Fe-Catalyzed C–C Bond Construction from Olefins via Radicals

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General Experimental.

Dry dichloromethane (DCM), toluene (PhMe), and tetrahydrofuran (THF) were obtained by passing the previously degassed solvents through an activated alumina column. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Indicated manipulations were performed under a N₂ atmosphere in an M. Braun glovebox maintained at or below 1 ppm O₂. Yields refer to chromatographically and spectroscopically (¹H NMR) homogeneous material, unless otherwise stated. Reactions were monitored by thin layer chromatography (TLC) carried out on 0.25 mm E. Merck silica plates (60F-254), using short-wave UV light as the visualizing agent and an acidic solution of vanillin and heat, p-anisaldehyde and heat, 2,4-dinitrophenylhydrazine and heat, or KMnO₄ and heat as developing agents. Flash column chromatography was performed using E. Merck silica gel (60, particle size 0.043–0.063 mm). NMR spectra were recorded on Bruker DRX-600, DRX-500, AMX-400, or AV-400 instruments and were calibrated using residual undeuterated solvent as an internal reference. The following abbreviations were used to explain NMR peak multiplicities: s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet, br=broad. High-resolution mass spectra (HRMS) were recorded on an Agilent LC/MSD TOF mass spectrometer by electrospray ionization time-of-flight (ESI-TOF) reflectron experiments. Hydrogen gas evolution was detected by injecting 500 µL of methane into the headspace of the sealed reaction vessel. At the end of reaction, 500 µL of headspace was drawn out and injected into an SSL injection port of a Thermo Scientific Trace 1300 GC. Solution ⁵⁷Fe Mössbauer samples were frozen in Delrin sample cups and recorded on a SEECo Mössbauer spectrometer with alternating constant acceleration; isomer shifts are relative to α-iron metal at 298 K. The sample temperature was maintained at 80 K in a Janis Research Company Inc. cryostate. The zero-field spectra were simulated using Lorentzian doublets using WMoss (SeeCo).
Experimental Procedures and Characterization Data for Substrates.

**Benzyl geranate (50).** To a solution of geranic acid (20.0 mg, 119 µmol, 1.0 equiv), EDCI·HCl (28.2 mg, 143 µmol, 1.2 equiv), and DMAP (1.5 mg, 11.9 µmol, 0.1 equiv) in DCM (0.60 mL) was added benzyl alcohol (12.3 µL, 119 µmol, 1.0 equiv). The reaction mixture was stirred at rt for 2.5 h, quenched with a saturated aqueous solution of NH₄Cl, and then extracted with EtOAc. The organic layers were combined, washed with brine, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. Purification by preparative TLC (SiO₂, 8:2 hexanes:DCM) gave an inconsequential mixture of E and Z isomers of benzyl geranate (50) as a colorless oil (15.2 mg, 58.8 µmol, 49%).

**Physical State:** colorless oil.

**¹H NMR** (600 MHz, CDCl₃): δ 7.39–7.30 (m, 10 H), 5.73–5.72 (m, 2 H), 5.14–5.13 (m, 2 H), 2.65 (t, J=7.8 Hz, 2 H), 2.18–2.16 (m, 9 H), 1.89 (s, 3 H), 1.68–1.67 (m, 6 H), and 1.61–1.60 (m, 6 H).

**¹³C NMR** (151 MHz, CDCl₃): δ 166.7, 166.2, 161.2, 160.9, 136.6, 132.7, 132.3, 128.7, 128.6, 128.31, 128.27, 128.18, 128.15, 123.8, 123.1, 116.0, 115.4, 65.6, 65.5, 41.2, 33.7, 26.9, 26.2, 25.8, 25.7, 19.1, 17.85, and 17.78. Peak overlapping was observed.

**HRMS** (m/z): calcd for C₁₇H₂₃O₂, [M+H]⁺, 259.1693; found, 259.1694.

**TLC:** R₉ 0.79 (8:2 hexanes:EtOAc).

**N-Benzylgeranamide (52).** To a solution of geranic acid (20.0 mg, 119 µmol, 1.0 equiv), EDCI·HCl (28.2 mg, 143 µmol, 1.2 equiv), and DMAP (1.5 mg, 11.9 µmol, 0.1 equiv) in DCM
(0.60 mL) was added benzylamine (13.0 µL, 119 µmol, 1.0 equiv). The reaction mixture was stirred at rt for 2.5 h, quenched with a saturated aqueous solution of NH₄Cl, and then extracted with EtOAc. The organic layers were combined, washed with brine, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. Purification by preparative TLC (SiO₂, 8:2 hexanes:EtOAc) gave an inconsequential 1:1 mixture of E and Z isomers of N-benzylgeranamide (52) as a colorless oil (21.7 mg, 84.3 µmol, 71%).

**Physical State:** colorless oil.

**¹H NMR** (600 MHz, CDCl₃): δ 7.35–7.27 (m, 10 H), 5.27 (br s, 1 H), 5.62 (br s, 1 H), 5.58 (s, 1 H), 5.56 (s, 1 H), 5.15 (t, J=7.2 Hz, 1 H), 5.07 (t, J=6.7 Hz, 1 H), 4.49–4.47 (m, 4 H), 2.64 (t, J=7.7 Hz), 2.18 (s, 3 H), 2.17–2.09 (m, 6 H), 1.84 (s, 3 H), 1.68 (s, 3 H), 1.64 (s, 3 H) and 1.60 (m, 6 H).

**¹³C NMR** (151 MHz, CDCl₃): δ 167.0, 166.6, 155.0, 154.1, 138.74, 138.72, 132.5, 132.4, 128.8, 128.03, 128.01, 127.6, 124.0, 123.3, 119.1, 117.8, 43.5, 41.0, 33.3, 26.8, 26.3, 25.83, 25.80, 24.9, 18.6, 17.9, and 17.8. Peak overlapping was observed.

**HRMS (m/z):** calcd for C₁₇H₂₄NO, [M+H]+, 258.1852; found, 258.1852.

**TLC:** Rᵋ 0.39 (8:2 hexanes:EtOAc).

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**tert-Butyl 3-(3-methylbut-2-en-1-yl)-1H-indole-1-carboxylate (67).** To a solution of prenylated indole S₂₁ (3.5 mg, 18.9 µmol, 1.0 equiv) and DMAP (0.2 mg, 1.89 µmol, 0.1 equiv) at 0 °C was added Boc₂O with stirring. The reaction mixture was warmed to rt, stirred for 30 min, and then concentrated under reduced pressure. Purification by preparative TLC (SiO₂, 9:1 hexanes:EtOAc) gave Boc indole 67 as a viscous, yellow oil (1.3 mg, 4.56 µmol, 24%).

**Physical State:** viscous, yellow oil.

**¹H NMR** (600 MHz, CDCl₃): δ 8.10 (br s, 1 H), 7.51 (d, J=7.8 Hz, 1 H), 7.33–7.29 (m, 2 H), 7.23 (dd, J=7.5, 7.5 Hz, 1 H), 5.39 (t, J=7.0, 7.0 Hz, 1 H), 3.38 (d, J=7.0 Hz, 2 H), 1.76 (s, 6 H), 1.67 and (s, 9 H).

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¹ Westermaier, M.; Mayr, H. *Org. Lett.* 2006, 8, 4791–4794.
$^{13}$C NMR (151 MHz, CDCl$_3$): δ 176.8, 150.1, 133.2, 130.8, 124.4, 122.5, 122.4, 121.6, 120.8, 119.2, 115.4, 83.4, 28.4, 25.9, 24.0, and 18.0.

HRMS ($m$/z): calcd for C$_{18}$H$_{24}$NO$_2$, [M+H]$^+$, 286.1801; found, 286.1800.

TLC: R$_f$ 0.60 (9:1 hexanes:EtOAc).

$^{13}$C NMR (151 MHz, CDCl$_3$): δ 178.9, 134.5, 123.0, 65.9, 51.1, 50.2, 42.4, 39.4, 38.9, 36.7, 33.3, 33.1, 27.4, 26.3, 23.9, 22.2, 22.0, 18.9, and 13.6.

HRMS ($m$/z): calcd for C$_{21}$H$_{37}$O$_2$, [M+H]$^+$, 321.2788; found, 321.2785.

TLC: R$_f$ 0.66 (9:1 hexanes:EtOAc).

2-((1S,8aS)-2,5,5,8a-tetramethyl-1,4,4a,5,6,7,8,8a-octahydronaphthalen-1-yl)ethyl pivalate (71). To a solution of a mixture of olefin isomers S3$^2$ (100.0 mg, 432 µmol, 1.0 equiv), pyridine (102 µL, 1.27 mmol, 3.0 equiv), and DMAP (10.3 mg, 84.6 µmol, 0.2 equiv) in DCM (2.1 mL) at 0 °C was added PivCl (104 µL, 846 µmol, 2.0 equiv). The resulting mixture was warmed to rt and stirred for 2h. The reaction mixture was then quenched with a saturated aqueous solution of NH$_4$Cl and extracted with Et$_2$O. The organic layers were combined, washed with brine, dried over MgSO$_4$, filtered, and concentrated under reduced pressure. Purification by flash column chromatography (SiO$_2$, 8:2→7:3 hexanes:DCM) furnished pivalate 71 as a colorless oil (36.0 mg, 112 µmol, 27%).

Physical State: colorless oil.

$^1$H NMR (600 MHz, CDCl$_3$): δ 5.43 (br s, 1 H), 4.21 (ddd, $J$=10.6, 8.5, 5.0 Hz), 3.98 (ddd, $J$=10.7, 7.7, 7.7 Hz, 1 H), 1.99 (br d, $J$=17.7 Hz, 1 H), 1.86 (br dd, $J$=12.3, 12.3 Hz, 2H), 1.78 (ddd, $J$=15.3, 8.1 Hz, 1 H), 1.72–1.68 (m, 4 H), 1.55–1.49 (m, 2 H), 1.46–1.40 (m, 2 H), 1.20 (s, 9 H), 1.18–1.13 (m, 2 H), 0.97 (ddd, $J$=13.0, 13.0 3.6 Hz, 1 H), 0.88 (s, 3 H), 0.86 (s, 3 H), and 0.76 (s, 3 H).

$^{13}$C NMR (151 MHz, CDCl$_3$): δ 178.9, 134.5, 123.0, 65.9, 51.1, 50.2, 42.4, 39.4, 38.9, 36.7, 33.3, 33.1, 27.4, 26.3, 23.9, 22.2, 22.0, 18.9, and 13.6.

HRMS ($m$/z): calcd for C$_{21}$H$_{37}$O$_2$, [M+H]$^+$, 321.2788; found, 321.2785.

TLC: R$_f$ 0.66 (9:1 hexanes:EtOAc).

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$^2$ Cebula, R. E.; Blanchard, J. L.; Boisclair, M. D.; Pal, K.; Bockovich, N. J. Bioorg. Med. Chem. Lett. 1997, 7, 2015.
Phenethyl(prop-1-en-2-yl)sulfide (182). Following the method of Kao and Lee,3 2-phenylethanethiol (670 µL, 5.00 mmol, 1.0 equiv) was added to a solution of KOH (560 mg, 10.0 mmol, 2.0 equiv), Cu₂O (35.8 mg, 250 µmol, 5 mol%), 1,10-phenanthroline (90.1 mg, 500 µmol, 10 mol%) and 2-bromopropene (533 µL, 6.00 mmol, 1.2 equiv) in 1,4-dioxane (2.5 mL). The reaction mixture was then heated at 110 °C with stirring for 12 h, cooled to rt, the reaction diluted with ethyl acetate, and filtered directly through a pad of Celite®. Concentration under reduced pressure and purification by flash column chromatography (SiO₂, 100:1 hexanes:EtOAc) furnished thioether 182 as a colorless oil (445 mg, 2.50 mmol, 50%).

Physical State: colorless oil.

1H NMR (600 MHz, CDCl₃): δ 7.33–7.30 (m, 2 H), 7.25–7.22 (m, 3 H), 5.04 (q, J=1.4 Hz, 1 H), 4.77 (q, J=0.7 Hz, 1 H), 2.98–2.92 (m, 4 H), and 1.99 (dd, J=1.4, 0.7 Hz, 3 H).

13C NMR (151 MHz, CDCl₃): δ 140.7, 140.5, 128.7, 128.6, 126.6, 106.8, 35.0, 32.9, and 23.7.

HRMS (m/z): calcd for C₁₁H₁₅S [M+H]+: 179.0889, found: 179.0893.

TLC: Rₓ=0.75 (10:1 hexanes:EtOAc).

Oct-1-en-1-yl(phenethyl)sulfide (193). Following the method of Lee, Baggiolini, and Uskoković,4 a solution of 2-phenylethanethiol (402 µL, 3.00 mmol, 1.0 equiv), oct-1-yne (664 µL, 4.50 mmol, 1.5 equiv), and 2,2’-azobis(2-methylpropionitrile) (24.6 mg, 150 µmol, 5 mol%) in 1,4-dioxane (3.0 mL) was heated at 85 °C with stirring for 11 h. The reaction mixture was cooled to rt, concentrated under reduced pressure, and purified by flash column chromatography (SiO₂, 100:1 hexanes:EtOAc) to furnish thioether 193 as 1:1.4 mixture of E:Z olefin isomers (574 mg, 2.31 mmol, 77%). Data is reported for the mixture of olefin isomers.

Physical State: colorless oil.

3 Kao, H.-L.; Lee, C.-F. Org. Lett. 2011, 13, 5204.
4 Lee, H. L.; Baggiolini, E. G.; Uskoković, M. R. Tetrahedron 1987, 43, 4887.
**1H NMR** (600 MHz, CDCl₃): δ 7.32–7.29 (m, 2 H), 7.24–7.20 (m, 3 H), 5.93–5.90 (m, 1 H), 5.69 (dt, J=15.0, 7.2 Hz, 0.58 H), 5.60 (dt, J=9.0, 7.2 Hz, 0.42 H), 2.94–2.87 (m, 4 H), 2.13 (dt, J=7.2, 7.2, 1.2 Hz, 0.84 H), 2.09 (dt, J=7.2, 7.2, 1.3 Hz, 1.16 H), 1.42–1.35 (m, 2 H), 1.33–1.26 (m, 6 H), and 0.90–0.88 (m, 3 H).

**13C NMR** (151 MHz, CDCl₃): δ 140.5, 140.4, 132.1, 130.6, 128.7, 128.7, 128.6, 126.5, 124.5, 122.2, 37.0, 36.2, 35.4, 34.4, 33.4, 31.9, 31.8, 29.4, 29.3, 29.1, 28.9, 22.8, 22.8, and 14.2. Peak overlapping was observed.

**HRMS (m/z):** calcd for C₁₆H₂₅S \([M+H]^+\): 249.1671, found: 249.1672.

**TLC:** Rₖ=0.55 (10:1 hexanes:EtOAc).

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(4-Methoxyphenyl)(oct-1-en-1-yl)sulfide (195). Following the method of Lee, Baggioni, and Uskoković, a solution of p-methoxybenzenethiol (369 µL, 3.00 mmol, 1.0 equiv), oct-1-yne (664 mL, 4.50 mmol, 1.5 equiv), and 2,2’-azobis(2-methylpropionitrile) (24.6 mg, 150 µmol, 5 mol%) in 1,4-dioxane (3.0 mL) was heated at 85 °C with stirring for 11 h. The reaction mixture was cooled to rt, concentrated under reduced pressure, and purified by flash column chromatography (SiO₂, 100:1 hexanes:EtOAc) to furnish thioether 195 as a 1:1 mixture of E:Z olefin isomers (480 mg, 1.92 mmol, 64%). Data is reported for the mixture of olefin isomers.

**Physical State:** colorless oil.

**1H NMR** (600 MHz, CDCl₃): δ 7.32–7.29 (m, 2 H), 6.87–6.85 (m, 2 H), 6.10–6.01 (m, 1 H), 5.80 (dt, J=15.0, 7.2 Hz, 0.5 H), 5.68 (dt, J=9.6, 7.2 Hz, 0.5 H), 3.80 (s, 3 H), 3.80 (s, 3 H), 2.22 (dt, J=7.2, 7.2 Hz, 1 H), 2.11 (dt, J=7.2, 7.2 Hz, 1 H), 1.46–1.26 (m, 8H), and 0.91–0.87 (m, 3 H).

**13C NMR** (151 MHz, CDCl₃): δ 159.0, 158.9, 134.7, 132.1, 131.9, 131.6, 127.0, 126.4, 125.0, 122.9, 114.8, 114.8, 55.5, 33.1, 31.8, 31.8, 29.2, 29.2, 29.1, 28.9, 22.8, 22.8, 14.3, and 14.2. Peak overlapping was observed.

**HRMS (m/z):** calcd for C₁₅H₂₃OS \([M+H]^+\): 251.1464, found: 251.1469.

**TLC:** Rₖ=0.55 (10:1 hexanes:EtOAc).
Isopropenyl 1,8-diaminonaphthyl boronamide (205). To a solution of trimethyl borate (500 µL, 4.48 mmol, 1.0 equiv) in THF (4.5 mL) under an Ar atmosphere was added a solution of freshly prepared isopropenylmagnesium bromide$^5$ (0.68 M in THF, 398 µL, 4.48 mmol, 1.0 equiv) at –20 °C with stirring. The reaction mixture turned milky white upon stirring at –20 °C for 30 min, at which point 1,8-diaminonaphthalene (710 mg, 4.48 mmol, 1.0 equiv) was added in one portion. After stirring for 70 min at –20 °C, the reaction mixture was warmed to rt and then quenched with a saturated aqueous solution of NH$_4$Cl. The organic layer was separated and the aqueous layer was extracted with EtOAc. The organic layers were combined, washed with brine, dried over MgSO$_4$, filtered, and concentrated under reduced pressure. Purification by flash column chromatography (SiO$_2$, 9:1 hexanes:EtOAc) furnished boronamide 205 as a white solid (555 mg, 2.67 mmol, 59%).

**Physical State:** white solid.

**Melting Point:** 91.4–91.6 °C.

$^1$H NMR (600 MHz, CDCl$_3$): δ 7.11 (dd, $J$=8.0, 8.0 Hz, 2 H), 7.02 (d, $J$=8.2 Hz, 2 H), 6.35 (d, $J$=7.3 Hz, 2 H), 5.76 (br s, 2 H), 5.57 (br s, 2 H), 5.51 (br s, 1 H), and 1.92 (s, 3 H).

$^{13}$C NMR (151 MHz, CDCl$_3$): δ 141.2, 136.5, 127.7, 124.6, 119.9, 117.7, 105.9, and 21.6. The boron–bound carbon was not observed due to quadrupolar relaxation.

$^{11}$B NMR (128 MHz, CDCl$_3$): δ 8.7.

HRMS ($m$/z): calcd for C$_{13}$H$_{14}$BN$_2$ [M+H]$^+$: 209.1245, found: 209.1252.

TLC: $R_s$=0.48 (9:1 hexanes:EtOAc).

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$^5$ Song, D.; Rostami, A.; West, F. G. *J. Am. Chem. Soc.* **2014**, *136*, 6884.
tert-Butyl((2-fluoroallyl)oxy)dimethylsilane (230). To a solution of 2-fluoro-2-propen-1-ol\(^6\) (439 mg, 5.77 mmol, 1.0 equiv) and imidazole (786 mg, 11.5 mmol, 2.0 equiv) in DCM (19 mL) was added TBSCl (1.30 g, 8.66 mmol, 1.5 equiv) at 0 °C with stirring. The reaction mixture was warmed to rt over 2 h and was quenched with a saturated aqueous solution of NH\(_4\)Cl. The organic layer was separated and the aqueous layer was extracted with Et\(_2\)O. The organic layers were combined, washed with brine, dried over MgSO\(_4\), filtered, and concentrated under reduced pressure. Purification by flash column chromatography (SiO\(_2\), pentane) furnished fluoride 230 as a colorless oil (1.05 g, 5.49 mmol, 95%).

Physical State: colorless oil.

\(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta\) 4.65 (ddt, \(J=17.2, 2.8, 0.7\) Hz, 1 H), 4.54 (ddt, \(J=49.3, 2.9, 1.2\) Hz, 1 H), 4.14 (dd, \(J=0.9, 0.9\) Hz, 1 H), 4.13 (dd, \(J=0.9, 0.9\) Hz, 1 H), 0.92 (s, 9 H), and 0.10 (s, 6 H).

\(^{13}\)C NMR (151 MHz, CDCl\(_3\)): \(\delta\) 165.1 (d, \(J=257.4\) Hz), 90.0 (d, \(J=17.4\) Hz), 60.9 (d, \(J=38.3\) Hz), 25.9, 18.5, and −5.3.

\(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \(\delta\) −108.4.

GC/MS (m/z): [M−t-Bu]\(^+\): 133.

TLC: \(R_f=0.74\) (9:1 hexanes:EtOAc).

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tert-Butyl((2-chloroallyl)oxy)dimethylsilane (232). To a solution of 2-chloro-2-propen-1-ol (200 mg, 2.16 mmol, 1.0 equiv) and imidazole (294 mg, 4.32 mmol, 2.0 equiv) in DCM (7.0 mL) was added TBSCl (489 mg, 3.24 mmol, 1.5 equiv) at 0 °C with stirring. The reaction mixture was warmed to rt over 75 min and was quenched with a saturated aqueous solution of NH\(_4\)Cl. The organic layer was separated and the aqueous layer was extracted with Et\(_2\)O. The organic layers were combined, washed with brine, dried over MgSO\(_4\), filtered, and concentrated under reduced pressure. Purification by flash column chromatography (SiO\(_2\), hexanes) furnished chloride 232 as a colorless oil (311 mg, 1.50 mmol, 69%).

Physical State: colorless oil.

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\(^6\) King, S. M.; Ma, X.; Herzon, S. B. J. Am. Chem. Soc. 2014, 136, 6884.
$^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 5.50 (dd, $J$=3.1, 1.6 Hz, 1 H), 5.29 (dd, $J$=2.9, 1.4 Hz, 1 H), 4.16 (dd, $J$=1.6, 1.6 Hz, 2 H), 0.92 (s, 9 H), and 0.10 (s, 6 H).

$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 140.6, 110.7, 65.9, 25.9, 18.5, and –5.3.

**GC/MS (m/z):** [M–t-Bu]$^+$: 149.

**TLC:** $R_f$=0.45 (9:1 hexanes:EtOAc).
Preparation of Fe(dibm)$_3$ (131).

**Iron(III) diisobutyrylmethane** (131). To a biphasic mixture of 2,6-dimethylheptane-3,5-dione (2.60 g, 16.6 mmol, 3.0 equiv) and NaOAc•3H$_2$O (2.27 g, 16.6 mmol, 3.0 equiv) in an aqueous solution of EtOH (1:1 EtOH:H$_2$O, 42 mL) was added ground FeCl$_3$•6H$_2$O (1.50 g, 5.55 mmol, 1.0 equiv). A red slurry formed and the reaction mixture was heated at 60 °C with stirring for 1 h. The slurry was cooled at rt over 10 min, cooled at 0 °C for 15 min, and then filtered to give an orange powder. The orange powder was rinsed with H$_2$O, collected, placed in an Erlenmeyer flask, and heated with an aqueous solution of EtOH (9:1 EtOH:H$_2$O, 30 mL) using a heat gun until fully dissolved to give a red, homogenous solution. The solution was cooled to rt and then to 0 °C to give red crystals, which were filtered and rinsed with a –78 °C aqueous solution of EtOH (9:1 EtOH:H$_2$O, 10 mL) to furnish Fe(dibm)$_3$ (131) as a red crystalline solid (1.91 g, 3.67 mmol, 66%). A small amount was recrystallized from MeOH to provide crystals suitable for X-ray analysis.

**Physical State**: red crystalline solid.

**Melting Point**: 99.2–99.5 °C.

**Elemental Analysis**: calcd for C$_{27}$H$_{45}$FeO$_6$: C, 62.19; H, 8.70; N, 0.00 found: C, 62.16; H, 8.64; N, 0.00.

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**Figure S1.** X-ray crystallographic structure of Fe(dibm)$_3$ (131).
The single crystal X-ray diffraction studies were carried out on a Bruker Kappa APEX-II CCD diffractometer equipped with Mo K\textalpha\ radiation ($\lambda=0.71073$ Å). A 0.115 x 0.053 x 0.044 mm red block was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 175(2) K using $\phi$ and $\varphi$ scans. Crystal-to-detector distance was 40 mm using variable exposure time (30 s or 60 s) depending on $\theta$ with a scan width of 1.0$^\circ$. Data collection was 100% complete to 25.00$^\circ$ in $\theta$. A total of 75632 reflections were collected covering the indices, -14<=$h<=$13, -23<=$k<=$23, -18<=$l<=$18. 6312 reflections were found to be symmetry independent, with a $R_{int}$ of 0.0793. Indexing and unit cell refinement indicated a primitive, monoclinic lattice. The space group was found to be $P2_1/c$. The data were integrated using the Bruker SAINT software program and scaled using the SADABS software program. Solution by direct methods (SHELXT) produced a complete phasing model consistent with the proposed structure.  

All nonhydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2013). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014. Crystallographic data are summarized in Table S1.

Table S1. Crystal data and structure refinement for Fe(dibm)$_3$ (131).

| Identification code | CCDC 1022625 |
|---------------------|--------------|
| Empirical formula   | C27 H45 Fe O6 |
| Molecular formula   | C27 H45 Fe O6 |
| Formula weight      | 521.48       |
| Temperature         | 175 K        |
| Wavelength          | 0.71073 Å    |
| Crystal system      | Monoclinic   |
| Space group         | P 1 21/n 1   |
| Unit cell dimensions| $a=11.3761(2)$ Å $\alpha = 90^\circ$, $b=18.9915(5)$ Å $\beta = 105.0130(14)^\circ$, $c=14.7639(4)$ Å $\gamma =90^\circ$. |
| Volume              | 3080.85(13) Å$^3$ |
| Z                   | 4            |
| Density (calculated)| 1.124 Mg/m$^3$ |
| Property                                      | Value                          |
|----------------------------------------------|--------------------------------|
| Absorption coefficient                       | 0.522 mm\(^{-1}\)              |
| F(000)                                        | 1124                           |
| Crystal size                                 | 0.115 x 0.053 x 0.044 mm\(^3\) |
| Crystal color, habit                         | Red Block                      |
| Theta range for data collection              | 1.786 to 26.423°.              |
| Index ranges                                 | -14<=h<=13, -23<=k<=23, -18<=l<=18 |
| Reflections collected                        | 75632                          |
| Independent reflections                      | 6312 [R(int)=0.0793]            |
| Completeness to theta=25.000°                | 100.0 %                        |
| Absorption correction                        | Semi-empirical from equivalents|
| Max. and min. transmission                   | 0.7454 and 0.7010              |
| Refinement method                            | Full-matrix least-squares on F\(^2\) |
| Data / restraints / parameters               | 6312 / 0 / 319                 |
| Goodness-of-fit on F\(^2\)                   | 1.053                          |
| Final R indices [I>2sigma(I)]                | R1=0.0579, wR2=0.1332           |
| R indices (all data)                         | R1=0.1076, wR2=0.1599           |
| Extinction coefficient                       | n/a                            |
| Largest diff. peak and hole                  | 0.447 and -0.395 e.Å\(^-3\)    |
Photographic Guide for the Preparation of Fe(dibm)$_3$ (131).

Figure S2. Reagents used in the synthesis of Fe(dibm)$_3$. From left to right: NaOAc•3H$_2$O, 2,6-dimethylheptane-3,5-dione, FeCl$_3$•6H$_2$O.

Figure S3. Setting up the synthesis of Fe(dibm)$_3$. From left to right: biphasic mixture of NaOAc•3H$_2$O and 2,6-dimethylheptane-3,5-dione in aqueous EtOH, after addition of FeCl$_3$•6H$_2$O.
Figure S4. Synthesis of Fe(dibm)$_3$. From left to right: heating the reaction mixture at 60 °C, cooling the reaction mixture to rt after heating at 60 °C for 1 h.

Figure S5. Cooling the slurry at 0 °C.
Figure S6. Filtering the slurry through a Büchner funnel.

Figure S7. Crude Fe(dibm)₃.
Figure S8. Recrystallization of Fe(dibm)$_3$ in an Erlenmeyer flask. From left to right: heating with a heat gun, dark red solution of fully dissolved Fe(dibm)$_3$.

Figure S9. Cooling of the solution at 0 °C. From left to right: immediately upon cooling, after cooling ca. 1 h.
Figure S10. Collecting the recrystallized Fe(dibm)$_3$. From left to right: filtering through a Büchner funnel, rinsing with aqueous EtOH precooled to −78 °C.

Figure S11. Recrystallized Fe(dibm)$_3$. 
Photographic Guide for the Olefin Cross-Coupling.

Figure S12. A. Weighing 30 mol% Fe(acac)₃. B. Weighing 1.0 equiv α-ionone. C. Addition of CD₃OD solvent and 2.5 equiv PhSiH₃. D. Reaction mixture prior to heating.
**Figure S13.** A. Heating the reaction mixture to 60 °C. B. Taking a TLC of the reaction mixture. C. The TLC plate visualized under short-wave UV light (left) and developed with vanillin (right). D. The reaction mixture immediately prior to addition of brine.
Figure S14. A. Initial stages of the work up: addition of Et₂O and brine initially giving a biphasic system (left), the first extraction resulting in a monophasic solution (middle), addition of a more Et₂O and minimal amount of H₂O causing phase separation (right). B. Red residue after concentrating the organic layers from the extractions. C. Filtering the red residue through a plug of SiO₂. D. Yellow oil after concentrating the filtrate.
Experimental Procedures and Characterization Data for the Olefin Cross-Coupling Products.

General Procedure 1. Reductive olefin cyclization and intermolecular olefin cross-coupling.

To a solution of donor olefin (1.0 equiv), acceptor olefin (intermolecular reactions only, 3.0 equiv), and Fe(acac)_3 (20–100 mol%) in either EtOH, EtOH/(CH₂OH)_2 (5:1) or DCE/(CH₂OH)_2, was added PhSiH₃ (1.0–2.5 equiv) [CAUTION: H₂ evolution is occasionally observed upon addition of PhSiH₃]. The resulting mixture was heated to 60 °C with stirring until TLC analysis indicated the consumption of starting material. The reaction mixture was then cooled to rt and diluted with brine. Addition of Et₂O and minimal amount of water resulted in both the solution of any solids and a phase separation. The organic layer was separated and the aqueous layer was extracted with Et₂O. The organic layers were combined, washed with brine, dried over MgSO₄, filtered, and concentrated under reduced pressure. The red residue was then dissolved in a minimal amount of DCM and flushed through a plug of silica using hexanes:EtOAc [typically 9:1, but a more polar solvent system was used for more polar products (see individual procedures for details)] as the eluent to remove the red compound(s) [presumably Fe(acac)₃ and/or derivatives of] from the crude. Concentration under reduced pressure gave a pale yellow or colorless oil or solid, which was then purified on SiO₂ (preparative TLC or flash column chromatography) to furnish the coupled product.

Miscellaneous Reaction Notes.

EtOH and EtOH/(CH₂OH)_2 both produced monophasic reaction mixtures, whereas DCE/(CH₂OH)_2 produced a biphasic reaction mixture. The monophasic reactions were generally faster than the biphasic ones. Reactions using stoichiometric Fe(acac)₃ proceeded faster than the ones using catalytic Fe(acac)₃. Regarding the catalyst loading of Fe(acac)₃, 30 mol% tended to give cleaner reactions by TLC than 20 mol%. For the work up, it is also possible to concentrate the crude reaction mixture under reduced pressure and then filter the red residue through SiO₂ (this process has only been used when EtOH or CD₃OD were used as the solvent). Common competitive reactions are the reduction of the donor and acceptor olefins to their saturated counterparts.
4a,8,8-Trimethyloctahydronaphthalen-2(1H)-one (38). To a solution of cyclohexenone 25 (20.0 mg, 104 µmol, 1.0 equiv) and Fe(acac)3 (11.0 mg, 31.2 µmol, 0.2 equiv) in ethanol (1.7 mL) and (CH2OH)2 (0.4 mL) was added PhSiH3 (32.0 µL, 260 µmol, 2.5 equiv). The resulting mixture was heated to 60 °C with stirring for 50 min, then cooled to rt, and diluted with H2O and brine. The organic layer was separated and the aqueous layer was extracted with Et2O. The organic layers were combined, washed with brine, dried over MgSO4, filtered, and concentrated under reduced pressure. The red residue was then dissolved in a minimal amount of DCM and flushed through a plug of silica using 9:1 hexanes:EtOAc as the eluent. Concentration under reduced pressure gave a pale yellow oil, which was then purified by flash column chromatography (SiO2, 95:5 hexanes:EtOAc) to furnish cis-decalin 38 as a colorless oil (12.2 mg, 62.8 µmol, 60%).

Physical State: colorless oil.

1H NMR (600 MHz, CDCl3): δ 2.54–2.44 (m, 2 H), 2.33 (dddd, J=16.1, 5.7, 2.1, 2.1 Hz, 1 H), 2.27 (ddd, J=13.3, 13.3, 5.7 Hz, 1 H), 1.57–1.53 (m, 2 H), 1.51 (ddd, J=7.1, 2.3, 2.3 Hz, 1 H), 1.44–1.42 (m, 1 H), 1.41–1.40 (m, 1 H), 1.37 (dddd, J=13.7, 7.5, 2.0, 2.0 Hz, 1 H), 1.32 (dd, J=14.0, 3.8 Hz, 1 H), 1.25 (br s, 1 H), 1.20 (s, 3 H), 0.92 (s, 3 H), and 0.82 (s, 3 H).

13C NMR (151 MHz, CDCl3): δ 213.6, 52.0, 42.4, 40.7, 39.3, 37.5, 34.7, 33.1, 33.0, 30.4, 23.2, and 18.4. Peak overlapping was observed.

HRMS (m/z): calcd for C13H23O [M+H]+: 195.1743; found: 195.1744.

TLC: Rf 0.42 (9:1 hexanes:EtOAc).

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7 Snider, B. B.; Rodini, D. J.; van Straten, J. J. Am. Chem. Soc. 1980, 102, 5872–5880.
1-(1,5,5-Trimethylbicyclo[4.1.0]heptan-7-yl)propan-2-one (45). To a solution of α-ionone (30.0 mg, 156 µmol, 1.0 equiv) and Fe(acac)_3 (55.1 mg, 156 µmol, 1.0 equiv) in ethanol (3.0 mL) was added PhSiH_3 (48.1 µL, 390 µmol, 2.5 equiv). The resulting mixture was heated to 60 °C with stirring for 15 min, then cooled to rt, and diluted with H_2O and brine. The organic layer was separated and the aqueous layer was extracted with Et_2O. The organic layers were combined, washed with brine, dried over MgSO_4, filtered, and concentrated under reduced pressure. The red residue was then dissolved in a minimal amount of DCM and flushed through a plug of silica using 9:1 hexanes:EtOAc as the eluent. Concentration under reduced pressure gave a pale yellow oil, which was then purified by flash column chromatography (SiO_2, 95:5 hexanes:EtOAc) to furnish cyclopropane 45 as a pale yellow oil (29.7 mg, 153 µmol, 98%).

Physical State: pale yellow oil with a sweet, peppery aroma.

^1H NMR (600 MHz, CDCl_3): δ 2.37 (dd, J=16.3, 7.2 Hz, 1 H), 2.33 (dd, J=16.3, 7.0 Hz, 1 H), 2.16 (s, 3 H), 1.62–1.52 (m, 3 H), 1.38–1.31 (m, 1 H), 1.21–1.13 (m, 2 H), 1.04 (s, 3 H), 1.02 (s, 3 H), 0.91 (s, 3 H), 0.67 (ddd, J=12.7, 7.1, 5.6 Hz, 1 H), and 0.14 (d, J=5.6 Hz, 1 H).

^13C NMR (151 MHz, CDCl_3): δ 209.7, 44.8, 38.2, 36.0, 32.3, 31.4, 29.88, 29.86, 28.5, 22.6, 21.8, 20.2, and 18.5.

HRMS (m/z): calcd for C_{13}H_{23}O [M+H]^+: 195.1743; found: 195.1743.

TLC: R_f 0.54 (9:1 hexanes:EtOAc).

(2R,4aS,8R,8aS)-8,8a,9,9-Tetramethylhexahydro-2H-2,4a-methanonaphthalen-6(5H)-one (47). To a solution of (+)-nootkatone (30.0 mg, 137 µmol, 1.0 equiv) and Fe(acac)_3 (14.6 mg, 41.2 µmol, 0.3 equiv) in ethanol (4.6 mL) and ethylene glycol (0.9 mL) was added PhSiH_3 (25.4
µL, 206 µmol, 1.5 equiv). The resulting mixture was heated to 60 °C with stirring for 30 min, then cooled to rt, and diluted with H2O and brine. The organic layer was separated and the aqueous layer was extracted with Et2O. The organic layers were combined, washed with brine, dried over MgSO4, filtered, and concentrated under reduced pressure. The red residue was then dissolved in a minimal amount of DCM and flushed through a plug of silica using 9:1 hexanes:EtOAc as the eluent. Concentration under reduced pressure gave a pale yellow oil, which was then purified by flash column chromatography (SiO2, 95:5 hexanes:EtOAc) to furnish bicyclo[2.2.1]heptane 47 as a colorless oil (19.5 mg, 88.5 µmol, 64%).

**Physical State:** colorless oil with a cedar aroma.

**1H NMR** (600 MHz, CDCl3): δ 2.41 (dddd, J=13.4, 6.7, 6.7, 6.7, 4.2 Hz, 1 H), 2.29 (dd, J=15.5, 1.8 Hz, 1 H), 2.21–2.15 (m, 2 H), 2.07 (ddd, J=14.5, 4.2, 1.8 Hz, 1 H), 1.92 (ddd, J=12.6, 3.5, 3.5 Hz, 1 H), 1.80–1.66 (m, 3 H), 1.46–1.38 (m, 1 H), 1.23–1.16 (m, 1 H), 1.09 (d, J=12.6 Hz, 1 H), 1.05 (s, 6 H), 0.94 (s, 3 H), and 0.89 (d, J=6.7 Hz, 3 H).

**13C NMR** (151 MHz, CDCl3): δ 213.4, 55.2, 50.2, 46.5, 45.3, 43.6, 42.5, 41.6, 39.0, 32.7, 26.6, 23.7, 22.6, 18.3, and 16.7.

**TLC:** Rf 0.69 (8:2 hexanes:EtOAc).

**HRMS (m/z):** calcd for C15H25O [M+H]+: 221.1900; found: 221.1902.

**TLC:** Rf 0.55 (8:2 hexanes:EtOAc).

2-(1,2,2-Trimethylcyclopentyl)acetaldehyde (49). To a biphasic mixture of citral (30.0 mg, 197 µmol, 1.0 equiv) and Fe(acac)3 (20.9 mg, 59.1 µmol, 0.3 equiv) in EtOH (3.2 mL) and ethylene glycol (0.7 mL) was added PhSiH3 (36.4 µL, 296 µmol, 1.5 equiv). The resulting mixture was heated to 60 °C with stirring for 20 min, then cooled to rt, and diluted with H2O and brine. The organic layer was separated and the aqueous layer was extracted with Et2O. The organic layers were combined, washed with brine, dried over MgSO4, filtered, and concentrated under reduced pressure. The red residue was then dissolved in a minimal amount of DCM and flushed through a plug of silica using 9:1 hexanes:EtOAc as the eluent. Concentration under reduced pressure gave
a pale yellow oil, which was then purified by flash column chromatography (SiO₂, 96:4 hexanes:EtOAc) to furnish cyclopentane 49 as a pale yellow oil (24.0 mg, 156 µmol, 79%).

**Physical State:** pale yellow oil.

**¹H NMR** (600 MHz, CDCl₃): δ 9.84 (t, J=3.2 Hz, 1 H), 2.27 (d, J=3.2 Hz, 2 H), 1.88–1.82 (m, 1 H), 1.70–1.64 (m, 3 H), 1.63–1.50 (m, 1 H), 1.49–1.45 (m, 1 H), 0.98 (s, 3 H), 0.88 (s, 3 H), and 0.87 (s, 3 H).

**¹³C NMR** (151 MHz, CDCl₃): δ 205.0, 51.0, 45.3, 44.2, 38.7, 36.9, 24.8, 23.7, 22.2, and 19.9.

**HRMS (m/z):** calcd for C₁₀H₁₉O, [M+H]⁺, 155.1430; found, 155.1420.

**TLC:** Rₚ 0.67 (9:1 hexanes:EtOAc).

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**Benzyl 2-(1,2,2-trimethylcyclopentyl)acetate (51).** To a solution of benzyl geranate (15.2 mg, 55.8 µmol, 1.0 equiv) and Fe(acac)₃ (20.8 mg, 55.8 µmol, 1.0 equiv) in ethanol (1.2 mL) was added PhSiH₃ (18.1 µL, 147 µmol, 2.5 equiv). The resulting mixture was heated to 60 °C with stirring for 13 h, then cooled to rt, and diluted with H₂O and brine. The organic layer was separated and the aqueous layer was extracted with Et₂O. The organic layers were combined, washed with brine, dried over MgSO₄, filtered, and concentrated under reduced pressure. The red residue was then dissolved in a minimal amount of DCM and flushed through a plug of silica using 95:5 hexanes:EtOAc as the eluent. Concentration under reduced pressure gave a pale yellow oil, which was then purified by preparative TLC (SiO₂, 95:5 hexanes:EtOAc) to furnish cyclopentane 51 as a pale yellow oil (11.6 mg, 44.6 µmol, 76%).

**Physical State:** pale yellow oil.

**¹H NMR** (600 MHz, CDCl₃): δ 7.37–7.36 (m, 4 H), 7.34–7.31 (m, 1 H), 5.12 (d, J=12.3 Hz, 1 H), 5.09 (d, J=12.3 Hz, 1 H), 2.29 (d, J=13.1 Hz, 1 H), 2.25 (d, J=13.1 Hz, 1 H), 1.89–1.83 (m, 1 H), 1.65–1.57 (m, 4 H), 1.47–1.44 (m, 1 H), 0.93 (s, 3 H), 0.87 (s, 3 H), and 0.85 (s, 3 H).

**¹³C NMR** (151 MHz, CDCl₃): δ 173.5, 136.3, 128.7, 128.4, 128.3, 66.1, 45.5, 44.2, 41.8, 39.1, 36.9, 24.7, 23.7, 21.4, and 19.6.

**HRMS (m/z):** calcd for C₁₇H₂₅O₂ [M+H]⁺: 261.1851; found: 261.1851.
**TLC:** R\textsubscript{f} 0.18 (95:5 hexanes:EtOAc).

*\textbf{N-Benzyl-2-(1,2,2-trimethylcyclopentyl)acetamide (53).} To a solution of \(N\)-benzyl geranamide (30.0 mg, 117 \(\mu\)mol, 1.0 equiv) and Fe(acac)\textsubscript{3} (41.2 mg, 117 \(\mu\)mol, 1.0 equiv) in ethanol (2.3 mL) was added PhSiH\textsubscript{3} (35.9 \(\mu\)L, 292 \(\mu\)mol, 2.5 equiv). The resulting mixture was heated to 60 °C with stirring for 30 min, then cooled to rt, and diluted with H\(_2\)O and brine. The organic layer was separated and the aqueous layer was extracted with Et\(_2\)O. The organic layers were combined, washed with brine, dried over MgSO\(_4\), filtered, and concentrated under reduced pressure. The red residue was then dissolved in a minimal amount of DCM and flushed through a plug of silica using 8:2 hexanes:EtOAc as the eluent. Concentration under reduced pressure gave a pale yellow oil, which was then purified by preparative TLC (SiO\(_2\), 95:5 hexanes:EtOAc) to furnish cyclopentane 53 as a pale yellow oil (11.6 mg, 44.6 \(\mu\)mol, 76%).

**Physical State:** pale yellow oil.

\(\text{\(^1H\) NMR}\) (400 MHz, CDCl\(_3\)): \(\delta\) 7.33–7.24 (m, 5 H), 5.65 (br s, 1 H), 4.46–4.37 (m, 2 H), 2.13 (d, \(J=12.9\) Hz, 1 H), 2.02 (d, \(J=12.9\) Hz, 1 H), 1.92–1.83 (m, 1 H), 1.66–1.56 (m, 4 H), 1.49–1.39 (m, 1 H), 0.93 (s, 3 H), 0.85 (s, 3 H), and 0.81 (s, 3 H).

\(\text{\(^{13}C\) NMR}\) (151 MHz, CDCl\(_3\)): \(\delta\) 172.8, 138.6, 128.8, 128.1, 127.6, 45.5, 44.2, 44.1, 43.8, 39.0, 37.0, 24.8, 23.6, 21.4, and 19.8.

**HRMS (\textit{m}/\textit{z}):** calcd for \(C_{17}H_{26}NO\) [M+H]\(^+\): 260.2009; found: 260.2009.

**TLC:** UV inactive and does not stain.

*\textbf{4-(1-Methylcyclohexyl)butan-2-one (58).} To a solution of 1-methylcyclohexene (30.0 mg, 312 \(\mu\)mol, 1.0 equiv) and Fe(acac)\textsubscript{3} (33.1 mg, 93.6 \(\mu\)mol, 0.3 equiv) in ethanol (1.3 mL) and ethylene glycol (0.3 mL) was added methyl vinyl ketone (78.0 \(\mu\)L, 936 \(\mu\)mol, 3.0 equiv), followed by
PhSiH₃ (57.7 µL, 468 µmol, 1.5 equiv). The resulting mixture was heated to 60 °C with stirring for 15 min, then cooled to rt, and diluted with H₂O and brine. The organic layer was separated and the aqueous layer was extracted with Et₂O. The organic layers were combined, washed with brine, dried over MgSO₄, filtered, and concentrated under reduced pressure. The red residue was then dissolved in a minimal amount of DCM and flushed through a plug of silica using 9:1 hexanes:EtOAc as the eluent. Concentration under reduced pressure gave a pale yellow oil, which was then purified by flash column chromatography (SiO₂, 94:6 hexanes:Et₂O) to furnish ketone 58 as a colorless oil (34.6 mg, 206 µmol, 66%). Spectroscopic data was identical to that reported in the literature.⁸

7-((tert-Butyldimethylsilyl)oxy)-5,5-dimethylheptan-2-one (60). To a solution of TBS silyl ether 59⁹ (30.0 mg, 150 µmol, 1.0 equiv) and Fe(acac)₃ (15.9 mg, 44.9 µmol, 0.3 equiv) in ethanol (2.5 mL) and ethylene glycol (0.5 mL) was added methyl vinyl ketone (37.4 µL, 449 µmol, 3.0 equiv), followed by PhSiH₃ (46.1 µL, 374 µmol, 2.5 equiv). The resulting mixture was heated to 60 °C with stirring for 1 h, then cooled to rt, and diluted with H₂O and brine. The organic layer was separated and the aqueous layer was extracted with Et₂O. The organic layers were combined, washed with brine, dried over MgSO₄, filtered, and concentrated under reduced pressure. The red residue was then dissolved in a minimal amount of DCM and flushed through a plug of silica using 9:1 hexanes:EtOAc as the eluent. Concentration under reduced pressure gave a pale yellow oil, which was then purified by preparative TLC (SiO₂, 8:2 hexanes:EtOAc) to furnish ketone 60 as a colorless oil (29.9 mg, 110 µmol, 73%). Spectroscopic data was identical to that reported in the literature.⁸

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⁸ Lackner, G. L.; Quasdorf, K. W.; Overman, L. E. J. Am. Chem. Soc. 2013, 135, 15342.
⁹ Sueiras, J.; Okamura, W. H. J. Am. Chem. Soc. 1980, 102, 6255.
**tert-Butyl 4-methyl-4-(3-oxobutyl)piperidine-1-carboxylate (62).** To a solution of piperidine 61\(^\text{10}\) (10.0 mg, 50.7 µmol, 1.0 equiv) and Fe(acac)\(_3\) (5.4 mg, 15.2 µmol, 0.3 equiv) in ethanol (0.8 mL) and ethylene glycol (0.2 mL) was added methyl vinyl ketone (12.7 µL, 152 µmol, 3.0 equiv), followed by PhSiH\(_3\) (15.6 µL, 127 µmol, 2.5 equiv). The resulting mixture was heated to 60 °C with stirring for 4 h, then cooled to rt, and diluted with H\(_2\)O and brine. The organic layer was separated and the aqueous layer was extracted with Et\(_2\)O. The organic layers were combined, washed with brine, dried over MgSO\(_4\), filtered, and concentrated under reduced pressure. The red residue was then dissolved in a minimal amount of DCM and flushed through a plug of silica using 8:2 hexanes:EtOAc as the eluent. Concentration under reduced pressure gave a pale yellow oil, which was then purified by preparative TLC (SiO\(_2\), 8:2 hexanes:EtOAc) to furnish piperidine 62 as a colorless oil (8.5 mg, 31.6 µmol, 62%). Spectroscopic data was identical to that reported in the literature.\(^8\)

**5-Phenylhexan-2-one (64).** To a solution of styrene (30.0 mg, 280 µmol, 1.0 equiv) and Fe(acac)\(_3\) (30.5 mg, 86.4 µmol, 0.3 equiv) in ethanol (1.2 mL) and ethylene glycol (0.2 mL) was added methyl vinyl ketone (72.0 µL, 864 µmol, 3.0 equiv), followed by PhSiH\(_3\) (53.2 µL, 432 µmol, 1.5 equiv). The resulting mixture was heated to 60 °C with stirring for 15 min, then cooled to rt, and diluted with H\(_2\)O and brine. The organic layer was separated and the aqueous layer was extracted with Et\(_2\)O. The organic layers were combined, washed with brine, dried over MgSO\(_4\), filtered, concentrated under reduced pressure, then purified by flash column chromatography (SiO\(_2\), 94:6 pentane:Et\(_2\)O) to furnish ketone 64 as a yellow oil (44.6 mg, 252 µmol, 87%).

\(^{10}\) Chen, M. H.; Abraham, J. A. *Tetrahedron Lett.* **1996**, *37*, 5233.
Spectroscopic data was identical to that reported in the literature.11

**5-(Pyridin-3-yl)hexan-2-one (66).** To a solution of 3-vinylpyridine12 (30.0 mg, 285 µmol, 1.0 equiv) and Fe(acac)₃ (100.8 mg, 285 µmol, 1.0 equiv) in ethanol (1.2 mL) and ethylene glycol (0.2 mL) was added methyl vinyl ketone (71.3 µL, 856 µmol, 3.0 equiv), followed by PhSiH₃ (53.7 µL, 428 µmol, 1.5 equiv). The resulting mixture was heated to 60 °C with stirring for 35 min, then cooled to rt, and diluted with H₂O and brine. The organic layer was separated and the aqueous layer was extracted with Et₂O. The organic layers were combined, washed with brine, dried over MgSO₄, filtered, concentrated under reduced pressure, then purified by flash column chromatography (SiO₂, Et₂O) to furnish ketone 66 as a colorless oil (21.0 mg, 118 µmol, 42%).

**Physical State:** colorless oil.

**¹H NMR** (600 MHz, CDCl₃): δ 8.46 (br d, J=4.7 Hz, 1 H), 8.43 (br s, 1 H), 7.49 (br d, J=7.9 Hz, 1 H), 7.24 (dd, J=7.8, 4.8 Hz, 1 H), 2.72 (ddq, J=6.8, 6.8, 6.8 Hz, 1 H), 2.35 (ddd, J=17.4, 9.2, 6.4 Hz, 1 H), 2.28 (ddd, J=17.5, 9.3, 5.7 Hz, 1 H), 2.07 (s, 3 H), 1.93 (dddd, J=14.8, 9.2, 6.3, 6.3 Hz, 1 H), 1.82 (dddd, J=14.5, 9.1, 9.1, 5.5 Hz, 1 H), and 1.28 (d, J=6.9 Hz, 3 H).

**¹³C NMR** (151 MHz, CDCl₃): δ 208.5, 149.3, 148.1, 141.7, 134.3, 123.7, 41.7, 36.9, 31.6, 30.2, and 22.2.

**HRMS (m/z):** calcd for C₁₁H₁₆NO [M+H]⁺: 178.1226; found: 178.1226.

**TLC:** Rᵥ 0.32 (Et₂O).

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**tert-Butyl 3-(3,3-dimethyl-6-oxoheptyl)-1H-indole-1-carboxylate (68).** To a solution of Boc indole 67 (30.0 mg, 105 µmol, 1.0 equiv) and Fe(acac)₃ (37.1 mg, 105 µmol, 1.0 equiv) in

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11 Gilbert, J. C.; Giamalva, D. H.; Baze, M. E. *J. Org. Chem.* 1985, 50, 2557.
12 Alunni, S.; Laureti, V.; Ottavi, L.; Ruzziconi, R. *J. Org. Chem.* 2003, 68, 718.
ethanol (0.5 mL) and ethylene glycol (0.1 mL) was added methyl vinyl ketone (26.3 µL, 315 µmol, 3.0 equiv), followed by PhSiH₃ (19.4 µL, 158 µmol, 1.5 equiv). The resulting mixture was heated to 60 °C with stirring for 35 min, then cooled to rt, and diluted with H₂O and brine. The organic layer was separated and the aqueous layer was extracted with Et₂O. The organic layers were combined, washed with brine, dried over MgSO₄, filtered, and concentrated under reduced pressure. The red residue was then dissolved in a minimal amount of DCM and flushed through a plug of silica using 9:1 hexanes:EtOAc as the eluent. Concentration under reduced pressure gave a pale yellow oil, which was then purified by flash column chromatography (SiO₂, 95:5 hexanes:EtOAc) to furnish ketone 68 as a colorless oil (12.9 mg, 36.1 µmol, 34%). Spectroscopic data was identical to that reported in the literature.⁸

5-Methylpentadecan-2-one (70). To a solution of 1-dodecene (30.0 mg, 178 µmol, 1.0 equiv) and Fe(acac)₃ (18.9 mg, 53.5 µmol, 0.3 equiv) in ethanol (0.74 mL) and ethylene glycol (0.15 mL) was added methyl vinyl ketone (44.6 µL, 535 µmol, 3.0 equiv), followed by PhSiH₃ (32.9 µL, 267 µmol, 1.5 equiv). The resulting mixture was heated to 60 °C with stirring for 1 h, then cooled to rt, and diluted with H₂O and brine. The organic layer was separated and the aqueous layer was extracted with Et₂O. The organic layers were combined, washed with brine, dried over MgSO₄, filtered, concentrated under reduced pressure, then purified by preparative flash column chromatography (SiO₂, 95:5 hexanes:Et₂O) to furnish ketone 70 as a colorless oil (17.1 mg, 71.2 µmol, 40%).

**Physical State:** colorless oil.

**¹H NMR** (600 MHz, CDCl₃): δ 2.47–2.36 (m, 2 H), 2.14 (s, 3 H), 1.62–1.58 (m, 1 H), 1.41–1.34 (m, 2 H), 1.32–1.26 (m, 18 H), and 0.89–0.85 (m, 6 H).

**¹³C NMR** (151 MHz, CDCl₃): δ 209.8, 41.7, 36.9, 32.6, 32.1, 30.9, 30.1, 30.0, 29.84, 29.80, 29.5, 27.1, 22.8, 19.6, and 14.3. Peak overlapping was observed.

**HRMS (m/z):** calcd for C₁₆H₃₃O [M+H]+: 241.2526; found: 241.2525.

**TLC:** Rₖ 0.50 (9:1 hexanes:EtOAc).
2-((1S,2S,8aS)-2,5,5,8a-Tetramethyl-2-(3-oxobutyl)decahydronaphthalen-1-yl)ethyl pivalate (72). To a solution of pivalate 71 (13.3 mg, 41.5 µmol, 1.0 equiv) and Fe(acac)₃ (14.7 mg, 41.5 µmol, 1.0 equiv) in ethanol (0.83 mL) was added methyl vinyl ketone (12.4 µL, 125 µmol, 3.0 equiv), followed by PhSiH₃ (12.8 µL, 104 µmol, 2.5 equiv). The resulting mixture was heated to 60 °C with stirring for 20 min, then cooled to rt, and concentrated under reduced pressure. The red residue was purified by preparative TLC (SiO₂, 9:1 hexanes:EtOAc) to furnish ketone 72 as a colorless solid (9.2 mg, 23.4 µmol, 56%). Spectroscopic data was identical to that reported in the literature.⁸

4-((8S,9S,13S,14S,17S)-3-Methoxy-13,17-dimethyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-17-yl)butan-2-one (74). To a solution of olefin 73¹³ (30.0 mg, 106 µmol, 1.0 equiv) and Fe(acac)₃ (11.3 mg, 31.9 µmol, 0.3 equiv) in ethanol (0.5 mL) and ethylene glycol (0.1 mL) was added methyl vinyl ketone (26.6 µL, 319 µmol, 3.0 equiv), followed by PhSiH₃ (19.6 µL, 159 µmol, 1.5 equiv). The resulting mixture was heated to 60 °C with stirring for 1 h, then cooled to rt, and diluted with H₂O and brine. The organic layer was separated and the aqueous layer was extracted with Et₂O. The organic layers were combined, washed with brine, dried over MgSO₄, filtered, and concentrated under reduced pressure. The red residue was then dissolved in a minimal amount of DCM and flushed through a plug of silica using 9:1 hexanes:EtOAc as the eluent. Concentration under reduced pressure gave a pale yellow oil, which was then purified by flash column chromatography (SiO₂, 95:5 hexanes:EtOAc) to furnish ketone 74 as a yellow oil (20.3 mg, 57.3 µmol, 54%).

¹³ Norden, S.; Bender, M.; Rullkötter, J.; Christoffers, J. Eur. J. Org. Chem. 2011, 4543–4550.
Spectroscopic data was identical to that reported in the literature.\(^8\)

![Diagram of 78](image)

**Methyl 3-(1-methylcyclohexyl)propanoate (78).** To a biphasic mixture of 1-methylcyclohexene (111 µL, 939 µmol, 3.0 equiv) and Fe(acac)\(_3\) (110 mg, 313 µmol, 1.0 equiv) in DCE (2.4 mL) and ethylene glycol (0.5 mL) was added methyl acrylate (27.0 mg, 313 µmol, 1.0 equiv), followed by PhSiH\(_3\) (58.0 µL, 470 µmol, 1.5 equiv). The resulting mixture was heated to 60 °C with stirring for 20 min, then cooled to rt, and diluted with H\(_2\)O and brine. The organic layer was separated and the aqueous layer was extracted with Et\(_2\)O. The organic layers were combined, washed with brine, dried over MgSO\(_4\), filtered, and concentrated under reduced pressure. The red residue was then purified by flash column chromatography (SiO\(_2\), 5:1 hexanes:EtOAc) to furnish ester 78 as a colorless oil (44.0 mg, 239 µmol, 76%). Spectroscopic data was identical to that reported in the literature.\(^8\)

![Diagram of 80](image)

**\(N,N\)-Dimethyl-3-(1-methylcyclohexyl)propanamide (80).** To a biphasic mixture of 1-methylcyclohexene (33.0 mg, 343 µmol, 1.0 equiv) and Fe(acac)\(_3\) (24.2 mg, 68.6 µmol, 0.2 equiv) in DCE (2.8 mL) and ethylene glycol (0.6 mL) was added \(N,N\)-dimethylacrylamide (106 µL, 1.03 mmol, 3.0 equiv), followed by PhSiH\(_3\) (64.0 µL, 515 µmol, 1.5 equiv). The resulting mixture was heated to 60 °C with stirring for 45 min, then cooled to rt, and diluted with H\(_2\)O and brine. The organic layer was separated and the aqueous layer was extracted with Et\(_2\)O. The organic layers were combined, washed with brine, dried over MgSO\(_4\), filtered, and concentrated under reduced pressure. The red residue was then purified by flash column chromatography (SiO\(_2\), 1:1 hexanes:EtOAc) to furnish amide 80 as a colorless oil (48.1 mg, 244 µmol, 71%). Spectroscopic data was identical to that reported in the literature.\(^8\)
3-(1-Methylcyclohexyl)propanenitrile (82). To a biphasic mixture of 1-methylcyclohexene (140 µL, 1.19 mmol, 3.0 equiv) and Fe(acac)$_3$ (27.9 mg, 79.0 µmol, 0.2 equiv) in DCE (3.3 mL) and ethylene glycol (0.7 mL) was added acrylonitrile (21.0 mg, 395 µmol, 1.0 equiv), followed by PhSiH$_3$ (73.0 µL, 593 µmol, 1.5 equiv). The resulting mixture was heated to 60 °C with stirring for 30 min, then cooled to rt, and diluted with H$_2$O and brine. The organic layer was separated and the aqueous layer was extracted with Et$_2$O. The organic layers were combined, washed with brine, dried over MgSO$_4$, filtered, and concentrated under reduced pressure. The red residue was then purified by preparative TLC (SiO$_2$, 10:1 hexanes:EtOAc) to furnish nitrile 82 as a colorless oil (42.3 mg, 280 µmol, 71%). Spectroscopic data was identical to that reported in the literature.$^8$

((2-(1-Methylcyclohexyl)ethyl)sulfonyl)benzene (84). To a biphasic mixture of 1-methylcyclohexene (63.0 µL, 1535 µmol, 3.0 equiv) and Fe(acac)$_3$ (62.9 mg, 178 µmol, 1.0 equiv) in DCE (1.5 mL) and ethylene glycol (0.3 mL) was added phenyl vinyl sulfone (30.0 mg, 178 µmol, 1.0 equiv), followed by PhSiH$_3$ (33.0 µL, 267 µmol, 1.5 equiv). The resulting mixture was heated to 60 °C with stirring for 30 min, then cooled to rt, and diluted with H$_2$O and brine. The organic layer was separated and the aqueous layer was extracted with Et$_2$O. The organic layers were combined, washed with brine, dried over MgSO$_4$, filtered, and concentrated under reduced pressure. The red residue was then purified by flash column chromatography (SiO$_2$, 5:1 hexanes:EtOAc) to furnish sulfone 84 as a colorless oil (26.5 mg, 99.5 µmol, 56%). Spectroscopic data was identical to that reported in the literature.$^8$
Dimethyl 2-(1-methylcyclohexyl)succinate (86). To a biphasic mixture of 1-methylcyclohexene (94.0 µL, 790 µmol, 3.0 equiv) and Fe(acac)₃ (18.6 mg, 52.6 µmol, 0.2 equiv) in DCE (0.3 mL) and ethylene glycol (0.3 mL) was added dimethyl fumarate (38.0 mg, 263 µmol, 1.0 equiv), followed by PhSiH₃ (49.0 µL, 395 µmol, 1.5 equiv). The resulting mixture was heated to 60 °C with stirring for 30 min, then cooled to rt, and diluted with H₂O and brine. The organic layer was separated and the aqueous layer was extracted with Et₂O. The organic layers were combined, washed with brine, dried over MgSO₄, filtered, and concentrated under reduced pressure. The red residue was then purified by preparative TLC (SiO₂, 5:1 hexanes:EtOAc) to furnish diester 86 as a colorless oil (57.3 mg, 236 µmol, 90%). Spectroscopic data was identical to that reported in the literature.

4-(1-Methylcyclohexyl)dihydrofuran-2(3H)-one (88). To a biphasic mixture of 1-methylcyclohexene (127 µL, 1.07 mmol, 3.0 equiv) and Fe(acac)₃ (50.3 mg, 142 µmol, 0.4 equiv) in DCE (3.0 mL) and ethylene glycol (0.6 mL) was added 2-furanone (30.0 mg, 356 mmol, 1.0 equiv), followed by PhSiH₃ (66.0 µL, 534 µmol, 1.5 equiv). The resulting mixture was heated to 60 °C with stirring for 20 min, then cooled to rt, and diluted with H₂O and brine. The organic layer was separated and the aqueous layer was extracted with Et₂O. The organic layers were combined, washed with brine, dried over MgSO₄, filtered, and concentrated under reduced pressure. The red residue was then purified by flash column chromatography (SiO₂, 5:1 hexanes:EtOAc) to furnish butyrolactone 88 as a colorless oil (39.8 mg, 219 µmol, 61%). Spectroscopic data was identical to that reported in the literature.
3-(1-Methylcyclohexyl)cyclopentan-1-one (90). To a biphasic mixture of 1-methylcyclohexene (20.3 mg, 211 μmol, 1.0 equiv) and Fe(acac)₃ (14.9 mg, 42.2 μmol, 3.0 equiv) in DCE (1.8 mL) and ethylene glycol (0.4 mL) was added cyclopent-2-enone (53.0 μL, 633 mmol, 3.0 equiv), followed by PhSiH₃ (39.0 μL, 317 μmol, 1.5 equiv). The resulting mixture was heated to 60 °C with stirring for 2 h, then cooled to rt, and diluted with H₂O and brine. The organic layer was separated and the aqueous layer was extracted with Et₂O. The organic layers were combined, washed with brine, dried over MgSO₄, filtered, and concentrated under reduced pressure. The red residue was then purified by flash column chromatography (SiO₂, 10:1 hexanes:EtOAc) to furnish cyclopentanone 90 as a colorless oil (24.9 mg, 133 μmol, 63%). Spectroscopic data was identical to that reported in the literature.⁸

1'-Methyl-[1,1'-bi(cyclohexan)]-3-one (92). To a biphasic mixture of 1-methylcyclohexene (34.0 mg, 353 μmol, 1.0 equiv) and Fe(acac)₃ (124.7 mg, 353 μmol, 1.0 equiv) in DCE (2.9 mL) and ethylene glycol (0.6 mL) was added cyclohex-2-enone (103 μL, 1.06 mmol, 3.0 equiv), followed by PhSiH₃ (5.0 μL, 530 μmol, 1.5 equiv). The resulting mixture was heated to 60 °C with stirring for 15 min, then cooled to rt, and diluted with H₂O and brine. The organic layer was separated and the aqueous layer was extracted with Et₂O. The organic layers were combined, washed with brine, dried over MgSO₄, filtered, and concentrated under reduced pressure. The red residue was then purified by preparative TLC (SiO₂, 5:1 hexanes:EtOAc) to furnish cyclohexanone 92 as a viscous, pale yellow oil (26.0 mg, 134 μmol, 38%).

**Physical State:** viscous, pale yellow oil.
$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 2.41 (dddd, $J$=13.6, 4.0, 2.0, 2.0 Hz, 1 H), 2.36 (dddd, $J$=14.2, 4.2, 2.1, 2.1 Hz, 1 H), 2.23 (ddd, $J$=13.8, 13.8, 6.4 Hz, 1 H), 2.13–2.02 (m, 2 H), 2.92 (d, $J$ =13.1 Hz, 1 H), 1.66–1.28 (m, 11 H), and 0.83 (s, 3 H).

$^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 213.5, 42.8, 41.7, 36.2, 35.8, 35.1, 26.5, 25.9, 25.2, 22.0, 21.9, and 19.9. Peak overlapping was observed.

HRMS (m/z): calcd for C$_{13}$H$_{23}$O $[\text{M+H}]^+$: 195.1749; found: 195.1746.

TLC: $R_f$ 0.45 (5:1 hexanes:EtoAc).

Methyl 6-((tert-butyldimethylsilyl)oxy)-4,4-dimethylhexanoate (94). To a biphasic mixture of TBS silyl ether $^9$ (36.3 mg, 181 $\mu$mol, 1.0 equiv) and Fe(acac)$_3$ (12.8 mg, 36.2 $\mu$mol, 0.2 equiv) in DCE (1.5 mL) and ethylene glycol (0.3 mL) was added methyl acrylate (49.0 $\mu$L, 543 $\mu$mol, 3.0 equiv), followed by PhSiH$_3$ (34.0 $\mu$L, 272 $\mu$mol, 1.5 equiv). The resulting mixture was heated to 60 ºC with stirring for 40 min, then cooled to rt, and diluted with H$_2$O and brine. The organic layer was separated and the aqueous layer was extracted with Et$_2$O. The organic layers were combined, washed with brine, dried over MgSO$_4$, filtered, and concentrated under reduced pressure. The red residue was then purified by flash column chromatography (SiO$_2$, 10:1 hexanes:EtoAc) to furnish ester 94 as a pale yellow oil (42.3 mg, 147 $\mu$mol, 81%).

Physical State: pale yellow oil.

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 3.65 (m, 5 H), 2.28 (m, 2 H), 1.56 (m, 2 H), 1.46 (t, $J$=7.3 Hz, 2 H), 0.882 (s, 6 H), 0.877 (s, 9 H), and 0.04 (s, 6 H).

$^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 174.9, 60.0, 51.7, 44.0, 37.2, 32.0, 29.6, 27.2, 26.1, 18.4, and –5.2.

HRMS (m/z): calcd for C$_{15}$H$_{33}$O$_3$Si $[\text{M+H}]^+$: 289.2199; found: 289.2200.

TLC: $R_f$ 0.40 (10:1 hexanes:EtoAc).
6-((tert-Butyldimethylsilyl)oxy)-N,N,4,4-tetramethylhexanamide (95). To a biphasic mixture of TBS silyl ether 59 (32.5 mg, 162 μmol, 1.0 equiv) and Fe(acac)₃ (11.4 mg, 32.4 μmol, 0.2 equiv) in DCE (1.6 mL) and ethylene glycol (0.3 mL) was added N,N-dimethylacrylamide (50.0 μL, 487 μmol, 3.0 equiv), followed by PhSiH₃ (30.0 μL, 243 μmol, 1.5 equiv). The resulting mixture was heated to 60 °C with stirring for 1 h, then cooled to rt, and diluted with H₂O and brine. The organic layer was separated and the aqueous layer was extracted with Et₂O. The organic layers were combined, washed with brine, dried over MgSO₄, filtered, and concentrated under reduced pressure. The red residue was then purified by flash column chromatography (SiO₂, 3:1 hexanes:EtOAc) to furnish amide 95 as a colorless oil (34.4 mg, 114 μmol, 70%).

**Physical State:** colorless oil.

**¹H NMR** (500 MHz, CDCl₃): δ 3.66 (t, 7.5 Hz, 2 H), 3.00 (s, 3 H), 2.93 (s, 3 H), 2.26 (m, 2 H), 1.54 (m, 2 H), 1.48 (t, J=7.6 Hz, 2 H), 0.90 (s, 6 H), 0.87 (s, 9 H), and 0.03 (s, 6 H).

**¹³C NMR** (126 MHz, CDCl₃): δ 173.7, 60.1, 44.2, 37.5, 35.6, 32.0, 28.6, 27.3, 26.1, 18.4, and −5.1.

**HRMS (m/z):** calcd for C₁₆H₃₆NO₂Si [M+H]⁺: 302.2515; found: 302.2517.

**TLC:** Rf 0.30 (3:1 hexanes:EtOAc).

6-((tert-Butyldimethylsilyl)oxy)-4,4-dimethylhexanenitrile (96). To a biphasic mixture of TBS silyl ether 59 (34.0 mg, 169 μmol, 1.0 equiv) and Fe(acac)₃ (23.9 mg, 67.9 μmol, 0.4 equiv) in DCE (1.4 mL) and ethylene glycol (0.3 mL) was added acrylonitrile (34 μL, 509 μmol, 3.0 equiv), followed by PhSiH₃ (31.0 μL, 254 μmol, 1.5 equiv). The resulting mixture was heated to 60 °C with stirring for 1 h, then cooled to rt, and diluted with H₂O and brine. The organic layer was separated and the aqueous layer was extracted with Et₂O. The organic layers were combined, washed with brine, dried over MgSO₄, filtered, and concentrated under reduced
pressure. The red residue was then purified by preparative TLC (SiO₂, 10:1 hexanes:EtOAc) to furnish nitrile 96 as a pale yellow oil (35.0 mg, 137 μmol, 81%).

**Physical State:** pale yellow oil.

**1H NMR** (500 MHz, CDCl₃): δ 3.66 (t, J=6.8 Hz, 2 H), 2.31 (m, 2 H), 1.67 (m, 2 H), 1.45 (t, J=6.7 Hz, 2 H), 0.92 (s, 3 H), 0.89 (s, 9 H), and 0.05 (s, 6 H).

**13C NMR** (126 MHz, CDCl₃): δ 120.7, 59.7, 43.2, 37.8, 32.4, 27.1, 26.1, 18.4, 12.6, and -5.3.

**HRMS (m/z):** calcd for C₁₄H₂₉NOSi [M+H]⁺: 256.2097; found: 256.2091.

**TLC:** Rₚ 0.40 (10:1 hexanes:EtOAc).

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3-(4-((tert-Butyldimethylsilyl)oxy)-2-methylbutan-2-yl)cyclopentan-1-one (97). To a biphasic mixture of TBS silyl ether 59 (38.5 mg, 192 μmol, 1.0 equiv) and Fe(acac)₃ (27.1 mg, 76.8 μmol, 0.4 equiv) in DCE (1.6 mL) and ethylene glycol (0.3 mL) was added cyclopent-2-enone (48.0 μL, 576 μmol, 3.0 equiv), followed by PhSiH₃ (35.0 μL, 288 μmol, 1.5 equiv). The resulting mixture was heated to 60 °C with stirring for 1 h, then cooled to rt, and diluted with H₂O and brine. The organic layer was separated and the aqueous layer was extracted with Et₂O. The organic layers were combined, washed with brine, dried over MgSO₄, filtered, and concentrated under reduced pressure. The red residue was then purified by flash column chromatography (SiO₂, 10:1 hexanes:EtOAc) to furnish cyclopentanone 97 as a colorless oil (32.8 mg, 115 μmol, 60%).

**Physical State:** colorless oil.

**1H NMR** (500 MHz, CDCl₃): δ 3.70 (dd, J=7.4, 7.4 Hz, 2 H), 2.32 (br dd, J=18.4, 8.2 Hz, 1 H), 2.22 (br dd, J=17.7, 7.0 Hz, 1 H), 2.17–2.06 (m, 2 H), 2.03–1.99 (m, 1 H), 1.94 (ddd, J=17.6, 12.4, 1.3 Hz, 1 H), 1.60 (dddd, J=11.9, 11.9, 11.9, 8.5 Hz, 1 H), 1.51 (ddd, J=7.1, 7.1, 2.4 Hz, 2 H), 0.91 (s, 3 H), 0.89 (s, 3 H), 0.88 (s, 9 H), and 0.05 (s, 6 H).

**13C NMR** (126 MHz, CDCl₃): δ 219.7, 59.9, 47.3, 43.3, 40.3, 39.4, 33.8, 26.1, 24.6, 24.3, 24.0, 18.4, and -5.2. Peak overlapping was observed.

**HRMS (m/z):** calcd for C₁₆H₃₅O₂Si [M+H]⁺: 285.2250; found: 285.2231.

**TLC:** Rₚ 0.35 (10:1 hexanes:EtOAc).
3-(4-((tert-Butyldimethylsilyl)oxy)-2-methylbutan-2-yl)-2-methylcyclopentan-1-one (99). To a biphasic mixture of TBS silyl ether 599 (30.0 mg, 150 µmol, 1.0 equiv) and Fe(acac)₃ (10.5 mg, 29.7 µmol, 0.2 equiv) in DCE (1.3 mL) and ethylene glycol (0.3 mL) was added cyclopent-2-enone (42.8 µL, 450 µmol, 3.0 equiv), followed by PhSiH₃ (28.0 µL, 225 µmol, 1.5 equiv). The resulting mixture was heated to 60 °C with stirring for 4 h, then cooled to rt, and diluted with H₂O and brine. The organic layer was separated and the aqueous layer was extracted with Et₂O. The organic layers were combined, washed with brine, dried over MgSO₄, filtered, and concentrated under reduced pressure. The red residue was then purified by flash column chromatography (SiO₂, 10:1 hexanes:EtOAc) to furnish a diastereomeric 2:1 mixture of cyclopentanones 99 as a colorless oil (16.8 mg, 56.3 µmol, 38%).

**Physical State:** colorless oil.

**¹H NMR** (500 MHz, CDCl₃): δ 3.71 (m, 4 H), 2.40–2.29 (m, 2 H), 2.18–2.08 (m, 2H), 1.95–1.93 (m, 4 H), 1.75–1.69 (m, 2 H), 1.65–1.58 (m, 4 H), 1.54–1.47 (m, 2 H), 1.18 (d, J=7.0 Hz, 3 H), 1.08 (d, J=7.6 Hz, 3 H), 1.00 (s, 3 H), 0.99 (s, 3 H), 0.96 (s, 3 H), 0.93 (s, 3 H), 0.89 (s, 18 H), and 0.05 (m, 12 H).

**¹³C NMR** (126 MHz, CDCl₃): δ 222.5, 222.1, 60.0, 59.9, 53.8, 50.8, 46.2, 45.5, 44.2, 43.2, 37.7, 37.4, 34.6, 34.5, 26.7, 26.1, 25.9, 25.6, 25.0, 22.4, 21.3, 18.4, 17.3, 12.9, 12.8, and –5.1. Peak overlapping was observed.

**HRMS (m/z):** calcd for C₁₇H₃₅O₂Si [M+H]⁺: 299.2406; found: 299.2403.

**TLC:** Rₜ 0.35 (10:1 hexanes:EtOAc).
9-(4-((tert-Butyldimethylsilyl)oxy)-2-methylbutan-2-yl)-9,10-dihydroacridine (101). To a biphasic mixture of TBS silyl ether 59 (23.8 mg, 118 µmol, 1.0 equiv) and Fe(acac)₃ (8.3 mg, 23.5 µmol, 0.2 equiv) in DCE (1.0 mL) and ethylene glycol (0.2 mL) was added acridine (23.6 mg, 132 µmol, 1.1 equiv), followed by PhSiH₃ (22.0 µL, 178 µmol, 1.5 equiv). The resulting mixture was heated to 60 °C with stirring for 3h, then cooled to rt, and diluted with H₂O and brine. The organic layer was separated and the aqueous layer was extracted with Et₂O. The organic layers were combined, washed with brine, dried over MgSO₄, filtered, and concentrated under reduced pressure. The red residue was then purified by flash column chromatography (SiO₂, 10:1 hexanes:EtOAc) to furnish dihydroacridine 101 as a colorless solid (21.6 mg, 56.6 µmol, 48%).

**Physical State:** colorless solid.

**¹H NMR** (400 MHz, CDCl₃): δ 7.17–7.12 (m, 4 H), 6.91 (dd, J=6.9, 6.9 Hz, 2 H), 6.76 (d, J=7.8 Hz, 2 H), 6.01 (s, 1 H), 3.76 (s, 1 H), 3.68 (dd, J=7.3, 7.3 Hz, 2 H), 1.50 (dd, J=7.3, 7.3 Hz, 2 H), 0.88 (s, 9 H), 0.79 (s, 6 H), and 0.03 (s, 6 H).

**¹³C NMR** (101 MHz, CDCl₃): δ 141.5, 131.3, 127.0, 121.3, 120.1, 113.7, 60.5, 52.8, 40.8, 40.3, 26.1, 24.5, 18.4, and -5.1.

**HRMS (m/z):** calcd for C₂₄H₃₅NOSi [M+H]⁺: 382.2566; found: 382.2560.

**TLC:** R₇ 08.40 (10:1 hexanes:EtOAc).
Experimental Procedures and Characterization Data for the Functionalized Olefin Cross-Coupling Products.

**General Procedure 2. Functionalized olefin cross-coupling.** To a solution of donor olefin in EtOH or n-PrOH was added anhydrous Na$_2$HPO$_4$, Fe(dibm)$_3$ or Fe(acac)$_3$, acceptor olefin, and PhSiH$_3$ [CAUTION: H$_2$ evolution is occasionally observed upon addition of PhSiH$_3$]. The resulting mixture was stirred at rt or heated in an oil bath preheated to 60 °C or 80 °C with stirring for the indicated time (typically until TLC analysis indicated the consumption of starting material). The reaction mixture was then cooled to rt and diluted with brine and EtOAc. The organic layer was separated and the aqueous layer was extracted with EtOAc. The organic layers were combined, washed with brine, dried over Na$_2$SO$_4$, filtered, and concentrated under reduced pressure. The resulting crude product was then purified on SiO$_2$ (preparative TLC or flash column chromatography) to furnish the coupled product.

3-(2-(((tert-Butyldimethylsilyl)oxy)propan-2-yl)cyclohexan-1-one (122). Following General Procedure 2, a mixture of tert-butyldimethyl(prop-1-en-2-yloxy)silane$^{14}$ (51.7 mg, 300 µmol, 3.0 equiv), cyclohex-2-enone (9.6 mg, 100 µmol, 1.0 equiv), Na$_2$HPO$_4$ (14.2 mg, 100 µmol, 1.0 equiv), Fe(dibm)$_3$ (2.6 mg, 5.0 µmol, 5 mol%), and PhSiH$_3$ (25.0 µL, 200 µmol, 2.0 equiv) in EtOH (0.50 mL) was heated at 60 °C with stirring for 1 h. Purification by flash column chromatography (SiO$_2$, 10:1 hexanes:EtOAc) furnished silyl ether 122 as a pale yellow oil (21.9 mg, 78.1 µmol, 78%).

**Physical State:** pale yellow oil.

$^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 2.48 (dddd, $J=13.9, 4.1, 2.1, 2.1$ Hz, 1 H), 2.34 (dddd, $J=14.3, 4.2, 2.2, 2.2, 2.2$ Hz, 1 H), 2.25–2.19 (m, 2 H), 2.09 (dddd, $J=3.2, 3.2, 3.2, 6.1, 12.6$ Hz, 1 H), 1.97 (dddddd, $J=13.0, 3.5, 3.5, 3.5, 1.8, 1.8, 1$ H), 1.64 (dddd, $J=12.4, 12.4, 3.6, 3.6$ Hz, 1 H),

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$^{14}$ Mikami, K.; Matsumoto, S.; Ishida, A.; Takamuku, S.; Suenobu, T.; Fukuzumi, S. *J. Am. Chem. Soc.* 1995, *117*, 11134.
1.56 (dddddd, J=13.4, 13.4, 13.4, 3.9, 3.9, 1 H), 1.46 (dddd, J=13.0, 13.0, 11.7, 3.3 Hz, 1 H), 1.22 (s, 3 H), 1.18 (s, 3 H), 0.86 (s, 9 H), 0.08 (s, 3 H), and 0.07 (s, 3 H).

$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 213.4, 74.6, 50.8, 43.3, 41.5, 28.1, 26.0, 25.3, 19.3, 18.4, and –2.0.

HRMS (m/z): calcd for C$_{15}$H$_{31}$O$_2$Si [M+H]$^+$: 271.2088, found: 271.2087.

TLC: R$_f$=0.55 (10:1 hexanes:EtOAc).

1'-(tert-Butyldimethylsilyl)oxy-[1,1'-bi(cyclohexan)]-3-one (123). A solution of PhSiH$_3$ (4.0 M in EtOH, 78.0 µL, 312 µmol, 2.0 equiv) was added slowly via syringe pump to a mixture of tert-butyl(cyclohex-1-en-1-yloxy)dimethylsilane$^{15}$ (99.4 mg, 468 µmol, 3.0 equiv), cyclohex-2-enone (15.0 mg, 156 µmol, 1.0 equiv), Na$_2$HPO$_4$ (22.1 mg, 156 µmol, 1.0 equiv), and Fe(dibm)$_3$ (4.1 mg, 7.8 µmol, 5 mol%) in EtOH (0.78 mL) while heating at 60 °C with stirring for 1 h. After work up Following General Procedure 2, purification by flash column chromatography (SiO$_2$, 96:4 hexanes:EtOAc) furnished silyl ether 123 as a white solid (17.8 mg, 57.3 µmol, 37%).

Physical State: white solid.

Melting Point: 59.0–60.0 °C.

$^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 2.38–2.30 (m, 3 H), 2.21 (ddd, J=13.6, 6.8, 6.8 Hz, 1 H), 2.12–2.03 (m, 2 H), 1.89–1.85 (m, 2 H), 1.74–1.72 (m, 1 H), 1.65–1.50 (m, 5 H), 1.39 (ddd, J=12.4, 12.4, 3.5 Hz, 1 H), 1.36–1.20 (m, 4 H), 0.87 (s, 9 H), 0.10 (s, 3 H), and 0.08 (s, 3 H).

$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 213.9, 76.6, 42.7, 42.1, 41.5, 36.8, 36.2, 26.1, 25.7, 25.4, 24.5, 23.1, 23.0, 18.7, –1.6, and –1.6.

HRMS (m/z) calcd for C$_{18}$H$_{35}$O$_2$Si [M+H]$^+$: 311.2401, found: 311.2402.

TLC: R$_f$=0.44 (9:1 hexanes:EtOAc)

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$^{15}$ Kopta, I.; Rathke, M. W. J. Org. Chem. 1981, 46, 3771.
5-((tert-Butyldimethylsilyloxy)-5-methylhexan-2-one (139). Following General Procedure 2, a mixture of tert-butyldimethyl(prop-1-en-2-yloxy)silane\(^\text{14}\) (17.3 mg, 100 µmol, 1.0 equiv), methyl vinyl ketone (24.9 µL, 300 µmol, 3.0 equiv), Na\(_2\)HPO\(_4\) (14.2 mg, 100 µmol, 1.0 equiv), Fe(dibm\(_3\)) (2.6 mg, 5.0 µmol, 5 mol%), and PhSiH\(_3\) (24.6 µL, 200 µmol, 2.0 equiv) in EtOH (0.50 mL) was heated at 60 °C with stirring for 1 h. Purification by flash column chromatography (SiO\(_2\), 97:3 hexanes:EtOAc) furnished silyl ether 139 as a colorless oil (16.8 mg, 68.8 µmol, 69%).

**Physical State**: colorless oil

\(\text{\(^1H\) NMR (600 MHz, CDCl}\(_3\))}: \(\delta\) 2.54 (t, \(J=7.8\) Hz, 2 H), 2.16 (s, 3 H), 1.69 (t, \(J=7.8\) Hz, 2 H), 1.20 (s, 6 H), 0.85 (s, 9 H), and 0.07 (s, 6 H).

\(\text{\(^13C\) NMR (151 MHz, CDCl}\(_3\))}: \(\delta\) 209.8, 72.8, 39.1, 38.5, 30.1, 29.9, 26.0, 18.2, and −1.9.

**HRMS (m/z)** calcld for C\(_{13}\)H\(_{29}\)O\(_2\)Si [M+H]\(^+\): 245.1931, found: 245.1928.

**TLC**: \(R_f\)=0.33 (97:3 hexanes:EtOAc)

4-((tert-Butyldimethylsilyloxy)-3,4-dimethylpentanal (140). Following General Procedure 2, a mixture of tert-butyldimethyl(prop-1-en-2-yloxy)silane\(^\text{14}\) (17.2 mg, 100 µmol, 1.0 equiv), (E)-but-2-enal (25.0 µL, 300 µmol, 3.0 equiv), Na\(_2\)HPO\(_4\) (14.2 mg, 100 µmol, 1.0 equiv), Fe(dibm\(_3\)) (2.6 mg, 5 µmol, 5 mol%), and PhSiH\(_3\) (25.0 µL, 200 µmol, 2.0 equiv) in EtOH (0.50 mL) was heated at 60 °C with stirring for 1 h. Purification by flash column chromatography (SiO\(_2\), 20:1 hexanes:EtOAc) furnished silyl ether 140 as a pale yellow oil (9.7 mg, 39.6 µmol, 40%).

**Physical State**: pale yellow oil.

\(\text{\(^1H\) NMR (600 MHz, CDCl}\(_3\))}: \(\delta\) 9.76 (dd, \(J=3.0, 1.8\) Hz, 1 H), 2.74 (dd, \(J=16.2, 3.0\) Hz, 1 H), 2.16 (ddd, \(J=16.2, 9.2, 3.0\) Hz, 1 H), 2.08 (dq, \(J=10.2, 6.5, 3.5, 1\) H), 1.23 (s, 3 H), 1.14 (s, 3 H), 0.92 (d, \(J=7.2\) Hz, 3 H), 0.85 (s, 9 H), 0.09 (s, 3 H) and 0.08 (s, 3 H).
$^{13}$C NMR (151 MHz, CDCl$_3$): δ 203.5, 75.4, 47.1, 40.0, 28.7, 26.0, 25.9, 18.3, 15.9, –1.9, and –2.0.

GC/MS (m/z): [M–Me]$^+$: 229, [M–t-Bu]$^+$: 187, [M–CH(CH$_3$)CH$_2$CHO]$^+$: 173.

TLC: $R_f$=0.45 (20:1 hexanes:EtOAc).

$^{13}$C NMR (151 MHz, C$_6$D$_6$): δ 209.8, 77.4, 42.6, 41.4, 36.0, 35.8, 30.2, 26.1, 25.3, 25.2, 22.9, 22.8, and 2.9.

HRMS (m/z) calcd for C$_{15}$H$_{29}$O$_2$Si [M+H]$^+$: 269.1931, found: 269.1933.

TLC: $R_f$=0.41 (9:1 hexanes:EtOAc)

I’-((Trimethylsilyl)oxy) -[1,1'-bi(cyclohexan)]-3-one (142). A solution of PhSiH$_3$ (4.0 M in EtOH, 78.0 µL, 312 µmol, 2.0 equiv) was added slowly via syringe pump to a mixture of (cyclohex-1-en-1-yloxy)trimethylsilane$^{16}$ (79.2 mg, 468 µmol, 3.0 equiv), cyclohex-2-enone (15.0 mg, 156 µmol, 1.0 equiv), Na$_2$HPO$_4$ (22.1 mg, 156 µmol, 1.0 equiv), and Fe(dibm)$_3$ (4.1 mg, 7.8 µmol, 5 mol%) in EtOH (0.78 mL) while heating at 60 °C with stirring for 1 h. After work up Following General Procedure 2, purification by flash column chromatography (SiO$_2$, 96:4 hexanes:EtOAc) furnished silyl ether 142 as a colorless oil (19.1 mg, 71.1 µmol, 46%).

Physical State: colorless oil.

$^1$H NMR (600 MHz, CDCl$_3$): δ 2.38 (dddd, $J$=14.0, 4.1, 2.1, 2.1 Hz, 1 H), 2.36–2.32 (m, 1 H), 2.26–2.20 (m, 2 H), 2.10 (dddd, $J$=16.4, 6.4, 3.4, 3.4 Hz, 1 H), 1.94 (dddd, $J$=11.8, 11.8, 3.8, 3.8 Hz, 1 H), 1.90–1.84 (m, 1 H), 1.71–1.67 (m, 1 H), 1.62–1.52 (m, 4 H), 1.51–1.31 (m, 7 H), and 0.12 (s, 9 H).

$^{13}$C NMR (151 MHz, C$_6$D$_6$): δ 209.8, 77.4, 42.6, 41.4, 36.0, 35.8, 30.2, 26.1, 25.3, 25.2, 22.9, 22.8, and 2.9.

HRMS (m/z) calcd for C$_{15}$H$_{29}$O$_2$Si [M+H]$^+$: 269.1931, found: 269.1933.

TLC: $R_f$=0.41 (9:1 hexanes:EtOAc)

$^{16}$ Lin, J.-M.; Liu, B.-S. Synth. Commun. 1997, 27, 739.
1'-(Triethylsilyloxy)-[1,1'-bi(cyclohexan)]-3-one (144). A solution of PhSiH₃ (4.0 M in EtOH, 78.0 µL, 312 µmol, 2.0 equiv) was added slowly via syringe pump to a mixture of (cyclohex-1-en-1-yl oxy)triethylsilane¹⁷ (99.4 mg, 468 µmol, 3.0 equiv), cyclohex-2-enone (15.0 mg, 156 µmol, 1.0 equiv), Na₂HPO₄ (22.1 mg, 156 µmol, 1.0 equiv), and Fe(dibm)₃ (4.1 mg, 7.8 µmol, 5 mol%) in EtOH (0.78 mL) while heating at 60 °C with stirring for 1 h. After work up Following General Procedure 2, purification by flash column chromatography (SiO₂, 95:5 hexanes:EtOAc) furnished silyl ether 144 as a colorless oil (15.9 mg, 51.2 µmol, 33%).

**Physical State:** colorless oil.

¹H NMR (600 MHz, CDCl₃): δ 2.35–2.30 (m, 3 H), 2.25–2.20 (m, 1 H), 2.12–2.10 (m, 1 H), 2.05–2.01 (m, 1 H), 1.88–1.83 (m, 2 H), 1.73–1.68 (m, 1 H), 1.59–1.50 (m, 5 H), 1.41–1.20 (m, 5 H), 0.96 (t, J=7.8 Hz, 9 H), and 0.60 (q, J=7.8 Hz, 6 H).

¹³C NMR (151 MHz, CDCl₃): δ 214.0, 76.4, 42.9, 42.2, 41.5, 37.0, 36.5, 25.8, 25.4, 24.6, 23.2, 23.1, 7.5, and 7.2.

HRMS (m/z): calcd for C₁₈H₃₅O₂Si [M+H]⁺: 311.2401, found: 311.2402.

TLC: Rₗ=0.44 (9:1 hexanes:EtOAc)

1'-(Triisopropylsilyloxy)-[1,1'-bi(cyclohexan)]-3-one (146). A solution of PhSiH₃ (4.0 M in EtOH, 78.0 µL, 312 µmol, 2.0 equiv) was added slowly via syringe pump to a mixture of (cyclohex-1-en-1-yl oxy)triisopropylsilane¹⁸ (119.1 mg, 468 µmol, 3.0 equiv), cyclohex-2-enone (15.0 mg, 156 µmol, 1.0 equiv), Na₂HPO₄ (22.1 mg, 156 µmol, 1.0 equiv), and Fe(dibm)₃ (4.1 mg, 7.8 µmol, 5 mol%) in EtOH (0.78 mL) while heating at 60 °C with stirring for 1 h. After work up Following General Procedure 2, purification by flash column chromatography (SiO₂, 95:5 hexanes:EtOAc) followed by preparative TLC (SiO₂, 95:5 hexanes:EtOAc) furnished silyl ether 146 as a colorless oil (4.3 mg, 13.3 µmol, 9%).

**Physical State:** colorless oil.

¹⁷ Shen, Z.-L.; Peng, Z.; Yang, C.-M.; Helberg, J.; Mayer, P.; Marek, I.; Knochel, P. Org. Lett. 2014, 16, 956.

¹⁸ Yu, J.-Q.; Wu, H.-C.; Corey, E. J. Org. Lett. 2005, 7, 5953.
$^1$H NMR (600 MHz, CDCl$_3$): δ 2.47 (dd, $J$=13.7, 13.7 Hz, 1 H), 2.38–2.33 (m, 2 H), 2.23 (ddd, $J$=13.7, 13.7, 6.0 Hz, 1 H), 2.16 (ddddd, $J$=12.1, 12.1, 3.8, 3.8 Hz, 1 H), 2.13–2.10 (m, 1 H), 2.06–
2.02 (m, 1 H), 1.87–1.84 (m, 2 H), 1.59–1.57 (m, 4 H), 1.41 (ddddd, $J$=13.1, 13.1, 3.7 Hz, 1 H), 1.33 (ddddd, $J$=12.8, 12.8, 3.2 Hz, 1 H), 1.29–1.22 (m, 3 H), 1.21–1.13 (m, 1 H), and 1.10–1.04 (m, 21 H).

$^{13}$C NMR (151 MHz, CDCl$_3$): δ 214.2, 76.4, 42.1, 41.6, 41.5, 37.5, 37.0, 25.6, 25.6, 24.4, 23.5, 23.5, 18.7, and 13.9.

HRMS (m/z) calcd for C$_{21}$H$_{41}$O$_2$Si [M+H]$^+$: 353.2870, found: 353.2868.

TLC: R$_f$=0.44 (9:1 hexanes:EtOAc).

Diethyl 2-(1-(tetrahydrofuran-2-yl)ethyl)malonate (148). Following General Procedure 2, a mixture of 2,3-dihydrofuran (14.0 mg, 200 µmol, 1.0 equiv), diethyl ethylidenemalonate (109.6 µL, 600 µmol, 3.0 equiv), Na$_2$HPO$_4$ (28.4 mg, 200 µmol, 1.0 equiv), Fe(dibm)$_3$ (5.2 mg, 10 µmol, 5 mol%), and PhSiH$_3$ (49.2 µL, 400 µmol, 2.0 equiv) in EtOH (1.0 mL) was heated at 60 °C with stirring for 1 h. Purification by flash column chromatography (SiO$_2$, 20:1→10:1 hexanes:EtOAc) furnished a 1:1.2 diastereomeric mixture of ethers 148 as a colorless oil (27.9 mg, 108.1 µmol, 54%).

Spectroscopic data was identical to that reported in the literature.  

Diethyl 2-(1-(tetrahydro-2H-pyran-2-yl)ethyl)malonate (150). Following General Procedure 2, a mixture of 3,4-dihydro-2H-pyran (16.8 mg, 200 µmol, 1.0 equiv), diethyl ethylidenemalonate (110 µL, 600 µmol, 3.0 equiv), Na$_2$HPO$_4$ (28.4 mg, 200 µmol, 1.0 equiv),

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19 Chu, L.; Ohta, C.; Zuo, Z.; MacMillan, D. W.C. J. Am. Chem. Soc. 2014, 136, 10886.
Fe(dibm)$_3$ (5.2 mg, 10 µmol, 5 mol%), and PhSiH$_3$ (49.2 µL, 400 µmol, 2.0 equiv) in EtOH (1.0 mL) was heated at 60 °C with stirring for 1 h. Purification by flash column chromatography (SiO$_2$, 50:1→20:1 hexanes:EtOAc) furnished a 1:1.8 diastereomeric mixture of ethers 150 as a colorless oil (41.1 mg, 15.1 µmol, 76%). Spectroscopic data was identical to that reported in the literature.$^{19}$

![151](image)

4-(Tetrahydro-2H-pyran-2-yl)butan-2-one (151). Following General Procedure 2, a mixture of 3,4-dihydro-2H-pyran (54.6 µL, 600 µmol, 3.0 equiv), methyl vinyl ketone (16.5 µL, 200 µmol, 1.0 equiv), Na$_2$HPO$_4$ (28.4 mg, 200 µmol, 1.0 equiv), Fe(dibm)$_3$ (5.2 mg, 10 µmol, 5 mol%), and PhSiH$_3$ (49.2 µL, 400 µmol, 2.0 equiv) in EtOH (1.0 mL) was stirred at rt for 1 h. Purification by flash column chromatography (SiO$_2$, 6:1→5:1 pentanes:Et$_2$O) furnished ether 151 as a colorless oil (13.5 mg, 86.5 µmol, 43%). Spectroscopic data was identical to that reported in the literature.$^{20}$

![153](image)

5-Butoxyhexan-2-one (153). Following General Procedure 2, a mixture of butyl vinyl ether (54.6 µL, 600 µmol, 3.0 equiv), methyl vinyl ketone (16.5 µL, 200 µmol, 1.0 equiv), Na$_2$HPO$_4$ (28.4 mg, 200 µmol, 1.0 equiv), Fe(dibm)$_3$ (5.2 mg, 10 µmol, 5 mol%), and PhSiH$_3$ (49.2 µL, 400 µmol, 2.0 equiv) in EtOH (1.0 mL) was heated at 60 °C with stirring for 1 h. Purification by flash column chromatography (SiO$_2$, 50:1→20:1 hexanes:EtOAc) furnished ether 153 as a colorless oil (17.6 mg, 102 µmol, 51%).

**Physical State:** colorless oil.

$^1$H NMR (600 MHz, CDCl$_3$): δ 3.46 (ddd, $J$=9.0, 6.0, 6.0 Hz, 1 H), 3.37–3.34 (m, 1 H), 3.26 (ddd, $J$=9.6, 6.6, 6.6 Hz, 1 H), 2.54–2.46 (m, 2 H), 2.13 (s, 3 H), 1.75–1.73 (m, 1 H), 1.71–1.64

$^{20}$ Mori, T.; Maniguchi, M.; Suzuki, F.; Doi, H.; Oku, A. *J. Chem. Soc., Perkin Trans. 1* 1998, 3623.
(m, 1 H), 1.53–1.46 (m, 2 H), 1.37–1.32 (m, 2 H), 1.11 (d, \(J=6.0\ \text{Hz},\ 3 \text{H}\)), and 0.90 (t, \(J=7.2\ \text{Hz},\ 3 \text{H}\)).

\(^{13}\text{C NMR}\ (151 \text{ MHz, CDCl}_3):\ \delta 209.2, 74.3, 68.3, 39.8, 32.3, 30.7, 30.1, 19.8, 19.5, \text{and} 14.0.

\text{HRMS (}\text{m/z}\text{): calcd for C}_{10}\text{H}_{21}\text{O}_2 [\text{M+H}]^+: 173.1536, \text{found: 173.1546.}

\text{TLC: R}_f=0.21 (10:1 \text{hexanes:EtoAc}).

\[ \text{Me} \quad \begin{array}{c} \text{CN} \\ \text{OPh} \end{array} \quad 155 \]

\textbf{4-Phenoxy-1-pentanitrile (155).} Following General Procedure 2, a mixture of phenyl vinyl ether (36.0 mg, 300 \(\mu\text{mol},\ 3.0\ \text{equiv}\)), acrylonitrile (6.58 \(\mu\text{L},\ 100 \mu\text{mol},\ 1.0\ \text{equiv}\)), Na\(_2\)HPO\(_4\) (14.2 mg, 100 \(\mu\text{mol},\ 1.0\ \text{equiv}\)), Fe(dibm)\(_3\) (2.6 mg, 5.0 \(\mu\text{mol},\ 5\ \text{mol}\%\)), and PhSiH\(_3\) (25.0 \(\mu\text{L},\ 200 \mu\text{mol},\ 2.0\ \text{equiv}\)) in EtOH (0.50 mL) was heated at 60 °C with stirring for 1 h. Purification by flash column chromatography (SiO\(_2\), 10:1 \text{hexanes:EtoAc}) furnished ether 155 as a pale yellow oil (10.4 mg, 59.3 \(\mu\text{mol},\ 59\\%\)).

\textbf{Physical State:} pale yellow oil.

\(^1\text{H NMR}\ (600 \text{ MHz, CDCl}_3):\ \delta 7.31–7.27 (m, 2 \text{H}), 6.97 (dddd, \(J=7.3,\ 7.3,\ 1.0,\ 1.0\ \text{Hz},\ 1 \text{H}\)), 6.91–6.90 (m, 2 \text{H}), 4.49 (dqd, \(J=4.4,\ 6.1,\ 7.9\ \text{Hz},\ 1 \text{H}\)), 2.54 (dd, \(J=7.2,\ 7.2\ \text{Hz},\ 2 \text{H}\)), 2.06–1.97 (m, 2 \text{H}), \text{and} 1.33 (d, \(J=6.1\ \text{Hz},\ 3 \text{H}\)).

\(^{13}\text{C NMR}\ (151 \text{ MHz, CDCl}_3):\ \delta 157.5, 129.8, 121.5, 119.7, 116.2, 71.8, 32.5, 19.5, \text{and} 13.8.

\text{HRMS (}\text{m/z}\text{): calcd for C}_{11}\text{H}_{14}\text{NO [M+H]}^+: 176.1070, \text{found: 176.1074.}

\text{TLC: R}_f=0.20 (10:1 \text{hexanes:EtoAc}).

\[ \text{Me} \quad \begin{array}{c} \text{O} \\ \text{OMe} \end{array} \quad 156 \]

\textbf{Methyl 4-phenoxypentanoate (156).} Following General Procedure 2, a mixture of phenyl vinyl ether (36.0 mg, 300 \(\mu\text{mol},\ 3.0\ \text{equiv}\)), methyl acrylate (9.00 \(\mu\text{L},\ 100 \mu\text{mol},\ 1.0\ \text{equiv}\)), Na\(_2\)HPO\(_4\) (14.2 mg, 100 \(\mu\text{mol},\ 1.0\ \text{equiv}\)), Fe(dibm)\(_3\) (2.6 mg, 5.0 \(\mu\text{mol},\ 5\ \text{mol}\%\)), and PhSiH\(_3\) (25.0 \(\mu\text{L},\ 200 \mu\text{mol},\ 2.0\ \text{equiv}\)) in EtOH (0.50 mL) was heated at 60 °C with stirring for 1 h. Purification
by flash column chromatography (SiO₂, 10:1 hexanes:EtOAc) furnished ether 156 as a pale yellow oil (12.1 mg, 58.1 µmol, 58%).

**Physical State:** pale yellow oil.

**¹H NMR** (600 MHz, CDCl₃): δ 7.27–7.25 (m, 2 H), 6.92 (ddddd, J=7.4, 7.4, 1.0, 1.0 Hz, 1 H), 6.88–6.66 (m, 2 H), 4.41 (dqd, J=4.7, 6.0, 7.5 Hz, 1 H), 3.65 (s, 3 H), 2.53–2.42 (m, 2 H), 2.04–1.93 (m, 2 H), and 1.30 (d, J=6.1 Hz, 3 H).

**¹³C NMR** (151 MHz, CDCl₃): δ 174.1, 158.0, 129.6, 120.9, 116.0, 72.7, 51.7, 31.7, 30.2, and 19.7.

**HRMS (m/z):** calcd for C₁₂H₁₇O₃ [M+H]⁺: 209.1172, found: 209.1169.

**TLC:** Rₓ=0.35 (10:1 hexanes:EtOAc).

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5-Phenoxy-2-hexanone (157). Following General Procedure 2, a mixture of phenyl vinyl ether (36.0 mg, 300 µmol, 3.0 equiv), methyl vinyl ketone (8.11 µL, 100 µmol, 1.0 equiv), Na₂HPO₄ (14.2 mg, 100 µmol, 1.0 equiv), Fe(dibm)₃ (2.6 mg, 5.0 µmol, 5 mol%), and PhSiH₃ (25.0 µL, 200 µmol, 2.0 equiv) in EtOH (0.50 mL) was heated at 60 °C with stirring for 1 h. Purification by flash column chromatography (SiO₂, 5:1 hexanes:EtOAc) furnished ether 157 as a pale yellow oil (5.9 mg, 30.6 µmol, 31%).

**Physical State:** pale yellow oil.

**¹H NMR** (600 MHz, CDCl₃): δ 7.28–7.25 (m, 2 H), 6.92 (dd, J=7.3, 7.3 Hz, 1 H), 6.87 (d, J=8.0 Hz, 2 H), 4.40 (dqd, J=6.1, 6.1, 6.1 Hz, 1 H), 2.66–2.55 (m, 2 H), 2.13 (s, 3 H), 1.98–1.89 (m, 2 H), and 1.29 (d, J=6.1 Hz, 3 H).

**¹³C NMR** (151 MHz, CDCl₃): δ 208.7, 158.0, 134.3, 129.7, 127.8, 120.8, 115.9, 72.8, 39.6, 30.6, 30.2, and 19.9.

**HRMS (m/z):** calcd for C₁₂H₁₇O₂ [M+H]⁺: 193.1223, found: 193.1226.

**TLC:** Rₓ=0.40 (10:1 hexanes:EtOAc).
Benzyl 2-(3-(benzyloxy)-3-oxopropyl)pyrrolidine-1-carboxylate (160). Following General Procedure 2, a mixture of benzyl 2,3-dihydro-1H-pyrrole-1-carboxylate\textsuperscript{21} (30.0 mg, 148 µmol, 1.0 equiv), benzyl acrylate (67.8 µL, 443 µmol, 3.0 equiv), Na\textsubscript{2}HPO\textsubscript{4} (21.0 mg, 148 µmol, 1.0 equiv), Fe(dibm)\textsubscript{3} (3.8 mg, 7.4 µmol, 5 mol%), and PhSiH\textsubscript{3} (109 µL, 886 µmol, 6.0 equiv) in EtOH (0.74 mL) was heated at 60 °C with stirring for 10 min. Purification by flash column chromatography (SiO\textsubscript{2}, 8:2 hexanes:EtOAc) furnished carbamate 160 as a pale yellow oil (35.4 mg, 96.3 µmol, 65%). Spectroscopic data was identical to that reported in the literature.\textsuperscript{19}

Benzyl 2-(3-oxocyclopentyl)pyrrolidine-1-carboxylate (161). Following General Procedure 2, a mixture of benzyl 2,3-dihydro-1H-pyrrole-1-carboxylate\textsuperscript{21} (30.0 mg, 148 µmol, 1.0 equiv), cyclopent-2-enone (37.5 µL, 443 µmol, 3.0 equiv), Na\textsubscript{2}HPO\textsubscript{4} (21.0 mg, 148 µmol, 1.0 equiv), Fe(dibm)\textsubscript{3} (3.8 mg, 7.4 µmol, 5 mol%), and PhSiH\textsubscript{3} (109 µL, 886 µmol, 6.0 equiv) in EtOH (0.74 mL) was heated at 60 °C with stirring for 10 min. Purification by flash column chromatography (SiO\textsubscript{2}, 6:4 hexanes:EtOAc) furnished a diastereomeric mixture of carbamates 161 as a pale yellow oil (31.6 mg, 110 µmol, 75%). Spectroscopic data was identical to that reported in the literature.\textsuperscript{19}

\textsuperscript{21} Simpkins, L. M. \textit{et al}. \textit{Bioorg. Med. Chem. Lett.} \textbf{2007}, \textit{17}, 6476.
**Dimethyl 2-(1-((benzyloxy)carbonyl)pyrrolidin-2-yl)succinate (162).** Following General Procedure 2, a mixture of benzyl 2,3-dihydro-1H-pyrrole-1-carboxylate\textsuperscript{21} (30.0 mg, 148 µmol, 1.0 equiv), dimethyl maleate (55.4 µL, 443 µmol, 3.0 equiv), Na\textsubscript{2}HPO\textsubscript{4} (21.0 mg, 148 µmol, 1.0 equiv), Fe(dibm\textsubscript{3}) (3.8 mg, 7.4 µmol, 5 mol%), and PhSiH\textsubscript{3} (36.4 µL, 296 µmol, 2.0 equiv) in EtOH (0.74 mL) was heated at 60 °C with stirring for 10 min. Purification by flash column chromatography (SiO\textsubscript{2}, 7:3 hexanes:EtOAc) furnished a diastereomeric mixture of carbamates 162 as a pale yellow oil (38.7 mg, 111 µmol, 75%). Spectroscopic data was identical to that reported in the literature.\textsuperscript{19}

![Image of 163](image)

**Diethyl 2-(1-((benzyloxy)carbonyl)pyrrolidin-2-yl)ethyl)malonate (163)** Following General Procedure 2, a mixture of benzyl 2,3-dihydro-1H-pyrrole-1-carboxylate\textsuperscript{21} (20.3 mg, 100 µmol, 1.0 equiv), diethyl 2-ethylidenemalonate (54.8 µL, 300 µmol, 3.0 equiv), Na\textsubscript{2}HPO\textsubscript{4} (14.2 mg, 100 µmol, 1.0 equiv), Fe(dibm\textsubscript{3}) (2.6 mg, 5.0 µmol, 5 mol%), and PhSiH\textsubscript{3} (24.6 µL, 200 µmol, 2.0 equiv) in EtOH (0.50 mL) was heated at 60 °C with stirring for 1 h. Purification by flash column chromatography (SiO\textsubscript{2}, 10:1→5:1 hexanes:EtOAc) furnished a diastereomeric mixture of carbamates 163 as a colorless oil (34.3 mg, 87.7 µmol, 88%). Spectroscopic data was identical to that reported in the literature.\textsuperscript{19}

![Image of 165](image)

**Benzyl 2-(3-oxocyclohexyl)piperidine-1-carboxylate (165).** Following General Procedure 2, a mixture of benzyl 3,4-dihydropyridine-1(2H)-carboxylate\textsuperscript{22} (21.7 mg, 100 µmol, 1.0 equiv), cyclohex-2-enone (58.0 µL, 600 µmol, 6.0 equiv), Na\textsubscript{2}HPO\textsubscript{4} (14.2 mg, 100 µmol, 1.0 equiv), Fe(dibm\textsubscript{3}) (7.9 mg, 15.0 µmol, 15 mol%), and PhSiH\textsubscript{3} (73.8 µL, 600 µmol, 6.0 equiv) in EtOH (0.50 mL) was heated at 60 °C with stirring for 1 h. Purification by flash column chromatography furnished a diastereomeric mixture of carbamates 165 as a colorless oil (30.6 mg, 93.6 µmol, 93%). Spectroscopic data was identical to that reported in the literature.\textsuperscript{19}

\textsuperscript{22} Okitsu, O.; Suzuki, R.; Kobayashi, S. *J. Org. Chem.* 2001, 66, 809.
chromatography (SiO₂, 5:1→3:1 hexanes:EtOAc) furnished a 1:1.5 diastereomeric mixture of carbamates 165 as a colorless oil (17.3 mg, 54.6 µmol, 55%). Data is reported for the mixture of diastereomers.

**Physical State:** colorless oil.

**1H NMR** (500 MHz, CDCl₃, 50 °C): δ 7.36–7.34 (m, 5 H), 5.18–5.09 (m, 2 H), 4.13–4.08 (m, 2 H), 2.76–2.70 (m, 1 H), 2.44–2.20 (m, 4 H), 2.13–2.01 (m, 2 H), 1.95–1.71 (m, 2 H), 1.68–1.42 (m, 6 H), and 1.39–1.30 (m, 1 H).

**13C NMR** (126 MHz, acetone-d₆, 45 °C): δ 210.1, 210.0, 156.5, 139.0, 129.6, 129.0, 128.9, 67.7, 67.7, 57.1, 56.8, 46.1, 45.4, 42.0, 41.9, 40.7, 37.9, 28.8, 27.2, 26.6, 26.2, 25.8, 20.1, and 20.0.

**HRMS (m/z):** calcd for C₁₉H₂₆NO₃ [M+H]+: 316.1907, found: 316.1925.

**TLC:** Rᵢ=0.27 (3:1 hexanes:EtOAc).

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Benzyl 2-(3-oxooctyl)piperidine-1-carboxylate (166). Following General Procedure 2, a mixture of benzyl 3,4-dihydropyridine-1(2H)-carboxylate 22 (21.7 mg, 100 µmol, 1.0 equiv), oct-1-en-3-one (44.9 µL, 300 µmol, 3.0 equiv), Na₂HPO₄ (14.2 mg, 100 µmol, 1.0 equiv), Fe(dibm)₃ (2.6 mg, 5.0 µmol, 5 mol%), and PhSiH₃ (24.6 µL, 200 µmol, 2.0 equiv) in EtOH (0.50 mL) was heated at 60 °C with stirring for 1 h. Purification by flash column chromatography (SiO₂, 20:1→10:1 hexanes:EtOAc) furnished carbamate 166 as a colorless oil (21.1 mg, 61.1 µmol, 61%).

**Physical State:** colorless oil.

**1H NMR** (600 MHz, CDCl₃): δ 7.36–7.35 (m, 5 H), 5.13–5.08 (m, 2 H), 4.29–4.27 (m, 1 H), 4.07–3.97 (m, 1 H), 2.83–2.75 (m, 1 H), 2.34–2.21 (m, 4 H), 2.08–1.99 (m, 1 H), 1.62–1.19 (m, 13 H), and 0.87 (t, J=7.2 Hz, 3 H).

**13C NMR** (151 MHz, CDCl₃): δ 210.9, 155.7, 137.1, 128.6, 128.1, 128.0, 67.1, 50.6, 43.1, 39.4, 39.2, 31.5, 29.2, 25.7, 23.7, 23.6, 22.6, 19.1, and 14.1.

**HRMS (m/z):** calcd for C₂₁H₃₁NO₃ [M+H]+: 346.2377, found: 346.2377.

**TLC:** Rᵢ=0.21 (5:1 hexanes:EtOAc).
1-(1-(3-Oxobutyl)cyclohexyl)pyrrolidin-2-one (168). Following General Procedure 2, a mixture of 1-(cyclohex-1-en-1-yl)pyrrolidin-2-one23 (16.5 mg, 100 µmol, 1.0 equiv), methyl vinyl ketone (24.9 µL, 300 µmol, 3.0 equiv), Na₂HPO₄ (14.2 mg, 100 µmol, 1.0 equiv), Fe(dibm)₃ (7.9 mg, 15 µmol, 15 mol%), and PhSiH₃ (73.8 µL, 600 µmol, 6.0 equiv) in EtOH (0.50 mL) was heated at 60 °C with stirring for 1 h. The reaction mixture was then cooled to rt and a second portion of methyl vinyl ketone (24.8 µL, 300 µmol, 3.0 equiv), Fe(dibm)₃ (7.9 mg, 15.0 µmol, 15 mol%), and PhSiH₃ (73.8 µL, 600 µmol, 6.0 equiv) was added. After heating the reaction mixture at 60 °C with stirring for 1 h and work up Following General Procedure 2, purification by flash column chromatography (SiO₂, 1:1→1:2 hexanes:EtOAc→EtOAc) furnished amide 168 as a colorless oil (16.6 mg, 70.0 µmol, 70%).

**Physical State**: colorless oil.

**¹H NMR** (600 MHz, CDCl₃): δ 3.39 (dd, J=7.2, 6.6 Hz, 2 H), 2.50 (dd, J=7.8, 7.2 Hz, 2 H), 2.35–2.32 (m, 4 H), 2.14 (s, 3 H), 1.94–1.90 (m, 4 H), 1.55–1.54 (m, 3 H), and 1.39–1.34 (m, 5 H).

**¹³C NMR** (151 MHz, CDCl₃): δ 209.2, 176.5, 59.4, 45.5, 38.3, 34.7, 33.6, 31.4, 30.2, 25.8, 22.6, and 18.3.

**HRMS (m/z)**: calcd for C₁₄H₂₄NO₂ [M+H]+: 238.1802, found: 238.1806.

**TLC**: Rᵣ=0.18 (1:2 hexanes:EtOAc).

Methyl 4-(benzyl(tert-butoxycarbonyl)amino)-4-methylpentanoate (170). Following General Procedure 2, a mixture of tert-butyl benzyl(prop-1-en-2-yl)carbamate²⁴ (74.2 mg, 300 µmol, 3.0 equiv), methyl acrylate (9.00 µL, 100 µmol, 1.0 equiv), Na₂HPO₄ (14.2 mg, 100 µmol, 1.0

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²³ Pan, C.; Cai, Q.; Ma, D. *Org. Lett.* 2004, 6, 1809.
²⁴ Bach, T.; Schröder, J. *Synthesis* 2001, 1117.
equiv), Fe(dibm)₃ (2.6 mg, 5.0 µmol, 5 mol%), and PhSiH₃ (25.0 µL, 200 µmol, 2.0 equiv) in EtOH (0.50 mL) was heated at 60 °C with stirring for 1 h. Purification by flash column chromatography (SiO₂, 5:1 hexanes:EtOAc) furnished carbamate 170 as a pale yellow oil (23.6 mg, 70.3 µmol, 70%).

**Physical State**: pale yellow oil.

**¹H NMR** (600 MHz, CDCl₃): δ 7.34–7.27 (m, 3 H), 7.21–7.20 (m, 2 H), 4.54 (s, 2 H), 3.66 (s, 3 H), 2.27–2.24 (m, 2 H), 2.22–2.19 (m, 2 H), 1.46 (s, 9 H), and 1.31 (s, 6 H).

**¹³C NMR** (151 MHz, CDCl₃): δ 174.4, 156.1, 141.1, 128.5, 126.6, 126.5, 80.1, 58.4, 51.7, 49.2, 36.0, 30.0, 28.6, and 27.9.

**HRMS (m/z)**: calcd for C₁⁹H₃₀NO₄ [M+H]+: 336.2175, found: 336.2172.

**TLC**: Rₛ=0.50 (5:1 hexanes:EtOAc).

**Benzyl (1-(3-oxocyclohexyl)ethyl)carbamate (172)**. Following General Procedure 2, a mixture of benzyl vinylcarbamate²⁵ (17.7 mg, 100 µmol, 1.0 equiv), cyclohex-2-enone (29.0 µL, 300 µmol, 3.0 equiv), Na₂HPO₄ (14.2 mg, 100 µmol, 1.0 equiv), Fe(dibm)₃ (7.9 mg, 15 µmol, 15 mol%), and PhSiH₃ (73.8 µL, 600 µmol, 6.0 equiv) in EtOH (0.50 mL) was heated at 60 °C with stirring for 1 h. The reaction mixture was then cooled to rt and a second portion of cyclohex-2-enone (29.0 µL, 300 µmol, 3.0 equiv), Fe(dibm)₃ (7.9 mg, 15.0 µmol, 15 mol%), and PhSiH₃ (73.8 µL, 600 µmol, 6.0 equiv) was added. After heating the reaction mixture at 60 °C with stirring for 1 h and work up Following General Procedure 2, purification by flash column chromatography (SiO₂, 5:1→3:1 hexanes:EtOAc) furnished a diastereomeric mixture of carbamates 172 as a colorless oil (13.1 mg, 47.6 µmol, 48%). Data is reported for the mixture of diastereomers.

**Physical State**: colorless oil.

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²⁵ Chanthamath, S.; Nguyen, D. T.; Shibatomi, K.; Iwasa, S. *Org. Lett.* **2013**, *15*, 772.
$^1$H NMR (500 MHz, CDCl$_3$, 50 °C): δ 7.37–7.30 (m, 5 H), 5.13–5.07 (m, 2 H), 4.54 (br s, 1 H), 3.77–3.72 (m, 1 H), 2.47–2.34 (m, 2 H), 2.27–2.20 (m, 1 H), 2.14–2.05 (m, 2 H), 1.95–1.79 (m, 2 H), 1.63–1.54 (m, 1 H), 1.44–1.33 (m, 1 H), and 1.16–1.14 (m, 3H).

$^{13}$C NMR (151 MHz, CDCl$_3$): δ 211.2, 211.2, 156.1, 156.0, 136.5, 128.7, 128.3, 128.3, 128.3, 127.3, 126.5, 50.9, 50.7, 44.9, 44.6, 44.6, 44.0, 42.3, 41.5, 41.4, 35.1, 34.8, 28.2, 27.2, 25.8, 25.4, 25.2, 25.1, 24.9, 22.0, 22.0, 18.7, and 18.2.

HRMS ($m/z$): calcd for C$_{16}$H$_{22}$NO$_3$ [M+H]$^+$: 276.1594, found: 276.1598.

TLC: $R_f$=0.16 (3:1 hexanes:EtOAc).

Benzyl benzyl(1-(3-oxocyclohexyl)ethyl)carbamate (174). Following General Procedure 2, a mixture of benzyl benzyl(vinyl)carbamate$^{26}$ (26.7 mg, 100 µmol, 1.0 equiv), cyclohex-2-enone (58.0 µL, 600 µmol, 6.0 equiv), Na$_2$HPO$_4$ (14.2 mg, 100 µmol, 1.0 equiv), Fe(dibm)$_3$ (7.9 mg, 15.0 µmol, 15 mol%), and PhSiH$_3$ (73.8 µL, 600 µmol, 6.0 equiv) in EtOH (0.50 mL) was heated at 60 °C with stirring for 1 h. Purification by flash column chromatography (SiO$_2$, 5:1→4:1 hexanes:EtOAc) furnished a 1:1.3 diastereomeric mixture of carbamates 174 as a colorless oil (29.0 mg, 79.4 µmol, 79%). Data is reported for the mixture of diastereomers.

Physical State: colorless oil.

$^1$H NMR (500 MHz, CDCl$_3$, 50 °C): δ 7.29–7.21 (m, 10 H), 5.18–5.15 (m, 2 H), 4.53–4.27 (m, 2 H), 3.92–3.65 (m, 1 H), 2.42–2.32 (m, 2 H), 2.21–2.17 (m, 1 H), 2.07–1.78 (m, 4 H), 1.59–1.33 (m, 2 H), 1.16 (d, $J$=6.5 Hz, 1.7 H), and 1.11 (d, $J$=6.7 Hz, 1.3 H).

$^{13}$C NMR (151 MHz, C$_6$D$_6$, 55 °C): δ 207.9, 207.7, 156.6, 139.8, 139.7, 137.5, 137.5, 128.6, 128.6, 128.5, 128.3, 127.3, 67.4, 58.0, 57.8, 48.8, 45.4, 45.3, 42.9, 42.7, 41.0, 28.9, 28.7, 25.0, 24.8, 17.2, and 16.3. Peak overlapping was observed.

HRMS ($m/z$): calcd for C$_{23}$H$_{28}$NO$_3$ [M+H]$^+$: 366.2064, found: 366.2064.

TLC: $R_f$=0.33 (3:1 hexanes:EtOAc).

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$^{26}$ Simone, F. D.; Saget, T.; Benfatti, F.; Almeida, S.; Waser, J. Chem. Eur. J. 2011, 17, 14527.
Benzyl 4-(benzyl((benzyloxy)carbonyl)amino)pentanoate (175). Following General Procedure 2, a mixture of benzyl benzyl(vinyl)carbamate \(^{26}\) (26.7 mg, 100 \(\mu\)mol, 1.0 equiv), benzyl acrylate (45.9 \(\mu\)L, 300 \(\mu\)mol, 3.0 equiv), \(\text{Na}_2\text{HPO}_4\) (14.2 mg, 100 \(\mu\)mol, 1.0 equiv), \(\text{Fe(dibm)}_3\) (2.6 mg, 5.0 \(\mu\)mol, 5 mol%), and \(\text{PhSiH}_3\) (24.6 \(\mu\)L, 200 \(\mu\)mol, 2.0 equiv) in EtOH (0.50 mL) was heated at 60 °C with stirring for 1 h. Purification by flash column chromatography (SiO\(_2\), 5:1 hexanes:EtOAc) furnished carbamate 175 as a colorless oil (31.7 mg, 73.5 \(\mu\)mol, 73%).

**Physical State:** colorless oil.

\(^1\text{H NMR}\) (500 MHz, CDCl\(_3\), 50 °C): \(\delta\) 7.40–7.26 (m, 15 H), 5.20 (s, 2 H), 5.12 (s, 2 H), 4.46 (s, 2 H), 5.20 (m, 1 H), 2.32 (m, 2 H), 2.00 (m, 1 H), 1.84 (m, 1 H), and 1.17 (d, \(J=6.5\ \text{Hz}\), 3 H).

\(^{13}\text{C NMR}\) (126 MHz, CDCl\(_3\), 50 °C): \(\delta\) 183.0, 172.8, 139.1, 136.8, 136.1, 128.5, 128.4, 128.2, 127.9, 127.9, 127.3, 127.0, 67.2, 66.2, 52.7, 47.7, 31.4, 29.9, and 19.0.

**HRMS (\(m/z\))**: calcd for C\(_{27}\)H\(_{30}\)NO\(_4\) [M+H]**+:** 432.2169, found: 432.2178.

**TLC:** \(R_f=0.42\) (3:1 hexanes:EtOAc).

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Methyl 4-(((benzyloxy)carbonyl)((\(S\))-1-phenylethyl)amino)pentanoate (177). Following General Procedure 2, a mixture of benzyl (\(S\))-1-phenylethyl(vinyl)carbamate\(^{27}\) (10.0 mg, 35.5 \(\mu\)mol, 1.0 equiv), methyl acrylate (19.3 \(\mu\)L, 213 \(\mu\)mol, 6.0 equiv), \(\text{Na}_2\text{HPO}_4\) (5.0 mg, 35.5 \(\mu\)mol, 1.0 equiv), \(\text{Fe(dibm)}_3\) (2.8 mg, 5.3 \(\mu\)mol, 15 mol%), and \(\text{PhSiH}_3\) (26.3 \(\mu\)L, 213 \(\mu\)mol, 6.0 equiv) in EtOH (0.18 mL) was heated at 60 °C with stirring for 1 h. Purification by preparative TLC (SiO\(_2\), 8:2 hexanes:EtOAc) furnished a 1:1.5 diastereomeric mixture of carbamates 177 as a colorless oil (9.0 mg, 24.4 \(\mu\)mol, 69%). Data is reported for the mixture of diastereomers.

**Physical State:** colorless oil.

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\(^{27}\) Tamura, O. *et al.* Tetrahedron 1994, 50, 3889.
**Methyl 4-((tert-butoxycarbonyl)((S)-1-phenylethyl)amino)pentanoate (179).** Following General Procedure 2, a mixture of tert-butyl (S)-(1-phenylethyl)(vinyl)carbamate\(^{27}\) (14.3 mg, 57.8 \(\mu\)mol, 1.0 equiv), methyl acrylate (31.4 \(\mu\)L, 347 \(\mu\)mol, 6.0 equiv), Na\(_2\)HPO\(_4\) (8.2 mg, 57.8 \(\mu\)mol, 1.0 equiv), Fe(dibm)\(_3\) (4.5 mg, 8.7 \(\mu\)mol, 15 mol%), and PhSiH\(_3\) (42.8 \(\mu\)L, 347 \(\mu\)mol, 6.0 equiv) in EtOH (0.29 mL) was heated at 60 °C with stirring for 1h. Purification by preparative TLC (SiO\(_2\), 9:1 hexanes:EtOAc) furnished a 1:1.4 diastereomeric mixture of carbamates 179 as a colorless oil (10.7 mg, 31.9 \(\mu\)mol, 55\%). Data is reported for the mixture of diastereomers.

**Physical State:** colorless oil.

**\(^1\)H NMR** (500 MHz, CDCl\(_3\), 50 °C): \(\delta\) 7.35–7.21 (m, 5 H), 5.26 (m, 1 H), 3.69 (s, 1.75 H), 3.54 (s, 1.25 H), 3.39–3.26 (m, 1 H), 2.36–2.25 (m, 1 H), 2.06–1.93 (m, 1 H), 1.81–1.67 (m, 2 H), 1.56–1.54 (m, 3 H), 1.48–1.44 (m, 9 H), 1.30 (d, \(J=6.7\) Hz, 1.25 H), and 0.90 (d, \(J=6.8\) Hz, 1.75 H).

**\(^{13}\)C NMR** (151 MHz, CDCl\(_3\)): \(\delta\) 173.5, 173.3, 127.7, 127.6, 126.8, 126.4, 79.3, 52.8, 52.0, 51.2, 51.0, 31.1, 30.9, 30.2, 30.2, 28.1, and 18.1. Peak overlapping was observed.

**HRMS (m/z):** calcd for C\(_{19}\)H\(_{29}\)NNaO\(_4\) [M+Na]\(^+\): 358.1989, found: 358.1988.

**TLC:** \(R_f=0.57\) (8:2 hexanes:EtOAc).
4-Methyl-4-(phenethylthio)pentanenitrile (183). Following General Procedure 2, a mixture of 182 (17.8 mg, 100 µmol, 1.0 equiv), acrylonitrile (19.8 µL, 300 µmol, 3.0 equiv), Na₂HPO₄ (14.2 mg, 100 µmol, 1.0 equiv), Fe(dibm)₃ (2.6 mg, 5.0 µmol, 5 mol%), and PhSiH₃ (24.6 µL, 200 µmol, 2.0 equiv) in EtOH (0.50 mL) was stirred at rt for 1 h. Purification by flash column chromatography (SiO₂, 50:1→20:1 hexanes:EtOAc) furnished thioether 183 as a colorless oil (15.2 mg, 65.2 µmol, 65%).

Physical State: colorless oil.

¹H NMR (600 MHz, CDCl₃): δ 7.31 (dd, J=7.8, 7.2 Hz, 2 H), 7.25–7.20 (m, 3 H), 2.84 (dd, J=8.4, 7.2 Hz, 2 H), 2.70 (dd, J=8.4, 7.2 Hz, 2 H), 2.43 (dd, J=8.4, 7.8 Hz, 2 H), 1.85 (dd, J=8.4, 7.8 Hz, 2 H), and 1.29 (s, 6 H).

¹³C NMR (151 MHz, CDCl₃): δ 140.5, 128.7, 128.6, 126.7, 120.3, 44.7, 37.4, 35.9, 29.6, 28.7, and 13.2.

HRMS (m/z): calcd for C₁₄H₂₀NS [M+H]⁺: 234.1311, found: 234.1312.

TLC: Rₗ=0.41 (10:1 hexanes:EtOAc).

N,N,4-Trimethyl-4-(phenethylthio)pentanamide (184). Following General Procedure 2, a mixture of 182 (17.8 mg, 100 µmol, 1.0 equiv), N,N-dimethylacrylamide (31.0 µL, 300 µmol, 3.0 equiv), Na₂HPO₄ (14.2 mg, 100 µmol, 1.0 equiv), Fe(dibm)₃ (2.6 mg, 5.0 µmol, 5 mol%), and PhSiH₃ (24.6 µL, 200 µmol, 2.0 equiv) in EtOH (0.50 mL) was stirred at rt for 1 h. Purification by flash column chromatography (SiO₂, 3:1→2:1 hexanes:EtOAc) furnished thioether 184 as a colorless oil (18.7 mg, 67.0 µmol, 67%).

Physical State: colorless oil.
**1H NMR** (600 MHz, CDCl₃): δ 7.30–7.27 (m, 2 H), 7.21–7.19 (m, 3 H), 2.99 (s, 3 H), 2.94 (s, 3 H), 2.83 (dd, J=7.8, 7.8 Hz, 2 H), 2.73 (dd, J=7.8, 7.8 Hz, 2 H), 2.43–2.40 (m, 2 H), 1.87–1.84 (m, 2 H), and 1.29 (s, 6 H).

**13C NMR** (151 MHz, CDCl₃): δ 173.0, 140.9, 128.6, 128.5, 126.4, 45.3, 37.4, 36.8, 36.2, 35.6, 29.5, 29.2, and 29.1.

**HRMS (m/z):** calcd for C₁₆H₂₆NOS [M+H]⁺: 280.1730, found: 280.1734.

**TLC:** Rₕ=0.58 (1:1 hexanes:EtOAc).

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**4-(Dodecylthio)pentanenitrile (186).** Following General Procedure 2, a mixture of lauryl vinyl sulfide²⁸ (22.8 mg, 100 µmol, 1.0 equiv), acrylonitrile (19.8 µL, 300 µmol, 3.0 equiv), Na₂HPO₄ (14.2 mg, 100 µmol, 1.0 equiv), Fe(dibm)₃ (2.6 mg, 5.0 µmol, 5 mol%), and PhSiH₃ (24.6 µL, 200 µmol, 2.0 equiv) in EtOH (0.50 mL) was stirred at 60 °C for 1 h. A solution of TBAF (1 M in THF, 600 µL, 600 µmol, 6.0 equiv) was then added and the reaction mixture was heated at 60 °C with stirring for 1 h. Purification by flash column chromatography (SiO₂, 100:1→50:1 hexanes:EtOAc) furnished thioether 186 as a colorless oil (13.6 mg, 48.1 µmol, 48%).

**Physical State:** colorless oil.

**1H NMR** (600 MHz, CDCl₃): δ 2.86–2.82 (m, 1 H), 2.61–2.47 (m, 2 H), 2.51 (dd, J=7.8, 7.2 Hz, 2 H), 1.92–1.86 (m, 1 H), 1.83–1.78 (m, 1 H), 1.59–1.55 (m, 2 H), 1.32 (d, J=6.6 Hz, 3 H), 1.37–1.26 (m, 18 H), and 0.88 (dd, J=7.2, 6.6 Hz, 3 H).

**13C NMR** (151 MHz, CDCl₃): δ 119.7, 39.1, 32.4, 32.1, 30.5, 29.9, 29.8, 29.8, 29.7, 29.7, 29.5, 29.4, 29.1, 22.8, 21.7, 15.1, and 14.3.

**HRMS (m/z):** calcd for C₁₇H₃₄NS [M+H]⁺: 284.2407, found: 284.2409.

**TLC:** Rₕ=0.33 (10:1 hexanes:EtOAc).

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²⁸ Foster, D. J.; Tobler, E. *J. Am. Chem. Soc.* 1961, 83, 851.
4-(Phenylthio)pentanenitrile (188). Following General Procedure 2, a mixture of phenyl vinyl sulfide (13.6 mg, 100 µmol, 1.0 equiv), acrylonitrile (19.6 µL, 300 µmol, 3.0 equiv), Na$_2$HPO$_4$ (14.2 mg, 100 µmol, 1.0 equiv), Fe(dibm)$_3$ (2.6 mg, 5.0 µmol, 5 mol%), and PhSiH$_3$ (73.8 µL, 600 µmol, 6.0 equiv) in EtOH (0.50 mL) was stirred at rt for 1 h. Purification by flash column chromatography (SiO$_2$, 50:1→20:1 hexanes:EtOAc) furnished thioether 188 as a colorless oil (12.8 mg, 67.0 µmol, 67%).

**Physical State**: colorless oil.

$^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.43–7.41 (m, 2 H), 7.34–7.31 (m, 2 H), 7.30–7.28 (m, 1 H), 3.27 (dqd, $J=6.8$, 6.8, 6.8 Hz, 1 H), 2.62–2.50 (m, 2 H), 1.92–1.83 (m, 2 H), and 1.32 (d, $J=7.2$ Hz, 3 H).

$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 133.5, 133.1, 129.2, 127.8, 119.4, 42.6, 32.0, 21.1, and 15.0.

HRMS ($m/z$): calcd for C$_{11}$H$_{14}$NS [M+H]$^+$: 192.0841, found: 192.0845.

TLC: $R_f=0.39$ (10:1 hexanes:EtOAc).

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$N,N$-Dimethyl-4-(phenylthio)pentanamide (189). Following General Procedure 2, a mixture of phenyl vinyl sulfide (13.6 mg, 100 µmol, 1.0 equiv), $N,N$-dimethylacrylamide (31.0 µL, 300 µmol, 3.0 equiv), Na$_2$HPO$_4$ (14.2 mg, 100 µmol, 1.0 equiv), Fe(dibm)$_3$ (2.6 mg, 5.0 µmol, 5 mol%), and PhSiH$_3$ (73.8 µL, 600 µmol, 6.0 equiv) in EtOH (0.50 mL) was stirred at rt for 1 h. Purification by flash column chromatography (SiO$_2$, 2:1→1:1 hexanes:EtOAc) furnished thioether 189 as a colorless oil (11.4 mg, 48.1 µmol, 48%).

**Physical State**: colorless oil.
**1H NMR** (600 MHz, CDCl₃): δ 7.38 (d, J=7.8 Hz, 2 H), 7.25 (dd, J=7.8, 7.2 Hz, 2 H), 7.21 (dd, J=7.2, 7.2 Hz, 1 H), 3.32 (ddq, J=6.7, 6.7, 6.7 Hz, 1 H), 2.96 (s, 3 H), 2.92 (s, 3 H), 2.55–2.49 (m, 2 H), 2.01–1.95 (m, 1 H), 1.87–1.81 (m, 1 H), and 1.32 (d, J=6.6 Hz, 3 H).

**13C NMR** (151 MHz, CDCl₃): δ 172.5, 135.2, 131.9, 129.0, 126.8, 43.2, 37.3, 35.5, 32.0, 30.7, and 21.7.

**HRMS (m/z):** calcd for C₁₃H₂₀NOS [M+H]⁺: 238.1260, found: 238.1267.

**TLC**: Rₑ=0.31 (1:1 hexanes:EtOAc).

**4-(1-(Butylthio)cyclohexyl)butan-2-one (191).** A solution of methyl vinyl ketone (49.6 µL, 600 µmol, 6.0 equiv) and PhSiH₃ (73.8 µL, 600 µmol, 6.0 equiv) in EtOH (0.50 mL) was added slowly via syringe pump to a mixture of butyl cyclohex-1-enyl sulfide²⁹ (17.0 mg, 100 µmol, 1.0 equiv), Na₂HPO₄ (14.2 mg, 100 µmol, 1.0 equiv), Fe(dibm)₃ (2.6 mg, 5.0 µmol, 5 mol%) in EtOH (0.5 mL) while stirring at rt for 1 h. After stirring at rt for an additional 1 h, a solution of TBAF (1 M in THF, 600 µL, 600 µmol, 6.0 equiv) was added and the reaction mixture was heated at 60 °C with stirring for 1 h. Purification by flash column chromatography (SiO₂, 100:1→50:1 hexanes:EtOAc) furnished thioether 191 as a colorless oil (11.8 mg, 48.8 µmol, 49%).

**Physical State**: colorless oil.

**1H NMR** (600 MHz, CDCl₃): δ 2.64 (dd, J=7.8, 7.8 Hz, 2 H), 2.31 (dd, J=7.8, 7.8 Hz, 2 H), 2.17 (s, 3 H), 1.76 (dd, J=7.8, 7.8 Hz, 2 H), 1.71–1.63 (m, 4 H), 1.54–1.36 (m, 9 H), 1.31–1.25 (m, 1 H), and 0.90 (t, J=7.2 Hz, 3 H).

**13C NMR** (151 MHz, CDCl₃): δ 209.3, 49.2, 38.6, 36.6, 33.1, 31.7, 30.4, 26.2, 26.2, 22.5, 22.1, and 13.9.

**HRMS (m/z):** calcd for C₁₄H₂₇OS [M+H]⁺: 243.1777, found: 243.1776.

**TLC**: Rₑ=0.62 (10:1 hexanes:EtOAc).

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²⁹ Labiad, B.; Villemin, D. *Synthesis* 1989, 143.
3-(1-(Butylthio)cyclohexyl)propanenitrile (192). Following General Procedure 2, a mixture of butyl cyclohex-1-enyl sulfide\textsuperscript{29} (17.0 mg, 100 µmol, 1.0 equiv), acrylonitrile (19.8 µL, 300 µmol, 3.0 equiv), Na\textsubscript{2}HPO\textsubscript{4} (14.2 mg, 100 µmol, 1.0 equiv), Fe(dibm)\textsubscript{3} (2.6 mg, 5.0 µmol, 5 mol%), and PhSiH\textsubscript{3} (24.6 µL, 200 µmol, 2.0 equiv) in EtOH (0.50 mL) was stirred at rt for 1 h. A solution of TBAF (1 M in THF, 600 µL, 600 µmol, 6.0 equiv) was then added and the reaction mixture was heated at 60 °C with stirring for 1 h. Purification by flash column chromatography (SiO\textsubscript{2}, 100:1→50:1 hexanes:EtOAc) furnished thioether 192 as a colorless oil (11.3 mg, 50.2 µmol, 50%).

**Physical State:** colorless oil.

\textsuperscript{1}H NMR (600 MHz, CDCl\textsubscript{3}): \(\delta\) 2.56–2.54 (m, 2 H), 2.31 (t, \(J=7.2\) Hz, 2 H), 1.86–1.83 (m, 2 H), 1.73–1.64 (m, 4 H), 1.60–1.34 (m, 9 H), 1.31–1.25 (m, 1 H), and 0.92 (t, \(J=7.2\) Hz, 3 H).

\textsuperscript{13}C NMR (151 MHz, CDCl\textsubscript{3}): \(\delta\) 120.7, 49.0, 36.0, 35.9, 31.6, 26.3, 26.0, 22.5, 21.9, 13.9, and 12.2.

**HRMS (\textit{m/z}):** calcd for C\textsubscript{13}H\textsubscript{24}NS \([\text{M+H}]^+: 226.1624, \text{found: 226.1621.}\)

**TLC:** \(R_f=0.65\) (10:1 hexanes:EtOAc).

4-(Phenethylthio)undecanenitrile (194). Following General Procedure 2, a mixture of 193 (24.8 mg, 100 µmol, 1.0 equiv), acrylonitrile (19.8 µL, 300 µmol, 3.0 equiv), Na\textsubscript{2}HPO\textsubscript{4} (14.2 mg, 100 µmol, 1.0 equiv), Fe(dibm)\textsubscript{3} (7.9 mg, 15.0 µmol, 15 mol%), and PhSiH\textsubscript{3} (73.8 µL, 600 µmol, 6.0 equiv) in EtOH (0.50 mL) was stirred at rt for 1 h. A second portion of acrylonitrile (19.8 µL, 300 µmol, 3.0 equiv), Fe(dibm)\textsubscript{3} (7.9 mg, 15 µmol, 15 mol%), and PhSiH\textsubscript{3} (73.8 µL, 600 µmol, 6.0 equiv) was added. After stirring at rt for an additional 1 h, a solution of TBAF (1 M in THF, 1.20 mL, 1.20 mmol, 12.0 equiv) was added and the reaction mixture was heated at
60 °C with stirring for 1 h. Purification by flash column chromatography (SiO₂, 100:1→50:1 hexanes:EtOAc) furnished thioether 194 as a colorless oil (12.1 mg, 39.9 µmol, 40%).

**Physical State:** colorless oil.

**¹H NMR** (600 MHz, CDCl₃): δ 7.31 (dd, J=7.8, 7.2 Hz, 2 H), 7.24–7.20 (m, 3 H), 2.87 (dd, J=8.4, 7.2 Hz, 2 H), 2.75 (dd, J=8.4, 7.2 Hz, 2 H), 2.67–2.63 (m, 1 H), 2.57–2.52 (m, 1 H), 2.49–2.44 (m, 1 H), 1.97–1.91 (m, 1 H), 1.75–1.69 (m, 1 H), 1.57–1.21 (m, 12 H), and 0.89 (dd, J=7.2, 6.6 Hz, 3 H).

**¹³C NMR** (151 MHz, CDCl₃): δ 140.4, 128.7, 128.6, 126.6, 119.9, 45.3, 36.5, 35.3, 32.1, 31.9, 30.5, 29.6, 29.3, 27.0, 22.8, 14.9, and 14.2.

**HRMS (m/z):** calcd for C₁₉H₃₀NS [M+H]⁺: 304.2093, found: 304.2099.

**TLC:** Rₛ=0.40 (10:1 hexanes:EtOAc).

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5-((4-Methoxyphenyl)thio)dodecan-2-one (196). A solution of methyl vinyl ketone (49.6 µL, 600 µmol, 6.0 equiv) and PhSiH₃ (73.8 µL, 600 µmol, 6.0 equiv) in EtOH (0.5 mL) was added slowly via syringe pump to a mixture of 195 (25.0 mg, 100 µmol, 1.0 equiv), Na₂HPO₄ (14.2 mg, 100 µmol, 1.0 equiv), Fe(dibm)₃ (2.6 mg, 5.0 µmol, 5 mol%) in EtOH (0.50 mL) while stirring at rt for 1 h. Purification by flash column chromatography (SiO₂, 50:1→20:1 hexanes:EtOAc) furnished thioether 196 as a colorless oil (11.2 mg, 34.8 µmol, 35%).

**Physical State:** colorless oil.

**¹H NMR** (600 MHz, CDCl₃): δ 7.34 (d, J=7.8 Hz, 2 H), 6.83 (d, J=7.8 Hz, 2 H), 3.80 (s, 3 H), 2.86–2.83 (m, 1 H), 2.66–2.69 (m, 2 H), 2.13 (s, 3 H), 1.89–1.83 (m, 1 H), 1.68–1.62 (m, 1 H), 1.51–1.42 (m, 4 H), 1.29–1.22 (m, 8 H), and 0.88 (dd, J=7.2, 6.6 Hz, 3 H).

**¹³C NMR** (151 MHz, CDCl₃): δ 208.8, 159.6, 135.8, 124.7, 114.6, 55.5, 50.0, 40.9, 34.9, 32.0, 30.2, 29.6, 29.3, 28.1, 27.0, 22.8, and 14.3.

**HRMS (m/z):** calcd for C₁₉H₃₁O₂S [M+H]⁺: 323.2039, found: 323.2047.

**TLC:** Rₛ=0.31 (10:1 hexanes:EtOAc).
4-(Benzo[d]thiazol-2-ylthio)-N,N-dimethylpentanamide (198). Following General Procedure 2, a mixture of 2-(vinylthio)benzo[d]thiazole $^{30}$ (19.3 mg, 100 µmol, 1.0 equiv), N,N-dimethylacrylamide (31.0 µL, 300 µmol, 3.0 equiv), Na$_2$HPO$_4$ (14.2 mg, 100 µmol, 1.0 equiv), Fe(dibm)$_3$ (2.6 mg, 5.0 µmol, 5 mol%), and PhSiH$_3$ (24.6 µL, 200 µmol, 2.0 equiv) in EtOH (0.50 mL) was stirred at rt for 1 h. Purification by flash column chromatography (SiO$_2$, 2:1→1:1 hexanes:EtOAc) furnished thioether 198 as a colorless oil (16.0 mg, 54.4 µmol, 54%).

**Physical State:** colorless oil.

$^1$H NMR (600 MHz, CDCl$_3$): δ 7.85 (d, $J$=8.4 Hz, 1 H), 7.75 (d, $J$=7.8 Hz, 1 H), 7.41 (dd, $J$=7.8, 7.2 Hz, 1 H), 7.29 (dd, $J$=7.8, 7.8 Hz, 1 H), 4.06 (dqd, $J$=6.8, 6.8, 6.8 Hz, 1 H), 2.94 (s, 3 H), 2.93 (s, 3 H), 2.58–2.49 (m, 2 H), 2.22–2.17 (m, 1 H), 2.07–2.00 (m, 1 H), and 1.55 (d, $J$=6.6 Hz, 3 H).

$^{13}$C NMR (151 MHz, CDCl$_3$): δ 172.1, 166.3, 153.4, 135.5, 126.1, 124.4, 121.7, 121.1, 44.6, 37.3, 35.6, 32.2, 30.8, and 22.1.

HRMS (m/z): calcd for C$_{14}$H$_{19}$N$_2$O$_2$ [M+H]$^+$: 295.0933, found: 295.0939.

TLC: R$_f$=0.24 (1:1 hexanes:EtOAc).

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$N,N,4$-Trimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanamide (202). Following General Procedure 2, a mixture of isopropenylboronic acid pinacol ester (30.0 mg, 179 µmol, 1.0 equiv), N,N-dimethylacrylamide (55.2 µL, 536 µmol, 3.0 equiv), Na$_2$HPO$_4$ (25.3 mg, 179 µmol, 1.0 equiv), Fe(acac)$_3$ (3.2 mg, 8.9 µmol, 5 mol%), and PhSiH$_3$ (66.0 µL, 536

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$^{30}$ Abele, E.; Dzenitis, O.; Rubina, K.; Lukevics, E. *Chem. Heterocycl. Compd.* 2002, *38*, 682.
µmol, 3.0 equiv) in EtOH (0.89 mL) was heated at 60 °C with stirring for 1 h. Purification by flash column chromatography (SiO₂, 1:1 hexanes:EtOAc) furnished boronic ester 202 as a pale yellow oil (33.8 mg, 126 µmol, 70%).

**Physical State:** pale yellow oil.

**¹H NMR** (600 MHz, CDCl₃): δ 3.02 (s, 3 H), 2.92 (s, 3 H), 2.31–2.28 (m, 2 H), 1.60–1.57 (m, 2 H), 1.21 (s, 12 H), and 0.94 (s, 6 H).

**¹³C NMR** (151 MHz, CDCl₃): δ 174.0, 83.1, 37.5, 36.3, 35.5, 31.0, 24.9, and 24.8. The boron–bound carbon was not observed due to quadrupolar relaxation.

**¹¹B NMR** (128 MHz, CDCl₃): δ 15.2.

**HRMS (m/z):** calcd for C₁₄H₂₉BNO₃ [M+H]+: 270.2235, found: 270.2234.

**TLC:** Rₛ=0.39 (1:1 hexanes:EtOAc).

![Structure of 202](image)

*N,N,4-Trimethyl-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)pentanamide* (204).

Following General Procedure 2 using THF as a cosolvent, a mixture of isopropenylboronic acid MIDA ester (30.0 mg, 152 µmol, 1.0 equiv), N,N-dimethylacrylamide (47.1 µL, 457 µmol, 3.0 equiv), Na₂HPO₄ (21.6 mg, 153 µmol, 1.0 equiv), Fe(acac)₃ (2.7 mg, 7.6 µmol, 5 mol%), and PhSiH₃ (56.3 µL, 457 µmol, 3.0 equiv) in EtOH (0.38 mL) and THF (0.38 mL) was heated at 60 °C with stirring for 30 min. Purification by flash column chromatography (SiO₂, 94:6→9:1 DCM:MeOH) furnished MIDA boronate 204 as a colorless amorphous solid (26.2 mg, 87.9 µmol, 58%).

**Physical State:** colorless amorphous solid.

**¹H NMR** (600 MHz, acetone-d₆): δ 4.18 (d, J=16.9 Hz, 2 H), 4.03 (d, J=16.8 Hz, 2 H), 3.28 (s, 3 H), 3.03 (s, 3 H), 2.84 (s, 3 H), 2.36–2.33 (m, 2 H), 1.66–1.64 (m, 2 H), and 0.95 (s, 6 H).

**¹³C NMR** (151 MHz, acetone-d₆): δ 173.9, 168.9, 64.0, 47.3, 37.4, 35.3, 35.1, 28.6, and 23.9.

The boron–bound carbon was not observed due to quadrupolar relaxation.

**¹¹B NMR** (128 MHz, acetone-d₆): δ –6.4.

**HRMS (m/z):** calcd for C₁₃H₂₄BN₂O₅ [M+H]+: 299.1773, found: 299.1779.
**N,N,4-Trimethyl-4-(1H-naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)pentanamide** (206).

Following General Procedure 2, a mixture of boronamide 205 (30.0 mg, 144 µmol, 1.0 equiv), N,N-dimethylacrylamide (44.6 µL, 433 µmol, 3.0 equiv), Na₂HPO₄ (20.5 mg, 144 µmol, 1.0 equiv), Fe(acac)₃ (2.6 mg, 7.2 µmol, 5 mol%), and PhSiH₃ (53.3 µL, 433 µmol, 3.0 equiv) in EtOH (0.72 mL) was heated at 60 °C with stirring for 50 min. Purification by flash column chromatography (SiO₂, 3:7→2:8 hexanes:EtOAc) furnished boronamide 206 as a colorless amorphous solid (31.6 mg, 102 µmol, 71%).

**Physical State**: colorless amorphous solid.

**¹H NMR** (600 MHz, CDCl₃): δ 7.10 (dd, J=7.4, 8.2 Hz, 2 H), 7.00, (dd, J=0.8, 8.3 Hz, 2 H), 6.34 (dd, J=0.9, 7.3 Hz, 2 H), 5.77 (br s, 2 H), 2.96 (s, 3 H), 2.92 (s, 3 H), 2.31–2.28(m, 2 H), 1.71–1.69 (m, 2 H), and 1.04 (s, 6 H).

**¹³C NMR** (151 MHz, CDCl₃): δ 173.5, 141.2, 136.4, 127.7, 119.6, 117.6, 105.9, 37.4, 36.5, 35.6, 30.2, and 25.7. The boron–bound carbon was not observed due to quadrupolar relaxation.

**¹¹B NMR** (128 MHz, CDCl₃): δ 14.2.

**HRMS (m/z)**: calcd for C₁₈H₂₅BN₃O [M+H]⁺: 310.2085, found: 310.2086.

**TLC**: Rₕ=0.21 (3:7 hexanes:EtOAc).

**Methyl 4-methyl-4-(1H-naphtho[1,8-de][1,3,2]diazaborinin-2(3H)-yl)pentanoate** (207).

Following General Procedure 2, a mixture of boronamide 205 (30.0 mg, 144 µmol, 1.0 equiv), methyl acrylate (39.2 µL, 433 µmol, 3.0 equiv), Na₂HPO₄ (20.5 mg, 144 µmol, 1.0 equiv),
Fe(acac)₃ (2.6 mg, 7.2 µmol, 5 mol%), and PhSiH₃ (53.3 µL, 433 µmol, 3.0 equiv) in EtOH (0.72 mL) was heated at 60 °C with stirring for 70 min. Purification by flash column chromatography (SiO₂, 9:1 hexanes:EtOAc) furnished boronamide 207 as a colorless oil (36.5 mg, 123 µmol, 86%).

**Physical State:** colorless oil.

**¹H NMR** (600 MHz, CDCl₃): δ 7.11 (dd, J=7.8 Hz, 2 H), 7.02 (d, J=8.1 Hz, 2 H), 6.34 (d, J=7.3 Hz, 2 H), 5.65 (br s, 2 H), 3.64 (s, 3 H), 2.34–2.31 (m, 2 H), 1.71–1.69 (m, 2 H), and 1.03 (s, 6 H).

**¹³C NMR** (151 MHz, CDCl₃): δ 174.7, 141.1, 136.4, 127.7, 119.6, 117.7, 105.9, 51.8, 36.4, 31.2, and 25.3. The boron–bound carbon was not observed due to quadrupolar relaxation.

**¹¹B NMR** (128 MHz, CDCl₃): δ 13.7.

**HRMS (m/z):** calcd for C₁₇H₂₂BN₂O₂ [M+H]⁺: 297.1769, found: 297.1769.

**TLC:** Rₓ=0.32 (9:1 hexanes:EtOAc).

Methyl 5-((tert-butyldimethylsilyl)oxy)-4-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanoate (209). Following General Procedure 2, a mixture of tert-butyldimethyl((2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl)oxy)silane³¹ (30.0 mg, 101 µmol, 1.0 equiv), methyl acrylate (27.3 µL, 302 µmol, 3.0 equiv), Na₂HPO₄ (14.3 mg, 101 µmol, 1.0 equiv), Fe(acac)₃ (1.8 mg, 5.0 µmol, 5 mol%), and PhSiH₃ (37.2 µL, 302 µmol, 3.0 equiv) in EtOH (0.50 mL) was heated at 60 °C with stirring for 70 min. Purification by flash column chromatography (SiO₂, 9:1 hexanes:EtOAc) furnished boronic ester 209 as a colorless oil (18.3 mg, 47.4 µmol, 47%).

**Physical State:** colorless oil.

³¹ Jang, H.; Zhugralin, A. R.; Lee, Y.; Hoveyda, A. H. *J. Am. Chem. Soc.* 2011, *133*, 7859.
1H NMR (600 MHz, CDCl3): δ 3.65 (s, 3 H), 3.48 (d, J=9.2 Hz, 1 H), 3.43 (d, J=9.2 Hz, 1 H), 2.34–2.31 (m, 2 H), 1.78 (ddd, J=7.2, 9.6, 13.3 Hz, 1 H), 1.58–1.52 (m, 1 H), 1.22 (s, 12 H), 0.91 (s, 3 H), 0.88 (s, 9 H), −0.02 (s, 3 H), and −0.02 (s, 3 H).

13C NMR (151 MHz, CDCl3): δ 174.9, 83.3, 69.9, 51.6, 30.8, 30.3, 26.1, 24.9, 18.8, 18.4, and −5.4. The boron–bound carbon was not observed due to quadrupolar relaxation.

11B NMR (128 MHz, CDCl3): δ 15.0.

HRMS (m/z): calcd for C19H40BO5Si [M+H]+: 387.2733, found: 387.2235.

TLC: Rf=0.47 (9:1 hexanes:EtOAc).

tert-Butyl (5-(dimethylamino)-2-methyl-5-oxo-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)carbamate (211). Following General Procedure 2, a mixture of tert-butyl (2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl)carbamate31 (15.0 mg, 53.0 µmol, 1.0 equiv), N,N-dimethylacrylamide (16.4 µL, 159 µmol, 3.0 equiv), Na2HPO4 (7.5 mg, 53.0 µmol, 1.0 equiv), Fe(acac)3 (0.9 mg, 2.7 µmol, 5 mol%), and PhSiH3 (19.6 µL, 159 µmol, 3.0 equiv) in EtOH (0.27 mL) was heated at 60 ºC with stirring for 1 h. Purification by preparative TLC (SiO2, 94:6 DCM:MeOH) furnished boronic ester 211 as a colorless oil (6.5 mg, 16.9 µmol, 32%).

Physical State: colorless oil.

1H NMR (600 MHz, CDCl3): δ 4.95 (br s, 1 H), 3.15 (dd, J=12.8, 6.1 Hz, 1 H), 3.04–3.01 (m, 4 H), 2.93 (s, 3 H), 2.34–2.31 (m, 2 H), 1.75–1.70 (m, 2 H), 1.42 (s, 9 H), 1.23 (s, 12 H), and 0.94 (s, 3 H).

13C NMR (151 MHz, CDCl3): δ 173.6, 156.3, 83.5, 47.2, 37.5, 35.6, 31.2, 29.9, 29.5, 28.6, 25.0, 24.9, and 19.9. The boron–bound carbon was not observed due to quadrupolar relaxation.

11B NMR (128 MHz, CDCl3): δ 14.5.

HRMS (m/z): calcd for C19H38BN2O5 [M+H]+: 385.2868, found: 385.2868.

TLC: Rf=0.25 (94:6 DCM:MeOH).
Methyl 4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)decanoate (213). Following General Procedure 2, a mixture of (E)-4,4,5,5-tetramethyl-2-(oct-1-en-1-yl)-1,3,2-dioxaborolane\textsuperscript{32} (23.8 mg, 100 \(\mu\)mol, 1.0 equiv), methyl acrylate (27.1 \(\mu\)L, 300 \(\mu\)mol, 3.0 equiv), \(\text{Na}_2\text{HPO}_4\) (14.2 mg, 100 \(\mu\)mol, 1.0 equiv), \(\text{Fe}(\text{acac})_3\) (1.8 mg, 5 \(\mu\)mol, 5 mol%), and \(\text{PhSiH}_3\) (37.0 \(\mu\)L, 300 \(\mu\)mol, 3.0 equiv) in EtOH (0.50 mL) was heated at 60 °C with stirring for 17 h. Purification by preparative TLC (SiO\(_2\), 9:1 hexanes:EtOAc) furnished boronic ester 213 as a colorless oil (18.9 mg, 57.9 \(\mu\)mol, 58%).

**Physical State:** colorless oil.

\(^1\text{H NMR}\) (600 MHz, CDCl\(_3\)): \(\delta\) 3.66 (s, 3 H), 2.34–2.26 (m, 2 H), 1.71–1.65 (m, 1 H), 1.63–1.59 (m, 1 H), 1.58–1.52 (m, 1 H), 1.32–1.18 (m, XX H), 0.87 (dd, \(J=6.8, 6.8\) Hz, 3 H), and 0.75 (d, \(J=6.7\) Hz, 2 H).

\(^{13}\text{C NMR}\) (151 MHz, CDCl\(_3\)): \(\delta\) 174.8, 83.1, 51.6, 36.3, 33.9, 32.0, 31.9, 31.6, 29.8, 26.8, 25.00, 24.97, 22.8, and 14.3. The boron–bound carbon was not observed due to quadrupolar relaxation.

\(^{11}\text{B NMR}\) (128 MHz, CDCl\(_3\)): \(\delta\) 14.7.

**HRMS (m/z):** calcd for C\(_{18}\)H\(_{36}\)BO\(_4\) [M+H]\(^+\): 327.2701, found: 327.2703.

**TLC:** \(R_f=0.41\) (9:1 hexanes:EtOAc).

Methyl 4-(dimethyl(phenyl)silyl)-4-methylpentanoate (217). Following General Procedure 2, a mixture of dimethyl(phenyl)(prop-1-en-2-yl)silane\textsuperscript{33} (17.6 mg, 100 \(\mu\)mol, 1.0 equiv), methyl acrylate (27.0 \(\mu\)L, 300 \(\mu\)mol, 3.0 equiv), \(\text{Na}_2\text{HPO}_4\) (14.2 mg, 100 \(\mu\)mol, 1.0 equiv), \(\text{Fe}(\text{acac})_3\)

\textsuperscript{32} Shirakawa, K.; Arase, A.; Hoshi, M. *Synthesis* 2004, 1814.

\textsuperscript{33} Casey, C. P.; Gohdes, M. A.; Meszaros, M. W. *Organometallics* 1986, 5, 196.
(17.7 mg, 50.0 µmol, 50 mol%), and PhSiH₃ (25.0 µL, 200 µmol, 2.0 equiv) in n-PrOH (0.50 mL) was heated at 80 °C with stirring for 1 h. Purification by flash column chromatography (SiO₂, 10:1 hexanes:EtOAc) furnished silane 217 as a pale yellow oil (16.2 mg, 61.2 µmol, 61%).

**Physical State:** pale yellow oil.

**¹H NMR** (600 MHz, CDCl₃): δ 7.52–7.50 (m, 2 H), 7.37–7.33 (m, 3 H), 3.64 (s, 3 H), 2.24–2.21 (m, 2 H), 1.65–1.62 (m, 2 H), 0.87 (s, 6 H), and 0.30 (s, 6 H).

**¹³C NMR** (151 MHz, CDCl₃): δ 175.2, 137.4, 134.7, 129.1, 127.7, 51.7, 33.3, 28.6, 22.5, 19.4, and –5.7.

**HRMS (m/z):** calcd for C₁₅H₂₄NaO₂Si [M+Na]+: 287.1438, found: 287.1432.

**TLC:** Rᵢ=0.60 (10:1 hexanes:EtOAc).

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Benzyl 4-(dimethyl(phenyl)silyl)-4-methylpentanoate (218). Following General Procedure 2, a mixture of dimethyl(phenyl)(prop-1-en-2-yl)silane³³ (17.6 mg, 100 µmol, 1.0 equiv), acrylic acid (45.0 µL, 300 µmol, 3.0 equiv), Fe(acac)₃ (17.7 mg, 50.0 µmol, 50 mol%), and PhSiH₃ (25.0 µL, 200 µmol, 2.0 equiv) in n-PrOH (0.50 mL) was heated at 80 °C with stirring for 1 h. Purification by flash column chromatography (SiO₂, 10:1 hexanes:EtOAc) furnished silane 218 as a pale yellow oil (18.4 mg, 54.0 µmol, 54%).

**Physical State:** pale yellow oil.

**¹H NMR** (600 MHz, CDCl₃): δ 7.52–7.50 (m, 2 H), 7.38–7.31 (m, 8 H), 5.09 (s, 2 H), 2.29–2.26 (m, 2 H), 1.68–1.65 (m, 2 H), 0.87 (s, 6 H), and 0.30 (s, 6 H).

**¹³C NMR** (151 MHz, CDCl₃): δ 174.6, 137.3, 136.2, 134.7, 129.1, 128.7, 128.3, 127.7, 66.3, 33.2, 28.7, 22.5, 19.4, and –5.7.

**HRMS (m/z):** calcd for C₂₁H₂₆NaO₂Si [M+Na]+: 363.1751, found: 363.1753.

**TLC:** Rᵢ=0.40 (20:1 hexanes:EtOAc).
4-(Dimethyl(phenyl)silyl)-4-methylpentanenitrile (219). Following General Procedure 2, a mixture of dimethyl(phenyl)(prop-1-en-2-yl)silane\textsuperscript{33} (17.6 mg, 100 µmol, 1.0 equiv), acrylonitrile (19.7 µL, 300 µmol, 3.0 equiv), Na\textsubscript{2}HPO\textsubscript{4} (14.2 mg, 100 µmol, 1.0 equiv), Fe(acac)\textsubscript{3} (17.7 mg, 50.0 µmol, 50 mol%), and PhSiH\textsubscript{3} (25.0 µL, 200 µmol, 3.0 equiv) in \textit{n}-PrOH (0.50 mL) was heated at 80 °C with stirring for 1 h. Purification by flash column chromatography (SiO\textsubscript{2}, 3:1 hexanes:EtOAc) furnished silane 219 as a pale yellow oil (19.5 mg, 84.2 µmol, 84%).

**Physical State:** pale yellow oil.

\textbf{\textsuperscript{1}H NMR} (600 MHz, CDCl\textsubscript{3}): δ 7.51–7.49 (m, 2 H), 7.39–7.36 (m, 3 H), 2.20–2.17 (m, 2 H), 1.71–1.69 (m, 2 H), 0.91 (s, 6 H), and 0.31 (s, 6 H).

\textbf{\textsuperscript{13}C NMR} (151 MHz, CDCl\textsubscript{3}): δ 136.5, 134.6, 129.4, 127.9, 121.0, 34.2, 22.0, 19.7, 11.4, and –6.0.

\textbf{HRMS (m/z):} calcd for C\textsubscript{14}H\textsubscript{21}NNaSi [M+Na]\textsuperscript{+}: 254.1336, found: 254.1346.

\textbf{TLC:} R\textsubscript{s}=0.60 (10:1 hexanes:EtOAc).

Dimethyl(2-methyl-4-(phenylsulfonyl)butan-2-yl)(phenyl)silane (220). Following General Procedure 2, a mixture of dimethyl(phenyl)(prop-1-en-2-yl)silane\textsuperscript{33} (17.6 mg, 100 µmol, 1.0 equiv), phenyl vinyl sulfone (50.5 mg, 300 µmol, 3.0 equiv), Fe(acac)\textsubscript{3} (17.7 mg, 50.0 µmol, 100 mol%), and PhSiH\textsubscript{3} (25.0 µL, 200 µmol, 2.0 equiv) in \textit{n}-PrOH (0.50 mL) was heated at 80 °C with stirring for 1 h. Purification by flash column chromatography (SiO\textsubscript{2}, 5:1 hexanes:EtOAc) furnished silane 220 as a white solid (12.3 mg, 35.4 µmol, 35%).

**Physical State:** white solid.

**Melting point:** 112.0–114.0 °C
$^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.84–7.82 (m, 2 H), 7.65–7.62 (m, 1 H), 7.55–7.52 (m, 2 H), 7.42–7.40 (m, 2 H), 7.37–7.34 (m, 1 H), 7.33–7.30 (m, 2 H), 2.95–2.93 (m, 2 H), 1.69–1.66 (m, 2 H), 0.82 (s, 6 H), and 0.25 (s, 6 H).

$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 139.3, 136.6, 134.5, 133.7, 129.3, 128.1, 127.9, 51.7, 30.6, 22.7, 19.2, and –5.9.

HRMS ($m/z$): calcd for C$_{19}$H$_{26}$NaO$_2$SSi [M+Na]$^+$: 369.1315, found: 369.1312.

TLC: $R_f$=0.40 (5:1 hexanes:EtOAc).

5-(Dimethyl(phenyl)silyl)-5-methylhexan-2-one (221). Following General Procedure 2, a mixture of dimethyl(phenyl)(prop-1-en-2-yl)silane$^{33}$ (17.6 mg, 100 $\mu$mol, 1.0 equiv), methyl vinyl ketone (49.0 $\mu$L, 600 $\mu$mol, 6.0 equiv), Na$_2$HPO$_4$ (14.2 mg, 100 $\mu$mol, 1.0 equiv), Fe(acac)$_3$ (17.7 mg, 50.0 $\mu$mol, 50 mol%), and PhSiH$_3$ (25.0 $\mu$L, 200 $\mu$mol, 2.0 equiv) in n-PrOH (0.50 mL) was heated at 80 °C with stirring for 1 h. Purification by flash column chromatography (SiO$_2$, 10:1 hexanes:EtOAc) furnished silane 221 as a pale yellow oil (14.8 mg, 59.5 $\mu$mol, 60%).

Physical State: pale yellow oil.

$^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.52–7.50 (m, 2 H), 7.37–7.33 (m, 3 H), 2.32–2.29 (m, 2 H), 2.08 (s, 3 H), 1.57–1.55 (m, 2 H), 0.87 (s, 6 H), and 0.30 (s, 6 H).

$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 210.0, 137.5, 134.7, 129.1, 127.7, 38.1, 32.1, 30.1, 22.5, 19.3, and –5.7.

HRMS ($m/z$): calcd for C$_{19}$H$_{26}$NaO$_2$SSi [M+Na]$^+$: 369.1315, found: 369.1312.

TLC: $R_f$=0.40 (5:1 hexanes:EtOAc).

5-(Dimethyl(phenyl)silyl)-5-methylhexan-2-one (221). Following General Procedure 2, a mixture of dimethyl(phenyl)(prop-1-en-2-yl)silane$^{33}$ (17.6 mg, 100 $\mu$mol, 1.0 equiv), methyl vinyl ketone (49.0 $\mu$L, 600 $\mu$mol, 6.0 equiv), Na$_2$HPO$_4$ (14.2 mg, 100 $\mu$mol, 1.0 equiv), Fe(acac)$_3$ (17.7 mg, 50.0 $\mu$mol, 50 mol%), and PhSiH$_3$ (25.0 $\mu$L, 200 $\mu$mol, 2.0 equiv) in n-PrOH (0.50 mL) was heated at 80 °C with stirring for 1 h. Purification by flash column chromatography (SiO$_2$, 10:1 hexanes:EtOAc) furnished silane 221 as a pale yellow oil (14.8 mg, 59.5 $\mu$mol, 60%).

Physical State: pale yellow oil.

$^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.52–7.50 (m, 2 H), 7.37–7.33 (m, 3 H), 2.32–2.29 (m, 2 H), 2.08 (s, 3 H), 1.57–1.55 (m, 2 H), 0.87 (s, 6 H), and 0.30 (s, 6 H).

$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 210.0, 137.5, 134.7, 129.1, 127.7, 38.1, 32.1, 30.1, 22.5, 19.3, and –5.7.

HRMS ($m/z$): calcd for C$_{19}$H$_{26}$NaO$_2$SSi [M+Na]$^+$: 369.1315, found: 369.1312.

TLC: $R_f$=0.40 (5:1 hexanes:EtOAc).
4-(Dimethyl(phenyl)silyl)-N,N,4-trimethylpentanamide (222). Following General Procedure 2, a mixture of dimethyl(phenyl)(prop-1-en-2-yl)silane (17.6 mg, 100 µmol, 1.0 equiv), N,N-dimethylacrylamide (31.0 µL, 300 µmol, 3.0 equiv), Na₂HPO₄ (14.2 mg, 100 µmol, 1.0 equiv), Fe(acac)₃ (17.7 mg, 50.0 µmol, 50 mol%), and PhSiH₃ (25.0 µL, 200 µmol, 2.0 equiv) in n-PrOH (0.50 mL) was heated at 80 °C with stirring for 1 h. Purification by flash column chromatography (SiO₂, 3:1 hexanes:EtOAc) furnished silane 222 as pale yellow oil (19.4 mg, 69.9 µmol, 70%).

**Physical State:** pale yellow oil.

**¹H NMR** (600 MHz, CDCl₃): δ 7.52–7.51 (m, 2 H), 7.37–7.33 (m, 3 H), 2.90 (s, 3 H), 2.86 (s, 3 H) 2.19–2.16 (m, 2 H), 1.64–1.62 (m, 2 H), 0.91 (s, 6 H), and 0.30 (s, 6 H).

**¹³C NMR** (151 MHz, CDCl₃): δ 174.0, 137.8, 134.7, 128.9, 127.7, 37.3, 33.6, 27.8, 22.9, 22.9, 19.6, and –5.7.

**HRMS (m/z):** calcd for C₁₆H₂₇NNaOSi [M+Na]⁺: 300.1754, found: 300.1754.

**TLC:** Rₛ=0.20 (3:1 hexanes:EtOAc).

![](image)

4-(Dimethyl(phenyl)silyl)-4-methylpentanoic acid (223). Omitting Na₂HPO₄ from the general procedure, a mixture of dimethyl(phenyl)(prop-1-en-2-yl)silane (17.6 mg, 100 µmol, 1.0 equiv), acrylic acid (21.0 µL, 300 µmol, 3.0 equiv), Fe(acac)₃ (17.7 mg, 50.0 µmol, 50 mol%), and PhSiH₃ (25.0 µL, 200 µmol, 2.0 equiv) in n-PrOH (0.50 mL) was heated at 80 °C with stirring for 1 h. Purification by flash column chromatography (SiO₂, 3:1 DCM:MeOH) furnished silane 223 as a white solid (13.3 mg, 53.1 µmol, 53%).

**Physical State:** white solid.

**¹H NMR** (600 MHz, CDCl₃): δ 7.52–7.50 (m, 2 H), 7.37–7.33 (m, 3 H), 2.26–2.24 (m, 2 H), 1.66–1.63 (m, 2 H), 0.88 (s, 6 H), and 0.30 (s, 6 H).

**¹³C NMR** (151 MHz, CDCl₃): δ 180.1, 137.3, 134.7, 129.1, 127.7, 33.1, 28.4, 22.5, 19.4, and –5.7.

**HRMS (m/z):** calcd for C₁₄H₂₂NaOSi [M+Na]⁺: 273.1821, found: 273.1290.
**TLC:** $R_f=0.25$ (50:1 DCM:MeOH).

4-(Dimethyl(phenyl)silyl)-$N,N$-dimethylpentanamide (225). Following General Procedure 2, a mixture of dimethyl(phenyl)(vinyl)silane $^{34}$ (16.2 mg, 100 µmol, 1.0 equiv), $N,N$-dimethylacrylamide (62.0 µL, 600 µmol, 6.0 equiv), Na$_2$HPO$_4$ (14.2 mg, 100 µmol, 1.0 equiv), Fe(acac)$_3$ (17.7 mg, 50.0 µmol, 50 mol%), and PhSiH$_3$ (25.0 µL, 200 µmol, 2.0 equiv) in n-PrOH (0.50 mL) was heated at 80 °C with stirring for 1 h. Purification by flash column chromatography (SiO$_2$, 2:1 PhMe:EtOAc) furnished silane 225 as a pale yellow oil (13.3 mg, 50.5 µmol, 51%).

**Physical State:** pale yellow oil.

$^1$H NMR (600 MHz, CDCl$_3$): δ 7.51–7.49 (m, 2 H), 7.35–7.32 (m, 3 H), 2.90 (s, 3 H), 2.87 (s, 3 H), 2.42–2.37 (m, 1 H), 2.18–2.13 (m, 1 H), 1.86–1.82 (m, 1 H), 1.46–1.35 (m, 1 H), 0.96 (d, $J=7.2$ Hz, 3 H), 0.92–0.87 (m, 1 H), 0.27 (s, 3 H), and 0.26 (s, 3 H).

$^{13}$C NMR (151 MHz, CDCl$_3$): δ 173.5, 134.1, 129.0, 128.9, 127.8, 37.3, 35.5, 32.8, 27.4, 19.4, 14.2, −4.6, and −5.0.

**HRMS (m/z):** calcd for C$_{15}$H$_{26}$NOSi [M+H]$^+$: 264.1778, found: 264.1779.

**TLC:** $R_f=0.45$ (2:1 PhMe:EtOAc).

5-(Dimethyl(phenyl)silyl)-4-methylpentanenitrile (227) and 4-(dimethyl(phenyl)silyl)hexanenitrile (227'). Following General Procedure 2, a mixture of $E$- and $Z$-dimethyl(phenyl)(prop-1-en-1-yl)silane $^{35}$ (17.6 mg, 100 µmol, 1.0 equiv), acrylonitrile

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$^{34}$ Merten, J. *et al.* Eur. J. Org. Chem. 2006, 1144.

$^{35}$ Fugami, K.; Oshima, K.; Utimoto, K.; Nozaki, H. Tetrahedron Lett. 1986, 27, 2161.
(19.7 μL, 300 μmol, 3.0 equiv), Na₂HPO₄ (14.2 mg, 100 μmol, 1.0 equiv), Fe(acac)₃ (17.7 mg, 50.0 μmol, 50 mol%), and PhSiH₃ (25.0 μL, 200 μmol, 3.0 equiv) in n-PrOH (0.50 mL) was heated at 80 °C with stirring for 1 h. Purification by flash column chromatography (SiO₂, 9:1 hexanes:EtOAc) furnished an approximately 2:1 diastereomeric mixture of silanes 227 and 227' as a pale yellow oil (8.3 mg, 36.0 μmol, 36%).

**Physical State:** pale yellow oil.

**¹H NMR** (600 MHz, CDCl₃): δ 7.52–7.49 (m, 2 H), 7.38–7.35 (m, 3 H), 2.31–2.18 (m, 2 H), 1.82–1.71 (m, 1 H), 1.68–1.47 (m, 2.67 H), 1.38 (dddd, J=14.3, 14.3, 7.4, 7.4 Hz, 0.33 H), 0.91–0.89 (m, 3 H), 0.86 (dd, J=14.8, 4.8 Hz, 0.67 H), 0.69 (dd, J=14.8, 8.8 Hz, 0.67 H), and 0.32–0.31 (m, 6 H).

**¹³C NMR** (151 MHz, CDCl₃): δ 139.4, 138.1, 133.9, 133.6, 129.3, 129.1, 128.1, 128.0, 120.0, 35.7, 29.0, 26.5, 25.5, 23.8, 22.2, 21.9, 16.9, 15.0, 13.6, –1.9, –2.1, –3.5, and –4.2. Peak overlapping was observed.

**HRMS (m/z):** calcld for C₁₄H₂₁NaNSi [M+Na]⁺: 254.1335, found: 254.1341.

**TLC:** R₅=0.41 (9:1 hexanes:EtOAc).

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5-((tert-Butyldimethylsilyl)oxy)-4-fluoro-N,N,4-trimethylpentanamide (231). Following General Procedure 2, a mixture of 230 (30.0 mg, 158 μmol, 1.0 equiv), N,N-dimethylacrylamide (48.7 μL, 473 μmol, 3.0 equiv), Na₂HPO₄ (22.4 mg, 158 μmol, 1.0 equiv), Fe(acac)₃ (55.7 mg, 158 μmol, 100 mol%), and PhSiH₃ (58.3 μL, 473 μmol, 3.0 equiv) in EtOH (0.53 mL) was heated at 60 °C with stirring for 1 h. Purification by flash column chromatography (SiO₂, 7:3 hexanes:EtOAc) furnished fluoride 231 as a pale yellow oil (22.2 mg, 76.2 μmol, 48%).

**Physical State:** pale yellow oil.

**¹H NMR** (600 MHz, CDCl₃): δ 3.62–3.55 (m, 2 H), 3.02 (s, 3 H), 2.94 (s, 3 H), 2.48–2.40 (m, 2 H), 2.07–2.89 (m, 2 H), 1.30 (d, J=21.8 Hz, 3 H), 0.89 (s, 9 H), 0.06 (s, 3 H), and 0.06 (s, 3 H).

**¹³C NMR** (151 MHz, CDCl₃): δ 172.7, 96.6 (d, J=171.5 Hz), 68.5 (d, J=28.6), 37.4, 35.6, 31.8 (d, J=21.7 Hz), 27.4, 26.0, 21.5 (d, J=24.1 Hz), 18.4, –5.29, and –5.34.

**¹⁹F NMR** (376 MHz, CDCl₃): δ –156.6.
HRMS (m/z): calcd for C_{14}H_{31}FNO_{2}Si [M+H]^+: 292.2103, found: 292.2105.

TLC: R_f=0.27 (7:3 hexanes:EtOAc).

5-((tert-Butyldimethylsilyl)oxy)-4-chloro-\textit{N},\textit{N},4-trimethylpentanamide (233). Following General Procedure 2, a mixture of 232 (30.0 mg, 145 μmol, 1.0 equiv), \textit{N},\textit{N}-dimethylacrylamide (44.9 μL, 435 μmol, 3.0 equiv), Na_{2}HPO_{4} (20.6 mg, 145 μmol, 1.0 equiv), Fe(acac)_{3} (51.2 mg, 145 μmol, 100 mol%), and PhSiH_{3} (53.6 μL, 435 μmol, 3.0 equiv) in EtOH (0.73 mL) was heated at 60 °C with stirring for 1 h. Purification by flash column chromatography (SiO_{2}, 7:3 hexanes:EtOAc) furnished chloride 233 as a pale yellow oil (26.9 mg, 87.4 μmol, 60%).

Physical State: pale yellow oil.

$^1$H NMR (600 MHz, CDCl$_3$): δ 3.67 (d, J=10.1 Hz, 1 H), 3.61 (d, J=10.1 Hz, 1 H), 3.03 (s, 3 H), 2.95 (s, 3 H), 2.52 (m, 2 H), 2.11 (m, 2 H), 1.51 (s, 3 H), 0.89 (s, 9 H), 0.07 (s, 3 H), and 0.07 (s, 3 H).

$^{13}$C NMR (151 MHz, CDCl$_3$): δ 172.6, 72.6, 71.2, 37.4, 35.6, 28.9, 27.1, 26.0, 18.4, –5.27, and –5.32.

HRMS (m/z): calcd for C_{14}H_{31}ClNO_{2}Si [M+H]^+: 308.1807, found: 308.1807.

TLC: R_f=0.35 (7:3 hexanes:EtOAc).

5-((tert-Butyldimethylsilyl)oxy)-4-chloro-4-methylpentanoic acid (234). Omitting Na_{2}HPO_{4} from the general procedure, a mixture of 232 (30.0 mg, 145 μmol, 1.0 equiv), acrylic acid (29.8 μL, 435 μmol, 3.0 equiv), Fe(acac)$_3$ (51.2 mg, 145 μmol, 100 mol%), and PhSiH$_3$ (53.7 μL, 435 μmol, 3.0 equiv) in EtOH (0.73 mL) was heated at 60 °C with stirring for 1 h. Purification by flash column chromatography (SiO$_2$, 8:2 hexanes:EtOAc), followed by preparative TLC (SiO$_2$, 7:3 hexanes:EtOAc) furnished chloride 234 as a pale yellow oil (18.9 mg, 67.3 μmol, 46%).
Physical State: pale yellow oil.

$^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 3.66 (d, $J$=10.1 Hz, 1 H), 3.60 (d, $J$=10.0 Hz, 1 H), 2.58–2.46 (m, 2 H), 2.15 (ddd, $J$=7.5, 8.6, 14.5 Hz, 1 H), 2.09 (ddd, $J$=6.7, 9.6, 14.5 Hz, 1 H), 1.52 (s, 3 H), 0.90 (s, 9 H), 0.07 (s, 3 H), and 0.07 (s, 3 H).

$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 178.6, 71.4, 70.7, 34.9, 29.5, 27.2, 25.9, 18.4, –5.31, and –5.35.

HRMS ($m/z$): calcd for C$_{12}$H$_{26}$ClO$_3$Si [M+H]$^+$: 281.1334, found: 281.1337.

TLC: $R_f$=0.31 (8:2 hexanes:EtOAc).

4-Chloro-5-((4-methoxybenzoyl)oxy)-4-methylpentanoic acid (236). Omitting Na$_2$HPO$_4$ from the general procedure, a mixture of 2-chloroallyl 4-methoxybenzoate$^6$ (22.6 mg, 100 µmol, 1.0 equiv), acrylic acid (20.6 µL, 300 µmol, 3.0 equiv), Fe(acac)$_3$ (35.3 mg, 100 µmol, 100 mol%), and PhSiH$_3$ (36.9 µL, 300 µmol, 3.0 equiv) in EtOH (0.50 mL) was heated to 60 °C with stirring for 1 h. Purification by flash column chromatography (SiO$_2$, 2:1→1:2 hexanes:EtOAc) furnished chloride 236 as a colorless oil (14.9 mg, 49.6 µmol, 50%).

Physical State: colorless oil.

$^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 8.00 (d, $J$=9.0 Hz, 2 H), 6.94 (d, $J$=9.0 Hz, 2 H), 4.39 (s, 2 H), 3.86 (s, 3H), 2.71–2.61 (m, 2 H), 2.29–2.24 (m, 1 H), 2.20–2.15 (m, 1 H), and 1.65 (s, 3 H).

$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 178.2, 165.7, 163.8, 131.9, 122.0, 113.9, 70.7, 68.9, 55.6, 35.5, 29.4, and 27.4.

HRMS ($m/z$): calcd for C$_{14}$H$_{18}$ClO$_5$ [M+H]$^+$: 301.0837, found: 301.0830.

TLC: $R_f$=0.50 (1:2 hexanes:EtOAc).
4-Chloro-5-hydroxy-N,N,4-trimethylpentanamide (238). Following General Procedure 2, a mixture of 2-chloro-2-propen-1-ol (30.0 mg, 324 µmol, 1.0 equiv), N,N-dimethylacrylamide (100 µL, 973 µmol, 3.0 equiv), Na₂HPO₄ (46.0 mg, 324 µmol, 1.0 equiv), Fe(acac)₃ (115 mg, 324 µmol, 100 mol%), and PhSiH₃ (120 µL, 973 µmol, 3.0 equiv) in EtOH (1.6 mL) was heated at 60 °C with stirring for 1 h. Purification by flash column chromatography (SiO₂, EtOAc), followed by preparative TLC (SiO₂, 95:5 DCM:MeOH) furnished chloride 238 as a pale yellow oil (42.1 mg, 217 µmol, 67%).

Physical State: pale yellow oil.

¹H NMR (600 MHz, CDCl₃): δ 4.29 (dd, J=6.0, 9.1 Hz, 1 H), 3.48–3.42 (m, 2 H), 3.05 (s, 3 H), 2.98 (s, 3 H), 2.68 (ddd, J=4.3, 8.9, 17.5 Hz, 1 H), 2.46–2.39 (m, 2 H), 1.91 (dddd, J=0.8, 4.3, 7.5, 15.4 Hz, 1 H), and 1.63 (s, 3 H).

¹³C NMR (151 MHz, CDCl₃): δ 173.3, 73.9, 68.6, 37.4, 36.0, 33.7, 28.6, and 28.5.

HRMS (m/z): calcd for C₈H₁₇ClNO₂ [M+H]+: 194.0942, found: 194.0943.

TLC: Rₛ=0.40 (EtOAc).

4-Bromo-5-((tert-butyldimethylsilyl)oxy)-N,N,4-trimethylpentanamide (240). A solution of N,N-dimethylacrylamide (62.0 µL, 600 µmol, 6.0 equiv), and PhSiH₃ (73.8 µL, 600 µmol, 6.0 equiv) in EtOH (0.50 mL) was added slowly via syringe pump to a mixture of ((2-bromoallyl)oxy)(tert-butyl)dimethylsilane₃⁶ (25.0 mg, 100 µmol, 1.0 equiv), Na₂HPO₄ (14.2 mg, 100 µmol, 1.0 equiv), and Fe(acac)₃ (35.3 mg, 100 µmol, 100 mol%) in EtOH (0.50 mL) while heating at 60 °C with stirring for 1 h. After work up Following General Procedure 2, purification by flash column chromatography (SiO₂, 5:1→3:1 hexanes:EtOAc) furnished bromide 240 as a colorless oil (14.8 mg, 42.4 µmol, 42%).

Physical State: colorless oil.

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³⁶ Charpentay, M.; Boudhar, A.; Hulot, C.; Blond, G.; Suffert, J. Tetrahedron 2013, 69, 7568.
$^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 3.77 (d, $J=10.2$ Hz, 1 H), 3.71 (d, $J=10.2$ Hz, 1 H), 3.05 (s, 3 H), 2.95 (s, 3 H), 2.61–2.56 (m, 1 H), 2.54–2.49 (m, 1 H), 2.20–2.11 (m, 2 H), 1.71 (s, 3 H), 0.89 (s, 9 H), 0.07 (s, 3 H), and 0.07 (s, 3 H).

$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 172.4, 71.8, 70.6, 37.4, 36.7, 35.6, 30.3, 28.5, 26.0, 18.4, and –5.3.

HRMS ($m/z$): calcd for C$_{14}$H$_{31}$BrNO$_2$Si [M+H]$^+$: 352.1302, found: 352.1308.

TLC: $R_f=0.45$ (2:1 hexanes:EtOAc).

5-((tert-Butyldimethylsilyl)oxy)-4-iodo-$N,N,4$-trimethylpentanamide (242). A solution of $N,N$-dimethylacrylamide (62.0 µL, 600 µmol, 6.0 equiv), and PhSiH$_3$ (73.8 µL, 600 µmol, 6.0 equiv) in EtOH (0.50 mL) was added slowly via syringe pump to a mixture of tert-butyl((2-iodoallyl)oxy)dimethylsilane$^{37}$ (29.8 mg, 100 µmol, 1.0 equiv), Na$_2$HPO$_4$ (14.2 mg, 100 µmol, 1.0 equiv), and Fe(acac)$_3$ (35.3 mg, 100 µmol, 100 mol%) in EtOH (0.50 mL) while heating at 60 °C with stirring for 1 h. After work up Following General Procedure 2, purification by flash column chromatography (SiO$_2$, 5:1→4:1 hexanes:EtOAc) furnished iodide 242 as a colorless oil (14.6 mg, 36.6 µmol, 37%).

Physical State: colorless oil.

$^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 3.76 (d, $J=10.2$ Hz, 1 H), 3.71 (d, $J=10.2$ Hz, 1 H), 3.06 (s, 3 H), 2.95 (s, 3 H), 2.61–2.56 (m, 1 H), 2.53–2.47 (m, 1 H), 2.10–2.04 (m, 1 H), 1.97–1.94 (m, 1 H), 1.90 (s, 3 H), 0.90 (s, 9 H), 0.07 (s, 3 H), and 0.07 (s, 3 H).

$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 172.3, 74.1, 57.3, 39.0, 37.4, 35.6, 32.7, 31.6, 26.0, 18.4, and –5.2.

HRMS ($m/z$): calcd for C$_{14}$H$_{31}$INO$_2$Si [M+H]$^+$: 400.1163, found: 400.1171.

TLC: $R_f=0.55$ (2:1 hexanes:EtOAc).

$^{37}$ Nicolaou, K. C. et al. J. Am. Chem. Soc. 2006, 128, 2244.
4-((8R,9S,13S,14S,17R)-17-((tert-Butyldimethylsilyl)oxy)-3-methoxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-17-yl)butan-2-one (244). Following General Procedure 2 using THF as a cosolvent, a mixture of tert-butyl(((8R,9S,13S,14S)-3-methoxy-13-methyl-7,8,9,11,12,13,14,15-octahydro-6H-cyclopenta[a]phenanthren-17-yl)oxy)dimethylsilane\(^{38}\) (19.9 mg, 50.0 µmol, 1.0 equiv), methyl vinyl ketone (24.8 µL, 300 µmol, 6.0 equiv), Na\(_2\)HPO\(_4\) (7.1 mg, 50.0 µmol, 1.0 equiv), Fe(dibm)\(_3\) (1.3 mg, 2.5 µmol, 5 mol%), and PhSiH\(_3\) (36.9 µL, 300 µmol, 6.0 equiv) in EtOH (0.12 mL) and THF (0.12 mL) was heated at 60 °C with stirring for 1 h. Purification by flash column chromatography (SiO\(_2\), 50:1→30:1 hexanes:EtOAc) furnished estrone derivative 244 as a white solid (10.0 mg, 21.3 µmol, 43%).

**Physical State:** white solid.

**Melting Point:** 72.2–74.9 °C.

\([\alpha]_D^{20}\) +22.0 (c=0.50, CHCl\(_3\)).

\(\text{\(^1\)}H \text{ NMR}\) (600 MHz, CDCl\(_3\)): δ 7.20 (d, J=8.4 Hz, 1 H), 6.71 (dd, J=8.4, 3.0 Hz, 1 H), 6.62 (d, J=3.0 Hz, 1 H), 3.78 (s, 3 H), 2.86–2.83 (m, 2 H), 2.64–2.59 (m, 2 H), 2.30–2.28 (m, 1 H), 2.17 (s, 3 H), 0.90 (s, 9 H), 0.83 (s, 3 H), 0.11 (s, 3 H), and 0.10 (s, 3 H).

\(\text{\(^{13}\)}C \text{ NMR}\) (151 MHz, CDCl\(_3\)): δ 209.6, 157.6, 138.2, 132.9, 126.4, 113.9, 111.6, 86.1, 55.4, 48.6, 48.2, 43.9, 40.0, 39.9, 35.5, 32.5, 32.2, 30.3, 30.0, 27.7, 26.6, 26.3, 23.5, 18.9, 15.5, –1.3, and –1.7.

**HRMS (m/z):** calcd for C\(_{29}\)H\(_{47}\)O\(_3\)Si [M+Na]\(^+\): 493.3108, found: 493.3109.

**TLC:** R\(_t\)=0.48 (10:1 hexanes:EtOAc).

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\(^{38}\) Mander, L. N.; Sethi, S. P. *Tetrahedron Lett.* 1984, 25, 5953.
4-((2R,4R,5S,6R)-4,5-Bis(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-2-yl)butan-2-one (246). A solution of methyl vinyl ketone (49.6 µL, 600 µmol, 12.0 equiv) and PhSiH₃ (73.8 µL, 600 µmol, 12.0 equiv) in EtOH (0.25 mL) was added slowly via syringe pump to a mixture of 3,4,6-tri-O-benzyl-D-glucal (20.8 mg, 50.0 µmol, 1.0 equiv), Na₂HPO₄ (7.1 mg, 50.0 µmol, 1.0 equiv), Fe(dibm)₃ (7.9 mg, 15 µmol, 30 mol%) in EtOH (0.25 mL) while heating at 60 °C with stirring for 2 h. After work up following General Procedure 2, purification by preparative TLC (SiO₂, 3:1 hexanes:EtOAc) furnished glucal derivative 246 as a colorless oil (16.7 mg, 34.1 µmol, 68%) and recovered starting material (5.1 mg, 12.2 µmol, 24%). Spectroscopic data was identical to that reported in the literature.³⁹

**Physical State:** colorless oil.

[α]ᵦ²⁰: +28.2 (c=0.50, CHCl₃).

**¹H NMR** (600 MHz, CDCl₃): δ 7.33–7.26 (m, 13 H), 7.21–7.20 (m, 2 H), 4.78 (d, J=10.8 Hz, 1 H), 4.60 (d, J=11.4 Hz, 1 H), 4.58 (d, J=11.4 Hz, 1 H), 4.56 (d, J=12.6 Hz, 1 H), 4.52 (d, J=10.8 Hz, 1 H), 4.51 (d, J=12.0 Hz, 1 H), 3.96–3.93 (m, 1 H), 3.82–3.78 (m, 1 H), 3.75–3.69 (m, 2 H), 3.66–3.63 (m, 1 H), 3.49 (dd, J=7.2, 7.2 Hz, 1 H), 2.59–2.54 (m, 1 H), 2.51–2.45 (m, 1 H), 2.12 (s, 3 H), 1.99–1.94 (m, 2 H), 1.83–1.78 (m, 1 H), and 1.68–1.63 (m, 1 H).

**¹H NMR** (600 MHz, C₆D₆): δ 7.30–7.10 (m, 15 H), 4.75 (d, J=11.4 Hz, 1 H), 4.54 (d, J=11.4 Hz, 1 H), 4.44–4.33 (m, 4 H), 3.91–3.72 (m, 5 H), 3.56 (dd, J=6.6, 6.6 Hz, 1 H), 2.23–2.10 (m, 2 H), 1.88–1.83 (m, 1 H), 1.78–1.74 (m, 1 H), 1.68 (s, 3 H), 1.67–1.64 (m, 1 H), and 1.55–1.52 (m, 1 H).

**¹³C NMR** (151 MHz, CDCl₃): δ 208.6, 138.6, 138.5, 138.4, 128.5, 128.5, 128.0, 127.9, 127.8, 127.7, 76.9, 76.7, 74.1, 73.5, 72.6, 71.6, 70.2, 69.2, 39.8, 33.7, 30.3, and 25.9.

**HRMS (m/z):** calcd for C₃₁H₃₇O₅ [M+H]⁺: 489.2636, found: 489.2646.

**TLC:** Rₛ=0.21 (3:1 hexanes:EtOAc).

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³⁹ Hutchinson, D. K.; Fuchs, P. L. *J. Am. Chem. Soc.* 1987, 109, 4930.
4-((2R,4R,5S,6R)-4,5-Dimethoxy-6-(methoxymethyl)tetrahydro-2H-pyran-2-yl)butan-2-one (248). A solution of methyl vinyl ketone (49.6 µL, 600 µmol, 6.0 equiv) and PhSiH₃ (73.8 µL, 600 µmol, 6.0 equiv) in EtOH (0.50 mL) was added slowly via syringe pump to a mixture of 3,4,6-tri-O-methyl-D-glucal(40 (18.8 mg, 100 µmol, 1.0 equiv), Na₂HPO₄ (14.2 mg, 100 µmol, 1.0 equiv), Fe(dibm)_3 (2.6 mg, 5.00 µmol, 5 mol%) in EtOH (0.50 mL) while heating at 60 °C with stirring for 1 h. The reaction mixture was then heated at 60 °C with stirring for another 1 h. After workup Following General Procedure 2, purification by flash column chromatography (SiO₂, 2:1→1:2 hexanes:EtOAc) furnished glucal derivative 248 as a colorless oil (16.5 mg, 63.5 µmol, 64%).

Physical State: colorless oil.

[α]_D⁰⁺=+34.2 (c=1.00, CHCl₃)

¹H NMR (600 MHz, CDCl₃): δ 3.89 (ddd, J=6.0, 4.5, 4.5 Hz, 1 H), 3.60 (dd, J=9.6, 5.4 Hz, 1 H), 3.56 (ddd, J=7.2, 2.4, 2.4 Hz, 1 H), 3.51 (dd, J=9.6, 3.0 Hz, 1 H), 3.49–3.46 (m, 4 H), 3.40 (s, 3 H), 3.38 (s, 3 H), 3.09 (dd, J=7.2, 7.2 Hz, 1 H), 2.56–2.50 (m, 2 H), 2.15 (s, 3 H), 1.98–1.92 (m, 1 H), 1.87 (ddd, J=13.8, 4.8, 4.2 Hz, 1 H), and 1.70–1.62 (m, 2 H).

¹³C NMR (151 MHz, CDCl₃): δ 208.6, 78.8, 78.0, 72.3, 71.6, 70.0, 59.7, 59.3, 57.1, 39.9, 33.0, 30.3, and 26.0.

HRMS (m/z): calcd for C₁₃H₂₅O₅ [M+H]⁺: 261.1697, found: 261.1706.

TLC: Rₜ=0.12 (1:1 hexanes:EtOAc).

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⁴⁰ Beaver, M. G.; Woerpel, K. A. J. Org. Chem. 2010, 75, 1107.
Experimental Procedures and Characterization Data for the Vinyl Sulfone Coupling Products.

**General Procedure 3. Vinyl sulfone coupling.** To a solution of donor olefin (1.0 equiv), vinyl sulfone 276\textsuperscript{41} (1.5 equiv), and Fe(acac)\textsubscript{3} (30 mol%) in EtOH (0.2 M), was added PhSiH\textsubscript{3} (1.5 equiv) [CAUTION: H\textsubscript{2} evolution is occasionally observed upon addition of PhSiH\textsubscript{3}]. The resulting mixture was heated to 60 °C with stirring for 1 h. The reaction mixture was then cooled to rt and diluted with brine. The organic layer was separated and the aqueous layer was extracted with Et\textsubscript{2}O. The organic layers were combined, washed with brine, dried over MgSO\textsubscript{4}, filtered, and concentrated under reduced pressure. The crude material was then purified on SiO\textsubscript{2} (preparative TLC or flash column chromatography) to furnish the coupled product.

![](image)

5-((4-(Benzyloxy)-3,3-dimethylbutyl)sulfonyl)-2-phenyl-2H-tetrazole (279). General Procedure 3 was followed using (((2-methylallyl)oxy)methyl)benzene\textsuperscript{42} (16.2 mg, 100 µmol) as the donor olefin to furnish sulfone 279 as a colorless oil (29.7 mg, 74.0 µmol, 74%).

**Physical State:** colorless oil.

\textsuperscript{1}H NMR (600 MHz, CDCl\textsubscript{3}): \(\delta\) 7.70–7.57 (m, 5 H), 7.36–7.26 (m, 5 H), 4.50 (s, 2 H), 3.77–3.74 (m, 2 H), 3.18 (s, 2 H), 1.94–1.91 (m, 2 H), and 0.99 (s, 3 H).

\textsuperscript{13}C NMR (151 MHz, CDCl\textsubscript{3}): \(\delta\) 153.6, 138.4, 133.2, 131.6, 129.8, 128.6, 127.7, 127.6, 125.3, 78.5, 73.4, 53.0, 34.6, 31.3, and 24.7.

**HRMS (m/z):** calcd for C\textsubscript{20}H\textsubscript{25}N\textsubscript{4}O\textsubscript{3}S [M+H]\textsuperscript{+}: 401.1642, found: 401.1644.

**TLC:** \(R_s=0.35\) (4:1 hexanes:EtOAc).

\textsuperscript{41} Rodrigo, E.; Morales, S.; Duce, S.; Ruano, J. L. G.; Cid, M. B. *Chem. Commun.* **2011**, *47*, 11267.

\textsuperscript{42} Blanc, A.; Toste, F. D. *Angew. Chem. Int. Ed.* **2006**, *45*, 2096.
**N-(2,2-Dimethyl-4-((2-phenyl-2H-tetrazol-5-yl)sulfonyl)butyl)benzamide (281).** General Procedure 3 was followed using N-(2-methylallyl)benzamide\(^{43}\) (17.5 mg, 100 µmol) as the donor olefin to furnish sulfone 281 as a white solid (33.6 mg, 81.0 µmol, 81%).

**Physical State:** white solid.

**Melting Point:** 107–109 °C.

1H NMR (600 MHz, CDCl\(_3\)): \(\delta\) 7.82 (d, \(J=7.3\) Hz, 2 H), 7.71 (d, \(J=7.3\) Hz, 2 H), 7.61 (dq, \(J=14.7, 7.2, 3\) H), 7.51 (t, \(J=7.3\) Hz, 1 H), 7.45 (t, \(J=7.5\) Hz, 2 H), 6.66 (br s, 1 H), 3.86–3.76 (m, 2 H), 3.37 (d, \(J=6.6\) Hz, 2 H), 2.00–1.89 (m, 2 H), and 1.04 (s, 6 H).

13C NMR (151 MHz, CDCl\(_3\)): \(\delta\) 168.1, 153.4, 134.3, 133.1, 131.8, 131.6, 129.8, 128.8, 127.2, 125.4, 52.6, 47.6, 35.2, 31.3, and 25.4.

HRMS (m/z): calcd for C\(_{20}\)H\(_{24}\)N\(_5\)O\(_3\)S [M+H]\(^+\): 414.1594, found: 414.1594.

TLC: R\(_f\)=0.35 (3:2 hexanes:EtOAc).

**3,7,7-Trimethyl-9-((2-phenyl-2H-tetrazol-5-yl)sulfonyl)nonanal (283).** General Procedure 3 was followed using 3,7-dimethyloct-7-enal (15.4 mg, 100 µmol) as the donor olefin to furnish sulfone 283 as a colorless oil (16.5 mg, 42.0 µmol, 42%).

**Physical State:** colorless oil.

1H NMR (600 MHz, CDCl\(_3\)): \(\delta\) 9.76 (s, 1 H), 7.70–7.59 (m, 5 H), 3.70–3.66 (m, 2 H), 2.41 (dd, \(J=16.2, 4.0\) Hz, 2 H), 2.25 (ddd, \(J=16.2, 7.8, 2.4\) Hz, 1 H), 2.10–2.04 (m, 1 H), 1.83–1.77 (m, 2 H), 1.35–1.17 (m, 6 H), 0.97 (d, \(J=6.7\) Hz, 3 H), and 0.94 (s, 6 H).

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\(^{43}\) Engel, N.; Steglich, W. *Angew. Chem.* 1978, 90, 719.
**13C NMR** (151 MHz, CDCl₃): δ 203.0, 153.6, 133.2, 131.6, 129.9, 125.2, 52.8, 51.2, 41.7, 37.7, 33.0, 28.2, 26.9, 21.3, and 20.1.

**HRMS (m/z):** calcd for C₁₉H₂₉N₄O₃S [M+H]⁺: 393.1955, found: 393.1956.

**TLC:** R₅=0.45 (4:1 hexanes:EtOAc).

**4-Butyl-4-(2-((2-phenyl-2H-tetrazol-5-yl)sulfonyl)ethyl)cyclohexan-1-one (285).** General Procedure 3 was followed using 4-butylcyclohexanone⁴⁴ (15.4 mg, 100 µmol) as the donor olefin to furnish sulfone 285 as a colorless oil (17.6 mg, 45.0 µmol, 45%).

**Physical State:** colorless oil.

**¹H NMR** (600 MHz, CDCl₃): δ 7.72–7.59 (m, 5 H), 3.72–3.70 (m, 2 H), 2.37 (t, J=6.9 Hz, 3 H), 2.08–2.05 (m, 2 H), 1.81–1.70 (m, 4 H), 1.46–1.43 (m, 2 H), 1.37 (q, J=7.3 Hz, 2 H), 1.32–1.27 (m, 2 H), and 0.95 (t, J=7.2 Hz, 3 H).

**¹³C NMR** (151 MHz, CDCl₃): δ 210.9, 153.4, 133.1, 131.7, 130.0, 125.1, 52.1, 37.1, 35.5, 34.9, 34.7, 28.2, 25.4, 23.5, and 14.2.

**HRMS (m/z):** calcd for C₁₉H₂₇N₄O₃S [M+H]⁺: 391.1798, found: 391.1797.

**TLC:** R₅=0.65 (3:2 hexanes:EtOAc).

**tert-Butyl 4-methyl-4-(2-((2-phenyl-2H-tetrazol-5-yl)sulfonyl)ethyl)piperidine-1-carboxylate (286).** General Procedure 3 was followed using tert-butyl 4-methyleneepiperidine-1-

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⁴⁴ Gui, J.; Pan, C.-M.; Jin, Y.; Qin, T.; Lo, J. C.; Lee, B. J.; Spergel, S. H.; Mertzman, M. E.; Pitts, W. J.; La Cruz, T. E.; Schmidt, M. A.; Darvatkar, N.; Natarajan, S. R.; Baran, P. S. Science 2015, 348, 886.
carboxylate\textsuperscript{10} (1.000 g, 5.07 mmol) as the donor olefin to furnish sulfone 286 as a colorless oil (1.659 g, 3.80 mmol, 75%).

**Physical State:** colorless oil.

\textsuperscript{1}H NMR (600 MHz, CDCl\textsubscript{3}): \(\delta\) 7.71–7.68 (m, 2 H), 7.65–7.59 (m, 3 H), 3.73–3.71 (m, 2 H), 3.62–3.60 (m, 2 H), 3.24–3.19 (m, 2 H), 1.92–1.89 (m, 2 H), 1.45 (s, 9 H), 1.44–1.34 (m, 4 H), and 1.03 (s, 3 H).

\textsuperscript{13}C NMR (151 MHz, CDCl\textsubscript{3}): \(\delta\) 154.9, 153.5, 136.9, 133.1, 131.7, 129.9, 125.2, 79.7, 51.9, 39.6, 36.5, 33.2, 31.6, 28.6, and 23.0.

HRMS (\(m/z\)): calcd for C\(_{20}\)H\(_{30}\)N\(_5\)O\(_3\)S [M+H]\(^+\): 436.2013, found: 436.2013.

TLC: \(R_f=0.40\) (1:1 hexanes:EtOAc).

Benzyl \(4\)-methyl-\(4\)-\((2\)-(2-phenyl-\(2\)H-tetrazol-5-yl)sulfonyl)ethyl)piperidine-1-carboxylate (288). General Procedure 3 was followed using benzyl 4-methylene piperidine-1-carboxylate (23.1 mg, 100 \(\mu\)mol) as the donor olefin to furnish sulfone 288 as a colorless oil (32.9 mg, 70.0 \(\mu\)mol, 70%).

**Physical State:** colorless oil.

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\) 7.72–7.58 (m, 5 H), 7.39–7.27 (m, 5 H), 5.12 (s, 2 H), 3.77–3.65 (m, 4 H), 3.34–3.26 (m, 2 H), 1.94–1.90 (m, 2 H), 1.47–1.35 (m, 4 H), and 1.05 (s, 3 H).

\textsuperscript{13}C NMR (151 MHz, CDCl\textsubscript{3}): \(\delta\) 155.4, 153.5, 136.9, 133.1, 131.7, 129.9, 128.7, 128.2, 128.1, 125.1, 67.3, 51.9, 40.0, 36.4, 33.2, 31.6, and 22.9.

HRMS (\(m/z\)): calcd for C\(_{23}\)H\(_{28}\)N\(_5\)O\(_4\)S [M+H]\(^+\): 470.1857, found: 470.1857.

TLC: \(R_f=0.55\) (3:2 hexanes:EtOAc).
2-Phenyl-5-((2-((1S,2R,5S)-2,6,6-trimethylbicyclo[3.1.1]heptan-2-yl)ethyl)sulfonyl)-2H-tetrazole (290). General Procedure 3 was followed using (−)-β-pinene (13.6 mg, 100 µmol) as the donor olefin to furnish sulfone 290 as a colorless oil (20.3 mg, 54.0 µmol, 54%).

**Physical State:** colorless oil.

\(^1\)H NMR (600 MHz, CDCl\(_3\)): δ 7.71–7.58 (m, 5 H), 3.73–3.66 (m, 2 H), 2.04–1.99 (m, 1 H), 1.92–1.87 (m, 2 H), 1.86–1.83 (m, 1 H), 1.71–1.69 (m, 1 H), 1.64–1.60 (m, 1 H), 1.57–1.53 (m, 1 H), 1.36–1.29 (m, 2 H), 1.12–1.10 (m, 1 H), 0.96 (s, 3 H), 0.92 (s, 3 H), and 0.91 (s, 3 H).

\(^{13}\)C NMR (151 MHz, CDCl\(_3\)): δ 153.7, 133.2, 131.6, 129.8, 125.2, 54.5, 51.2, 46.5, 43.2, 42.6, 34.8, 29.5, 27.1, 23.9, 23.44, 23.35, and 19.5.

HRMS (m/z): calcd for C\(_{19}\)H\(_{27}\)N\(_4\)O\(_2\)S [M+H]\(^+\): 375.1849, found: 375.1849.

TLC: R\(_f\)=0.35 (10:1 hexanes:EtOAc).

5-((3-Methyl-3-(6-methyl-7-oxabicyclo[4.1.0]heptan-3-yl)butyl)sulfonyl)-2-phenyl-2H-tetrazole (292). General Procedure 3 was followed using a mixture of cis and trans (+)-limonene oxide (15.2 mg, 100 µmol) as the donor olefin to furnish sulfone 292 as a colorless oil (33.3 mg, 85.0 µmol, 85%).

**Physical State:** colorless oil.

\(^1\)H NMR (600 MHz, CDCl\(_3\)): δ 7.71–7.68 (m, 2 H), 7.65–7.59 (m, 3 H), 3.70–3.61 (m, 2 H), 3.06 (br s, 0.5 H), 2.99 (d, J=5.3 Hz, 0.5 H), 2.10 (dddd, J=14.3, 4.3, 2.4, 2.4 Hz, 0.5 H), 2.04 (dddd, J=14.5, 3.2, 3.2 Hz, 0.5 H), 1.94 (m, 0.5 H), 1.90–1.77 (m, 2.5 H), 1.66–1.60 (m, 1 H), 1.52–1.45 (m, 1 H), 1.37–1.32 (m, 1 H), 1.31–1.30 (m, 3 H), 1.21–1.07 (m, 1.5 H), 0.97 (dddd, J=12.6, 12.6, 12.6, 6.1 Hz, 0.5 H), and 0.90–0.88 (m, 6 H).

\(^{13}\)C NMR (151 MHz, CDCl\(_3\)): δ 153.5, 133.2, 131.64, 131.61, 129.9, 125.21, 125.18, 61.3, 59.4, 57.7, 52.6, 52.5, 41.3, 37.0, 35.0, 34.6, 31.7, 31.3, 29.8, 26.8, 25.5, 24.5, 24.30, 24.26, 24.1, 24.0, 23.0, and 20.0.

HRMS (m/z): calcd for C\(_{19}\)H\(_{27}\)N\(_4\)O\(_3\)S [M+H]\(^+\): 391.1798, found: 391.1799.
**TLC:** R<sub>f</sub>=0.45 (4:1 hexanes:EtOAc).

![Image of 2,3-Dimethyl-5-((2-phenyl-2H-tetrazol-5-yl)sulfonyl)pentan-2-ol (294)](image)

**2,3-Dimethyl-5-((2-phenyl-2H-tetrazol-5-yl)sulfonyl)pentan-2-ol (294).** General Procedure 3 was followed using 2-methylbut-3-en-2-ol (8.6 mg, 100 µmol) as the donor olefin to furnish sulfone 294 as a colorless oil (17.7 mg, 51.0 µmol, 51%).

**Physical State:** colorless oil.

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>): δ 7.73–7.58 (m, 5 H), 3.92–3.87 (m, 1 H), 3.82–3.76 (m, 1 H), 2.32–2.27 (m, 1 H), 1.74–1.62 (m, 2 H), 1.23 (s, 3 H), 1.16 (s, 3 H), and 0.99 (d, J=6.7 Hz, 3 H).

**<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>): δ 153.6, 133.2, 131.6, 129.9, 125.2, 73.3, 55.5, 43.0, 28.8, 25.4, 24.5, and 15.2.

**HRMS (m/z):** calcd for C<sub>14</sub>H<sub>20</sub>N<sub>4</sub>NaO<sub>3</sub>S [M+Na]<sup>+</sup>: 347.1148, found: 347.1152.

**TLC:** R<sub>f</sub>=0.45 (3:2 hexanes:EtOAc).

![Image of 2-(2-Methyl-4-((2-phenyl-2H-tetrazol-5-yl)sulfonyl)butyl)phenol (296)](image)

**2-(2-Methyl-4-((2-phenyl-2H-tetrazol-5-yl)sulfonyl)butyl)phenol (296).** General Procedure 3 was followed using 2-allylphenol (13.4 mg, 100 µmol) as the donor olefin to furnish sulfone 296 as a yellow oil (16.8 mg, 45.0 µmol, 45%).

**Physical State:** yellow oil.

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>): 7.67–7.57 (m, 5 H), 7.10–7.05 (m, 2 H), 6.88–6.85 (m, 1 H), 6.74–6.72 (m, 1 H), 3.85 (ddd, J=14.4, 11.4, 5.0 Hz, 1 H), 3.75 (ddd, J=14.5, 11.4, 4.9 Hz, 1 H), 2.70 (dd, J=13.5, 6.6 Hz, 1 H), 2.49 (dd, J=13.5, 7.4 Hz, 1 H), 2.06–2.01 (m, 1 H), 1.98–1.92 (m, 1 H), 1.85–1.79 (m, 1 H), and 0.99 (d, J=6.7 Hz, 3 H).

**<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>): δ 153.64, 153.60, 133.2, 131.6, 131.5, 129.8, 127.7, 126.4, 125.3, 121.0, 115.6, 54.4, 36.7, 32.9, 28.1, and 19.6.

**HRMS (m/z):** calcd for C<sub>18</sub>H<sub>21</sub>N<sub>4</sub>O<sub>3</sub>S [M+H]<sup>+</sup>: 373.1329, found: 373.1331.
**TLC:** R<sub>t</sub>=0.30 (4:1 hexanes:EtOAc).

![Chemical structure](image)

**N-Carbamoyl-2-isopropyl-4-methyl-6-((2-phenyl-2H-tetrazol-5-yl)sulfonyl)hexanamide** (298). General Procedure 3 was followed using apronal (18.4 mg, 100 µmol) as the donor olefin to furnish a 1:1 diastereomeric mixture of sulfoamides 298 as a colorless oil (19.0 mg, 45.0 µmol, 45%).

**Physical State:** colorless oil.

**1H NMR** (600 MHz, CDCl<sub>3</sub>): δ 9.96 (s, 0.5 H), 9.61 (s, 0.5 H), 8.32 (br s, 1 H), 7.69–7.67 (m, 2 H), 7.65–7.58 (m, 3 H), 5.64 (br s, 0.5 H), 5.61 (br s, 0.5 H), 3.79 (ddd, J=14.4, 11.9, 4.5 Hz, 0.5 H), 3.74 (dd, J=8.2, 6.1 Hz, 1 H), 3.66 (ddd, J=14.4, 11.8, 4.8 Hz, 0.5 H), 2.21–2.16 (m, 1 H), 2.13–2.08 (m, 0.5 H), 1.93–1.79 (m, 1.5 H), 1.76–1.67 (m, 1 H), 1.60–1.55 (m, 1 H), 1.55–1.50 (m, 1 H), 1.39 (ddd, J=14.1, 9.5, 3.1 Hz, 0.5 H), 1.27 (ddd, J=13.6, 9.9, 3.6 Hz, 0.5 H), and 0.98–0.93 (m, 9 H).

**13C NMR** (151 MHz, CDCl<sub>3</sub>): δ 177.7, 177.2, 155.4, 155.3, 153.52, 153.50, 133.2, 131.6, 129.9, 125.3, 125.2, 60.5, 54.3, 54.2, 52.1, 52.0, 36.3, 35.4, 31.4, 30.6, 30.5, 29.4, 27.5, 21.2, 20.5, 20.4, 20.3, 20.2, 19.2, and 14.3. Peak overlapping was observed.

**HRMS (m/z):** calcd for C<sub>18</sub>H<sub>27</sub>N<sub>6</sub>O<sub>4</sub>S [M+H]<sup>+</sup>: 423.1809, found: 423.1807.

**TLC:** R<sub>t</sub>=0.50 (1:1 hexanes:EtOAc).

![Chemical structure](image)
(3aR,5R,6S,6aR)-5-((R)-2,2-Dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-yl 4-methyl-6-((2-phenyl-2H-tetrazol-5-yl)sulfonyl)hexanoate (300). General Procedure 3 was followed using (3aR,5R,6S,6aR)-5-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-yl pent-4-enoate\textsuperscript{45} (34.2 mg, 100 µmol) as the donor olefin to furnish a diastereomeric mixture of sulfones \textbf{300} as a colorless oil (31.4 mg, 52.0 µmol, 52%).

**Physical State:** colorless oil.

\textsuperscript{1}H NMR (600 MHz, CDCl\textsubscript{3}): \(\delta \) 7.71–7.68 (m, 2 H), 7.65–7.59 (m, 3 H), 5.87 (dd, \(J=3.7, 1.3 \text{ Hz}, 1 \text{ H})\), 5.26 (dd, \(J=4.9, 2.3 \text{ Hz}, 2 \text{ H})\), 4.48 (dd, \(J=4.0, 4.0 \text{ Hz}, 1 \text{ H})\), 4.22–4.18 (m, 2 H), 4.10–4.07 (m, 1 H), 4.03–4.00 (m, 1 H), 3.82–3.69 (m, 2 H), 2.46–2.33 (m, 2 H), 1.99 (dddd, \(J=16.5, 10.7, 5.2, 5.2 \text{ Hz}, 1 \text{ H})\), 1.85–1.78 (m, 1 H), 1.78–1.69 (m, 2 H), 1.58–1.53 (m, 1 H), 1.52 (s, 3 H), 1.40 (s, 3 H), 1.31–1.30 (m, 6 H), and 0.99 (dd, \(J=6.6, 1.1 \text{ Hz}, 3 \text{ H})\).

\textsuperscript{13}C NMR (151 MHz, CDCl\textsubscript{3}): \(\delta \) 172.1, 172.0, 153.5, 133.1, 131.6, 130.4, 129.9, 125.2, 121.4, 112.4, 110.1, 109.5, 105.2, 83.5, 80.8, 79.9, 76.29, 76.27, 72.6, 67.5, 54.2, 54.1, 31.7, 31.6, 31.5, 31.1, 28.4, 27.0, 26.9, 26.3, 25.4, 18.9. Peak overlapping was observed.

**HRMS (m/z):** calcd for C\textsubscript{26}H\textsubscript{36}N\textsubscript{4}NaO\textsubscript{9}S [M+Na]\textsuperscript{+}: 603.2095, found: 603.2097.

**TLC:** \(R_\text{f}=0.55\) (3:2 hexanes:EtOAc).

5-((3-((\textit{tert}-Butyldimethylsilyl)oxy)-3-methylbutyl)sulfonyl)-2-phenyl-2H-tetrazole (303). General Procedure 3 was followed using \textit{tert}-butyldimethyl(prop-1-en-2-yloxy)silane\textsuperscript{14} (17.2 mg, 100 µmol) as the donor olefin to furnish sulfone \textbf{303} as a white solid (22.2 mg, 54.0 µmol, 54%). A small amount was recrystallized from hexanes and DCM to provide crystals suitable for X-ray analysis.

**Physical State:** white solid.

**Melting Point:** 47–48 °C.

\textsuperscript{45} Dao, H. T.; Li, C.; Michaudel, Q. Maxwell, B. D.; Baran, P. S. \textit{J. Am. Chem. Soc.} 2015, 137, 8046.
$^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.71–7.69 (m, 2 H), 7.64–7.57 (m, 3 H), 3.87–3.84 (m, 2 H), 2.06–2.03 (m, 2 H), 1.30 (s, 6 H), 0.87 (s, 9 H), and 0.11 (s, 6 H).
$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 153.6, 133.2, 131.6, 129.8, 125.2, 72.2, 52.8, 36.7, 29.8, 25.9, 18.2, and –2.04.
HRMS ($m/z$): calcd for C$_{18}$H$_{31}$N$_4$O$_3$SSi [M+H]$^+$: 411.1881, found: 411.1881.
TLC: $R_f$=0.70 (4:1 hexanes:EtOAc).

Figure S15. X-ray crystallographic structure of sulfone 303.

The single crystal X-ray diffraction studies were carried out on a Bruker Kappa APEX-II CCD diffractometer equipped with Mo K$_\alpha$ radiation ($\lambda$=0.71073 Å). A 0.223 x 0.087 x 0.065 mm piece of a colorless block was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using $\phi$ and $\omega$ scans. Crystal-to-detector distance was 70 mm and exposure time was 5 seconds per frame using a scan width of 1.0°. Data collection was 100% complete to 25.00° in $\theta$. A total of 70378 reflections were collected covering the indices, -9<=$h<=$9, -19<=$k<=$19, -44<=$l<=$44. 8817 reflections were found to be symmetry independent, with a R$_{int}$ of 0.0455. Indexing and unit cell refinement indicated a primitive, monoclinic lattice. The space group was found to be $P2_1/c$. The data were integrated using the Bruker SAINT software program and scaled using the SADABS software program. Solution by direct methods (SHELXT) produced a complete phasing model consistent with the proposed structure.

All nonhydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014. Crystallographic data are summarized in Table S2.
Table S2. Crystal data and structure refinement for sulfone 303.

| Parameter                                      | Value                                           |
|------------------------------------------------|-------------------------------------------------|
| Identification code                            | CCDC 1522560                                    |
| Empirical formula                              | C19.50 H33.50 N4 O3 S Si                        |
| Molecular formula                              | C18 H30 N4 O3 S Si, 0.25(C6 H14)                 |
| Formula weight                                 | 432.15                                          |
| Temperature                                    | 100.0 K                                         |
| Wavelength                                     | 0.71073 Å                                       |
| Crystal system                                 | Monoclinic                                      |
| Space group                                    | P 1 21/c 1                                      |
| Unit cell dimensions                           | a=8.0108(3) Å, α = 90°, b=16.3497(5) Å, β = 90.004(2)°, c=36.6816(12) Å, γ = 90°. |
| Volume                                         | 4804.3(3) Å³                                     |
| Z                                              | 8                                               |
| Density (calculated)                           | 1.195 Mg/m³                                      |
| Absorption coefficient                         | 0.210 mm⁻¹                                      |
| F(000)                                         | 1860                                            |
| Crystal size                                   | 0.223 x 0.087 x 0.065 mm³                        |
| Crystal color, habit                           | Colorless Block                                 |
| Theta range for data collection                | 1.669 to 25.370°                                |
| Index ranges                                   | -9<=h<=9, -19<=k<=19, -44<=l<=44                 |
| Reflections collected                          | 70378                                           |
| Independent reflections                        | 8817 [R(int)=0.0455]                             |
| Completeness to theta=25.000°                  | 100.0 %                                         |
| Absorption correction                          | Semi-empirical from equivalents                 |
| Max. and min. transmission                     | 0.0916 and 0.0638                               |
| Refinement method                              | Full-matrix least-squares on F²                  |
| Data / restraints / parameters                 | 8817 / 0 / 529                                  |
| Goodness-of-fit on F²                           | 1.104                                           |
| Final R indices [I>2σ(I)]                      | R1=0.0549, wR2=0.1423                           |
| R indices (all data)                           | R1=0.0698, wR2=0.1513                           |
| Extinction coefficient                         | n/a                                             |
| Largest diff. peak and hole                    | 0.499 and -0.318 e.Å⁻³                          |
5-((2-(1-((tert-Butyldimethylsilyl)oxy)cyclohexyl)ethyl)sulfonyl)-2-phenyl-2H-tetrazole (304). General Procedure 3 was followed using tert-butyl(cyclohex-1-en-1-yloxy)dimethylsilane\textsuperscript{15} (21.2 mg, 100 µmol) as the donor olefin to furnish sulfone 304 as a colorless oil (26.1 mg, 58.0 µmol, 58%).

**Physical State:** colorless oil.

\textsuperscript{1}H NMR (600 MHz, CDCl\textsubscript{3}): \(\delta 7.71–7.70\) (m, 2 H), \(7.64–7.59\) (m, 3 H), \(3.83–3.80\) (m, 2 H), \(2.16–2.13\) (m, 2 H), \(1.69–1.64\) (m, 2 H), \(1.61–1.54\) (m, 4 H), \(1.53–1.48\) (m, 1 H), \(1.41–1.34\) (m, 2 H), \(1.33–1.27\) (m, 1 H), \(0.88\) (s, 9 H), and \(0.12\) (s, 6 H).

\textsuperscript{13}C NMR (151 MHz, CDCl\textsubscript{3}): \(\delta 153.7, 133.2, 131.6, 129.8, 125.2, 74.4, 52.2, 38.6, 31.6, 26.1, 25.6, 23.2, 18.5,\) and \(-1.7\).

HRMS (m/z): calcld for C\textsubscript{21}H\textsubscript{34}N\textsubscript{4}NaO\textsubscript{3}Si [M+Na]\textsuperscript{+}: 473.2013, found: 473.2009.

TLC: \(R_f=0.75\) (4:1 hexanes:EtOAc).

Benzyl 2-(2-((2-phenyl-2H-tetrazol-5-yl)sulfonyl)ethyl)piperidine-1-carboxylate (305). General Procedure 3 was followed using benzyl 3,4-dihydropyridine-1(2H)-carboxylate\textsuperscript{22} (21.7 mg, 100 µmol) as the donor olefin to furnish sulfone 305 as a colorless oil (28.2 mg, 62.0 µmol, 62%).

**Physical State:** colorless oil.

\textsuperscript{1}H NMR (600 MHz, CDCl\textsubscript{3}): \(\delta 7.68–7.66\) (m, 2 H), \(7.63–7.57\) (m, 3 H), \(7.37–7.34\) (m, 4 H), \(7.33–7.29\) (m, 1 H), \(5.17–5.10\) (m, 2 H), \(4.54–4.44\) (br s, 1 H), \(4.16–4.05\) (br s, 1 H), \(3.78–3.51\) (m, 2 H), \(2.98–2.82\) (br s, 1 H), \(2.54–2.48\) (m, 1 H), \(2.03–1.94\) (m, 1 H), \(1.76–1.68\) (m, 1 H), \(1.67–1.52\) (m, 4 H), and \(1.48–1.36\) (m, 1 H).

\textsuperscript{13}C NMR (151 MHz, CDCl\textsubscript{3}): \(\delta 153.4, 136.6, 133.1, 131.6, 129.8, 128.7, 128.3, 128.1, 125.1, 67.5, 53.7, 49.6, 39.3, 29.0, 25.3, 23.1,\) and 19.0.
HRMS (m/z): calcd for C_{22}H_{26}N_{5}O_{4}S [M+H]^+: 456.1700, found: 456.1701.
TLC: R_f=0.60 (3:2 hexanes:EtOAc).

2-Phenyl-5-((3-(phenylthio)butyl)sulfonyl)-2H-tetrazole (306). General Procedure 3 was followed using phenyl vinyl sulfide (13.6 mg, 100 µmol) as the donor olefin to furnish sulfone 303 as a white solid (18.3 mg, 49.0 µmol, 49%).

Physical State: colorless oil.

H NMR (600 MHz, CDCl₃): δ 7.69–7.55 (m, 5 H), 7.44–7.42 (m, 2 H), 7.33–7.27 (m, 3 H), 4.03–3.91 (m, 2 H), 3.36–3.31 (m, 1 H), 2.22–2.10 (m, 2 H), and 1.36 (d, J=6.9 Hz, 3 H).

C NMR (151 MHz, CDCl₃): δ 153.5, 133.5, 132.9, 131.7, 129.92, 129.88, 129.3, 128.1, 125.2, 53.9, 42.4, 28.7, and 21.2.

HRMS (m/z): calcd for C_{17}H_{19}N_{4}O_{2}S_{2} [M+H]^+: 375.0944, found: 375.0946.
TLC: R_f=0.50 (4:1 hexanes:EtOAc).

5-((3-Methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)sulfonyl)-2-phenyl-2H-tetrazole (307). General Procedure 3 was followed using isopropenylboronic acid pinacol ester (16.8 mg, 100 µmol) as the donor olefin to furnish sulfone 307 as a colorless oil (31.7 mg, 78.0 µmol, 78%).

Physical State: colorless oil.

H NMR (600 MHz, CDCl₃): δ 7.70–7.67 (m, 2 H), 7.64–7.58 (m, 3 H), 3.80–3.78 (m, 2 H), 1.85–1.83 (m, 2 H), 1.23 (s, 12 H), and 1.00 (s, 6 H).

C NMR (151 MHz, CDCl₃): δ 153.6, 133.3, 131.2, 129.8, 125.3, 83.7, 53.9, 32.0, 24.8, and 24.5.

HRMS (m/z): calcd for C_{18}H_{28}BN_{4}O_{4}S [M+H]^+: 407.1919, found: 407.1917.
TLC: R_f=0.50 (4:1 hexanes:EtOAc).
2-Phenyl-5-((2-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentyl)ethyl)sulfonyl)-2\textit{H}-tetrazole (309). General Procedure 3 was followed using cyclopentenylboronic acid pinacol ester (19.4 mg, 100 µmol) as the donor olefin to furnish sulfone 309 as a white solid (13.4 mg, 31.0 µmol, 31%).

**Physical State:** white solid.

**Melting Point:** 107–108 °C.

**\textit{\textit{1H NMR}} (600 MHz, CDCl\textsubscript{3}):** δ 7.70–7.68 (m, 2 H), 7.64–7.58 (m, 3 H), 3.80–3.78 (m, 2 H), 1.91–1.89 (m, 2 H), 1.86–1.82 (m, 2 H), 1.67–1.57 (m, 4 H), 1.34–1.29 (m, 2 H), and 1.24 (s, 12 H).

**\textit{\textit{13C NMR}} (151 MHz, CDCl\textsubscript{3}):** δ 153.6, 133.3, 131.5, 129.8, 125.3, 83.7, 54.9, 35.2, 29.8, 25.3, and 24.8.

**HRMS (m/z):** calcd for C\textsubscript{20}H\textsubscript{30}BN\textsubscript{4}O\textsubscript{4}S [M+H]\textsuperscript{+}: 433.2075, found: 433.2074.

**TLC:** R\textsubscript{f}=0.65 (4:1 hexanes:EtOAc).

2-Chloro-2-methyl-4-((2-phenyl-2\textit{H}-tetrazol-5-yl)sulfonyl)butan-1-ol (310). General Procedure 3 was followed using 2-chloroprop-2-en-1-ol (9.2 mg, 100 µmol) as the donor olefin to furnish sulfone 310 as a white solid (25.1 mg, 76.0 µmol, 76%).

**Physical State:** white solid.

**Melting Point:** 107–108 °C.

**\textit{\textit{1H NMR}} (600 MHz, CDCl\textsubscript{3}):** δ 7.70–7.68 (m, 2 H), 7.66–7.60 (m, 3 H), 4.03 (ddd, J=14.7, 11.8, 4.3 Hz, 1 H), 3.95 (ddd, J=14.7, 11.9, 4.8 Hz, 1 H), 3.75 (dd, J=12.0, 4.0 Hz, 1 H), 3.67 (dd, J=12.0, 6.4 Hz, 1 H), 2.56 (ddd, J=14.2, 11.9, 4.3 Hz, 1 H), 2.37–2.32 (m, 2 H), and 1.63 (s, 3 H).

**\textit{\textit{13C NMR}} (151 MHz, CDCl\textsubscript{3}):** δ 153.4, 133.0, 131.7, 129.9, 125.2, 71.5, 70.7, 52.7, 33.1, and 26.9.
HRMS (m/z): calcd for C_{12}H_{16}ClN_{4}O_{3}S [M+H]^+: 331.0626, found: 331.0625.
TLC: R_f = 0.50 (3:2 hexanes:EtOAc).

2-Bromo-2-methyl-4-((2-phenyl-2H-tetrazol-5-yl)sulfonyl)butan-1-ol (312). General Procedure 3 was followed using 2-bromoprop-2-en-1-ol (13.6 mg, 100 µmol) as the donor olefin to furnish sulfone 312 as a white solid (20.2 mg, 54.0 µmol, 54%).

Physical State: white solid.

Melting Point: 107–108 °C.

$^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.71–7.69 (m, 2 H), 7.66–7.60 (m, 3 H), 4.06 (ddd, $J$=14.7, 11.8, 4.2 Hz, 1 H), 3.97 (ddd, $J$=14.7, 11.9, 4.9 Hz, 1 H), 3.81 (dd, $J$=12.1, 4.5 Hz, 1 H), 3.69 (dd, $J$=12.2, 7.0 Hz, 1 H), 2.62 (ddd, $J$=14.4, 11.8, 4.2 Hz, 1 H), 2.41–2.36 (m, 2 H), and 1.81 (s, 3 H).

$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 153.4, 133.0, 131.8, 130.0, 125.2, 71.5, 68.4, 53.9, 34.2, and 28.3.

HRMS (m/z): calcd for C$_{12}$H$_{16}$BrN$_4$O$_3$S [M+H]$^+$: 375.0121, found: 375.0121.
TLC: R_f = 0.50 (3:2 hexanes:EtOAc).

$t$ert-Butyl 4-ethyl-4-methylpiperidine-1-carboxylate (313). To a degassed solution of sulfone 286 (65.3 mg, 150 µmol, 1.0 equiv) in THF/H$_2$O (10:1, 3.0 mL) was added SmI$_2$ in THF 0.1 M, 9.0 mL, 900 µmol, 6.0 equiv. The resulting light yellow solution was stirred at rt for 30 min and monitored via TLC. Upon completion, the reaction was quenched with a saturated aqueous solution of NaHCO$_3$ and extracted with EtOAc. The combined organic layers were washed with brine, dried over Na$_2$SO$_4$, filtered, and concentrated under reduced pressure. The crude material
was purified by column chromatography (SiO2, 10:1 hexanes:E2O) to furnish piperidine 286 as a colorless oil (13.3 mg, 58.5 µmol, 39%).

**Physical State**: colorless oil.

**1H NMR** (600 MHz, CDCl3): $\delta$ 3.57–3.48 (br s, 2 H), 3.19 (ddd, $J$=13.2, 9.2, 3.8 Hz, 2 H), 1.45 (s, 9 H), 1.35–1.23 (m, 6 H), 0.89 (s, 3 H), and 0.82 (t, $J$=7.5 Hz, 3 H).

**13C NMR** (151 MHz, CDCl3): $\delta$ 155.2, 79.3, 40.1, 36.5, 34.0, 31.4, 28.6, 22.9, and 7.7.

**HRMS (m/z)**: calcd for C13H26NO [M+H]+: 228.1958, found: 228.1959.

**TLC**: $R_f$=0.28 (10:1 hexanes:E2O).

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**tert-Butyl 4-methyl-4-(3-phenyl-2-((2-phenyl-2H-tetrazol-5-yl)sulfonyl)propyl)piperidine-1-carboxylate (314).** To a solution of sulfone 286 (43.5 mg, 100 µmol, 1.0 equiv) in THF (500 µL) at –78 °C under Ar was added a solution of LiHMDS in THF (1 M, 220 µL, 220 µmol, 1.1 equiv). After stirring for 30 min at –78 °C, a solution of benzyl bromide (13.1 µL, 110 µmol, 1.1 equiv) in THF (200 µL) was added. The reaction mixture was stirred for an additional 30 min at –78 °C for 30 min, warmed to 0 °C over 1 h, and then stirred for 30 min at 0 °C. The reaction was quenched with a saturated aqueous solution of NH4Cl and extracted with EtOAc. The combined organic layers were washed with brine, dried over Na2SO4, filtered, and concentrated under reduced pressure. The crude material was purified by column chromatography (SiO2, 4:1 hexanes:EtOAc) to furnish benzylated 314 as a colorless oil (40.1 mg, 76.3 µmol, 76%).

**Physical State**: colorless oil.

**1H NMR** (600 MHz, CDCl3): $\delta$ 7.65–7.58 (m, 5 H), 7.29–7.21 (m, 5 H), 4.15–4.09 (m, 1 H), 3.60 (br s, 1 H), 3.54–3.45 (m, 1 H), 3.39 (dd, $J$=14.1, 5.5 Hz, 1 H), 3.01–2.93 (m, 2 H), 2.90 (dd, $J$=14.1, 8.3 Hz, 1 H), 2.35 (dd, $J$=15.6, 4.2 Hz, 1 H), 1.55 (dd, $J$=15.5, 3.9 Hz, 1 H), 1.43 (s, 9 H), 1.33–1.24 (m, 1 H), 1.16–1.06 (m, 3 H), and 0.72 (s, 3 H).

**13C NMR** (151 MHz, CDCl3): $\delta$ 154.9, 153.3, 135.4, 133.1, 131.6, 129.8, 129.7, 128.9, 127.7, 125.5, 79.5, 63.0, 38.9, 38.0, 36.7, 32.0, 28.6, and 22.3.

**HRMS (m/z)**: calcd for C27H36N5O4S [M+H]+: 526.2483, found: 526.2481.
TLC: R_f=0.42 (4:1 hexanes:EtOAc).

*tert*-Butyl 4-(3-methoxy-3-oxo-2-((2-phenyl-2H-tetrazol-5-yl)sulfonyl)propyl)-4-methylpiperidine-1-carboxylate (315). To a solution of sulfone 286 (43.5 mg, 100 µmol, 1 equiv) in anhydrous THF (500 µL) at –78 °C under Ar was added a solution of LiHMDS in THF (1 M, 400 µL, 400 µmol, 4.0 equiv). After 1 min, methyl chloroformate (15.5 µL, 200 µmol, 2.0 equiv) was added. The mixture was stirred at –78 °C for 30 min, warmed to 0 °C over 1 h, and stirred at 0 °C for an additional 2 h. The reaction was quenched with a saturated aqueous solution of NH₄Cl and extracted with EtOAc. The combined organic layers were washed with saturated NaHCO₃ and brine, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The crude material was purified by column chromatography (SiO₂, 3:1 hexanes:EtOAc) to furnish ester 315 as a colorless oil (40.2 mg, 81.4 µmol, 81%).

Physical State: colorless oil.

^1^H NMR (600 MHz, CDCl₃): δ 7.66–7.63 (m, 1 H), 7.62–7.57 (m, 5 H), 4.57 (br d, J=9.7 Hz, 1 H), 3.71 (s, 3 H), 3.66–3.52 (m, 2 H), 3.19–3.09 (m, 2 H), 2.22 (dd, J=14.4, 10.1 Hz, 1 H), 2.19 (dd, J=14.4, 2.0 Hz, 1 H), 1.45 (s, 9 H), 1.38–1.24 (m, 4 H), and 0.95 (s, 3 H).

^1^C NMR (151 MHz, CDCl₃): δ 165.4, 154.9, 152.7, 133.0, 131.8, 129.7, 126.0, 79.8, 67.5, 54.0, 39.6, 37.3, 36.4, 32.2, 28.6, and 22.6.

HRMS (m/z): calcd for C₂₂H₃₂N₅O₆S [M+H]^+: 494.2068; found 494.2065.

TLC: R_f=0.24 (3:1 hexanes:EtOAc).

*tert*-Butyl (E)-4-(3-(4-bromophenyl)allyl)-4-methylpiperidine-1-carboxylate (316). To a solution of sulfone 286 (43.6 mg, 100 µmol, 1.0 equiv) and p-bromobenzaldehyde (20.4 mg, 110
µmol, 1.1 equiv) in THF (1.0 mL) at –78 °C was added a solution of KHMDS in PhMe (0.5 M, 240 µL, 120 µmol, 1.2 equiv). The resulting mixture was stirred at –78 °C for 30 min and then warmed to rt over 2 h. The reaction was quenched with a saturated aqueous solution of NH₄Cl and extracted with Et₂O. The combined organic layers were washed with brine, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The crude material was purified by column chromatography (SiO₂, 10:1 hexanes:Et₂O) to furnish the E olefin 316 exclusively as a colorless oil (20.8 mg, 52.7 µmol, 53% yield).

**Physical State:** colorless oil.

**¹H NMR** (600 MHz, CDCl₃): δ 7.42–7.40 (m, 2 H), 7.21–7.19 (m, 2 H), 6.32 (d, J=15.8 Hz, 1 H), 6.21 (dt, J=15.2, 7.5 Hz, 1 H), 3.58 (br s, 2 H), 3.22 (ddd, J=13.3, 9.3, 3.7 Hz, 2 H), 2.16 (d, J=7.5 Hz, 2 H), 1.45 (s, 9 H), 1.44–1.39 (m, 2 H), 1.36–1.29 (m, 2 H), and 0.98 (s, 3 H).

**¹³C NMR** (151 MHz, CDCl₃): δ 155.2, 136.6, 131.7, 127.7, 127.3, 120.8, 79.4, 45.3, 40.0, 36.8, 32.6, 28.6, and 23.8. Peak overlapping was observed.

**HRMS (m/z):** calcd for C₂₀H₂₉BrNO₂ [M+H]+: 394.1376, found: 394.1379.

**TLC:** Rᵣ=0.43 (10:1 hexanes:Et₂O).

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**Sodium 2-(1-((tert-butoxycarbonyl)-4-methylpiperidin-4-yl)ethane-1-sulfinate** (317). To a solution of sulfone 286 (43.6 mg, 100 µmol, 1.0 equiv) in MeOH (1.5 mL) was added NaOMe (21.6 mg, 400 µmol, 4 equiv) under Ar. The reaction mixture was stirred at rt for 1.5 h, after which AcOH (35 µL, 600 µmol, 6 equiv) was added. The reaction mixture was concentrated under reduced pressure and then azeotroped with PhMe. The crude material was purified by column chromatography (DCM→9:1 DCM:MeOH→3:1 DCM:MeOH→MeOH) to provide sodium sulfinate 317 as a white solid (11.0 mg, 35.1 µmol, 35% yield).

**Physical State:** white solid.

**Melting Point:** 225 °C (decomp).

**¹H NMR** (600 MHz, D₂O): δ 3.57 (br s, 2 H), 3.30 (br s, 2 H), 2.93–2.90 (m, 2 H), 1.74–1.72 (m, 2 H), 1.46 (s, 9 H), 1.43–1.35 (m, 4 H), and 0.98 (s, 3 H).
\[^{13}\text{C NMR}\] (151 MHz, CDCl\(_3\)): \(\delta\) 156.7, 81.5, 46.2, 35.8, 35.1, 30.5, 27.7, 27.5, and 22.1.

HRMS ([m/z]): calcd for C\(_{13}\)H\(_{25}\)NNaO\(_4\)S [M+H]\(^+\): 314.1396, found: 314.1399.

TLC: \(R_s=0.33\) (9:1 DCM:MeOH).

**tert-Butyl 4-(2-bromo-2-(2-phenyl-2H-tetrazol-5-yl)sulfonyl)ethyl)-4-methylpiperidine-1-carboxylate (318).** To a solution of sulfone 286 (218 mg, 500 \(\mu\)mol, 1 equiv) in THF (500 \(\mu\)L) at \(-78^\circ\text{C}\) under Ar was added a solution of LiHMDS in THF (1M, 1.75 mL, 1.75 mmol, 3.5 equiv) dropwise. After 15 min, \(N\)-bromosuccinimide (267 mg, 1.50 mmol, 3.0 equiv) was added and the mixture was stirred at \(-78^\circ\text{C}\) for 50 min, warmed to rt, and stirred for additional 2 h. The reaction mixture was quenched with a saturated aqueous solution of \(\text{NH}_4\text{Cl}\) and extracted with EtOAc. The combined organic layers were washed with brine, dried over Na\(_2\)SO\(_4\), filtered, and concentrated under reduced pressure. The crude material was purified by column chromatography (SiO\(_2\), 4:1 hexanes:EtOAc) to furnish bromide 318 as a colorless oil (121.4 mg, 236 \(\mu\)mol, 47%).

**Physical State:** colorless oil.

\[^1\text{H NMR}\] (600 MHz, CDCl\(_3\)): \(\delta\) 7.68–7.64 (m, 1 H), 7.62–7.60 (m, 4 H), 5.27 (dd, \(J=9.0, 1.8\) Hz, 1 H), 3.60 (br s, 2 H), 3.25–3.18 (m, 2 H), 2.64 (dd, \(J=15.8, 1.7\) Hz, 1 H), 2.18 (dd, \(J=15.8, 9.0\) Hz, 1 H), 1.53 (ddd, \(J=13.5, 9.4, 4.2\) Hz, 1 H), 1.49–1.42 (m, 11 H), 1.41–1.35 (m, 1 H), and 1.11 (s, 3 H).

\[^{13}\text{C NMR}\] (151 MHz, CDCl\(_3\)): \(\delta\) 154.9, 151.6, 132.9, 131.9, 129.7, 125.9, 79.8, 60.0, 41.2, 39.5, 36.7, 32.7, 28.6, and 23.2.

HRMS ([m/z]): calcd for C\(_{20}\)H\(_{29}\)BrN\(_5\)O\(_4\)S [M+H]\(^+\): 514.1118; found 514.1121.

TLC: \(R_s=0.38\) (4:1 hexanes:EtOAc).
**tert-Butyl 4-(2,2-dichloro-2-((2-phenyl-2H-tetrazol-5-yl)sulfonyl)ethyl)-4-methylpiperidine-1-carboxylate (319).** To a solution of sulfone 286 (87.1 mg, 200 µmol, 1 equiv) in THF (200 µL) at –78 °C under Ar was added a solution of LiHMDS in THF (1M, 700 µL, 700 µmol, 3.5 equiv). After 15 min, N-chlorosuccinimide (80.1 mg, 600 µmol, 3.0 equiv) was added, and the mixture was stirred at –78 °C for 50 min, warmed to rt, and stirred for additional 2 h. The reaction mixture was quenched with a saturated aqueous solution of NH₄Cl and the extracted with EtOAc. The combined organic layers were washed with brine, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The crude material was purified by column chromatography (SiO₂, 4:1 hexanes:EtOAc) to furnish dichloride 319 as a yellow oil (70.1 mg, 139 µmol, 70% yield).

**Physical State:** yellow oil.

**¹H NMR** (600 MHz, CDCl₃): δ 7.68–7.64 (m, 1 H), 7.62–7.57 (m, 2 H), 7.56–7.53 (m, 2 H), 3.72–3.63 (m, 2 H), 3.25–3.13 (m, 2 H), 2.81 (s, 2 H), 1.74–1.65 (m, 2 H), 1.63–1.55 (m, 2 H), 1.45 (s, 9 H), and 1.32 (s, 3 H).

**¹³C NMR** (151 MHz, CDCl₃): δ 154.9, 149.7, 133.3, 131.9, 129.5, 126.5, 101.0, 79.8, 48.7, 39.4, 38.1, 35.1, 28.6, and 23.3.

**HRMS (m/z):** calcd for C₂₀H₂₈Cl₂N₅O₄S [M+H]⁺: 504.1234, found: 504.1236.

**TLC:** Rₚ=0.33 (4:1 hexanes:EtOAc).

**tert-Butyl 4-(2,2-difluorovinyl)-4-methylpiperidine-1-carboxylate (320).** To a solution of sulfone 286 (43.5 mg, 100 µmol, 1.0 equiv) in THF (200 µL) at –78 °C under Ar was added a solution of LHMDS in THF (1 M, 200 µL, 200 µmol, 2.0 equiv). After 15 min, a solution of N-
fluorobenzenesulfonimide (94.6 mg, 300 µmol, 3 equiv) in THF (800 µL) was added, the mixture was stirred at –78 °C for 50 min and then warmed to rt. After stirring for 1.5 h, the reaction mixture was cooled to –78 °C and a solution of KHMDS in PhMe (0.5 M, 1.2 mL, 6.0 equiv) was added. The reaction mixture was stirred for 1 h at –78 °C and then quenched with a saturated aqueous solution of NH₄Cl and extracted with EtOAc. The combined organic layers were dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The crude material was purified by column chromatography (SiO₂, 4:1 hexanes:EtOAc) to give difluorovinyl 320 as a yellow oil (20.3 mg, 77.7 µmol, 78%).

**Physical State:** yellow oil.

**1H NMR** (600 MHz, CDCl₃): δ 4.10 (dd, J=29.2, 5.5 Hz, 1 H), 3.71 (br s, 2 H), 3.05–3.01 (m, 2 H), 1.65–1.62 (mv, 2 H), 1.45 (s, 9 H), 1.40–1.32 (m, 2 H), 1.13 (s, 3 H).

**13C NMR** (151 MHz, CDCl₃): δ 155.5 (dd, J=289.2, 282.7 Hz), 155.0, 85.2 (dd, J=19.7, 15.4 Hz), 79.5, 40.6, 37.7, 31.6–31.4 (m), 28.6, and 27.9 (m).

**19F NMR** (376 MHz, CDCl₃): δ –84.68 (d, J=49.4 Hz, 1 F) and –85.79 (d, J=49.4 Hz, 1 F)

**HRMS (m/z):** calcd for C₁₃H₂₂F₂NO₂ [M+H]⁺: 262.1613, found: 262.1610.

**TLC:** R₅=0.67 (4:1 hexanes:EtOAc).

\[ \text{N-(2,2-dimethyl-4-((2-phenyl-2H-tetrazol-5-yl)sulfonyl)butyl-3,4-^{13}C}_2\text{benzamide}} \quad (322). \]

General Procedure 3 was followed using N-(2-methylallyl)benzamide (17.5 mg, 100 µmol) as the donor olefin and 13C-labeled vinyl sulfone 321⁴⁶ (33.3 mg, 150 µmol) as the acceptor olefin to furnish sulfone 322 as a colorless oil (35.3 mg, 85.0 µmol, 85%).

**Physical State:** colorless oil.

**1H NMR** (600 MHz, CDCl₃): 7.83–7.81 (m, 2 H), 7.71–7.81 (m, 2 H), 7.64–7.58 (m, 3 H), 7.52–7.50 (m, 1 H), 7.47–7.45 (m, 2 H), 6.64 (br t, J=6.6 Hz), 3.82 (ddt, J=138.3, 12.6, 3.9 Hz, 2 H), 3.37 (dd, J=6.6, 4.0 Hz, 2 H), 1.93 (ddt, J=130.6, 12.7, 4.9 Hz, 2 H), and 1.05 (d, J=4.6 Hz, 6 H).

⁴⁶ Prepared from (1³CH₂Cl)₂ in an analogous manner to that used to synthesize vinyl sulfone 276.⁴¹
$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 168.1, 153.4 (d, $J$=10.8 Hz), 134.4, 133.2, 131.8, 131.6, 129.8, 128.8, 127.2, 125.4, 52.6 (d, $J$=33.1 Hz), 47.6, 35.2 (d, $J$=35.2 Hz), 31.3 (d, $J$=33.0 Hz), and 25.5.

HRMS (m/z): calcd for C$_{18}^{13}$C$_2$H$_{24}$N$_2$O$_3$S [M+H]$^+$: 416.1661, found: 416.1662.

TLC: $R_f$=0.35 (3:2 hexanes:EtOAc).
Experimental Procedures and Characterization Data for the Olefin-Based Minisci Reaction Products.

General Procedure 4. Olefin-based Minisci reaction. A culture tube was charged with desired heterocycle (1 equiv), Fe(acac)₃ (1 equiv), and donor olefin (3 equiv). The flask was evacuated and backfilled with argon. A solution of THF/MeOH (4:1, 0.1–0.2 M) was added, and the mixture was stirred vigorously. BF₃•Et₂O (neat, 2.0 equiv) was then added, the culture tube was placed into an oil bath preheated to 60 °C, PhSiH₃ (1.0–1.5 equiv) was added, and the reaction mixture stirred for 1 h at this temperature. The reaction mixture was then cooled to rt and quenched with saturated aqueous solution of NaHCO₃. The organic layer was separated and the aqueous layer was extracted with EtOAc. The organic layers were combined, washed with brine, dried over MgSO₄, filtered, and concentrated under reduced pressure. The residue was then dissolved in CH₂Cl₂ and filtered over silica gel (eluted with hexanes/EtOAc). Concentration under reduced pressure and purification on SiO₂ (preparative TLC or flash column chromatography) furnished the coupled product.

2-(4-((tert-Butyldimethylsilyl)oxy)-2-methylbutan-2-yl)quinoline (335) Following General Procedure 4 with the following modifications, a mixture of quinoline N-oxide (30 mg, 210 µmol, 1.0 equiv), TBS silyl ether 59⁹ (124 mg, 630 µmol, 3.0 equiv), PhSiH₃ (10.2 µL, 840 µmol, 4.0 equiv), Fe(acac)₃ (73 mg, 210 µmol, 1.0 equiv), and BF₃•Et₂O (77 µL, 630 µmol, 3.0 equiv) in THF/MeOH (4:1, 1.0 mL) was heated to 60 °C with stirring for 1 h. Purification by preparative TLC (19:1 hexanes:EtOAc) afforded quinoline 335 as a pale yellow oil (49 mg, 150 µmol, 71%).

Physical State: pale yellow oil.

¹H NMR (600 MHz, CDCl₃): δ 8.06 (d, J=7.8 Hz, 1 H), 8.04 (d, J=8.5 Hz, 1 H), 7.76 (dd, J=8.0, 1.4 Hz, 1 H), 7.66 (ddd, J=8.4, 6.8, 1.4 Hz, 1 H), 7.50 (d, J=8.6 Hz, 1 H), 7.49–7.46 (m, 1 H), 3.55 (t, J=7.6 Hz, 1 H), 2.13 (t, J=7.6 Hz, 1 H), 1.47 (s, 6 H), 0.82 (s, 9 H), and -0.05 (s, 6 H).
$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 168.0, 147.6, 135.9, 129.6, 129.1, 127.4, 126.6, 125.8, 118.7, 60.6, 45.8, 40.3, 28.6, 26.1, 18.4, and –5.2.

HRMS ($m$/z): calcd for C$_{20}$H$_{32}$NOSi [M+H]$^+$: 330.2248, found: 330.2248.

TLC: $R_f$=0.74 (10:1 hexanes:EtOAc).

4-Methyl-2-(1-methylcyclohexyl)quinoline (338). From lepidine: Following General Procedure 4, a mixture of lepidine (30 mg, 210 $\mu$mol, 1.0 equiv), Fe(acac)$_3$ (74 mg, 210 $\mu$mol, 1.0 equiv), 1-methyl-1-cyclohexene (61 mg, 630 $\mu$mol, 3.0 equiv), BF$_3$•Et$_2$O (52 $\mu$L, 420 $\mu$mol, 2.0 equiv), and PhSiH$_3$ (26 $\mu$L, 150 $\mu$mol, 1.0 equiv) in THF/MeOH (4:1, 1.0 mL) was heated at 60 °C with stirring for 1 h. Purification by preparative TLC (9:1 hexanes:EtOAc) afforded quinoline 338 as a pale yellow oil (33 mg, 138 $\mu$mol, 66%).

From lepidine N-oxide: Following General Procedure 4, a mixture of lepidine N-oxide (16 mg, 100 $\mu$mol, 1.0 equiv), Fe(acac)$_3$ (35 mg, 100 $\mu$mol, 1.0 equiv), 1-methyl-1-cyclohexene (29 mg, 300 $\mu$mol, 3.0 equiv), BF$_3$•Et$_2$O (25 $\mu$L, 200 $\mu$mol, 2.0 equiv), and PhSiH$_3$ (18 $\mu$L, 150 $\mu$mol, 1.5 equiv) in THF/MeOH (4:1, 0.5 mL) was heated at 60 °C with stirring for 1 h. Purification by preparative TLC (DCM) afforded quinoline 338 as a pale yellow oil (12.7 mg, 53 $\mu$mol, 53%).

Physical State: pale yellow oil.

$^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 8.05 (d, $J$=8.4 Hz, 1 H), 7.94 (dd, $J$=8.3, 1.3 Hz, 1 H), 7.65 (ddd, $J$=8.3, 6.7, 1.4 Hz, 1 H), 7.49 (ddd, $J$=8.1, 6.8, 1.3 Hz, 1 H), 7.33 (s, 1 H), 2.69 (s, 3 H), 2.36 (dd, $J$=12.9, 6.9 Hz, 2 H), 1.66–1.57 (m, 4 H), 1.52–1.42 (m, 4 H), and 1.29 (s, 3 H).

$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 168.4, 147.7, 143.6, 130.1, 128.7, 126.6, 125.5, 123.5, 119.5, 41.4, 37.3, 29.3, 26.5, 23.1, and 19.2.

HRMS ($m$/z): calcd for C$_{17}$H$_{22}$N [M+H]$^+$: 240.1747, found: 240.1744.

TLC: $R_f$=0.75 (DCM).
4-Bromo-2-(1-methylcyclohexyl)quinoline (339). From 4-bromoquinoline: Following General Procedure 4, a mixture of 4-bromoquinoline (21 mg, 100 µmol, 1.0 equiv), Fe(acac)₃ (35 mg, 100 µmol, 1.0 equiv), 1-methyl-1-cyclohexene (29 mg, 300 µmol, 3.0 equiv), BF₃•Et₂O (25 µL, 200 µmol, 2.0 equiv), and PhSiH₃ (18.5 µL, 150 µmol, 1.5 equiv) in THF/MeOH (4:1, 500 µL) was heated at 60 °C with stirring for 1 h. Purification by preparative TLC (9:1 hexanes:EtOAc) afforded quinoline 339 as a pale yellow oil (12 mg, 40 µmol, 40%).

From 4-bromoquinoline N-oxide: Following General Procedure 4, a mixture of 4-bromoquinoline N-oxide (22 mg, 100 µmol, 1.0 equiv), Fe(acac)₃ (35 mg, 100 µmol, 1.0 equiv), 1-methyl-1-cyclohexene (29 mg, 300 µmol, 3.0 equiv), BF₃•Et₂O (25 µL, 200 µmol, 2.0 equiv), and PhSiH₃ (18.5 µL, 150 µmol, 1.5 equiv) in THF/MeOH (4:1, 500 µL) was heated at 60 °C with stirring for 1 h. Purification by preparative TLC (10:1 hexanes:EtOAc) afforded quinoline 339 as a pale yellow oil (14.3 mg, 47 µmol, 47%).

**Physical State:** pale yellow oil.

**¹H NMR** (600 MHz, CDCl₃): δ 8.15 (dd, J=8.5, 1.4 Hz, 1 H), 8.07 (dt, J=8.5, 0.8 Hz, 1 H), 7.80 (s, 1 H), 7.73 (ddd, J=8.4, 6.9, 1.4 Hz, 1 H), 7.59 (ddd, J=8.2, 6.8, 1.2 Hz, 1 H), 2.39–2.30 (m, 2 H), 1.65 (tdd, J=10.3, 7.3, 3.1 Hz, 4 H), 1.53–1.44 (m, 4 H), and 1.32 (s, 3 H).

**¹³C NMR** (151 MHz, CDCl₃): δ 168.8, 148.5, 134.1, 123.0 (2C), 127.0, 126.5, 126.1, 123.0, 41.8, 37.3, 30.0, 26.4, and 23.0.

**HRMS (m/z):** calcd for C₁₆H₁₉NBr [M+H]⁺: 304.0695, found: 304.0698.

**TLC:** Rₛ=0.72 (9:1 hexanes:EtOAc).

5-Bromo-2-(1-methylcyclohexyl)quinoline (340). From 5-bromoquinoline: Following General Procedure 4, a mixture of 5-bromoquinoline (21 mg, 100 µmol, 1.0 equiv), Fe(acac)₃ (35 mg,
100 μmol, 1.0 equiv), 1-methyl-1-cyclohexene (29 mg, 300 μmol, 3.0 equiv), BF₃•Et₂O (25 μL, 200 μmol, 2.0 equiv), and PhSiH₃ (12 μL, 100 μmol, 1.0 equiv) in THF/MeOH (4:1, 500 μL) was heated at 60 °C with stirring for 1 h. Purification by preparative TLC (19:1 hexanes:EtOAc) afforded quinoline 339 as a pale yellow oil (12 mg, 40 μmol, 40%).

From 5-bromoquinoline N-oxide: Following General Procedure 4, a mixture of 5-bromoquinoline N-oxide (22 mg, 100 μmol, 1.0 equiv), Fe(acac)₃ (35 mg, 100 μmol, 1.0 equiv), 1-methyl-1-cyclohexene (29 mg, 300 μmol, 3.0 equiv), BF₃•Et₂O (25 μL, 200 μmol, 2.0 equiv), and PhSiH₃ (18 μL, 150 μmol, 1.5 equiv) in THF/MeOH (4:1, 500 μL) was heated at 60 °C with stirring for 1 h. Purification by preparative TLC (20:1 hexanes:EtOAc) afforded quinoline 339 as a pale yellow oil (16.7 mg, 55 μmol, 55%).

**Physical State:** pale yellow oil.

**1H NMR** (600 MHz, CDCl₃): δ 8.43 (dd, J=8.9, 0.9 Hz, 1 H), 8.02 (dt, J=8.5, 1.0 Hz, 1 H), 7.74 (dd, J=7.5, 1.1 Hz, 1 H), 7.59 (d, J=8.9 Hz, 1 H), 7.51 (dd, J=8.4, 7.5 Hz, 1 H), 2.41–2.32 (m, 2 H), 1.69–1.56 (m, 4 H), 1.49–1.40 (m, 4 H), and 1.30 (s, 3 H).

**13C NMR** (151 MHz, CDCl₃): δ 169.6, 148.6, 135.4, 129.5, 129.4, 129.2, 126.0, 121.7, 120.1, 41.6, 37.3, 29.4, 26.4, and 23.0.

**HRMS (m/z):** calcd for C₁₆H₁₉NBr [M+H]⁺: 304.0695, found: 304.0694.

**TLC:** Rₛ=0.72 (10:1 hexanes:EtOAc).

3-(1-Methylcyclohexyl)quinoxalin-2-ol (341). Following General Procedure 4, a mixture of 2-quinoxalinol (15 mg, 100 μmol, 1.0 equiv), Fe(acac)₃ (35 mg, 100 μmol, 1.0 equiv), 1-methyl-1-cyclohexene (29 mg, 300 μmol, 3.0 equiv), BF₃•Et₂O (25 μL, 200 μmol, 2.0 equiv), and PhSiH₃ (18 μL, 100 μmol, 1.5 equiv) in THF/MeOH (4:1, 500 μL) was heated at 60 °C with stirring for 1 h. Chloranil (0.052 g, 0.2 mmol, 2.0 equiv) was then added to the reaction mixture, which was stirred at 60 °C for an additional 2 h. Purification by preparative TLC (4:1 hexanes:EtOAc) afforded quinoxaline 339 as a white solid (17.3 mg, 71 μmol, 71%).

**Physical State:** white solid.

**Melting Point:** 162–163 °C.
\(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta \) 12.36 (br s, 1 H), 7.84 (dd, \(J=8.0, 1.3 \) Hz, 1 H), 7.48 (ddd, \(J=8.4, 7.3, 1.4 \) Hz, 1 H), 7.34–7.29 (m, 2 H), 2.53 (ddd, \(J=12.2, 7.6, 3.6 \) Hz, 2 H), 1.70 (ddd, \(J=13.0, 8.9, 3.5 \) Hz, 2 H), 1.66–1.59 (m, 2 H), 1.58–1.52 (m, 2 H), 1.49 (s, 3 H), and 1.49–1.45 (m, 2 H).

\(^{13}\)C NMR (151 MHz, CDCl\(_3\)): \(\delta \) 165.4, 156.2, 132.6, 131.2, 129.7, 129.3, 123.9, 115.1, 42.9, 35.9, 26.8, 24.8, and 23.1.

HRMS (m/z): calcd for C\(_{15}\)H\(_{19}\)NO [M+H]\(^+\): 243.1492, found: 243.1495.

TLC: \(R_f=0.44\) (4:1 hexanes:EtOAc).

4-Chloro-2-(1-methylcyclohexyl)quinoline (342). Following General Procedure 4, a mixture of 4-chloroquinoline (30 mg, 180 \(\mu\) mol, 1.0 equiv), Fe(acac)\(_3\) (65 mg, 180 \(\mu\) mol, 1.0 equiv), 1-methyl-1-cyclohexene (53 mg, 540 \(\mu\) mol, 3.0 equiv), BF\(_3\)•Et\(_2\)O (45 \(\mu\) L, 360 \(\mu\) mol, 2.0 equiv), and PhSiH\(_3\) (23 \(\mu\) L, 360 \(\mu\) mol, 1.0 equiv) in THF/MeOH (4:1, 1.0 mL) was heated at 60 °C with stirring for 1 h. Purification by preparative TLC (9:1 hexanes:EtOAc) afforded quinoline 342 as a pale yellow oil (23 mg, 72 \(\mu\) mol, 49%).

Physical State: pale yellow oil.

\(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta \) 8.17 (dd, \(J=8.4, 1.4 \) Hz, 1 H), 8.06 (dt, \(J=8.5, 0.9 \) Hz, 1 H), 7.72 (ddd, \(J=8.4, 6.8, 1.4 \) Hz, 1 H), 7.58 (s, 1 H), 7.59–7.55 (m, 1 H), 2.32 (ddd, \(J=13.9, 7.6 \) Hz, 2 H), 1.67–1.57 (m, 4 H), 1.51–1.43 (m, 4 H), and 1.29 (s, 3 H).

\(^{13}\)C NMR (151 MHz, CDCl\(_3\)): \(\delta \) 168.9, 148.7, 142.5, 130.0, 129.9, 126.7, 124.7, 123.9, 119.1, 41.8, 37.2, 29.3, 26.4, and 23.0.

HRMS (m/z): calcd for C\(_{16}\)H\(_{19}\)ClN [M+H]\(^+\): 260.1200, found: 260.1201.

TLC: \(R_f=0.73\) (10:1 hexanes:EtOAc).
Methyl 6-\textit{(tert}-butyl)nicotinate (343). From methyl nicotinate: Following General Procedure 4 with the following modifications, methyl nicotinate (14 mg, 100 µmol, 1.0 equiv) and Fe(acac)$_3$ (35 mg, 100 µmol, 1.0 equiv) were dissolved in THF/MeOH (4:1, 500 µL), and the mixture was cooled to –78 °C. Condensed isobutylene (95 µL, ca. 1.00 mmol, ca. 10 equiv) was added to the mixture via a cooled syringe. BF$_3$\textbullet Et$_2$O (50 µL, 400 µmol, 4.0 equiv) and PhSiH$_3$ (50 µL, 400 µmol, 4.0 equiv) were then added, and the mixture was heated at 60 °C with stirring for 1 h. Purification by preparative TLC (9:1 hexanes:EtOAc) afforded pyridine 343 as a pale yellow oil (7.2 mg, 37 µmol, 37%).

From methyl nicotinate $N$-oxide: Following General Procedure 4 with the following modifications, methyl nicotinate $N$-oxide (16 mg, 100 µmol, 1.0 equiv) and Fe(acac)$_3$ (35 mg, 100 µmol, 1.0 equiv) were dissolved in THF/MeOH (4:1, 0.5 mL), and the mixture was cooled to –78 °C. Condensed isobutylene (95 µL, ca. 1.00 mmol, ca. 10 equiv) was added to the mixture via a cooled syringe. BF$_3$\textbullet Et$_2$O (50 µL, 400 µmol, 4.0 equiv) and PhSiH$_3$ (50 µL, 400 µmol, 4.0 equiv) were then added, and the mixture was heated at 60 °C with stirring for 1 h. Purification by preparative TLC (9:1 hexanes:EtOAc) afforded pyridine 343 as a pale yellow oil (4.5 mg, 23 µmol, 23%).

Spectroscopic data was identical to that reported in the literature.$^{47}$

\[
\begin{align*}
\text{2-(1-Methylcyclohexyl)quinoline (345). From quinoline: Following General Procedure 4, a} \\
\text{mixture of quinoline (30 mg, 230 µmol, 1.0 equiv), Fe(acac)$_3$ (35 mg, 100 µmol, 1.0 equiv), 1-} \\
\text{methyl-1-cyclohexene (29 µg, 690 µmol, 3.0 equiv), BF$_3$\textbullet Et$_2$O (25 µL, 440 µmol, 2.0 equiv),} \\
\text{and PhSiH$_3$ (18.5 µL, 150 µmol, 1.5 equiv), and THF/MeOH (4:1, 1.15 mL) was heated at 60 °C} \\
\text{with stirring for 1 h afforded both quinoline 345 (44% by $^1$H NMR with 1,2-dichloroethane as an} \\
\text{internal standard) and tetrahydroquinoline 346 (34% by $^1$H NMR with 1,2-dichloroethane as an} \\
\text{internal standard). A small sample was purified by preparative TLC (9:1 hexanes:EtOAc) to} \\
\text{obtain an analytically pure sample of quinoline 345 as a pale yellow oil.}
\end{align*}
\]

$^{47}$ El Din, M. G.; Knaus, E. E.; Giam, C.-S. Can. J. Chem. 1982, 60, 1821.
Physical State: pale yellow oil.

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.06 (ddd, $J$=11.9, 8.5, 0.9 Hz, 2 H), 7.76 (dd, $J$=8.0, 1.4 Hz, 1 H), 7.66 (ddd, $J$=8.4, 6.9, 1.5 Hz, 1 H), 7.55–7.42 (m, 2 H), 2.36 (dd, $J$=13.8, 7.4 Hz, 2 H), 1.73–1.57 (m, 2 H), 1.50–1.42 (m, 6 H), and 1.30 (s, 3 H).

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 168.7, 147.9, 135.9, 129.6, 129.0, 127.4, 126.5, 125.7, 118.9, 41.6, 37.4, 29.3, 26.5, and 23.1.

HRMS ($m/z$): calcd for C$_{16}$H$_{20}$N [M+H]$^+$: 226.1590, found: 226.1591.

TLC: $R_f$=0.83 (10:1 hexanes:EtOAc).

4-(1-Methylcyclohexyl)-1,2,3,4-tetrahydroquinoline (346). Following General Procedure 4, a mixture of quinoline (30 mg, 230 µmol, 1.0 equiv), Fe(acac)$_3$ (35 mg, 100 µmol, 1.0 equiv), 1-methyl-1-cyclohexene (29 µg, 690 µmol, 3.0 equiv), BF$_3$•Et$_2$O (25 µL, 440 µmol, 2.0 equiv), and PhSiH$_3$ (18.5 µL, 150 µmol, 1.5 equiv), and THF/MeOH (4:1, 1.15 mL) was heated at 60 °C with stirring for 1 h afforded both quinoline 345 (44% by $^1$H NMR with 1,2-dichloroethane as an internal standard) and tetrahydroquinoline 346 (34% by $^1$H NMR with 1,2-dichloroethane as an internal standard). A small sample was purified by preparative TLC (9:1 hexanes:EtOAc) to obtain an analytically pure sample of tetrahydroquinoline 346 as a pale yellow oil.

Physical State: pale yellow oil.

$^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 6.99 (ddd, $J$=7.9, 7.2, 1.6 Hz, 1 H), 6.94 (dd, $J$=7.5, 1.6 Hz, 1 H), 6.55 (td, $J$=7.3, 1.2 Hz, 1 H), 6.45 (dd, $J$=7.9, 1.2 Hz, 1 H), 3.81 (s, 1 H), 3.44–3.32 (m, 2 H), 2.63 (dd, $J$=5.8, 2.5 Hz, 1 H), 2.19 (ddt, $J$=13.9, 4.8, 2.2 Hz, 1 H), 1.70 (dddd, $J$=13.8, 12.5, 7.3, 5.4 Hz, 1 H), 1.61–1.35 (m, 7 H), 1.33–1.18 (m, 3 H), and 0.79 (s, 3 H).

$^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 145.2, 131.3, 127.1, 122.4, 115.2, 113.5, 39.9, 37.6, 37.4, 36.2, 26.5, 22.8, 22.5, and 22.1.

HRMS ($m/z$): calcd for C$_{16}$H$_{24}$N [M+H]$^+$: 230.1903, found: 230.1905.

TLC: $R_f$=0.59 (10:1 hexanes:EtOAc).
6-Fluoro-2-(1-methylcyclohexyl)quinoline (349). Following General Procedure 4, a mixture of 6-fluoroquinoline N-oxide (16 mg, 100 µmol, 1.0 equiv), Fe(acac)₃ (35 mg, 100 µmol, 1.0 equiv), 1-methyl-1-cyclohexene (29 mg, 300 µmol, 3.0 equiv), BF₃•Et₂O (25 µL, 200 µmol, 2.0 equiv), and PhSiH₃ (18 µL, 150 µmol, 1.5 equiv) in THF/MeOH (4:1, 500 µL) was heated at 60 °C with stirring for 1 h. Purification by preparative TLC (20:1 hexanes:EtOAc) afforded quinoline 349 as a yellow oil (12.7 mg, 52 µmol, 52%).

**Physical State:** pale yellow oil.

**¹H NMR** (600 MHz, CDCl₃): δ 8.04 (dd, J=9.2, 5.4 Hz, 1 H), 8.02 (d, J=9.2 Hz, 1 H), 7.51 (dd, J=8.7, 0.8 Hz, 1 H), 7.42 (dd, J=9.1, 8.4, 2.8 Hz, 1 H), 7.37 (dd, J=8.9, 2.9 Hz, 1 H), 2.38–2.29 (m, 2 H), 1.68–1.56 (m, 4 H), 1.45 (m, 4 H), 1.29 (s, 3 H).

**¹³C NMR** (151 MHz, CDCl₃): δ 168.0, 160.2 (d, J=246.4 Hz), 144.9, 135.3 (d, J=5.0 Hz), 131.9 (d, J=9.1 Hz), 126.9 (d, J=9.9 Hz), 119.6, 119.0 (d, J=25.5 Hz), 110.3 (d, J=21.4 Hz), 41.6, 37.3, 29.3, 26.5, and 23.0.

**¹⁹F NMR** (376 MHz, CDCl₃): δ –115.7.

**HRMS (m/z):** calcld for C₁₆H₁₉NF [M+H]⁺: 244.1496, found: 244.1498.

**TLC:** Rₛ=0.71 (10:1 hexanes:EtOAc).
Mechanistic Studies.

Catalysis by $[{\text{Fe(acac)}}_2{(OEt)}_2]$. In an N$_2$-filled glove box, TBS silyl ether 59 (40 mg, 200 µmol, 1.0 equiv), benzyl acrylate (30 µL, 200 µmol, 1.0 equiv) and PhSiH$_3$ (50 µL, 400 µmol, 2.0 equiv) were added to a 25 mL resealable tube. A solution of $[{\text{Fe(acac)}}_2{(OEt)}_2]$ 350 (4.2 mg, 7.0 µmol, 3.5 mol%) in EtOH (1.0 mL) was then added. The resulting reaction mixture was stirred at rt for 15 min to give ester 368 in 65±8% yield, as determined by $^1$H NMR using 1,3,5-trimethoxybenzene (34 mg, 200 µmol, 1.0 equiv) as an internal standard. The mixture was then heated at 60 °C and cooled to rt to yield a brown yellow crystal suitable for X-ray diffraction.

Figure S16. X-ray crystallographic structure of Fe(acac)$_2$•2EtOH.

Low-temperature diffraction data ($\omega$-scans) were collected on a Rigaku SCX Mini diffractometer coupled to a Rigaku Mercury275R CCD with Mo K\(\alpha\) radiation ($\lambda=0.71073$ Å) for the structure of 353-EtOH. The diffraction images were processed and scaled using Rigaku Oxford Diffraction software (CrysAlisPro; Rigaku OD: The Woodlands, TX, 2015). The structure was solved with SHELXT and was refined against $F^2$ on all data by full-matrix least squares with SHELXL (Sheldrick, G. M. *Acta Cryst.* **2008**, *A64*, 112.). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions.

$^{48}$ Wu, C.-H. S.; Rossman, G. R.; Gray, H. B.; Hammond, G. S.; Schugar, H. J. *Inorg. Chem.* **1972**, *11*, 990.
positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). The only exception is H10B, which was found in the difference map and semi-freely refined with the aid of a O-H distance restraint of 0.90(2), which is near the O-H value suggested by the difference map. One reflection was obscured due to instrument artifacts and subsequently omitted. Crystallographic data are summarized in Table S3.

Table S3. Crystal data and structure refinement for Fe(acac)$_2$•2EtOH.

| Property                                         | Value                                      |
|--------------------------------------------------|--------------------------------------------|
| Identification code                               | CCDC 1522544                               |
| Empirical formula                                | C$_{14}$H$_{26}$FeO$_6$                    |
| Formula weight                                    | 346.20                                     |
| Temperature                                       | 93(2) K                                    |
| Wavelength                                        | 0.71073 Å                                  |
| Crystal system                                    | Triclinic                                   |
| Space group                                       | P-1                                        |
| Unit cell dimensions                              | a=5.2765(5) Å, b=8.7572(7) Å, c=9.3297(8) Å |
| Volume                                           | 405.30(6) Å                                |
| Z                                                | 1                                          |
| Density (calculated)                             | 1.418 Mg/m$^3$                             |
| Absorption coefficient                           | 0.953 mm$^{-1}$                            |
| F(000)                                           | 184                                        |
| Crystal size                                      | 0.500 x 0.200 x 0.020 mm$^3$               |
| Theta range for data collection                  | 2.450 to 26.446°                           |
| Index ranges                                      | -6<=$h$<=$6$, -10<=$k$<=$10$, -11<=$l$<=$11$ |
| Reflections collected                            | 6541                                       |
| Independent reflections                          | 1670 [R(int)=0.0354]                       |
| Completeness to theta=25.242°                     | 99.9 %                                     |
| Absorption correction                            | Semi-empirical from equivalents            |
Max. and min. transmission 1.00000 and 0.96624

Refinement method Full-matrix least-squares on F²

Data / restraints / parameters 1670 / 1 / 104

Goodness-of-fit on F² 1.101

Final R indices [I>2sigma(I)] R1=0.0286, wR2=0.0630

R indices (all data) R1=0.0312, wR2=0.0643

Largest diff. peak and hole 0.355 and -0.377 e.Å⁻³

Reduction of [Fe(acac)₂(OEt)]₂ to [Fe(acac)₂]₂ by PhSiH₃. In an N₂-filled glove box, [Fe(acac)₂OEt]₂ (150 mg, 250 µmol, 1.0 equiv) was dissolved in toluene (15 mL). PhSiH₃ (90 µL, 730 µmol, 2.9 equiv) was then added and the reaction mixture was stirred for 4 h at rt [CAUTION: H₂ evolution was observed]. The toluene was removed under reduced pressure and the remaining solids were washed with pentane (10 mL) and dried under reduced pressure to furnish [Fe(acac)₂]₂ (110 mg, 217 µmol, 88%) as an orange powder. A small sample (25 mg) of this solid was dissolved in 1.0 mL of THF and cooled to –38 °C to yield a yellow-green crystal suitable for X-ray diffraction.

Physical State: orange powder.

¹H NMR (400 MHz, C₆D₆): δ 45.7 (s, 2 H) and –24.5 (s, 12 H) ppm.

Elemental Analysis: calcd for C₁₀H₁₄FeO₄: C, 47.28; H, 5.55. Found: C, 47.68; H, 5.52.

Figure S17. X-ray crystallographic structure of Fe(acac)₂•2THF.
Low-temperature diffraction data (ω-scans) were collected on a Rigaku SCX Mini diffractometer coupled to a Rigaku Mercury275R CCD with Mo Kα radiation (λ=0.71073 Å) for the structure of 353-THF. The diffraction images were processed and scaled using the Rigaku CrystalClear software (CrystalClear and CrystalStructure; Rigaku/MSC: The Woodlands, TX, 2005). The structure was solved with SHELXT and was refined against F² on all data by full-matrix least squares with SHELXL (Sheldrick, G. M. *Acta Cryst*. 2008, A64, 112.). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). Atom C5 is disordered over two positions. No special restraints were required for refinement. The site occupancy was freely refined and subsequently constrained to a value of 0.5, which was near the converged value obtained for the site occupancy. The two positions are distinguished by the suffixes "a" and "b." The hydrogen atoms on and adjacent to C5a and C5b were placed and constrained to geometrically expected positions. The reflection (1 1 0) was omitted as it was obscured by the beam stop. Crystallographic data are summarized in Table S4.

**Table S4.** Crystal data and structure refinement for Fe(acac)₂•2THF.

| Property                        | Value                                      |
|---------------------------------|--------------------------------------------|
| Identification code             | CCDC 1522543                               |
| Empirical formula               | C18 H30 Fe O6                              |
| Formula weight                  | 398.27                                     |
| Temperature                     | 173(2) K                                   |
| Wavelength                      | 0.71073 Å                                  |
| Crystal system                  | Monoclinic                                 |
| Space group                     | C2/c                                       |
| Unit cell dimensions            | a=15.4305(11) Å                           |
|                                | α = 90°                                    |
|                                | b=11.1187(8) Å                            |
|                                | β = 116.126(4)°                            |
|                                | c=12.8932(9) Å                            |
|                                | γ=90°                                      |
| Volume                          | 1986.0(3) Å³                              |
| Z                               | 4                                          |
| Density (calculated)            | 1.332 Mg/m³                                |
Absorption coefficient 0.788 mm⁻¹
F(000) 848
Crystal size 0.300 x 0.220 x 0.120 mm³
Theta range for data collection 2.517 to 27.619°.
Index ranges -20≤h≤20, -14≤k≤14, -16≤l≤16
Reflections collected 13589
Independent reflections 2291 [R(int)=0.0398]
Completeness to theta=25.242° 99.7 %
Absorption correction Semi-empirical from equivalents
Max. and min. transmission 1.000 and 0.808
Refinement method Full-matrix least-squares on F²
Data / restraints / parameters 2291 / 0 / 126
Goodness-of-fit on F² 1.006
Final R indices [I>2sigma(I)] R1=0.0330, wR2=0.0866
R indices (all data) R1=0.0480, wR2=0.0950
Largest diff. peak and hole 0.273 and -0.407 e.Å⁻³

**Control for direct PhSiH₃ oxidative addition/reductive elimination pathway.** In an N₂-filled glove box, Fe(acac)₃ (7.0 mg, 20 µmol, 1.0 equiv) was dissolved in 1.0 mL of C₆D₆ in a J. Young tube. After adding a paramagnetic internal standard capillary consisting of 7.6 Mm nickelocene in C₇D₈ to this J. Young tube, the concentration of Fe(acac)₃ was determined to be 15.9 mM. 1,3,5-Trimethoxybenzene (3.4 mg, 20 µmol, 1 equiv) was then added to the J. Young tube as a diamagnetic internal standard. PhSiH₃ (2.5 µL, 20 µmol, 1 equiv) was then added and the reaction was monitored by ¹H NMR spectroscopy after 5 min at rt and 1 h at 60 °C. No reaction was observed between Fe(acac)₃ and PhSiH₃.
Figure S18. Paramagnetic region of the $^1$H NMR spectra before and after the addition of PhSiH$_3$ to Fe(acac)$_3$.
Identification of the Fe species present by Mössbauer spectroscopy. In an N2-filled glove box, TBS silyl ether 59 (40.0 mg, 200 µmol, 1.0 equiv), benzyl acrylate (30 µL, 200 µmol, 1.0 equiv) and PhSiH3 (50 µL, 400 µmol, 2.0 equiv) were added to a 25 mL resealable tube. A solution of $^{57}$Fe(acac)$_3$ 49,50 (4.0 mg, 10 µmol, 5 mol%) in EtOH (1 mL) was then added. The resulting reaction mixture was heated at 60 °C for 10 min and brought back into a N2-filled

49 Xiao, Y.; Koutmos, M.; Case, D. A.; Coucouvanis, D.; Wang, H.; Cramer, S. P. *Dalton Trans.* 2006, 2192.
50 Zhang, Y. C.; Tang, J. Y.; Hu, X. Y. *J. Alloys Compd.* 2008, 462, 24.
glovebox to prepare a solution Mössbauer sample. For comparison, [Fe(acac)₂]₂ (50 mg, 100 µmol) was dissolved in hot EtOH (2.0 mL) in an N₂-filled glovebox. About 1 mL of this solution was frozen in a Delrin sample cup at −196 °C and placed into the spectrometer at 80 K.

Figure S20. Zero-field Mössbauer spectrum of the catalytic reaction at 80 K. The black circles are the data, the red line (δ=1.25 mm/s, ΔE₀=2.59 mm/s) is the fit, and the blue line is the residual.
Figure S21. Zero-field Mössbauer spectrum of [Fe(acac)₂]₂ in EtOH at 80 K. The black circles are the data, the red line (δ=1.24 mm/s, ΔE_Q=2.60 mm/s) is the fit, and the blue line is the residual.

**Oxidation of [Fe(acac)₂]₂ to Fe(acac)₃ by O₂.** In an N₂-filled glove box, [Fe(acac)₂]₂ (50 mg, 100 µmol, 1.0 equiv) was dissolved in 5 mL of toluene in a 100 mL resealable tube. The headspace of the resealable tube was then filled with O₂ (830 mbar, 3.0 mmol, 30 equiv) and stirred for 18 h. The presence of Fe(acac)₃ was indicated by ¹H NMR spectroscopy.
Figure S22. $^1$H NMR spectrum of Fe(acac)$_2$ exposed to O$_2$.

Oxidation of [Fe(acac)$_2$]$_2$ to Fe(acac)$_3$ by air. In an N$_2$-filled glovebox, [Fe(acac)$_2$]$_2$ (5.0 mg, 10 µmol) was dissolved in 500 µL of C$_6$D$_6$ in a J. Young tube. After acquiring the $^1$H NMR spectrum of this solution, the J. Young tube was exposed to air for 10 s and the $^1$H NMR spectrum was acquired again. Additionally, a sample of [Fe(acac)$_2$]$_2$ (50 mg) that had been stored in an N$_2$-filled glovebox was exposed to air overnight. The resultant solids were packed in Delrin sample cup and placed into the spectrometer at 80 K. A small sample of the same solids (15 mg) were dissolved in 2.0 mL of hot hexanes and cooled to −38 °C to grow crystals suitable for X-ray diffraction. The resultant structure and unit cell from this diffraction is consistent with that of Fe(acac)$_3$. However, the Mössbauer spectrum of the material indicates the presence of a currently unidentified iron(III) species separate from Fe(acac)$_3$. For comparison, solid Fe(acac)$_3$ was packed in a Delrin sample cup and placed into the spectrometer at 80 K.
Figure S23. $^1$H NMR spectrum of Fe(acac)$_2$ exposed to air.

Figure S24. Zero-field Mössbauer spectrum of [Fe(acac)$_2$]$_2$ after air exposure at 80 K. The black circles are the data, the black line is a simulation with fit parameters. Red line ($\delta$=0.53 mm/s, $\Delta$E
=0 mm/s) is the fit for Fe(acac)$_3$, and blue line ($\delta=0.52$ mm/s, $\Delta E_Q=0.72$ mm/s) is the fit for the unidentified Fe species and the gray line is the residual.

**Figure S25.** Zero-field Mössbauer spectrum of Fe(acac)$_3$ at 80 K. The black circles are the data, the red line ($\delta=0.53$ mm/s, $\Delta E_Q=0$ mm/s) is the fit for Fe(acac)$_3$, and blue line is the residual. The broad signal for Fe(acac)$_3$ is presumably due to slow relaxation.
Preparation of PhSi(OEt)H₂. Following the procedure of Gunji, Yamashita, Ikeno, and Yamada,⁵¹ in an N₂-filled glove box, Cu(hfac)₂ (580 mg, 1.2 mmol, 16 mol%) was dissolved with 15 mL of CH₂Cl₂ in a 500 mL resealable tube and frozen at –196 °C. EtOH (6.5 mL, 110 mmol, 1.5 equiv) and PhSiH₃ (9.3 mL, 75 mmol, 1.0 equiv) were then added. After the reaction solution was frozen, the resealable tube was closed, taken out the glovebox and opened to N₂ on a Schlenk line. The reaction mixture was stirred at 0 °C for 90 min [CAUTION: substantial H₂ evolution is observed upon thawing]. The resealable tube was brought back to the glovebox, where 60 mL of hexanes were added. The solution was then concentrated under reduced pressure to remove the solvents. The resulting crude was distilled at 120 mtorr from a flask at 55 °C to a receiving flask at –78 °C to furnish 90% pure PhSi(OEt)H₂ (2.1 g, 14 mmol, 18%) as a colorless oil. The major impurity was PhSi(OEt)₂H.

Physical State: colorless oil.

¹H NMR (400 MHz, C₆D₆): δ 7.60–7.58 (m, 2 H), 7.19–7.12 (m, 3 H), 5.21 (s, 2 H), 3.58 (q, J=7.0 Hz, 2 H), and 1.04 (t, J=7.0 Hz, 3 H) ppm.

Fe(acac)₂-catalyzed ethanolysis of PhSiH₃. In an N₂-filled glove box, [Fe(acac)₂]₂ (1.0 mg, 2.0 µmol, 5 mol%) and PhSiH₃ (50 µL, 40 µmol, 1.0 equiv) was added with 1.0 mL of C₆D₆ to a J. Young tube. After adding an internal standard capillary consisting of 4.8 mM of 1,3,5-trimethoxybenzene in toluene-d₈ to this J. Young tube, the concentration of PhSiH₃ was determined to be 34 mM. EtOH (10 µL, 0.17 mmol, 4.3 equiv) was then added and the reaction was monitored by ¹H NMR spectroscopy after 1 h at rt, 1 h at 60 °C, and 2 h at 60 °C.

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⁵¹ Gunji, Y.; Yamashita, Y.; Ikeno, T.; Yamada, T. Chem. Lett. 2006, 35, 714.
Fe(acac)\(_2\)-catalyzed ethanolysis of PhSi(OEt)\(_2\)H. In an N\(_2\)-filled glove box, PhSi(OEt)H\(_2\) (90% pure, 7.4 mg, 48 \(\mu\)mol, 1.5 equiv) was added to a J. Young tube with 500 \(\mu\)L of C\(_6\)D\(_6\). After adding an internal standard capillary consisting of 4.8 mM 1,3,5-trimethoxybenzene in toluene-\(d_8\) to this J. Young tube, the concentration of PhSi(OEt)H\(_2\) was determined to be 66 mM. EtOH (2.0 \(\mu\)L, 33 \(\mu\)mol, 1.0 equiv) was then added to the J. Young tube. No reaction was between PhSi(OEt)H\(_2\) and EtOH was observed by \(^1\)H NMR spectroscopy after 1 h at rt and then after heating at 60 °C for 1 h. [Fe(acac)\(_2\)]\(_2\) (1.0 mg, 2.0 \(\mu\)mol, 6 mol%) was then added to the J. Young tube. After 10 min, the \(^1\)H NMR spectrum of resulting mixture indicated the presence of PhSi(OEt)\(_2\)H. Additional conversion of PhSi(OEt)H\(_2\) to PhSi(OEt)\(_2\)H was observed after 1 h at
rt. Additional EtOH (2.0 µL, 33 µmol, 1.0 equiv) was then added, after which the conversion of PhSi(OEt)₂H to PhSi(OEt)₃ was immediately observable by ¹H NMR spectroscopy. Heating at 60 °C for 2 h resulted in further ethanolysis of PhSi(OEt)₂H to PhSi(OEt)₃.

**Figure S27.** Monitoring of the ethanolysis of PhSi(OEt)H₂ by ¹H NMR spectroscopy.

**Use of PhSi(OEt)H₂ as the terminal reductant.** In an N₂-filled glove box, TBS silyl ether 59⁹ (40.0 mg, 200 µmol, 1.0 equiv), benzyl acrylate (30 µL, 200 mmol, 1.0 equiv) and PhSi(OEt)H₂ (63 mg, 400 mmol, 2.0 equiv) were added to a 25 mL resealable tube. A solution of Fe(acac)₃ (4.9 mg, 14 µmol, 5 mol%) in EtOH (1.0 mL) was then added. The resulting reaction mixture
was stirred at rt for 15 min to give ester 368 in 76±13% yield, as determined by \(^1\)H NMR using 1,3,5-trimethoxybenzene (34 mg, 200 \(\mu\)mol, 1.0 equiv) as an internal standard.

**Deuteration study with PhSiD\(_3\).** Following General Procedure 2, a mixture of tert-butylidimethyl(prop-1-en-2-yloxy)silane\(^{14}\) (17.3 mg, 100 \(\mu\)mol, 1.0 equiv), methyl vinyl ketone (24.9 \(\mu\)L, 300 \(\mu\)mol, 3.0 equiv), Na\(_2\)HPO\(_4\) (14.2 mg, 100 \(\mu\)mol, 1.0 equiv), Fe(dibm)\(_3\) (2.6 mg, 5.0 \(\mu\)mol, 5 mol%), and a solution of PhSiD\(_3\)\(^{52}\) (7.4 M in Et\(_2\)O, 270 \(\mu\)L, 200 \(\mu\)mol, 2.0 equiv) in EtOH (0.23 mL) was heated at 60 °C with stirring for 1 h. Purification by flash column chromatography (SiO\(_2, 97:3\) hexanes:EtOAc) furnished deuterated 371 as a colorless oil (15.8 mg, 66.1 \(\mu\)mol, 66%).

**Physical State**: colorless oil.

\(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta\) 2.56–2.52 (m, 2 H), 2.16 (s, 3 H), 1.71–1.67 (m, 2 H), 1.20 (s, 3 H), 1.19–1.18 (m, 2 H), 0.85 (s, 9 H), 0.07 (s, 3 H), and 0.07 (s, 3 H).

\(^{13}\)C NMR (151 MHz, CDCl\(_3\)): \(\delta\) 209.7, 72.8, 39.1, 38.5, 30.5, 29.6 (t, \(J = 19.5\) Hz), 25.9, 18.3, –1.9, and –1.9.

**HRMS (m/z)** calcd for C\(_{13}\)H\(_{28}\)DO\(_2\)Si [M+H]\(^+\): 246.1994, found: 246.1996.

**TLC**: \(R_f = 0.33\) (97:3 hexanes:EtOAc).

**Cyclopropane ring-opening experiment.** Following General Procedure 2, a mixture of tert-butyl((1-cyclopropylvinyl)oxy)dimethylsilane\(^{53}\) (65.0 mg, 331 \(\mu\)mol, 3.0 equiv), methyl acrylate (10.0 \(\mu\)L, 110 \(\mu\)mol, 1.0 equiv), Na\(_2\)HPO\(_4\) (15.7 mg, 110 \(\mu\)mol, 1.0 equiv), Fe(dibm)\(_3\) (2.9 mg, 5.5 \(\mu\)mol, 5 mol%), and PhSiH\(_3\) (27.2 \(\mu\)L, 221 \(\mu\)mol, 2.0 equiv) in EtOH (0.55 mL) was heated at

\(^{52}\) Fung, B. M.; Wei, I. Y. *J. Am. Chem. Soc.* 1970, 92, 1497.

\(^{53}\) Saito, I.; Nagata, R.; Yuba, K; Matsuura, T. *Tetrahedron Lett.* 1983, 24, 1737.
60 °C with stirring for 1 h. Purification by preparative TLC (SiO₂, 95:5 hexanes:EtOAc) furnished silyl ether 373 as a pale yellow oil (2.5 mg, 6.71 µmol, 6%).

**Physical State**: pale yellow oil.

**¹H NMR** (600 MHz, CDCl₃): δ 3.68 (s, 3 H), 3.62 (s, 3 H), 2.78 (dd, J=7.1, 7.1 Hz, 1 H), 2.43 (ddd, J=16.0, 11.2, 5.1 Hz, 1 H), 2.35 (ddd, J=15.7, 11.3, 5.5 Hz, 1 H), 2.08 (ddd, J=13.4, 6.8, 6.8 Hz, 1 H), 2.03–1.83 (m, 6 H), 1.84–1.71 (m, 2 H), 1.69–1.59 (m, 2 H), 1.15 (s, 3 H), 0.86 (s, 9 H), 0.09 (s, 3 H), and 0.07 (s, 3 H).

**¹³C NMR** (151 MHz, CDCl₃): δ 176.6, 174.6, 76.0, 55.4, 53.6, 51.8, 44.6, 36.7, 30.3, 29.2, 26.1, 24.9, 24.5, 22.5, –1.68, and –1.72.

**HRMS (m/z)** calcd for C₁₉H₃₉O₅Si [M+H]⁺: 375.2561, found: 375.2569.

**TLC**: Rᵢ=0.60 (9:1 hexanes:EtOAc).

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**Three component coupling reaction.** To a solution of TBS silyl ether 59 (40.0 mg, 200 µmol, 1.0 equiv), benzyl acrylate (45.9 µL, 300 µmol, 1.5 equiv), benzaldehyde (61.2 µL, 600 µmol, 3.0 equiv), Fe(acac)₃ (21.2 mg, 60 µmol, 30 mol%), and EtOH (35.0 µL, 600 µmol, 3.0 equiv) in THF (1.0 mL) was added PhSiH₃ (37.0 µL, 300 µmol, 1.5 equiv). The resulting mixture was heated to 60 °C with stirring for 17 h. The reaction mixture was then cooled to rt and diluted with brine. The organic layer was separated and the aqueous layer was extracted with EtOAc. The organic layers were combined, washed with brine, dried over MgSO₄, filtered, and concentrated under reduced pressure. The crude material was then purified by flash column chromatography (SiO₂, 9:1 hexanes:EtOAc) followed by preparative TLC (SiO₂, 8:2 hexanes:acetone) to furnish alcohol 378 as a colorless oil (18.9 mg, 40.0 µmol, 20%).

**Physical State**: colorless oil.

**¹H NMR** (600 MHz, CDCl₃): δ 7.35–7.29 (m, 8 H), 7.17–7.13 (m, 2 H), 4.92 (dd, J=14.7, 12.3 Hz, 2 H), 4.82 (d, J=5.9 Hz, 1 H), 3.43 (dd, J=7.5, 7.5 Hz, 2 H), 2.79 (ddd, J=10.2, 5.9, 1.5 Hz, 1 H), 2.60 (br s, 1 H), 1.84 (dd, J=14.2, 10.2 Hz, 1 H), 1.67 (dd, J=14.2, 1.6 Hz, 1 H), 1.45–1.33 (m, 2 H), 0.88 (s, 9 H), 0.78 (s, 3 H), 0.73 (s, 3 H), and 0.02 (s, 6 H).
$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 175.6, 141.4, 135.5, 128.60, 128.56, 128.43, 128.37, 128.0, 126.5, 75.3, 66.8, 59.9, 49.7, 44.3, 39.3, 32.3, 27.3, 27.1, 26.1, 18.4, and –5.1. Peak overlapping was observed.

HRMS ($m/z$) calcd for C$_{28}$H$_{43}$O$_4$Si [M+H]$^+$: 471.2925, found: 471.2924.

TLC: $R_f$=0.32 (9:1 hexanes:EtOAc).

Deuteration study with ethanol-$d_1$. Following General Procedure 2, a mixture of tert-butyldimethyl(prop-1-en-2-yloxy)silane$^{14}$ (17.3 mg, 100 µmol, 1.0 equiv), methyl vinyl ketone (24.9 µL, 300 µmol, 3.0 equiv), Na$_2$HPO$_4$ (14.2 mg, 0.1 mmol, 1.0 equiv), Fe(dibm)$_3$ (2.6 mg, 5.0 µmol, 5 mol%), and PhSiH$_3$ (24.6 µL, 200 µmol, 2.0 equiv) in ethanol-$d_1$ (0.50 mL) was heated at 60 °C with stirring for 1 h. Purification by flash column chromatography (SiO$_2$, 97:3 hexanes:EtOAc) furnished deuterated 379 as a colorless oil (16.5 mg, 68.1 µmol, 68%).

Physical State: colorless oil.

$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ 209.8, 72.8, 38.8 (t, $J$=18.8 Hz), 38.5, 30.1, 29.9, 26.0, 18.2, –1.9, and –1.9. Peak overlapping was observed.

HRMS ($m/z$) calcd for C$_{13}$H$_{28}$DO$_2$Si [M+H]$^+$: 246.1994, found: 246.1996.

TLC: $R_f$=0.33 (97:3 hexanes:EtOAc).
Determination of the Reactant Orders of an Olefin Cross-Coupling Model System.

Order in donor 59. The order in donor was determined by studying the initial rate of the olefin cross-coupling of donor 59 with acceptor 131 using different concentrations of donor 59. To a 0.5–2 mL tapered microwave vial was added TBS silyl ether 59 (50–125 µmol), benzyl acrylate (30.6 µL, 200 µmol), Fe(acac)₃ (10.6 mg, 30.0 µmol), and butyl butyrate (internal standard, 8.00–9.00 mg). A magnetic stir bar was placed in the vial, which was then sealed with a blue PTFE/white silicone septum cap. The vessel was briefly purged with Ar using a balloon filled with Ar and then placed under positive Ar pressure. Degassed EtOH that was sparged in a sonicator with Ar for ca. 10 min (500 µL) was then added. The mixture was stirred at rt until it became homogenous, after which PhSiH₃ (18.5 µL, 150 µmol) was quickly added. The reaction vessel was immediately submerged in an oil bath that was preheated 40 °C. Aliquots of the reaction mixture were taken via syringe at 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 15, 25, 40, and 60 min, immediately diluted in EtOAc, and analyzed by GC/FID to determine the rate of the formation of ester 368. A plot of ln [59] vs. ln initial rate gave a straight line ($R^2=0.97996$) with a slope of 0.4586, indicative of approximately half order dependence on [59].

**Figure S28.** Plot indicates approximately half order dependence on [59] for the model system.
Order in acceptor 131. The order in acceptor was determined by studying the initial rate of the olefin cross-coupling of donor 59 with acceptor 131 using different concentrations of acceptor 131. To a 0.5–2 mL tapered microwave vial was added TBS silyl ether 59 (20.0 mg, 100 µmol), benzyl acrylate (150–300 µmol), Fe(acac)₃ (10.6 mg, 30.0 µmol), and butyl butyrate (internal standard, 8.00–9.00 mg). A magnetic stir bar was placed in the vial, which was then sealed with a blue PTFE/white silicone septum cap. The vessel was briefly purged with Ar using a balloon filled with Ar and then placed under positive Ar pressure. Degassed EtOH that was sparged in a sonicator with Ar for ca. 10 min (500 µL) was then added. The mixture was stirred at rt until it became homogenous, after which PhSiH₃ (18.5 µL, 150 µmol) was quickly added. The reaction vessel was immediately submerged in an oil bath that was preheated 40 °C. Aliquots of the reaction mixture were taken via syringe at 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 15, 25, 40, and 60 min, immediately diluted in EtOAc, and analyzed by GC/FID to determine the rate of the formation of ester 368. A plot of ln [131] vs. ln initial rate gave a straight line (R²=0.95364) with a slope of –0.8288, indicative of approximately inverse first order dependence on [131].

![Chemical Reaction Diagram]

**Figure S29.** Plot indicates approximately inverse first order dependence on [131] for the model system.
Order in Fe(acac)₃. The order in Fe(acac)₃ was determined by studying the initial rate of the olefin cross-coupling of donor 59 with acceptor 131 using different concentrations of Fe(acac)₃. To a 0.5–2 mL tapered microwave vial was added TBS silyl ether 59 (20.0 mg, 100 µmol), benzyl acrylate (30.6 µL, 200 µmol), Fe(acac)₃ (10.0–50.0 µmol), and butyl butyrate (internal standard, 8.00–9.00 mg). A magnetic stir bar was placed in the vial, which was then sealed with a blue PTFE/white silicone septum cap. The vessel was briefly purged with Ar using a balloon filled with Ar and then placed under positive Ar pressure. Degassed EtOH that was sparged in a sonicator with Ar for ca. 10 min (500 µL) was then added. The mixture was stirred at rt until it became homogenous, after which PhSiH₃ (18.5 µL, 150 µmol) was quickly added. The reaction vessel was immediately submerged in an oil bath that was preheated 40 °C. Aliquots of the reaction mixture were taken via syringe at 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 15, 25, 40, and 60 min, immediately diluted in EtOAc, and analyzed by GC/FID to determine the rate of the formation of ester 368. A plot of ln [Fe(acac)₃] vs. ln initial rate gave a straight line (R²=0.97569) with a slope of 0.5856, indicative of approximately half order dependence on [Fe(acac)₃].

![Chemical diagram]

**Figure S30.** Plot indicates approximately half order dependence on [Fe(acac)₃] for the model system.
Order in PhSiH₃. The order in PhSiH₃ was determined by studying the initial rate of the olefin cross-coupling of donor 59 with acceptor 131 using different concentrations of PhSiH₃. To a 0.5–2 mL tapered microwave vial was added TBS silyl ether 59 (20.0 mg, 100 µmol), benzyl acrylate (30.6 µL, 200 µmol), Fe(acac)₃ (10.6 mg, 30.0 µmol), and butyl butyrate (internal standard, 8.00–9.00 mg). A magnetic stir bar was placed in the vial, which was then sealed with a blue PTFE/white silicone septum cap. The vessel was briefly purged with Ar using a balloon filled with Ar and then placed under positive Ar pressure. Degassed EtOH that was sparged in a sonicator with Ar for ca. 10 min (500 µL) was then added. The mixture was stirred at rt until it became homogenous, after which PhSiH₃ (50.0–250 µmol) was quickly added. The reaction vessel was immediately submerged in an oil bath that was preheated 40 °C. Aliquots of the reaction mixture were taken via syringe at 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 15, 25, 40, and 60 min, immediately diluted in EtOAc, and analyzed by GC/FID to determine the rate of the formation of ester 368. A plot of ln [PhSiH₃] vs. ln initial rate gave a straight line (R²=0.98683) with a slope of 1.1990, indicative of approximately first order dependence on [PhSiH₃].

![Chemical reaction diagram]

Figure S31. Plot indicates approximately first order dependence on [PhSiH₃] for the model system.
Kinetic Isotope Effect.

Synthesis of phenylsilane-$d_3$ (S14). Following a modification of the method of Fung and Wei,$^{52}$ LiAlD$_4$ (262 mg, 6.24 mmol, 1 equiv) was suspended in Et$_2$O (6.2 mL) under Ar and cooled to 0 °C with stirring. PhSiCl$_3$ (1.00 mL, 6.24 mmol, 1.0 equiv) was added dropwise and the reaction mixture was warmed to rt and then refluxed at 45 °C for 3.5 h. The reaction mixture was then cooled to 0 °C, where it was carefully quenched with ice cold H$_2$O. The organic layer was separated and held at 0 °C and the aqueous layer extracted with ice cold Et$_2$O at 0 °C. The organic layers were combined, washed with ice cold brine at 0 °C, dried over MgSO$_4$, filtered, and concentrated under reduced pressure at 0 °C at 40 mbar [CAUTION: concentrating below 40 mbar (e.g., 11 mbar) can result in the total loss of product] to furnish pure PhSiD$_3$ as a colorless oil (596 mg, 5.36 mmol, 86%).

Spectroscopic data was identical to that reported in the literature.$^{54}$

Reaction progress curve of an olefin cross-coupling model system using PhSiH$_3$. To a 0.5–2 mL tapered microwave vial was added TBS silyl ether 59$^9$ (40.1 mg, 200 µmol, 1.0 equiv), benzyl acrylate (45.9 µL, 300 µmol, 1.5 equiv), Fe(acac)$_3$ (7.06 mg, 20.0 µmol, 10 mol%), and butyl butyrate (internal standard, 8.48 mg). A magnetic stir bar was placed in the vial, which was then sealed with a blue PTFE/white silicone septum cap. The vessel was briefly purged with Ar using a balloon filled with Ar and then placed under positive Ar pressure. Degassed EtOH that was sparged in a sonicator with Ar for ca. 10 min (1.00 mL) was then added. The mixture was stirred at rt until it became homogenous, after which PhSiH$_3$ (37.0 µL, 300 µmol, 1.5 equiv) was quickly added. The reaction vessel was immediately submerged in an oil bath that was preheated 40 °C. Aliquots of the reaction mixture were taken via syringe at 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 15,$^{54}$ Kumar, A.; Pandiakumar, A. K.; Samuelson, A. G. *Tetrahedron* 2014, 70, 3185.
20, 25, 30, 35, 40, 45, 50, 55, and 60 min, immediately diluted in EtOAc, and analyzed by GC/FID to determine the rate of the formation of ester 368.

![Figure S32](image)

**Figure S32.** Reaction progress curve for the coupling of 59 with 131 using PhSiH₃.

**Reaction progress curve of an olefin cross-coupling model system using PhSiD₃.** To a 0.5–2 mL tapered microwave vial was added TBS silyl ether 59⁹ (40.1 mg, 200 µmol, 1.0 equiv), benzyl acrylate (45.9 µL, 300 µmol, 1.5 equiv), Fe(acac)₃ (7.06 mg, 20.0 µmol, 10 mol%), and butyl butyrate (internal standard, 8.44 mg). A magnetic stir bar was placed in the vial, which was then sealed with a blue PTFE/white silicone septum cap. The vessel was briefly purged with Ar using a balloon filled with Ar and then placed under positive Ar pressure. Degassed EtOH that was sparged in a sonicator with Ar for ca. 10 min (1.00 mL) was then added. The mixture was stirred at rt until it became homogenous, after which PhSiD₃ (38.0 µL, 300 µmol, 1.5 equiv) was quickly added. The reaction vessel was immediately submerged in an oil bath that was preheated 40 °C. Aliquots of the reaction mixture were taken via syringe at 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 15,
20, 25, 30, 35, 40, 45, 50, 55, and 60 min, immediately diluted in EtOAc, and analyzed by GC/FID to determine the rate of the formation of ester 368.

Figure S33. Reaction progress curve for the coupling of 59 with 131 using PhSiD₃.

**Determination of the kinetic isotope effect.** The first 10 min of Figures S32 and S33 were overlaid and a linear trendline was drawn between 5–10 min of each reaction progress curve to obtain the initial rates of the reaction (Figure S31). Minutes 1–4 were not included to account for the reaction’s induction period. Dividing the slope of the trendline for the reaction using PhSiH₃ by the slope of the trendline for the reaction using PhSiD₃ gave $k_H/k_D=1.2116/0.8199=1.5$. 
Figure S34. Overlay of the first 10 minutes of Figures S32 and S33 to show the kinetic isotope effect of the olefin cross-coupling.
Hammett Analysis of the Olefin Cross-Coupling.

**General Procedure 5. Determination of the initial rate of reaction of the coupling of \( p \)-substituted styrenes with acceptor 131.** To a 0.5–2 mL tapered microwave vial was added the \( p \)-substituted styrene (100 \( \mu \)mol, 1.0 equiv), benzyl acrylate (31.6 \( \mu \)L, 300 \( \mu \)mol, 2.0 equiv), Fe(acac)\(_3\) (10.6 mg, 30.0 \( \mu \)mol, 30 mol%), and butyl butyrate (internal standard, 8.29–8.91 mg). A magnetic stir bar was placed in the vial, which was then sealed with a blue PTFE/white silicone septum cap. The vessel was briefly purged with Ar using a balloon filled with Ar and then placed under positive Ar pressure. Degassed EtOH that was sparged in a sonicator with Ar for ca. 10 min (500 \( \mu \)L) was then added. The mixture was stirred at rt until it became homogenous, after which PhSiH\(_3\) (18.5 \( \mu \)L, 150 \( \mu \)mol, 1.5 equiv) was quickly added. The reaction vessel was immediately submerged in an oil bath that was preheated 40 °C. Aliquots of the reaction mixture were taken via syringe at 1, 2, 3, 4, 5, 6, 7, 8, 9, and 10 min, immediately diluted in EtOAc, and analyzed by GC/FID to determine the rate of the formation of the product.
No substitution on the styrene. General Procedure 5 was followed using styrene (10.4 mg, 100 µmol, 1.0 equiv) as the donor olefin and butyl butyrate (8.66 mg) as the internal standard. A plot of time vs. product yield gave a straight line ($R^2=0.98783$), where the slope indicated an initial rate of 0.5784% per min for the formation of 398.

![Chemical reaction](image)

**Figure S35.** Initial rate of the formation of 398 from the coupling of styrene (63) with 131.
**p-Methoxy substitution on the styrene.** General Procedure 5 was followed using styrene 395 (13.4 mg, 100 µmol, 1.0 equiv) as the donor olefin and butyl butyrate (8.66 mg) as the internal standard. A plot of time vs. product yield gave a straight line ($R^2=0.99167$), where the slope indicated an initial rate of 0.8602% per min for the formation of S15.

![Reaction Progress p-Methoxy](image)

**Figure S36.** Initial rate of the formation of S15 from the coupling of styrene 395 with 131.
**p-Methyl substitution on the styrene.** General Procedure 5 was followed using styrene S16 (11.8 mg, 100 µmol, 1.0 equiv) as the donor olefin and butyl butyrate (8.66 mg) as the internal standard. A plot of time vs. product yield gave a straight line ($R^2=0.99488$), where the slope indicated an initial rate of 0.8497% per min for the formation of S17.

![Reaction Progress p-Methyl](image)

**Figure S37.** Initial rate of the formation of S17 from the coupling of styrene S16 with 131.
**p-Fluoro substitution on the styrene.** General Procedure 5 was followed using styrene S18 (12.2 mg, 100 µmol, 1.0 equiv) as the donor olefin and butyl butyrate (8.91 mg) as the internal standard. A plot of time vs. product yield gave a straight line (R²=0.98864), where the slope indicated an initial rate of 0.7976% per min for the formation of S19.

![Reaction Progress p-Fluoro](image)

**Figure S38.** Initial rate of the formation of S19 from the coupling of styrene S18 with 131.
**p-Phenyl substitution on the styrene.** General Procedure 5 was followed using styrene S20 (18.0 mg, 100 µmol, 1.0 equiv) as the donor olefin and butyl butyrate (8.29 mg) as the internal standard. A plot of time vs. product yield gave a straight line ($R^2=0.98959$), where the slope indicated an initial rate of 0.3351% per min for the formation of S21.

![Reaction Progress p-Phenyl](image)

**Figure S39.** Initial rate of the formation of S21 from the coupling of styrene S20 with 131.
**p-Chloro substitution on the styrene.** General Procedure 5 was followed using styrene 396 (13.9 mg, 100 µmol, 1.0 equiv) as the donor olefin and butyl butyrate (8.66 mg) as the internal standard. A plot of time vs. product yield gave a straight line ($R^2=0.99925$), where the slope indicated an initial rate of 0.3642% per min for the formation of S22.

![Reaction Progress p-Chloro](image)

**Figure S40.** Initial rate of the formation of S22 from the coupling of styrene 396 with 131.
**p-Bromo substitution on the styrene.** General Procedure 5 was followed using styrene S23 (18.3 mg, 100 µmol, 1.0 equiv) as the donor olefin and butyl butyrate (8.66 mg) as the internal standard. A plot of time vs. product yield gave a straight line (R²=0.99629), where the slope indicated an initial rate of 0.3647% per min for the formation of S24.

![Reactivity progress p-Bromo](image)

**Figure S41.** Initial rate of the formation of S24 from the coupling of styrene S23 with 131.
**p-Trifluoromethyl substitution on the styrene.** General Procedure 5 was followed using styrene S25 (17.2 mg, 100 µmol, 1.0 equiv) as the donor olefin and butyl butyrate (8.55 mg) as the internal standard. A plot of time vs. product yield gave a straight line ($R^2 = 0.99198$), where the slope indicated an initial rate of 0.4458% per min for the formation of S26.

![Diagram](image)

**Figure S42.** Initial rate of the formation of S26 from the coupling of styrene S25 with 131.
**p-N,N-Dimethylcarboxamido substitution on the styrene.** General Procedure 5 was followed using styrene S27 (17.5 mg, 100 µmol, 1.0 equiv) as the donor olefin and butyl butyrate (8.69 mg) as the internal standard. A plot of time vs. product yield gave a straight line ($R^2=0.98855$), where the slope indicated an initial rate of 0.1579% per min for the formation of S28.

![Reaction Progress p-N,N-Dimethylcarboxamido](image)

**Figure S43.** Initial rate of the formation of S28 from the coupling of styrene S27 with 131.
**p**-Carboxymethyl substitution on the styrene. General Procedure 5 was followed using styrene 397 (16.2 mg, 100 µmol, 1.0 equiv) as the donor olefin and butyl butyrate (8.58 mg) as the internal standard. A plot of time vs. product yield gave a straight line (R²=0.99403), where the slope indicated an initial rate of 0.2056% per min for the formation of S29.

**Figure S44.** Initial rate of the formation of S29 from the coupling of styrene 397 with 131.
**p-Cyano substitution on the styrene.** General Procedure 5 was followed using styrene S30 (12.9 mg, 100 µmol, 1.0 equiv) as the donor olefin and butyl butyrate (8.47 mg) as the internal standard. A plot of time vs. product yield gave a straight line ($R^2=0.99400$), where the slope indicated an initial rate of 0.2398% per min for the formation of S31.

![Reaction Progress p-Cyano](image)

**Figure S45.** Initial rate of the formation of S31 from the coupling of styrene S30 with 131.
Construction of the Hammett plot. The initial reaction rates from Figures S36–S45 for the \( p \)-substituted styrenes were divided by the initial reaction rate from Figure S35 for styrene (63) to give values for \( k_X/k_H \). The values for \( \log(k_X/k_H) \) were then plotted against known values of \( \sigma^{-55} \) to obtain a Hammett plot for the olefin cross-coupling of \( p \)-substituted styrenes.

| \( p \)-Substituent | \( \sigma^- \) | Initial Rate | \( k_X/k_H \) | \( \log(k_X/k_H) \) |
|---------------------|----------------|--------------|----------------|-------------------|
| H                   | n/a            | 0.5784       | n/a            | n/a               |
| OMe                 | -0.26          | 0.8602       | 1.4872         | 0.1724            |
| Me                  | -0.17          | 0.8497       | 1.4691         | 0.1670            |
| F                   | -0.03          | 0.7976       | 1.3790         | 0.1396            |
| Ph                  | 0.02           | 0.3351       | 0.5794         | -0.2371           |
| Cl                  | 0.19           | 0.3642       | 0.6297         | -0.2009           |
| Br                  | 0.25           | 0.3647       | 0.6305         | -0.2003           |
| CF₃                 | 0.65           | 0.4458       | 0.7707         | -0.1131           |
| CONMe₂              | 0.70           | 0.1579       | 0.2730         | -0.5638           |
| CO₂Me               | 0.75           | 0.2056       | 0.3555         | -0.4492           |
| CN                  | 1.00           | 0.2337       | 0.4040         | -0.3936           |

Table S5. Tabular data used to construct the Hammett plot.

Figure S46. Hammett plot of the olefin cross-coupling of \( p \)-substituted styrenes.

\(^{55}\) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165.
Determination of the Reactant Orders of the Olefin Cross-Coupling of \( p \)-Methoxystyrene (395).

**Order in donor 395.** The order in donor was determined by studying the initial rate of the olefin cross-coupling of donor 395 with acceptor 131 using different concentrations of donor 395. To a 0.5–2 mL tapered microwave vial was added styrene 395 (50–150 \( \mu \text{mol} \)), benzyl acrylate (30.6 \( \mu \text{L} \), 200 \( \mu \text{mol} \)), \( \text{Fe(acac)}_3 \) (10.6 mg, 30.0 \( \mu \text{mol} \)), and butyl butyrate (internal standard, 8.00–9.00 mg). A magnetic stir bar was placed in the vial, which was then sealed with a blue PTFE/white silicone septum cap. The vessel was briefly purged with Ar using a balloon filled with Ar and then placed under positive Ar pressure. Degassed EtOH that was sparged in a sonicator with Ar for ca. 10 min (500 \( \mu \text{L} \)) was then added. The mixture was stirred at rt until it became homogenous, after which PhSiH\(_3\) (18.5 \( \mu \text{L} \), 150 \( \mu \text{mol} \)) was quickly added. The reaction vessel was immediately submerged in an oil bath that was preheated 40 °C. Aliquots of the reaction mixture were taken via syringe at 1, 2, 3, 4, and 5 min, immediately diluted in EtOAc, and analyzed by GC/FID to determine the rate of the formation of ester S15. A plot of \( \ln [395] \) vs. \( \ln \text{initial rate} \) gave a straight line (\( R^2=0.54821 \)) with a slope of –0.1323, indicative of approximately zero order dependence on [395].

**Figure S47.** Plot indicates approximately zero order dependence on [395] for the system using styrene 395.
Order in acceptor 131. The order in acceptor was determined by studying the initial rate of the olefin cross-coupling of donor 395 with acceptor 131 using different concentrations of acceptor 131. To a 0.5–2 mL tapered microwave vial was added styrene 395 (13.4 mg, 100 µmol), benzyl acrylate (150–300 µmol), Fe(acac)$_3$ (10.6 mg, 30.0 µmol), and butyl butyrate (internal standard, 8.00–9.00 mg). A magnetic stir bar was placed in the vial, which was then sealed with a blue PTFE/white silicone septum cap. The vessel was briefly purged with Ar using a balloon filled with Ar and then placed under positive Ar pressure. Degassed EtOH that was sparged in a sonicator with Ar for ca. 10 min (500 µL) was then added. The mixture was stirred at rt until it became homogenous, after which PhSiH$_3$ (18.5 µL, 150 µmol) was quickly added. The reaction vessel was immediately submerged in an oil bath that was preheated 40 °C. Aliquots of the reaction mixture were taken via syringe at 1, 2, 3, 4, and 5 min, immediately diluted in EtOAc, and analyzed by GC/FID to determine the rate of the formation of ester S15. A plot of ln [131] vs. ln initial rate gave a straight line ($R^2$=0.95047) with a slope of 0.6339, indicative of approximately half order dependence on [131].

**Figure S48.** Plot indicates approximately half order dependence on [131] for the system using styrene 395.
Order in Fe(acac)$_3$. The order in Fe(acac)$_3$ was determined by studying the initial rate of the olefin cross-coupling of donor 395 with acceptor 131 using different concentrations of Fe(acac)$_3$. To a 0.5–2 mL tapered microwave vial was added styrene 395 (13.4 mg, 100 µmol), benzyl acrylate (30.6 µL, 200 µmol), Fe(acac)$_3$ (10.0–50.0 µmol), and butyl butyrate (internal standard, 8.00–9.00 mg). A magnetic stir bar was placed in the vial, which was then sealed with a blue PTFE/white silicone septum cap. The vessel was briefly purged with Ar using a balloon filled with Ar and then placed under positive Ar pressure. Degassed EtOH that was sparged in a sonicator with Ar for ca. 10 min (500 µL) was then added. The mixture was stirred at rt until it became homogenous, after which PhSiH$_3$ (18.5 µL, 150 µmol) was quickly added. The reaction vessel was immediately submerged in an oil bath that was preheated 40 °C. Aliquots of the reaction mixture were taken via syringe at 1, 2, 3, 4, and 5 min, immediately diluted in EtOAc, and analyzed by GC/FID to determine the rate of the formation of ester S15. A plot of ln [Fe(acac)$_3$] vs. ln initial rate gave a straight line ($R^2=0.93486$) with a slope of 0.3245, indicative of approximately half order dependence on [Fe(acac)$_3$].

![Chemical Reaction](image)

**Figure S49.** Plot indicates approximately half order dependence on [Fe(acac)$_3$] for the system using styrene 395.
**Order in PhSiH₃.** The order in PhSiH₃ was determined by studying the initial rate of the olefin cross-coupling of donor 395 with acceptor 131 using different concentrations of PhSiH₃. To a 0.5–2 mL tapered microwave vial was added styrene 395 (13.4 mg, 100 µmol), benzyl acrylate (30.6 µL, 200 µmol), Fe(acac)₃ (10.6 mg, 30.0 µmol), and butyl butyrate (internal standard, 8.00–9.00 mg). A magnetic stir bar was placed in the vial, which was then sealed with a blue PTFE/white silicone septum cap. The vessel was briefly purged with Ar using a balloon filled with Ar and then placed under positive Ar pressure. Degassed EtOH that was sparged in a sonicator with Ar for ca. 10 min (500 µL) was then added. The mixture was stirred at rt until it became homogenous, after which PhSiH₃ (50.0–250 µmol) was quickly added. The reaction vessel was immediately submerged in an oil bath that was preheated 40 °C. Aliquots of the reaction mixture were taken via syringe at 1, 2, 3, 4, and 5 min, immediately diluted in EtOAc, and analyzed by GC/FID to determine the rate of the formation of ester S15. A plot of ln [PhSiH₃] vs. ln initial rate gave a straight line (R²=0.87481) with a slope of 0.5847, indicative of approximately half order dependence on [PhSiH₃].

![Figure S50](image-url)

**Figure S50.** Plot indicates approximately half order dependence on [PhSiH₃] for the system using styrene 395.
Determination of the Reactant Orders of the Olefin Cross-Coupling of $p$-Chlorostyrene (396).

Order in donor 396. The order in donor was determined by studying the initial rate of the olefin cross-coupling of donor 396 with acceptor 131 using different concentrations of donor 396. To a 0.5–2 mL tapered microwave vial was added styrene 396 (50–150 µmol), benzyl acrylate (30.6 µL, 200 µmol), Fe(acac)$_3$ (10.6 mg, 30.0 µmol), and butyl butyrate (internal standard, 8.00–9.00 mg). A magnetic stir bar was placed in the vial, which was then sealed with a blue PTFE/white silicone septum cap. The vessel was briefly purged with Ar using a balloon filled with Ar and then placed under positive Ar pressure. Degassed EtOH that was sparged in a sonicator with Ar for ca. 10 min (500 µL) was then added. The mixture was stirred at rt until it became homogenous, after which PhSiH$_3$ (18.5 µL, 150 µmol) was quickly added. The reaction vessel was immediately submerged in an oil bath that was preheated 40 °C. Aliquots of the reaction mixture were taken via syringe at 1, 2, 3, 4, and 5 min, immediately diluted in EtOAc, and analyzed by GC/FID to determine the rate of the formation of ester S22. A plot of ln [396] vs. ln initial rate gave a straight line ($R^2=0.44855$) with a slope of −0.1554, indicative of approximately zero order dependence on [396].

Figure S51. Plot indicates approximately zero order dependence on [396] for the system using styrene 396.
Order in acceptor 131. The order in acceptor was determined by studying the initial rate of the olefin cross-coupling of donor 396 with acceptor 131 using different concentrations of acceptor 131. To a 0.5–2 mL tapered microwave vial was added styrene 396 (13.9 mg, 100 µmol), benzyl acrylate (150–300 µmol), Fe(acac)₃ (10.6 mg, 30.0 µmol), and butyl butyrate (internal standard, 8.00–9.00 mg). A magnetic stir bar was placed in the vial, which was then sealed with a blue PTFE/white silicone septum cap. The vessel was briefly purged with Ar using a balloon filled with Ar and then placed under positive Ar pressure. Degassed EtOH that was sparged in a sonicator with Ar for ca. 10 min (500 µL) was then added. The mixture was stirred at rt until it became homogenous, after which PhSiH₃ (18.5 µL, 150 µmol) was quickly added. The reaction vessel was immediately submerged in an oil bath that was preheated 40 °C. Aliquots of the reaction mixture were taken via syringe at 1, 2, 3, 4, and 5 min, immediately diluted in EtOAc, and analyzed by GC/FID to determine the rate of the formation of ester S22. A plot of ln [131] vs. ln initial rate gave a straight line (R²=0.97094) with a slope of 0.7275, indicative of approximately half order dependence on [131].

**Figure S52.** Plot indicates approximately half order dependence on [131] for the system using styrene 396.
Order in Fe(acac)$_3$. The order in Fe(acac)$_3$ was determined by studying the initial rate of the olefin cross-coupling of donor 396 with acceptor 131 using different concentrations of Fe(acac)$_3$. To a 0.5–2 mL tapered microwave vial was added styrene 396 (13.9 mg, 100 µmol), benzyl acrylate (30.6 µL, 200 µmol), Fe(acac)$_3$ (10.0–50.0 µmol), and butyl butyrate (internal standard, 8.00–9.00 mg). A magnetic stir bar was placed in the vial, which was then sealed with a blue PTFE/white silicone septum cap. The vessel was briefly purged with Ar using a balloon filled with Ar and then placed under positive Ar pressure. Degassed EtOH that was sparged in a sonicator with Ar for ca. 10 min (500 µL) was then added. The mixture was stirred at rt until it became homogenous, after which PhSiH$_3$ (18.5 µL, 150 µmol) was quickly added. The reaction vessel was immediately submerged in an oil bath that was preheated 40 °C. Aliquots of the reaction mixture were taken via syringe at 1, 2, 3, 4, and 5 min, immediately diluted in EtOAc, and analyzed by GC/FID to determine the rate of the formation of ester S22. A plot of ln [Fe(acac)$_3$] vs. ln initial rate gave a straight line ($R^2=0.98127$) with a slope of 0.3468, indicative of approximately half order dependence on [Fe(acac)$_3$].

![Figure S53](image.png)

**Figure S53.** Plot indicates approximately half order dependence on [Fe(acac)$_3$] for the system using styrene 396.
**Order in PhSiH₃.** The order in PhSiH₃ was determined by studying the initial rate of the olefin cross-coupling of donor 396 with acceptor 131 using different concentrations of PhSiH₃. To a 0.5–2 mL tapered microwave vial was added styrene 396 (13.9 mg, 100 µmol), benzyl acrylate (30.6 µL, 200 µmol), Fe(acac)₃ (10.6 mg, 30.0 µmol), and butyl butyrate (internal standard, 8.00–9.00 mg). A magnetic stir bar was placed in the vial, which was then sealed with a blue PTFE/white silicone septum cap. The vessel was briefly purged with Ar using a balloon filled with Ar and then placed under positive Ar pressure. Degassed EtOH that was sparged in a sonicator with Ar for ca. 10 min (500 µL) was then added. The mixture was stirred at rt until it became homogenous, after which PhSiH₃ (50.0–250 µmol) was quickly added. The reaction vessel was immediately submerged in an oil bath that was preheated 40 °C. Aliquots of the reaction mixture were taken via syringe at 1, 2, 3, 4, and 5 min, immediately diluted in EtOAc, and analyzed by GC/FID to determine the rate of the formation of ester S22. A plot of ln [PhSiH₃] vs. ln initial rate gave a straight line (R²=0.93838) with a slope of 0.3773, indicative of approximately half order dependence on [PhSiH₃].

**Figure S54.** Plot indicates approximately half order dependence on [PhSiH₃] for the system using styrene 396.
Determination of the Reactant Orders of the Olefin Cross-Coupling of \( p \)-Carboxymethylstyrene (397).

**Order in donor 397.** The order in donor was determined by studying the initial rate of the olefin cross-coupling of donor 397 with acceptor 131 using different concentrations of donor 397. To a 0.5–2 mL tapered microwave vial was added styrene 397 (50–150 \( \mu \)mol), benzyl acrylate (30.6 \( \mu \)L, 200 \( \mu \)mol), Fe(acac)\(_3\) (10.6 mg, 30.0 \( \mu \)mol), and butyl butyrate (internal standard, 8.00–9.00 mg). A magnetic stir bar was placed in the vial, which was then sealed with a blue PTFE/white silicone septum cap. The vessel was briefly purged with Ar using a balloon filled with Ar and then placed under positive Ar pressure. Degassed EtOH that was sparged in a sonicator with Ar for ca. 10 min (500 \( \mu \)L) was then added. The mixture was stirred at rt until it became homogenous, after which PhSiH\(_3\) (18.5 \( \mu \)L, 150 \( \mu \)mol) was quickly added. The reaction vessel was immediately submerged in an oil bath that was preheated 40 °C. Aliquots of the reaction mixture were taken via syringe at 1, 2, 3, 4, and 5 min, immediately diluted in EtOAc, and analyzed by GC/FID to determine the rate of the formation of ester S29. A plot of ln [397] vs. ln initial rate gave a straight line (\( R^2 = 0.97789 \)) with a slope of 0.9040, indicative of approximately first order dependence on [397].

![Figure S55](image)

**Figure S55.** Plot indicates approximately first order dependence on [397] for the system using styrene 397.
Order in acceptor **131**. The order in acceptor was determined by studying the initial rate of the olefin cross-coupling of donor **397** with acceptor **131** using different concentrations of acceptor **131**. To a 0.5–2 mL tapered microwave vial was added styrene **397** (16.2 mg, 100 µmol), benzyl acrylate (150–300 µmol), Fe(acac)_3 (10.6 mg, 30.0 µmol), and butyl butyrate (internal standard, 8.00–9.00 mg). A magnetic stir bar was placed in the vial, which was then sealed with a blue PTFE/white silicone septum cap. The vessel was briefly purged with Ar using a balloon filled with Ar and then placed under positive Ar pressure. Degassed EtOH that was sparged in a sonicator with Ar for ca. 10 min (500 µL) was then added. The mixture was stirred at rt until it became homogenous, after which PhSiH₃ (18.5 µL, 150 µmol) was quickly added. The reaction vessel was immediately submerged in an oil bath that was preheated 40 °C. Aliquots of the reaction mixture were taken via syringe at 1, 2, 3, 4, and 5 min, immediately diluted in EtOAc, and analyzed by GC/FID to determine the rate of the formation of ester **S29**. A plot of ln [**131**] vs. ln initial rate gave a straight line (R²=0.94436) with a slope of 0.8790, indicative of approximately first order dependence on [**131**].

**Figure S56.** Plot indicates approximately first order dependence on [**131**] for the system using styrene **397**.
Order in Fe(acac)_3. The order in Fe(acac)_3 was determined by studying the initial rate of the olefin cross-coupling of donor 397 with acceptor 131 using different concentrations of Fe(acac)_3. To a 0.5–2 mL tapered microwave vial was added styrene 397 (16.2 mg, 100 µmol), benzyl acrylate (30.6 µL, 200 µmol), Fe(acac)_3 (10.0–50.0 µmol), and butyl butyrate (internal standard, 8.00–9.00 mg). A magnetic stir bar was placed in the vial, which was then sealed with a blue PTFE/white silicone septum cap. The vessel was briefly purged with Ar using a balloon filled with Ar and then placed under positive Ar pressure. Degassed EtOH that was sparged in a sonicator with Ar for ca. 10 min (500 µL) was then added. The mixture was stirred at rt until it became homogenous, after which PhSiH_3 (18.5 µL, 150 µmol) was quickly added. The reaction vessel was immediately submerged in an oil bath that was preheated 40 °C. Aliquots of the reaction mixture were taken via syringe at 1, 2, 3, 4, and 5 min, immediately diluted in EtOAc, and analyzed by GC/FID to determine the rate of the formation of ester S29. A plot of ln [Fe(acac)_3] vs. ln initial rate gave a straight line (R^2=0.88819) with a slope of 0.5213, indicative of approximately half order dependence on [Fe(acac)_3].

![Chemical Reaction Diagram](image_url)

**Figure S57.** Plot indicates approximately half order dependence on [Fe(acac)_3] for the system using styrene 397.
Order in PhSiH$_3$. The order in PhSiH$_3$ was determined by studying the initial rate of the olefin cross-coupling of donor 397 with acceptor 131 using different concentrations of PhSiH$_3$. To a 0.5–2 mL tapered microwave vial was added styrene 397 (16.2 mg, 100 µmol), benzyl acrylate (30.6 µL, 200 µmol), Fe(acac)$_3$ (10.6 mg, 30.0 µmol), and butyl butyrate (internal standard, 8.00–9.00 mg). A magnetic stir bar was placed in the vial, which was then sealed with a blue PTFE/white silicone septum cap. The vessel was briefly purged with Ar using a balloon filled with Ar and then placed under positive Ar pressure. Degassed EtOH that was sparged in a sonicator with Ar for ca. 10 min (500 µL) was then added. The mixture was stirred at rt until it became homogenous, after which PhSiH$_3$ (50.0–250 µmol) was quickly added. The reaction vessel was immediately submerged in an oil bath that was preheated 40 °C. Aliquots of the reaction mixture were taken via syringe at 1, 2, 3, 4, and 5 min, immediately diluted in EtOAc, and analyzed by GC/FID to determine the rate of the formation of ester S29. A plot of ln [PhSiH$_3$] vs. ln initial rate gave a straight line ($R^2$=0.96270) with a slope of 0.4320, indicative of approximately half order dependence on [PhSiH$_3$].

![Plot](image)

**Figure S58.** Plot indicates approximately half order dependence on [PhSiH$_3$] for the system using styrene 397.
Second-Generation Conditions for the Olefin Cross-Coupling.

Reaction progress curve of an olefin cross-coupling model system in the absence of styrene.
To a 0.5–2 mL tapered microwave vial was added TBS silyl ether 59 (40.1 mg, 200 µmol, 1.0 equiv), benzyl acrylate (45.9 µL, 300 µmol, 1.5 equiv), Fe(acac)₃ (7.06 mg, 20.0 µmol, 10 mol%), and butyl butyrate (internal standard, 8.48 mg). A magnetic stir bar was placed in the vial, which was then sealed with a blue PTFE/white silicone septum cap. The vessel was briefly purged with Ar using a balloon filled with Ar and then placed under positive Ar pressure. Degassed EtOH that was sparged in a sonicator with Ar for ca. 10 min (1.00 mL) was then added. The mixture was stirred at rt until it became homogenous, after which PhSiH₃ (37.0 µL, 300 µmol, 1.5 equiv) was quickly added. The reaction vessel was immediately submerged in an oil bath that was preheated 40 °C. Aliquots of the reaction mixture were taken via syringe at 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, and 60 min, immediately diluted in EtOAc, and analyzed by GC/FID to determine the rate of the formation of ester 368.
**Figure S59.** Reaction progress curve for the coupling of 59 with 131 in the absence of styrene as an additive.
Reaction progress curve of an olefin cross-coupling model system in the presence of styrene. To a 0.5–2 mL tapered microwave vial was added TBS silyl ether 59 (40.1 mg, 200 µmol, 1.0 equiv), benzyl acrylate (45.9 µL, 300 µmol, 1.5 equiv), Fe(acac)₃ (7.06 mg, 20.0 µmol, 10 mol%), styrene (2.1 mg, 20.0 µmol, 10 mol%), and butyl butyrate (internal standard, 8.47 mg). A magnetic stir bar was placed in the vial, which was then sealed with a blue PTFE/white silicone septum cap. The vessel was briefly purged with Ar using a balloon filled with Ar and then placed under positive Ar pressure. Degassed EtOH that was sparged in a sonicator with Ar for ca. 10 min (1.00 mL) was then added. The mixture was stirred at rt until it became homogenous, after which PhSiH₃ (37.0 µL, 300 µmol, 1.5 equiv) was quickly added. The reaction vessel was immediately submerged in an oil bath that was preheated 40 °C. Aliquots of the reaction mixture were taken via syringe at 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, and 60 min, immediately diluted in EtOAc, and analyzed by GC/FID to determine the rate of the formation of ester 368.
Figure S60. Reaction progress curve for the coupling of 59 with 131 in the presence of styrene as an additive.
Reaction progress curve of an olefin cross-coupling model system using styrene as the donor olefin. To a 0.5–2 mL tapered microwave vial was added styrene (20.8 mg, 200 µmol, 1.0 equiv), benzyl acrylate (45.9 µL, 300 µmol, 1.5 equiv), Fe(acac)$_3$ (7.06 mg, 20.0 µmol, 10 mol%), and butyl butyrate (internal standard, 8.56 mg). A magnetic stir bar was placed in the vial, which was then sealed with a blue PTFE/white silicone septum cap. The vessel was briefly purged with Ar using a balloon filled with Ar and then placed under positive Ar pressure. Degassed EtOH that was sparged in a sonicator with Ar for ca. 10 min (1.00 mL) was then added. The mixture was stirred at rt until it became homogenous, after which PhSiH$_3$ (37.0 µL, 300 µmol, 1.5 equiv) was quickly added. The reaction vessel was immediately submerged in an oil bath that was preheated 40 °C. Aliquots of the reaction mixture were taken via syringe at 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, and 60 min, immediately diluted in EtOAc, and analyzed by GC/FID to determine the rate of the formation of ester 398.
Figure S61. Reaction progress curve for the coupling of styrene with 131.

Figure S62. Overlay of the first 10 minutes of Figures S59–S61 to show how styrene influences the induction period of the olefin cross-coupling.
Effect of the styrene additive on the yield of the olefin cross-coupling. To a solution of TBS silyl ether 59 (20.0 mg, 100 µmol, 1.0 equiv), benzyl acrylate (30.6 µL, 200 µmol, 2.0 equiv), Fe(acac)3 (3.53 mg, 10.0 µmol, 10 mol%), and butyl butyrate (internal standard, 8.80 mg) in degassed EtOH (500 µL) under Ar was added PhSiH3 (18.5 µL, 150 µmol, 1.5 equiv). The reaction mixture was immediately heated to 40 °C and stirred overnight to give ester 368 in 62% yield, as determined by GC/FID. The reaction mixture then concentrated under reduced pressure. Purification of the crude material by preparative TLC (SiO2, 95:5 hexanes:Et2O) furnished ester 368 as a colorless oil (22.7 mg, 62.4 µmol, 62%). Repeating the reaction with the inclusion of styrene (1.04 mg, 10.0 µmol, 10 mol%) gave ester 368 in 88% yield, as determined by GC/FID.

Physical State: colorless oil.

1H NMR (600 MHz, CDCl3): δ 7.38–7.31 (m, 5 H), 5.10 (s, 2 H), 3.66 (t, J=7.3 Hz, 2 H), 2.34 (m, 2 H), 1.59 (m, 2 H), 1.46 (t, J=7.4 Hz, 2 H), 0.89 (s, 3 H), 0.88 (s, 9 H), and 0.04 (s, 6 H).

13C NMR (151 MHz, CDCl3): δ 174.3, 136.2, 128.7, 128.4, 128.3, 66.3, 60.0, 44.0, 37.1, 32.0, 29.8, 27.3, 26.1, 18.4, and –5.1.

HRMS (m/z): calcd for C21H37O3Si [M+H]+: 365.2506, found: 365.2516.

TLC: Rf=0.51 (9:1 hexanes:EtOAc).

General Procedure 6. Second-generation conditions for the (functionalized) olefin cross-coupling. To a solution of Fe(acac)3 or Fe(dibm)3 (10.0 µmol, 5 mol%) and styrene (1.1 µL, 10.0 µmol, 5 mol%) in degassed THF (0.8 mL) and degassed (CH2OH)2 (0.2 mL) under Ar was added PhSiH3 (1.2 µL, 10.0 µmol, 5 mol%). After stirring at rt for 30–60 min, the donor olefin (200 µmol, 1.0 equiv), acceptor olefin (300 µmol, 1.5 equiv), and additional PhSiH3 (37.0 µL, 300 µmol, 1.5 equiv) were added sequentially. The reaction mixture was heated to and stirred at 30 °C or 70 °C overnight, cooled to rt, and diluted with brine. The organic layer was separated and the aqueous layer was extracted with EtOAc. The organic layers were combined, washed with brine, dried over MgSO4, filtered, and concentrated under reduced pressure. The crude material was then purified on SiO2 (preparative TLC or flash column chromatography) to furnish the coupled product.
Methyl 6-((tert-butyldimethylsilyl)oxy)-4,4-dimethylhexanoate (94). General Procedure 6 was followed using TBS silyl ether 59\(^9\) (40.0 mg, 200 µmol, 1.0 equiv) as the donor olefin, methyl acrylate (27.2 µL, 300 µmol, 1.5 equiv) as the acceptor olefin, and Fe(acac)\(_3\) (3.53 mg, 10.0 µmol, 5 mol%) as the catalyst. After heating at 30 °C overnight, work up and purification by flash column chromatography (SiO\(_2\), 95:5 hexanes:Et\(_2\)O) furnished ester 94 as a pale yellow oil (38.6 mg, 134 µmol, 67%). Repeating the reaction with the omission of styrene gave ester 94 as a pale yellow oil (23.3 mg, 80.8 µmol, 40%). Spectroscopic data was identical to that obtained for the analogous reaction using the first-generation conditions.

tert-Butyl 4-methyl-4-(3-oxobutyl)piperidine-1-carboxylate (62). General Procedure 6 was followed using piperidine 61\(^10\) (39.5 mg, 200 µmol, 1.0 equiv) as the donor olefin, methyl vinyl ketone (25.0 µL, 300 µmol, 1.5 equiv) as the acceptor olefin, and Fe(acac)\(_3\) (3.53 mg, 10.0 µmol, 5 mol%) as the catalyst. After heating at 70 °C overnight, work up and purification by flash column chromatography (SiO\(_2\), 8:2 hexanes:EtOAc) furnished piperidine 62 as a colorless oil (36.3 mg, 135 µmol, 67%). Repeating the reaction with the omission of styrene gave piperidine 62 as a colorless oil (28.0 mg, 104 µmol, 52%). Spectroscopic data was identical to that obtained for the analogous reaction using the first-generation conditions.
5-Methylpentadecan-2-one (70). General Procedure 6 was followed using 1-dodecene (33.7 mg, 200 µmol, 1.0 equiv) as the donor olefin, methyl vinyl ketone (25.0 µL, 300 µmol, 1.5 equiv) as the acceptor olefin, and Fe(acac)₃ (3.53 mg, 10.0 µmol, 5 mol%) as the catalyst. After heating at 70 °C overnight, work up and purification by flash column chromatography (SiO₂, 95:5 hexanes:Et₂O) furnished ketone 70 as a colorless oil (21.0 mg, 87.3 µmol, 44%). Repeating the reaction with the omission of styrene gave ketone 70 as a colorless oil (16.3 mg, 67.8 µmol, 34%). Spectroscopic data was identical to that obtained for the analogous reaction using the first-generation conditions.

7-((tert-Butyldimethylsilyl)oxy)-5,5-dimethylheptan-2-one (60). General Procedure 6 was followed using TBS silyl ether 59 (40.0 mg, 200 µmol, 1.0 equiv) as the donor olefin, methyl vinyl ketone (25.0 µL, 300 µmol, 1.5 equiv) as the acceptor olefin, and Fe(acac)₃ (3.53 mg, 10.0 µmol, 5 mol%) as the catalyst. After heating at 70 °C overnight, work up and purification by flash column chromatography (SiO₂, 95:5 hexanes:Et₂O) furnished ketone 60 as a colorless oil (32.4 mg, 119 µmol, 59%). Repeating the reaction with the omission of styrene gave ketone 60 as a colorless oil (32.8 mg, 120 µmol, 60%). Spectroscopic data was identical to that obtained for the analogous reaction using the first-generation conditions.
4-Chloro-5-hydroxy-N,N,4-trimethylpentanamide (238). General Procedure 6 was followed using 2-chloro-2-propen-1-ol (18.5 mg, 200 µmol, 1.0 equiv) as the donor olefin, N,N-dimethyl acrylamide (30.9 µL, 300 µmol, 1.5 equiv) as the acceptor olefin, and Fe(acac)₃ (3.53 mg, 10.0 µmol, 5 mol%) as the catalyst. After heating at 30 °C overnight, work up and purification by flash column chromatography (SiO₂, EtOAc) furnished chloride 238 as a pale yellow oil (22.7 mg, 117 µmol, 59%). Repeating the reaction with the omission of styrene gave chloride 238 as a pale yellow oil (17.6 mg, 90.9 µmol, 45%).

Spectroscopic data was identical to that obtained for the analogous reaction using the first-generation conditions.

4-((8S,9S,13S,14S,17S)-3-Methoxy-13,17-dimethyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-17-yl)butan-2-one (74). General Procedure 6 was followed using olefin 73¹³ (56.5 mg, 200 µmol, 1.0 equiv) as the donor olefin, methyl vinyl ketone (25.0 µL, 300 µmol, 1.5 equiv) as the acceptor olefin, and Fe(acac)₃ (3.53 mg, 10.0 µmol, 5 mol%) as the catalyst. After heating at 70 °C overnight, work up and purification by flash column chromatography (SiO₂, 95:5 hexanes:EtOAc) furnished ketone 74 as a yellow oil (31.1 mg, 87.7 µmol, 44%). Repeating the reaction with the omission of styrene gave ketone 74 as a yellow oil (34.2 mg, 96.5 µmol, 48%).

Spectroscopic data was identical to that obtained for the analogous reaction using the first-generation conditions.
**Methyl 4-(dimethyl(phenyl)silyl)-4-methylpentanoate (217).** General Procedure 6 was followed using dimethyl(phenyl)(prop-1-en-2-yl)silane\textsuperscript{33} (35.2 mg, 200 µmol, 1.0 equiv) as the donor olefin, methyl acrylate (27.2 µL, 300 µmol, 1.5 equiv) as the acceptor olefin, and Fe(acac)\textsubscript{3} (3.53 mg, 10.0 µmol, 5 mol%) as the catalyst. After heating at 30 °C overnight, work up and purification by flash column chromatography (SiO\textsubscript{2}, 95:5 hexanes:EtOAc) furnished silane 217 as a pale yellow oil (35.8 mg, 135 µmol, 68%). Repeating the reaction with the omission of styrene gave silane 217 as a pale yellow oil (34.0 mg, 129 µmol, 64%). Spectroscopic data was identical to that obtained for the analogous reaction using the first-generation conditions.

![Structure of 156](image)

**Methyl 4-phenoxy pentanoate (156).** General Procedure 6 was followed using phenyl vinyl ether (24.0 mg, 200 µmol, 1.0 equiv) as the donor olefin, methyl acrylate (27.2 µL, 300 µmol, 1.5 equiv) as the acceptor olefin, and Fe(dibm)\textsubscript{3} (5.21 mg, 10.0 µmol, 5 mol%) as the catalyst. After heating at 70 °C overnight, work up and purification by flash column chromatography (SiO\textsubscript{2}, 93:7 hexanes:EtOAc) furnished ether 156 as a pale yellow oil (25.2 mg, 121 µmol, 61%). Repeating the reaction with the omission of styrene gave ether 156 as a pale yellow oil (20.0 mg, 96.0 µmol, 48%). Spectroscopic data was identical to that obtained for the analogous reaction using the first-generation conditions.

![Structure of 122](image)

**3-((tert-Butyldimethylsilyl)oxy)propan-2-yl)cyclohexan-1-one (122).** General Procedure 6 was followed using tert-butyldimethyl(prop-1-en-2-yloxy)silane\textsuperscript{14} (34.5 mg, 200 µmol, 1.0 equiv) as the donor olefin, cyclohex-2-enone (29.0 µL, 300 µmol, 1.5 equiv) as the acceptor olefin, and Fe(dibm)\textsubscript{3} (5.21 mg, 10.0 µmol, 5 mol%) as the catalyst. After heating at 30 °C
overnight, work up and purification by flash column chromatography (SiO₂, 9:1 hexanes:EtOAc) furnished silyl ether **122** as a pale yellow oil (13.8 mg, 51.0 µmol, 26%). Repeating the reaction with the omission of styrene gave silyl ether **122** as a pale yellow oil (23.0 mg, 85.0 µmol, 43%). Spectroscopic data was identical to that obtained for the analogous reaction using the first-generation conditions.

**Methyl 4-(benzyl(tert-butoxycarbonyl)amino)-4-methylpentanoate (170).** General Procedure 6 was followed using tert-butyl benzyl(prop-1-en-2-yl)carbamate**24** (49.5 mg, 200 µmol, 1.0 equiv) as the donor olefin, methyl acrylate (27.2 µL, 300 µmol, 1.5 equiv) as the acceptor olefin, and Fe(dibm)₃ (5.21 mg, 10.0 µmol, 5 mol%) as the catalyst. After heating at 30 °C overnight, work up and purification by flash column chromatography (SiO₂, 85:15 hexanes:EtOAc) furnished carbamate **170** as a pale yellow oil (38.3 mg, 114 µmol, 57%). Repeating the reaction with the omission of styrene gave carbamate **170** as a pale yellow oil (40.7 mg, 121 µmol, 61%). Spectroscopic data was identical to that obtained for the analogous reaction using the first-generation conditions.

**N,N-Dimethyl-4-(phenylthio)pentanamide (189).** General Procedure 6 was followed using phenyl vinyl sulfide (24.0 mg, 200 µmol, 1.0 equiv) as the donor olefin, N,N-dimethyl acrylamide (30.9 µL, 300 µmol, 1.5 equiv) as the acceptor olefin, and Fe(dibm)₃ (5.21 mg, 10.0 µmol, 5 mol%) as the catalyst. After heating at 30 °C overnight, work up and purification by flash column chromatography (SiO₂, 1:2 hexanes:EtOAc) furnished thioether **189** as a colorless oil (17.0 mg, 71.6 µmol, 36%). Repeating the reaction with the omission of styrene gave thioether **189** as a colorless oil (27.3 mg, 115 µmol, 58%).
Spectroscopic data was identical to that obtained for the analogous reaction using the first-generation conditions.

\[ \text{N,N,4-Trimethyl-4-(1\text{-}H-\text{naphtho}[1,8-de][1,3,2]diazaborinin-2(3H)-yl)pentanamide} \quad (206). \]

General Procedure 6 was followed using boronamide 205 (42.0 mg, 200 µmol, 1.0 equiv) as the donor olefin, \(N,N\)-dimethyl acrylamide (30.9 µL, 300 µmol, 1.5 equiv) as the acceptor olefin, and Fe(acac)\(_3\) (3.53 mg, 10.0 µmol, 5 mol%) as the catalyst. After heating at 30 °C overnight, work up and purification by flash column chromatography (SiO\(_2\), 1:9 hexanes:EtOAc) furnished boronamide 206 as a colorless amorphous solid (17.6 mg, 56.9 µmol, 29%). Repeating the reaction with the omission of styrene gave boronamide 206 as a colorless amorphous solid (20.5 mg, 66.3 µmol, 33%). Spectroscopic data was identical to that obtained for the analogous reaction using the first-generation conditions.

\[ \text{3-((tert-Butyldimethylsilyl)oxy)-2-methylbutan-2-yl)cyclopentan-1-one} \quad (97). \]

General Procedure 6 was followed using TBS silyl ether 59 (40.0 mg, 200 µmol, 1.0 equiv) as the donor olefin, cyclopent-2-enone (25.1 µL, 300 µmol, 1.5 equiv) as the acceptor olefin, and Fe(acac)\(_3\) (3.53 mg, 10.0 µmol, 5 mol%) as the catalyst. After heating at 30 °C overnight, work up and purification by flash column chromatography (SiO\(_2\), 10:1 hexanes:EtOAc) furnished cyclopentanone 97 as a colorless oil (25.4 mg, 89.3 µmol, 45%). Repeating the reaction with the omission of styrene gave cyclopentanone 97 as a colorless oil (31.4 mg, 110 µmol, 55%). Spectroscopic data was identical to that obtained for the analogous reaction using the first-generation conditions.
Me

Me

Me

Me

Me

Me

47
Me
Bn\text{-}N\text{-}N\text{Cbz} 175

ppm
n-C$_2$H$_5$S$^-$CN

ppm

186
n-C₆H₅S

Me

O

191 ppm
The image shows a chemical structure with the following elements:

- A sulfenyl group (S\(\text{S}^\text{a}
\))
- A nitrogen (N)
- An oxygen (O)
- Two methyl groups (Me)
- A dimethylamino group (NMe\(_2\))

The molecule is labeled with the number 198.
(pin)B
n-C₆H₁₃
OMe
(pin)B\text{O}M_{e}$

n-C$_{6}H_{13}$

213

ppm
n-BuSO₂Pt
Me\(-\)SO$_2$Na

$\text{Boc}$

$\text{Me}$

$\text{Na}$

$\text{Boc}$

317
Fe(acac)$_2$
