Nickel-Catalyzed Reductive Conjugate Addition to Enones Via Allylnickel Intermediates

Ruja Shrestha,† Stephanie C. M. Dorn and Daniel J. Weix*.
*Department of Chemistry, University of Rochester, Rochester, NY 14627
†Present Address: Department of Chemistry, University of California, Berkeley, CA 94720

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I. Chemicals.

Nickel Sources:

Ni(acac)$_2$ (Strem Chemicals) was used as received and stored in a Vacuum Atmospheres nitrogen filled glove box or stored on benchtop in a desiccator over CaSO$_4$.

Ligands:

2,9-dimethyl-1,10-phenanthroline (neocuproine, Aldrich), 1,10-phenanthroline (Aldrich), 3,4,7,8-tetramethylphenanthroline (Aldrich), 4,7-diphenyl-1,10-phenanthroline (Acros), 5,5'-dimethyl-2,2'-bipyridine (Aldrich), 4,4'-di-tert-butyl-2,2'-bipyridine (Aldrich), 4,4'-dimethoxy-2,2'-bipyridine (Aldrich), 2,2'-bipyridyl (Aldrich), 2,2'-biquinoline (Aldrich), pyridine (Aldrich), 4,4',4"-tri-*tert*-butyl-2,2':6',2"-terpyridine (Aldrich) were used as received. The ligands were either stored in a Vacuum Atmospheres nitrogen filled glove box or stored on benchtop in a desiccator over CaSO$_4$.

Reducing Agent:

Manganese powder -325 mesh (Aldrich) was used as received.

Enones:

2-cyclohexen-1-one (Alfa Aesar), 2-cyclopenten-1-one (Aldrich), 2-cyclohepten-1-one (Aldrich) 4-hexen-3-one (Aldrich), *trans*-2-methyl-2-butenal (TCI America), 3-methyl-3-penten-2-one (TCI America) were used as received.

Haloarenes:

Iodobenzene (Aldrich), 1-iodo-2-methylbenzene (Aldrich), 1-iodo-3-methylbenzene (Aldrich), 1-iodo-4-methylbenzene (Aldrich), 1-iodo-2-methoxybenzene (Alfa Aesar), 1-iodo-4-methoxybenzene (Aldrich), ethyl-3-iodobenzoate (Alfa Aesar), methyl-4-bromobenzoate (Lancaster), 1-iodo-3-(trifluoromethyl)benzene (Alfa Aesar), 1-bromo-4-(trifluoromethyl)benzene (Aldrich), 2-fluoro-4-iodo-1-methylbenzene (Aldrich), 1-(4-iodophenyl)ethanone (Aldrich), 1-(4-bromophenyl)ethanone (Aldrich), 2-iodobenzonitrile (Acros), 2-bromobenzonitrile (Aldrich), 4-bromobenzonitrile (Aldrich), 1-bromo-4-(methylsulfonyl)benzene (Acros), 1-fluoro-4-iodobenzene (TCI), 1-chloro-4-iodobenzene (Alfa Aesar), 1-bromo-4-iodobenzene (Aldrich), (4-iodophenyl)sulfurpentafluoride (TCI), and 2-bromopropene (GFS chemicals) were used as received. 5-iodobenzo[*d*][1,3]dioxole (Matrix Scientific) was filtered through a short, dry, activated basic alumina pad (1.5 cm) before use. 4-iodo-*N,N*-dimethylaniline,[1] 2-(4-iodophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane,[2] 2,2,2-trifluoro-*N*-(4-iodophenyl)acetamide,[3] 4-iodobenzaldehyde,[4] and 4-iodophenyl acetate[5] were prepared using literature procedures.

Silylating Reagents:

All silyl reagents were purchased from Gelest and used as received. Impure silyl reagents led to decreased yields, so care must be taken to avoid moisture during manipulation and storage.

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(1) Elmorsy, S. S.; Badawy, D. S.; Nour, M. A.; Pelter, A. *Tetrahedron Lett.* **1991**, *46*, 5421.
(2) Matteson, D. S.; Man, H-W. *J. Org. Chem.* **1994,** *59*, 5734.
(3) Melissaris, A. P.; Litt, M. H. *J. Org. Chem.* **1994**, *59*, 5818.
(4) Orita, A.; Miyamoto, K.; Nakashima, M.; Ye, F.; Otera, J. *Adv. Synth. Catal.* **2004**, *346*, 767.
(5) Yeung, C. S.; Dong, V. M. *J. Am. Chem. Soc.* **2008**, *130*, 7826.

Solvents:

Anhydrous solvents: *N,N*-dimethylacetamide (DMA, Alfa Aesar), 1-methyl-2-pyrrolidinone (NMP, Fluka), 1,3-Dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (DMPU, Aldrich), and 1,3-dimethyl-2-imidazolidinone (DMI, Aldrich), were used as received. Anhydrous *N,N*-dimethylformamide (DMF) and acetonitrile were prepared from ACS grade, inhibitor free solvent by passage though activated alumina and molecular sieves in a Glass Contour solvent purification system. Anhydrous tetrahydrofuran was prepared from ACS grade, inhibitor free solvents by passage through activated alumina and molecular sieves in a Vacuum Atmospheres solvent purification system. All solvents were stored in a Vacuum Atmospheres glove box in an amber bottle over 4 Å molecular sieves. Water content was routinely measured using Karl-Fisher titration (Metrohm) and was less than 30 ppm.

Other Reagents:

Dodecane (Aldrich), tetrabutylammonium fluoride (Aldrich), tetrabutylammonium difluorotriphenylsilicate (Aldrich), HF-pyridine (70% HF, 30% pyridine, Aldrich) potassium fluoride (Aldrich), glacial acetic acid (Mallinckrodt) and tetrakis(dimethylamino)ethylene (Aldrich) were purchased commercially and used without further purification.

II. Methods.

NMR Spectroscopy:

^{1}H and ^{13}C NMR spectra were recorded on a Bruker model Avance-500 MHz (126 MHz, ^{13}C) or a Bruker model Avance-400 MHz (101 MHz, ^{13}C) spectrometers operating at 500.13 MHz and 400.13 proton NMR frequency respectively, and data analysis was performed using the iNMR software package (version 4.2.0, Nucleomatica, September 2011). NMR chemical shifts are reported in ppm and referenced to the residual solvent peak $CDCl_3$ (δ = 7.26 ppm, ^{1}H; δ = 77.16 ppm ^{13}C) as an internal standard or trifluorotoluene (δ = 0.00 ppm, ^{19}F) as an external standard unless otherwise noted. Chemical shifts are reported in parts per million (ppm), multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broad). Coupling constants, *J*, are reported in Hertz.

Infrared Spectroscopy (IR):

Infrared (IR) spectra were recorded on a Shimadzu FT/IR-8400S Fourier Transform Infrared Spectrophotometer and were reported in wavenumbers (cm^{-1}).

Ultraviolet-Visible Spectroscopy:

UV-Vis spectra (300-800 nm) were recorded on a Cary 50 spectrometer using quartz screw-cap cuvettes.

Gas Chromatography:

GC analyses were performed on an Agilent 7890A GC equipped with dual DB-5 columns (20 m x 180 µm x 0.18 µm), dual FID detectors and with hydrogen as the carrier gas.

The analysis method used in all cases was 1 µL injection of sample, injector temperature of 300 ºC, 100:1 split ratio, initial inlet pressure was 20.3 psi but varied as the column flow was held constant at 1.8 mL/min for the duration of the run. <u>Method A:</u> Initial oven temperature of 50 ºC was held for 0.46 min followed by a temperature ramp up to 300 ºC at 65 ºC/min and finally the temperature was held at 300 ºC for 0.69 min. Total run time was ~ 5 min. FID temperature was 325 ºC. <u>Method B:</u> injector temperature of 300 °C, 20:1 split ratio, initial inlet pressure was 24.1 psi but varied as the column flow was held constant at 1.8 mL/min for the duration of the run. Initial oven temperature of 100 °C was held for 0.46 min followed by a temperature ramp up to 300 °C at 65 °C/min and finally the temperature was held at 300 °C for 3.4 min. Total run time was ~ 7 min. FID temperature was 325 °C.

Gas Chromatography/Mass Spectrometry:

GC/MS analyses were performed on a Shimadzu GCMS-QP2010 equipped with an RTX-XLB column (30 m x 0.25 mm x 0.28 µm) with a quadrupole mass analyzer with helium as the carrier gas. The analysis method used in all cases was 5 µL injection of sample, injector temp of 225 ºC, 10:1 split ratio, initial inlet pressure was 10.0 psi, but varied as the column flow was held constant at 0.95 mL/min for the duration of the run, the interface temperature was held at 250 ºC, and the electron impact (EI, 30 eV) ion source was held at 250 ºC. Initial oven temperature was held at 100 ºC for 3 min with the detector off followed by a temperature ramp, with the detector on, to 300 ºC at 40 ºC/min, and finally the temperature was held at 300 ºC for 3 min. Total run time was 15.00 min. Data are reported in the form of m/z (intensity relative to the base peak = 100, ion).

High Resolution Mass Spectrometry:

High resolution mass spectra (HRMS) under electron impact ionization (+ mode) were obtained on a Micromass 70-VSE instrument at the University of Illinois Mass Spectrometry Lab. The 70-VSE mass spectrometer was purchased in part with a grant from the Division of Research Resources, National Institutes of Health (RR 04648).

Thin Layer / Column Chromatography:

Thin layer chromatography was performed on EMD Chemicals TLC Silica Gel 60 F_{254} plates. Visualization was accomplished with ultraviolet light and potassium permanganate ($KMnO_4$) stain. Flash chromatography was performed using EMD silica gel 60, particle size 0.040-0.063 mm using standard techniques.

III. General Procedures.

(A) Procedure for reactions set up in a glove box and run under nitrogen:

*This procedure was used for optimization experiments and control reactions (**Tables 1, 2, S1, S2 and Figures S9 and S10**).*

In a nitrogen-filled glove box, the required amount of appropriate metal complex and ligand was weighed into an oven-dried 1-dram vial containing a teflon-coated stir bar (10 mm × 3 mm). Solvent, haloarene, electrophilic olefin, silylating reagent, Mn^0, and dodecane (10.0 µL internal standard) were then added. The reaction vials were capped with a PTFE-faced silicone septum, removed from the glove box and stirred at 1200 rpm in a heating block set to the indicated temperature. After 30 min – 24 h reaction time, 10 µL aliquots of the reaction mixture were removed with a 50-µL gas-tight syringe and quenched with 10 µL of 1 M aqueous $NaHSO_4$, diluted with diethyl ether (1 mL), and filtered through a short silica gel pad (1.5 cm) in a pipette. The filtrate was analyzed by gas chromatography and the reported percent yield was calculated versus the dodecane internal standard.

(B) Procedure for reactions set up on bench and run under air to isolate silyl enol ether products.

*This procedure was used for isolation purposes (**Schemes 1-4**)*

No precautions were taken to exclude air or moisture besides using anhydrous-grade *N*,*N*-dimethylacetamide (DMA) and oven-dried 1-dram vials and stir bars.

On the benchtop, $Ni(acac)_2$ (2.56 mg, 0.01 mmol, 0.01 equiv), neocuproine (2.08 mg, 0.01 mmol, 0.01 equiv), solid substrates and manganese powder (110 mg, 2.00 mmol, 2.00 equiv) were weighed directly into a 1-dram vial equipped with a teflon-coated stir bar (10 mm × 3 mm). DMA (3 mL), haloarene, electrophilic olefin, and silylating reagent were added using an automatic pipet. The vial was then capped with a PTFE-faced silicone septum, and stirred at 1200 rpm while the temperature was maintained at 20 °C or 40 °C.

The reaction progress was followed by GC analysis. 10 µL aliquots of reaction mixture were removed with a 50-µL gas-tight syringe, quenched with 10 µL of 1 M aqueous $NaHSO_4$, diluted with diethyl ether (1 mL), and filtered through a short silica gel pad (1.5 cm) in a pipette. The filtrate was analyzed by gas chromatography (Method A or B). Upon completion (judged as <1 Area % of starting materials remaining by GC analysis) the reaction mixture was purified using silica gel column chromatography (5.5” l × 1.5” d column). In cases where mixed fractions of the desired product were obtained, the mixed fractions were combined, concentrated under reduced pressure, and the residue was re-subjected to column chromatography. The purity of the desired product was determined by gas chromatography and ^1H NMR spectroscopy.

(C) Procedure for reactions set up on bench and run under air to isolate ketone product

No precautions were taken to exclude air or moisture besides using anhydrous-grade *N*,*N*-dimethylacetamide (DMA) and oven-dried 1-dram vials and stir bars.

On the benchtop, $Ni(acac)_2$ (2.6 mg, 0.01 mmol, 0.01 equiv), 2,2’-bipyridyl (1.6 mg, 0.01 mmol, 0.01 equiv), solid substrates and manganese powder (110 mg, 2.00 mmol, 2.00 equiv) were weighed directly into a 1-dram vial equipped with a teflon-coated stir bar (10 mm × 3 mm). DMA (3 mL), haloarene, electrophilic olefin, and silicon reagent were added using an automatic pipet. The vial was then capped with a PTFE-faced silicone septum, and stirred at 20 °C at 1200 rpm for 10 – 20 h.

The reaction progress was followed by GC analysis. 10 µL aliquots of reaction mixture were removed with a 50-µL gas-tight syringe, quenched with 10 µL of 1 M aqueous $NaHSO_4$, diluted with diethyl ether (1 mL), and filtered through a short silica gel pad (1.5 cm) in a pipette. The filtrate was analyzed by gas chromatography (Method A or B). Upon completion (judged as <1 Area % of starting materials remaining by GC analysis) the reaction mixture was filtered through a short pad of celite (1.5 cm) in a pipette and flushed with Et_2O (25 mL) into a 50 mL round bottom flask. The filtrate was concentrated under reduced pressure. The resulting residue was subjected to deprotection conditions.

Upon completion (judged as <1 Area % of silyl enol ether product remaining by GC analysis), aqueous work-up was performed and NMR yield of the desired ketone product was calculated versus 1,2-dichloroethane.

(i) Deprotection with KF

*This procedure was used for isolation purposes (**Scheme 1**)*

General procedure (III)(C) was followed with 4-hexen-3-one (114 μL, 1.00 mmol, 1.00 equiv), iodobenzene (112 μL, 1.00 mmol, 1.00 equiv) and chlorotriethylsilane (185 μL, 1.10 mmol, 1.10 equiv). The resulting residue was dissolved in methanol (16 mL), and KF (116 mg, 2.00 mmol, 2.00 equiv) was added *in small portions* at 20 °C.[6] *Addition of KF in one portion resulted in no deprotection and recovery of starting silyl enol ether.* The progress of deprotection was followed by GC analysis. Upon completion (judged as <1 Area % of silyl enol ether product remaining by GC analysis) MeOH was removed under reduced pressure and the resulting residue was purified using silica gel column chromatography (7.5” l × 1.5” d column). In cases where mixed fractions of the desired product were obtained, the mixed fractions were combined, concentrated under reduced pressure, and the residue was re-subjected to column chromatography. The purity of the desired product was determined by gas chromatography and ^{1}H NMR spectroscopy.

(ii) Deprotection with 2.0 M HCl

General procedure (III)(C) was followed with 4-hexen-3-one (114 μL, 1.00 mmol, 1.00 equiv), iodobenzene (112 μL, 1.00 mmol, 1.00 equiv) and chlorotriethylsilane (185 μL, 1.10 mmol, 1.10 equiv). The resulting residue was treated with 2.0 M HCl (2 mL) and stirred at 20 °C for 12 h. Upon completion (judged as <1 Area % of silyl enol ether product remaining by GC analysis) the mixture was extracted with diethyl ether (3 x 5 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting residue was dissolved in $CDCl_3$ (2.0 mL), and 1,2-dichloroethane internal standard (25 μL) was added. The NMR yield of desired ketone product was determined versus the internal standard (33%).

(iii) Deprotection with Tetrabutylammonium Fluoride

General procedure (III)(C) was followed with 4-hexen-3-one (114 μL, 1.00 mmol, 1.00 equiv), iodobenzene (112 μL, 1.00 mmol, 1.00 equiv) and chlorotriethylsilane (185 μL, 1.10 mmol, 1.10 equiv). The resulting residue was diluted with THF (9.5 mL), treated with tetrabutylammonium fluoride (1.1 mL, 1 M in THF) and stirred 20 °C for 12 h. Upon completion (judged as <1 Area % of silyl enol ether product remaining by GC analysis) the mixture was quenched with saturated sodium bicarbonate (100 mL) and extracted with diethyl ether (3 x 40 mL). The organic layers were combined, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting residue was dissolved in $CDCl_3$ (2.0 mL), and 1,2-dichloroethane internal standard (25 μL) was added. The NMR yield of desired ketone product was determined versus the internal standard (10%).

(iv) Deprotection with Tetrabutylammonium Difluorotriphenylsilicate (TBAT)

General procedure (III)(C) was followed with 4-hexen-3-one (114 μL, 1.00 mmol, 1.00 equiv), iodobenzene (112 μL, 1.00 mmol, 1.00 equiv) and chlorotriethylsilane (185 μL, 1.10 mmol, 1.10 The resulting residue was diluted with THF (9.5 mL), treated with TBAT (564 mg, 1.04 mmol, 1.10 equiv) and stirred at 20 °C for 1 h.[7] Upon completion (judged as <1 Area % of silyl enol ether product remaining by GC analysis) the mixture was quenched with saturated sodium bicarbonate (100 mL) and extracted with diethyl ether (3 x 40 mL). The organic layers were combined, dried over $MgSO_4$, filtered, and

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(6) Oppolzer, W.; Snowden, R. L., *Helv. Chim. Acta* **1981**, *64*, 2592

(7) Coombs, T. C.; Huang, W.; Garnier-Amblard, E. C.; Liebeskind, L. S., *Organometallics* **2010**, *29*, 5083

concentrated under reduced pressure. The resulting residue was dissolved in $CDCl_3$ (2.0 mL), and 1,2-dichloroethane internal standard (25 μL) was added. The NMR yield of desired ketone product was determined versus the internal standard (52%).

(v) Deprotection with HF-pyridine

General procedure (III)(C) was followed with 4-hexen-3-one (114 μL, 1.00 mmol, 1.00 equiv), iodobenzene (112 μL, 1.00 mmol, 1.00 equiv) and chlorotriethylsilane (185 μL, 1.10 mmol, 1.10 equiv). The resulting residue was diluted with THF (8.6 mL), cooled to 0 ^{o}C, HF-pyridine (1.0 mL) was added drop-wise.[8] The solution was stirred at 0 ^{o}C for 1 h hour, then warmed to 20 °C over two hours. Upon completion (judged as <1 Area % of silyl enol ether product remaining by GC analysis) the mixture was quenched with saturated sodium bicarbonate (100 mL), extracted with diethyl ether (3 x 40 mL), and dichloromethane (2 x 30 mL). The organic layers were combined, washed with copper(II) sulfate (1 M, 30 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting residue was dissolved in $CDCl_3$ (2.0 mL), and 1,2-dichloroethane internal standard (25 μL) was added. The NMR yield of desired ketone product was determined versus the internal standard (59%).

Note:
a) The deprotection sequence may be performed at 20 °C without a significant change in yield.
b) The reaction run with 4'-iodoacetophenone (246 mg, 1.00 mmol, 1.00 equiv) in place of iodobenzene at 20 °C provided NMR yield of ketone product in 49%.
c) The reaction run with 4-iodoanisole (234 mg, 1.00 mmol, 1.00 equiv) in place of iodobenzene at 20 °C provided NMR yield of ketone product in 53%.

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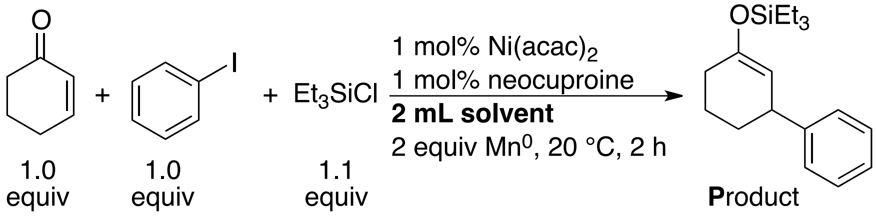
(8) Black, W. C.; Giroux, A.; Greidanus, G., *Tetrahedron Lett.* **1996**, *37*, 4471.

IV. Optimization Experiments.

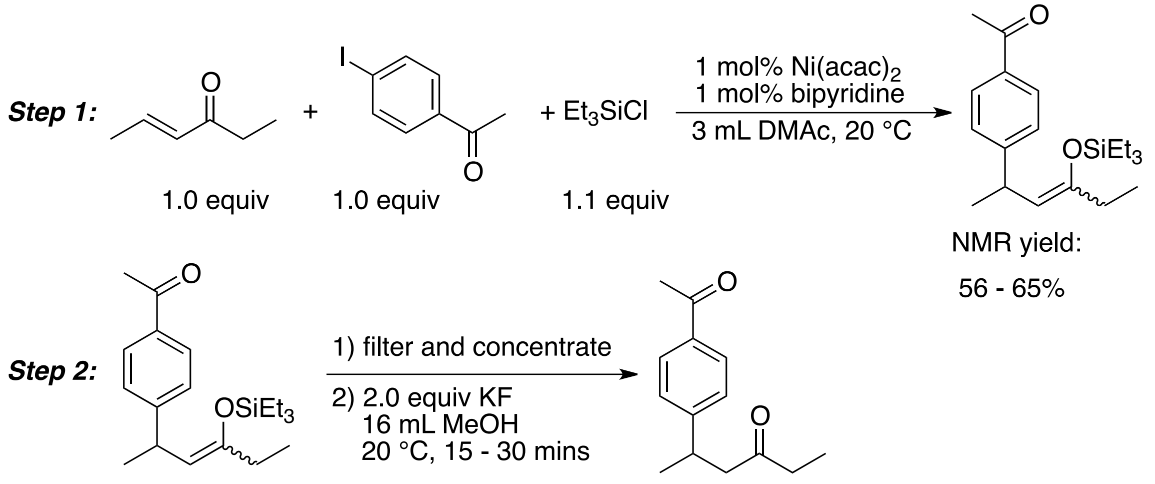
(A) Table S1: Effect of Solvent on Product Yield.[a]



Entry	Solvent	Yield **P** (%)[b]
1[c]	DMA (Standard Condition)	75
2	NMP	75
3	DMPU	71
4	DMF	57
5	DMI	49
6	THF	51[d]

[a] General procedure (III)(A) was followed, reactions were run on 0.5 mmol scale for 2 h and monitored by GC analysis. [b] Corrected GC yield vs the dodecane internal standard. [c] Reaction complete in 30 mins. [d] Obtained as a mixture of 10:1 ratio of deprotected:protected product (**P**).

(B) Table S2: Deprotection of Silyl Enol Ether[a]

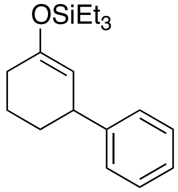


Entry	Deprotection Condition	Yield (%)[b]
1	2.0 M HCl	33
2	TBAF	10
3	TBAT	52
4	HF-pyridine	59
5	KF	61

[a] General procedure (III)(C) was followed, reactions were run on 1.0 mmol scale for 12 - 24 h and monitored by GC analysis. [b] NMR yield of ketone product, over two steps, versus 1,2-dichloroethane.

V. Compound Characterization.

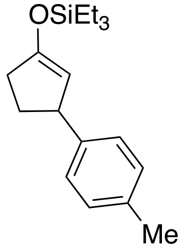
triethyl((1,4,5,6-tetrahydro-[1,1'-biphenyl]-3-yl)oxy)silane (1) (Scheme 1)



General procedure **(III)(B)** was followed with 2-cyclohexen-1-one (96.8 μL, 1.00 mmol, 1.00 equiv), iodobenzene (111 μL, 1.00 mmol, 1.00 equiv) and chlorotriethylsilane (185 μL, 1.10 mmol, 1.10 equiv). After 1 h, the reaction mixture was purified by silica gel column chromatography to afford faint yellow oil.

Data for **1**, **Scheme 1**
TLC: R_f 0.3 (1% EtOAc in hexanes) [silica gel treated with 0.1% Et_3N, UV and $KMnO_4$ stain]
GC Method: A
Yield: Run 1 (221 mg, 77%)
Yield: Run 2 (208 mg, 72%)
Average Yield: 75%
^1H NMR (400 MHz, $CDCl_3$)
δ 7.32-7.29 (m, 2H), 7.24-7.18 (m, 3H), 4.95 (t, *J* = 1.5 Hz, 1H), 3.51-3.46 (m, 1H), 2.21-2.06 (m, 2H), 1.97-1.91 (m, 1H), 1.83-1.76 (m, 1H), 1.70-1.62 (m, 1H), 1.46-1.39 (m, 1H), 1.01 (t, *J* = 7.9 Hz, 9H), 0.71 (q, *J* = 7.8 Hz, 6H).
^{13}C NMR (101 MHz; $CDCl_3$)
δ 152.1, 147.5, 128.4, 127.8, 126.1, 107.5, 41.7, 32.9, 29.9, 21.8, 6.9, 5.3
IR
1662 cm^{-1} (C=C), 1176 cm^{-1} (C-O)
LRMS *m/z* (%relative intensity, ion): (EI+, 30 eV)
288.20 (36.54, M^+), 157.10 (42.31, M^+ - $C_6H_{15}OSi$), 131.05 (6.13, M^+ - $C_{12}H_{13}$), 115.05 (27.55, M^+ - $C_{12}H_{13}O$)
HRMS (EI+):
Calc. for $C_{18}H_{28}OSi$ $[M]^+$: 288.1909; Found: 288.1915

triethyl((3-(*p*-tolyl)cyclopent-1-en-1-yl)oxy)silane (2) (Scheme 1)

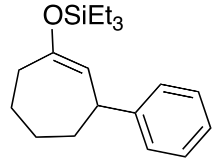


General procedure **(III)(B)** was followed with 2-cyclopenten-1-one (83.7 μL, 1.00 mmol, 1.00 equiv), 1-iodo-4-methylbenzene (218 mg, 1.00 mmol, 1.00 equiv) and chlorotriethylsilane (185 μL, 1.10 mmol, 1.10 equiv). The reaction was heated to 40 °C. After 1 h, the reaction mixture was purified by silica gel column chromatography to afford faint yellow oil.

Data for **2**, **Scheme 1**
TLC: R_f 0.3 (100% hexanes) [silica gel treated with 0.1% Et_3N, UV and $KMnO_4$ stain]
GC Method: A
Yield: Run 1 (289 mg, 80%)

Yield: Run 2 (222 mg, 77%)
Average Yield: 79%
^{1}H NMR (500 MHz, $CDCl_3$)
δ 7.13-7.09 (m, 4H), 4.73 (q, *J* = 1.8 Hz, 1H), 3.83 (q, *J* = 6.7 Hz, 1H), 2.42-2.34 (m, 3H), 2.32 (s, 3H), 1.69 (qd, *J* = 9.4, 7.2 Hz, 1H), 1.01 (t, *J* = 7.9 Hz, 9H), 0.73 (q, *J* = 7.9 Hz, 6H).
^{13}C NMR (126 MHz; $CDCl_3$)
δ 156.6, 145.1, 135.5, 129.2, 127.1, 106.5, 47.6, 33.7, 32.5, 21.1, 6.8, 5.0
LRMS *m/z* (%relative intensity, ion): (EI+, 30 eV)
288.15 (36.18, M^+), 273.15 (15..49, M^+ - CH_3), 259.10 (15.33, M^+ - C_2H_5), 197.10 (6.70, M^+ - C_7H_7), 157.10 (39.35, M^+ - $C_6H_{15}OSi$), 131.10 (6.13, M^+ - $C_{12}H_{13}$), 115.10 (27.29, M^+ - $C_{12}H_{13}O$)
HRMS (EI+):
Calc. for $C_{18}H_{28}OSi$ $[M]^+$: 288.1910; Found: 288.1914

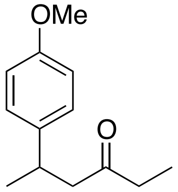
triethyl((3-phenylcyclohept-1-en-1-yl)oxy)silane (3) (Scheme 1)



General procedure **(III)(B)** was followed with 2-cyclohepten-1-one (110.0 μL, 1.00 mmol, 1.00 equiv), iodobenzene (112 μL, 1.00 mmol, 1.00 equiv) and chlorotriethylsilane (185 μL, 1.10 mmol, 1.10 equiv). After 1 h, the reaction mixture was purified by silica gel column chromatography to afford faint yellow oil.

Data for **3**, **Scheme 1**
TLC: R_f 0.4 (1% EtOAc in hexanes) [silica gel treated with 0.1% Et_3N, UV and $KMnO_4$ stain]
GC Method: A
Yield: Run 1 (188 mg, 62%)
Yield: Run 2 (203 mg, 67%)
Average Yield: 65%
^{1}H NMR (500 MHz, $CDCl_3$)
δ 7.31-7.28 (m, 2H), 7.23-7.17 (m, 3H), 5.04 (d, *J* = 4.4 Hz, 1H), 3.45 (d, br, *J* = 9.9 Hz, 1H), 2.48-2.43 (m, 1H), 2.28-2.24 (m, 1H), 1.88-1.73 (m, 4H), 1.67-1.55 (m, 2H), 0.98 (t, *J* = 7.9 Hz, 9H), 0.66 (q, *J* = 8.0 Hz, 6H).
^{13}C NMR (126 MHz; $CDCl_3$)
δ 155.1, 148.7, 128.5, 127.3, 125.8, 113.6, 43.6, 36.8, 35.3, 29.5, 25.2, 6.9, 5.2
LRMS *m/z* (%relative intensity, ion): (EI+, 30 eV)
302.20 (33.25, M^+), 287.20 (7.59, M^+ - CH_3), 273.15 (12.63, M^+ - C_2H_5), 131.10 (8.28, M^+ - $C_{13}H_{15}$), 171.10 (23.27, M^+ - $C_6H_{15}OSi$), 115.10 (22.92, M^+ - $C_{13}H_{15}O$)
HRMS (EI+):
Calc. for $C_{19}H_{30}OSi$ $[M]^+$: 302.2066; Found: 302.2074

5-(4-methoxyphenyl)hexan-3-one [141244-87-3] (4, Scheme 1)

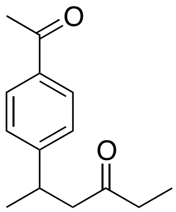


General procedure **(III)(C)(i)** was followed with 4-hexen-3-one (114 μL, 1.00 mmol, 1.00 equiv), 4-iodoanisole (234 mg, 1.00 mmol, 1.00 equiv) and chlorotriethylsilane (185 μL, 1.10 mmol, 1.10 equiv).

After deprotection, the crude mixture was purified by silica gel column chromatography to afford faint yellow oil.

Data for **4**, **Scheme 1**
TLC: R_f 0.3 (5% EtOAc in hexanes) [UV stain]
GC Method: A
Yield: Run 1 (99.9 mg, 48%)
Yield: Run 2 (98.6 mg, 48%)
Average Yield: 48%
^{1}H NMR (400 MHz, $CDCl_3$)
δ 7.12 (d, *J* = 8.6 Hz, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 3.78 (s, 3H), 3.27 (sextet, *J* = 7.1 Hz, 1H), 2.64 (qd, *J* = 18.2, 7.2 Hz, 2H), 2.39-2.22 (m, 2H), 1.23 (d, *J* = 7.0 Hz, 3H), 0.98 (t, *J* = 7.3 Hz, 3H)
^{13}C NMR (101 MHz; $CDCl_3$)
δ 210.7, 158.1, 138.5, 127.8, 114.0, 55.3, 51.2, 36.8, 34.9, 22.3, 7.7
LRMS *m/z* (%relative intensity, ion): (EI+, 30 eV)
206.05 (15.22, M^+), 135.10 (100.00, M^+ - C_4H_7O), 57.05 (14.54, M^+ - $C_{10}H_{13}O$)
HRMS (EI+):
Calc. for $C_{13}H_{18}O_2$ $[M]^+$: 206.1307; Found: 206.1312

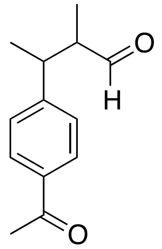
5-(4-acetylphenyl)hexan-3-one (5, Scheme 1)



General procedure **(III)(C)(i)** was followed with 4-hexen-3-one (114 μL, 1.00 mmol, 1.00 equiv), 4'-iodoacetophenone (246 mg, 1.00 mmol, 1.00 equiv) and chlorotriethylsilane (185 μL, 1.10 mmol, 1.10 equiv). After deprotection, the crude mixture was purified by silica gel column chromatography to afford faint yellow oil.

Data for **5**, **Scheme 1**
TLC: R_f 0.3 (20% EtOAc in hexanes) [UV stain]
GC Method: A
Yield: Run 1 (132 mg, 61%)
Yield: Run 2 (118 mg, 54%)
Average Yield: 58%
^{1}H NMR (400 MHz, $CDCl_3$)
δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 3.40 (q, *J* = 7.0 Hz, 1H), 2.70 (qd, *J* = 16.1, 7.1 Hz, 2H), 2.57 (s, 3H), 2.42-2.24 (m, 2H), 1.27 (d, *J* = 7.0 Hz, 3H), 0.99 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (101 MHz; $CDCl_3$)
δ 209.8, 197.7, 152.1, 135.4, 128.7, 127.1, 50.2, 36.6, 35.4, 26.6, 21.8, 7.6
LRMS *m/z* (%relative intensity, ion): (EI+, 30 eV)
218.10 (36.88, M^+), 203.05 (26.20, M^+ - CH_3), 175.10 (7.35, M^+ - C_2H_3O), 147.10 (100.00, M^+ - C_4H_7O), 119.05 (6.25, M^+ - $C_6H_{11}O$)
HRMS (EI+):
Calc. for $C_{14}H_{18}O_2$ $[M]^+$: 218.1307; Found: 218.1299

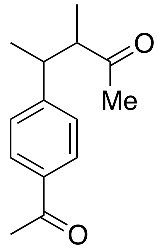
3-(4-acetylphenyl)-2-methylbutanal (6, Scheme 1)



General procedure **(III)(C)(i)** was followed with *trans*-2-methyl-2-butenal (97.0 μL, 1.00 mmol, 1.00 equiv), 4'-iodoacetophenone (246 mg, 1.00 mmol, 1.00 equiv) and chlorotriethylsilane (185 μL, 1.10 mmol, 1.10 equiv). After deprotection, the crude mixture was purified by silica gel column chromatography to afford a 1:1 mixture of diastereomers of desired product as a faint yellow oil.

Data for **6, Scheme 1**
TLC: R_f 0.3 (20% EtOAc in hexanes) [UV stain]
GC Method: A
Yield: Run 1 (104 mg, 51%)
Yield: Run 2 (104 mg, 51%)
Average Yield: 51%
^{1}H NMR (500 MHz, CDCl$_3$)
δ 9.65 (d, *J* = 2.9 Hz, 1H), 9.54 (d, *J* = 1.8 Hz, 1H), 7.87 (dd, *J* = 8.3, 3.5 Hz, 4H), 7.28-7.23 (m, 4H), 3.20 (quintet, *J* = 7.1 Hz, 1H), 3.09-3.03 (m, 1H), 2.63-2.54 (m, 8H), 1.27 (dd, *J* = 14.9, 7.0 Hz, 6H), 1.05 (d, *J* = 7.0 Hz, 3H), 0.85 (d, *J* = 7.0 Hz, 3H).
^{13}C NMR (126 MHz; CDCl$_3$)
δ 204.1, 204.0, 197.7, 150.0, 149.4, 135.8, 135.7, 128.7, 127.9, 127.7, 52.5, 52.3, 40.8, 40.0, 26.6, 19.9, 17.2, 12.4, 10.4
LRMS *m/z* (%relative intensity, ion): (EI+, 30 eV)
204.05 (32.36, M^+), 189.00 (10.87, M^+ - CH_3), 161.10 (12.48, M^+ - C_2H_3O), 147.05 (100.00, M^+ - C_3H_5O)
HRMS (EI+):
Calc. for $C_{13}H_{16}O_2$ $[M]^+$: 204.1150; Found: 204.1161

3-(4-acetylphenyl)-2-methylbutanal (7, Scheme 1)

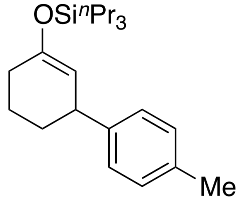


General procedure **(III)(C)(i)** was followed with 3-methyl-3-penten-2-one (112 μL, 1.00 mmol, 1.00 equiv), 4'-iodoacetophenone (246 mg, 1.00 mmol, 1.00 equiv) and chlorotriethylsilane (185 μL, 1.10 mmol, 1.10 equiv). After deprotection, the crude mixture was purified by silica gel column chromatography to afford 6:1 ratio of major:minor diastereomers as a faint yellow oil.

Data for **7, Scheme 1**
TLC: R_f 0.3 (20% EtOAc in hexanes) [UV stain]
GC Method: A
Yield: Run 1 (109 mg, 50%)
Yield: Run 2 (107 mg, 49%)

Average Yield: 50%
^{1}H NMR (400 MHz, CDCl$_3$)
major diastereomer:
δ 7.90 (d, *J* = 8.2 Hz, 2H), 7.26 (s, *J* = 8.3 Hz, 2H), 3.04-2.97 (m, 1H), 2.76-2.71 (m, 1H), 2.59 (s, 3H), 2.20 (s, 3H), 1.21 (d, *J* = 6.8 Hz, 3H), 0.84 (d, *J* = 7.0 Hz, 3H)
minor diastereomer:
7.90 (d, *J* = 8.2 Hz, 2H), 7.26 (s, *J* = 8.3 Hz, 2H), 3.12-3.08 (m, 1H), 2.82-2.77 (m, 1H), 2.57 (s, 3H), 1.90 (s, 3H), 1.25 (d, *J* = 7.0 Hz, 3H), 0.90 (d, *J* = 6.7 Hz, 3H)
^{13}C NMR (126 MHz; CDCl$_3$)
δ 212.3, 197.8, 150.5, 135.8, 128.8, 127.9, 53.6, 42.8, 29.5, 26.7, 20.6, 16.1
LRMS *m/z* (%relative intensity, ion): (EI+, 30 eV)
218.05 (31.31, M$^+$), 203.05 (7.49, M$^+$ - CH$_3$), 175.10 (11.53, M$^+$ - C$_2$H$_3$O), 147.05 (100.00, M$^+$ - C$_4$H$_7$O)
HRMS (EI+):
Calc. for C$_{14}$H$_{18}$O$_2$ [M]$^+$: 218.1307; Found: 218.1317

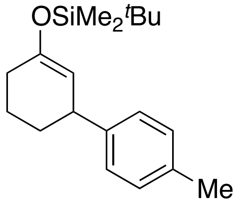
((4'-methyl-1,4,5,6-tetrahydro-[1,1'-biphenyl]-3-yl)oxy)tri-*n*-propylsilane (8) (Scheme 1)



General procedure **(III)(B)** was followed with 2-cyclohexen-1-one (96.8 μL, 1.00 mmol, 1.00 equiv), 1-iodo-4-methylbenzene (218 mg, 1.00 mmol, 1.00 equiv) and chlorotri-*n*-propylsilane (241 μL, 1.10 mmol, 1.10 equiv). After 1 h, the reaction mixture was purified by silica gel column chromatography to afford faint yellow oil.

Data for **8**, **Scheme 1**
TLC: R$_f$ 0.4 (1% EtOAc in hexanes) [silica gel treated with 0.1% Et$_3$N, UV and KMnO$_4$ stain]
GC Method: A
Yield: Run 1 (307 mg, 89%)
Yield: Run 2 (321 mg, 93%)
Average Yield: 91%
^{1}H NMR (500 MHz, CDCl$_3$)
δ 7.12 (s, 4H), 4.902-4.896 (m, 1H), 3.47-3.43 (m, 1H), 2.33 (s, 3H), 2.17-2.02 (m, 2H), 1.94-1.88 (m, 1H), 1.81-1.74 (m, 1H), 1.68-1.59 (m, 1H), 1.47-1.39 (m, 7H), 0.99 (t, *J* = 7.3 Hz, 9H), 0.71-0.68 (m, 6H).
^{13}C NMR (126 MHz; CDCl$_3$)
δ 152.0, 144.6, 135.5, 129.1, 127.7, 107.5, 41.2, 33.0, 30.0, 21.8, 21.1, 18.5, 17.2, 16.9
LRMS *m/z* (%relative intensity, ion): (EI+, 30 eV)
344.25 (4.65, M$^+$), 329.20 (2.51, M$^+$ - CH$_3$), 301.20 (14.87, M$^+$ - C$_3$H$_7$), 173.10 (8.75, M$^+$ - C$_{13}$H$_{15}$), 171.10 (18.30, M$^+$ - C$_9$H$_{21}$OSi), 157.10 (3.49, M$^+$ - C$_{13}$H$_{15}$O), 91.05 (5.19, M$^+$ - C$_{15}$H$_{29}$OSi),
HRMS (EI+):
Calc. for C$_{22}$H$_{36}$OSi [M]$^+$: 344.2535; Found: 344.2529

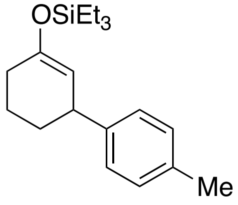
tert-butyldimethyl((4'-methyl-1,4,5,6-tetrahydro-[1,1'-biphenyl]-3-yl)oxy)silane (9) (Scheme 1)



General procedure **(III)(B)** was followed with 2-cyclohexen-1-one (96.8 μL, 1.00 mmol, 1.00 equiv), 1-iodo-4-methylbenzene (218 mg, 1.00 mmol, 1.00 equiv) and *tert*-butylchlorodimethylsilane (166 mg, 1.10 mmol, 1.10 equiv). After 1 h, the reaction mixture was purified by silica gel column chromatography to afford faint yellow oil.

Data for **9**, **Scheme 1**
TLC: R_f 0.4 (1% EtOAc in hexanes) [silica gel treated with 0.1% Et_3N, UV and $KMnO_4$ stain]
GC Method: A
Yield: Run 1 (268 mg, 88%)
Yield: Run 2 (276 mg, 86%)
Average Yield: 87%
^{1}H NMR (500 MHz, $CDCl_3$)
δ 7.14-7.10 (m, 4H), 4.92-4.91 (m), 3.45-3.42 (m, 1H), 2.33 (s, 3H), 2.18-2.02 (m, 2H), 1.94-1.88 (m, 1H), 1.81-1.75 (m, 1H), 1.67-1.60 (m, 1H), 1.43-1.36 (m, 1H), 0.94 (s, 9H), 0.17 (d, *J* = 6.3 Hz, 6H).
^{13}C NMR (126 MHz; $CDCl_3$)
δ 152.0, 144.5, 135.6, 129.1, 127.7, 108.2, 41.3, 32.9, 30.0, 25.9, 21.8, 21.1, 18.2, -4.09, -4.19
LRMS *m/z* (%relative intensity, ion): (EI+, 30 eV)
302.20 (48.97, M^+), 287.10 (8.67, $M^+ - CH_3$), 273.15 (19.67, $M^+ - C_2H_5$), 211.05 (7.33, $M^+ - C_7H_7$), 171.10 (30.87, $M^+ - C_{18}H_{28}OSi$), 131.05 (10.94, $M^+ - C_{13}H_{15}$), 91.00 (8.16, $M^+ - C_{12}H_{23}OSi$),
HRMS (EI+):
Calc. for $C_{19}H_{30}OSi$ $[M]^+$: 302.2066; Found: 302.2068

triethyl((4'-methyl-1,4,5,6-tetrahydro-[1,1'-biphenyl]-3-yl)oxy)silane (10) (Scheme 2)

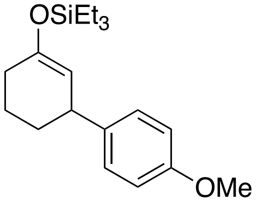


General procedure **(III)(B)** was followed with 2-cyclohexen-1-one (96.8 μL, 1.00 mmol, 1.00 equiv), 1-iodo-4-methylbenzene (218 mg, 1.00 mmol, 1.00 equiv) and chlorotriethylsilane (185 μL, 1.10 mmol, 1.10 equiv). After 1 h, the reaction mixture was purified by silica gel column chromatography to afford faint yellow oil.

Data for **10**, **Scheme 2**
TLC: R_f 0.3 (1% EtOAc in hexanes) [silica gel treated with 0.1% Et_3N, UV and $KMnO_4$ stain]
GC Method: A
Yield: Run 1 (260 mg, 86%)
Yield: Run 2 (258 mg, 85%)
Average Yield: 86%

^{1}H NMR (400 MHz, $CDCl_3$)
δ 7.17-7.10 (m, 4H), 4.93 (t, *J* = 1.2 Hz, 1H), 3.46-3.42 (m, 1H), 2.33 (s, 3H), 2.21-2.03 (m, 2H), 1.95-1.88 (m, 1H), 1.83-1.74 (m, 1H), 1.69-1.59 (m, 1H), 1.45-1.36 (m, 1H), 1.01 (t, *J* = 7.9 Hz, 9H), 0.69 (q, *J* = 7.9 Hz, 6H).
^{13}C NMR (101 MHz; $CDCl_3$)
δ 151.9, 144.5, 135.5, 129.1, 127.7, 107.7, 41.3, 32.9, 29.9, 21.8, 21.1, 6.9, 5.3
LRMS *m/z* (%relative intensity, ion): (EI+, 30 eV)
302.20 (40.91, M^+), 287.15 (M^+ - CH_3), 171.10 (26.30, M^+ - $C_6H_{15}OSi$), 131.10 (9.70, M^+ - $C_{13}H_{15}$), 115.05 (25.74, M^+ - $C_{13}H_{15}O$), 91.00 (7.86, M^+ - $C_{12}H_{23}OSi$)
HRMS (EI+):
Calc. for $C_{19}H_{30}OSi$ $[M]^+$: 302.2066; Found: 302.2072

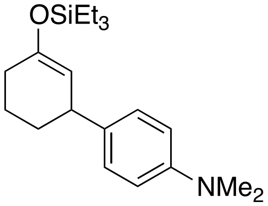
triethyl((4'-methoxy-1,4,5,6-tetrahydro-[1,1'-biphenyl]-3-yl)oxy)silane (11) (Scheme 2)



General procedure **(III)(B)** was followed with 2-cyclohexen-1-one (96.8 μL, 1.00 mmol, 1.00 equiv), 1-iodo-4-methoxybenzene (234 mg, 1.00 mmol, 1.00 equiv) and chlorotriethylsilane (185 μL, 1.10 mmol, 1.10 equiv). After 1 h, the reaction mixture was purified by silica gel column chromatography to afford faint yellow oil.

Data for **11**, **Scheme 2**
TLC: R_f 0.3 (3% EtOAc in hexanes) [silica gel treated with 0.1% Et_3N, UV and $KMnO_4$ stain]
GC Method: A
Yield: Run 1 (278 mg, 88%)
Yield: Run 2 (263 mg, 83%)
Average Yield: 86%
^{1}H NMR (400 MHz, $CDCl_3$)
δ 7.14 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 4.92-4.91 (m, 1H), 3.80 (s, 3H), 3.45-3.41 (m, 1H), 2.19-2.03 (m, 2H), 1.94-1.87 (m, 1H), 1.81-1.73 (m, 1H), 1.68-1.58 (m, 1H), 1.44-1.34 (m, 1H), 1.01 (t, *J* = 7.9 Hz, 9H), 0.70 (q, *J* = 7.9 Hz, 6H).
^{13}C NMR (101 MHz; $CDCl_3$)
δ 158.0, 151.9, 139.6, 128.7, 113.8, 107.8, 55.4, 40.8, 33.0, 29.9, 21.7, 6.9, 5.3
LRMS *m/z* (%relative intensity, ion): (EI+, 30 eV)
318.20 (<1.00, M^+), 203.05 (76.52, M^+ - $C_6H_{15}Si$), 187.10 (2.22, M^+ - $C_6H_{15}OSi$), 131.00 (40.86, $C_{13}H_{15}O$), 115.05 (27.13, M^+ - $C_{13}H_{15}O_2$), 107.00 (3.48, M^+ - $C_{12}H_{23}OSi$)
HRMS (EI+):
Calc. for $C_{19}H_{30}O_2Si$ $[M]^+$: 318.2015; Found: 318.2021

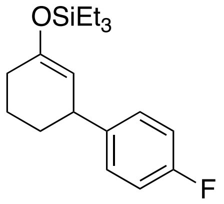
***N,N*-dimethyl-5'-((triethylsilyl)oxy)-1',2',3',4'-tetrahydro-[1,1'-biphenyl]-4-amine (12) (Scheme 2)**



General procedure **(III)(B)** was followed with 2-cyclohexen-1-one (96.8 μL, 1.00 mmol, 1.00 equiv), 4-iodo-*N,N*-dimethylaniline (247 mg, 1.00 mmol, 1.00 equiv) and chlorotriethylsilane (185 μL, 1.10 mmol, 1.10 equiv). After 1 h, the reaction mixture was purified by silica gel column chromatography to afford faint yellow oil.

Data for **12**, **Scheme 2**
TLC: R_f 0.3 (3% EtOAc in hexanes) [silica gel treated with 0.1% Et_3N, UV and $KMnO_4$ stain]
GC Method: B
Yield: Run 1 (243 mg, 73%)
Yield: Run 2 (259 mg, 78%)
Average Yield: 76%
^{1}H NMR (400 MHz, $CDCl_3$)
δ 7.11 (d, *J* = 8.7 Hz, 2H), 6.72 (d, *J* = 8.7 Hz, 2H), 4.94-4.93 (m, 1H), 3.42-3.37 (m, 1H), 2.92 (s, 6H), 2.19-2.02 (m, 2H), 1.92-1.86 (m, 1H), 1.82-1.73 (m, 1H), 1.67-1.57 (m, 1H), 1.44-1.35 (m, 1H), 1.00 (t, *J* = 7.9 Hz, 9H), 0.70 (q, *J* = 8.0 Hz, 6H).
^{13}C NMR (101 MHz; $CDCl_3$)
δ 151.6, 149.3, 135.7, 128.4, 113.0, 108.2, 41.1, 40.6, 33.0, 30.0, 21.8, 6.9, 5.3
LRMS *m/z* (%relative intensity, ion): (EI+, 30 eV)
331.25 (100.00, M^+), 302.20 (29.13, M^+ - C_2H_5), 287.20 (9.82, M^+ - C_2H_6N), 200.10 (20.41, M^+ - $C_6H_{15}OSi$), 115.05 (9.10, M^+ - $C_{14}H_{18}NO$)
HRMS (EI+):
Calc. for $C_{20}H_{33}NOSi$ $[M]^+$: 331.2331; Found: 331.2334

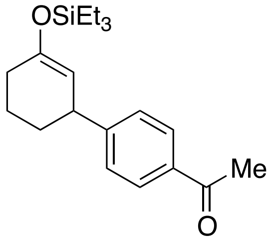
triethyl((4'-fluoro-1,4,5,6-tetrahydro-[1,1'-biphenyl]-3-yl)oxy)silane (13) (Scheme 2)



General procedure **(III)(B)** was followed with 2-cyclohexen-1-one (96.8 μL, 1.00 mmol, 1.00 equiv), 1-fluoro-4-iodobenzene (115 μL, 1.00 mmol, 1.00 equiv) and chlorotriethylsilane (185 μL, 1.10 mmol, 1.10 equiv). After 1 h, the reaction mixture was purified by silica gel column chromatography to afford faint yellow oil.

Data for **13**, **Scheme 2**
TLC: R_f 0.3 (1% EtOAc in hexanes) [silica gel treated with 0.1% Et_3N, UV and $KMnO_4$ stain]
GC Method: A
Yield: Run 1 (245 mg, 80%)
Yield: Run 2 (268 mg, 87%)
Average Yield: 84%
^{1}H NMR (400 MHz, $CDCl_3$)
δ 7.17 (dd, *J* = 8.5, 5.6 Hz, 2H), 6.97 (t, *J* = 8.7 Hz, 2H), 4.894-4.887 (m, 1H), 3.48-3.44 (m, 1H), 2.19-2.03 (m, 2H), 1.94-1.87 (m, 1H), 1.81-1.59 (m, 2H), 1.44-1.34 (m, 1H), 1.00 (t, *J* = 7.9 Hz, 9H), 0.70 (q, *J* = 7.9 Hz, 6H).
^{13}C NMR (101 MHz; $CDCl_3$)
δ 161.4 (d, *J* = 242.9 Hz), 152.3, 143.1, 129.1 (d, *J* = 7.7 Hz), 115.1 (d, *J* = 20.8 Hz), 107.3, 40.9, 32.9, 29.9, 21.6, 6.9, 5.3
^{19}F NMR (376 MHz; $CDCl_3$)
δ 66.73
LRMS *m/z* (%relative intensity, ion): (EI+, 30 eV)
306.20 (24.16, M^+), 277.10 (14.25, M^+ - C_2H_5), 175.09 (13.82, M^+ - $C_6H_{15}OSi$), 115.05 (10.01, M^+ - $C_{12}H_{12}FO$)
HRMS (EI+):
Calc. for $C_{18}H_{27}FOSi$ $[M]^+$: 306.1815; Found: 306.1832

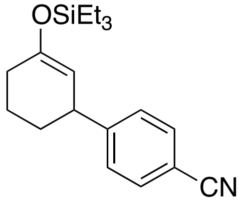
1-(5'-((triethylsilyl)oxy)-1',2',3',4'-tetrahydro-[1,1'-biphenyl]-4-yl)ethanone (14) (Scheme 2)



General procedure **(III)(B)** was followed with 2-cyclohexen-1-one (96.8 μL, 1.00 mmol, 1.00 equiv), 1-(4-iodophenyl)ethanone (246 mg, 1.00 mmol, 1.00 equiv) and chlorotriethylsilane (185 μL, 1.10 mmol, 1.10 equiv). After 1 h, the reaction mixture was purified by silica gel column chromatography to afford faint yellow oil.

Data for **14, Scheme 2**
TLC: R_f 0.3 (3% EtOAc in hexanes) [silica gel treated with 0.1% Et_3N, UV and $KMnO_4$ stain]
GC Method: A
Yield: Run 1 (273 mg, 83%)
Yield: Run 2 (280 mg, 85%)
Average Yield: 84%
^{1}H NMR (400 MHz, $CDCl_3$)
δ 7.90 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 4.90-4.89 (m, 1H), 3.56-3.52 (m, 1H), 2.59 (s, 3H), 2.21-2.05 (m, 2H), 1.98-1.91 (m, 1H), 1.82-1.62 (m, 2H), 1.45-1.37 (m, 1H), 1.00 (t, *J* = 7.9 Hz, 9H), 0.70 (q, *J* = 8.0 Hz, 6H).
^{13}C NMR (101 MHz; $CDCl_3$)
δ 198.0, 153.3, 152.7, 135.4, 128.6, 128.0, 106.4, 41.7, 32.5, 29.8, 26.7, 21.6, 6.9, 5.2
LRMS *m/z* (%relative intensity, ion): (EI+, 30 eV)
330.20 (71.26, M^+), 301.15 (100.00, M^+ - C_2H_5), 287.15 (77.63, M^+ - C_2H_3O), 199.05 (11.62, M^+ - $C_6H_{15}OSi$), 115.05 (37.51, M^+ - $C_{14}H_{15}O_2$)
HRMS (EI+):
Calc. for $C_{20}H_{30}O_2Si$ $[M]^+$: 330.2015; Found: 330.2024

5'-((triethylsilyl)oxy)-1',2',3',4'-tetrahydro-[1,1'-biphenyl]-4-carbonitrile (15) (Scheme 2)



General procedure **(III)(B)** was followed with 2-cyclohexen-1-one (96.8 μL, 1.00 mmol, 1.00 equiv), 4-bromobenzonitrile (182 mg, 1.00 mmol, 1.00 equiv) and chlorotriethylsilane (185 μL, 1.10 mmol, 1.10 equiv). After 1 h, the reaction mixture was purified by silica gel column chromatography to afford faint yellow oil.

Data for **15, Scheme 2**
TLC: R_f 0.3 (2% EtOAc in hexanes) [silica gel treated with 0.1% Et_3N, UV and $KMnO_4$ stain]
GC Method: A
Yield: Run 1 (270 mg, 86%)
Yield: Run 2 (254 mg, 81%)
Average Yield: 84%
^{1}H NMR (400 MHz, $CDCl_3$)

δ 7.58 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 4.86-4.85 (m, 1H), 3.56-3.51 (m, 1H), 2.21-2.04 (m, 2H), 1.97-1.90 (m, 1H), 1.80-1.60 (m, 2H), 1.42-1.35 (m, 1H), 1.00 (t, *J* = 7.9 Hz, 9H), 0.69 (q, *J* = 7.9 Hz, 6H).

^{13}C NMR (101 MHz; $CDCl_3$)

δ 153.2, 132.3, 128.6, 119.3, 117.5, 109.9, 105.8, 41.8, 32.4, 29.8, 21.5, 6.9, 5.2

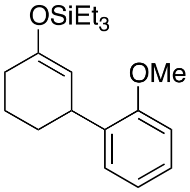
LRMS *m/z* (%relative intensity, ion): (EI+, 30 eV)

313.20 (59.13, M^+), 284.15 (100.00, $M^+ - C_2H_5$), 115.05 (27.61, $M^+ - C_{13}H_{12}NO$)

HRMS (EI+):

Calc. for $C_{19}H_{27}NOSi$ $[M]^+$: 313.1862; Found: 313.1871

triethyl((2'-methoxy-1,4,5,6-tetrahydro-[1,1'-biphenyl]-3-yl)oxy)silane (16) (Scheme 3)



General procedure **(III)(B)** was followed with 2-cyclohexen-1-one (96.8 μL, 1.00 mmol, 1.00 equiv), 1-iodo-2-methoxybenzene (130 μL, 1.00 mmol, 1.00 equiv) and chlorotriethylsilane (185 μL, 1.10 mmol, 1.10 equiv). After 1 h, the reaction mixture was purified by silica gel column chromatography to afford faint yellow oil.

NOTE: Employing 156 μL (1.20 mmol, 1.20 equiv) of iodo-2-methoxybenzene instead of 1.00 equiv provided 121 mg, 38% of the desired product.

Data for **16**, **Scheme 3**

TLC: R_f 0.3 (1% EtOAc in hexanes) [silica gel treated with 0.1% Et_3N, UV and $KMnO_4$ stain]

GC Method: A

Yield: Run 1 (202 mg, 63%)

Yield: Run 2 (209 mg, 66%)

Average Yield: 65%

^{1}H NMR (500 MHz, $CDCl_3$)

δ 7.23-7.16 (m, 2H), 6.92 (td, *J* = 7.4, 1.1 Hz, 1H), 6.85 (dd, *J* = 8.1, 0.9 Hz, 1H), 4.88-4.88 (m, 1H), 3.94-3.90 (m, 1H), 3.83 (s, 3H), 2.17-2.04 (m, 2H), 1.94-1.88 (m, 1H), 1.74-1.59 (m, 2H), 1.38 (dddd, *J* = 12.7, 9.6, 6.8, 3.0 Hz, 1H), 1.01 (t, *J* = 7.9 Hz, 9H), 0.70 (q, *J* = 8.0 Hz, 6H).

^{13}C NMR (126 MHz; $CDCl_3$)

δ 157.0, 152.1, 135.3, 128.7, 126.9, 120.4, 110.3, 107.4, 55.4, 33.7, 30.13, 30.05, 21.4, 6.9, 5.3

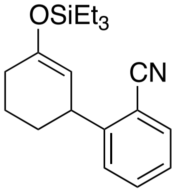
LRMS *m/z* (%relative intensity, ion): (EI+, 30 eV)

318.20 (<1.00, M^+), 203.05 (77.59, $M^+ - C_6H_{15}Si$), 131.05 (40.86, $C_{13}H_{15}O$)

HRMS (EI+):

Calc. for $C_{19}H_{30}O_2Si$ $[M]^+$: 318.2015; Found: 318.2019

5'-((triethylsilyl)oxy)-1',2',3',4'-tetrahydro-[1,1'-biphenyl]-2-carbonitrile (17) (Scheme 3)

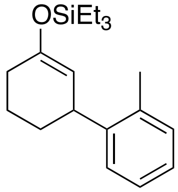


General procedure **(III)(B)** was followed with 2-cyclohexen-1-one (96.8 μL, 1.00 mmol, 1.00 equiv), 2-iodobenzonitrile (229 mg, 1.00 mmol, 1.00 equiv) and chlorotriethylsilane (185 μL, 1.10 mmol, 1.10

equiv). After 1 h, the reaction mixture was purified by silica gel column chromatography to afford faint yellow oil.

Data for **17**, **Scheme 3**
TLC: R_f 0.3 (5% EtOAc in hexanes) [silica gel treated with 0.1% Et_3N, UV and $KMnO_4$ stain]
GC Method: A
Yield: Run 1 (179 mg, 57%)
Yield: Run 2 (161 mg, 51%)
Average Yield: 54%
^{1}H NMR (400 MHz, $CDCl_3$)
δ 7.61 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.53 (td, *J* = 7.7, 1.2 Hz, 1H), 7.41-7.39 (m, 1H), 7.29 (dd, *J* = 7.6, 1.1 Hz, 1H), 4.84-4.84 (m, 1H), 3.98-3.93 (m, 1H), 2.22-2.02 (m, 3H), 1.79-1.67 (m, 2H), 1.45-1.37 (m, 1H), 1.00 (t, *J* = 7.9 Hz, 9H), 0.70 (q, *J* = 8.0 Hz, 6H).
^{13}C NMR (101 MHz; $CDCl_3$)
δ 153.5, 151.2, 132.97, 132.83, 128.4, 126.6, 118.2, 112.0, 105.4, 39.8, 31.6, 29.8, 21.4, 6.9, 5.2
LRMS *m/z* (%relative intensity, ion): (EI+, 30 eV)
313.15 (4.78, M^+), 284.10 (100.00, M^+ - C_2H_5), 211.00 (1.89, M^+ - C_7H_4N), 197.95 (4.11, M^+ - $C_6H_{15}Si$), 182.05 (6.02, M^+ - $C_6H_{15}OSi$), 131.00 (1.48, M^+ - $C_{13}H_{12}N$), 115.00 (8.70, M^+ - $C_{13}H_{12}NO$), 102.05 (1.24, M^+ - $C_{12}H_{23}OSi$)
HRMS (EI+):
Calc. for $C_{19}H_{27}NOSi$ $[M]^+$: 313.1862; Found: 313.1871

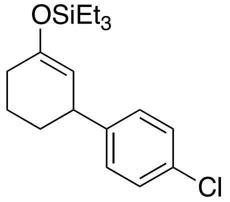
triethyl((2'-methyl-1,4,5,6-tetrahydro-[1,1'-biphenyl]-3-yl)oxy)silane (18) (Scheme 3)



General procedure **(III)(B)** was followed with 2-cyclohexen-1-one (96.8 μL, 1.00 mmol, 1.00 equiv), 1-iodo-2-methylbenzene (128 μL, 1.00 mmol, 1.00 equiv) and chlorotriethylsilane (185 μL, 1.10 mmol, 1.10 equiv). After 1 h, the reaction mixture was purified by silica gel column chromatography to afford faint yellow oil.

Data for **18**, **Scheme 3**
TLC: R_f 0.3 (1% EtOAc in hexanes) [silica gel treated with 0.1% Et_3N, UV and $KMnO_4$ stain]
GC Method: A
Yield: Run 1 (113 mg, 37%)
^{1}H NMR (500 MHz, $CDCl_3$)
δ 7.30 (t, *J* = 6.9 Hz, 1H), 7.24-7.21 (m, 1H), 7.20-7.15 (m, 2H), 4.96 (t, *J* = 1.4 Hz, 1H), 3.77 (ddd, *J* = 7.6, 5.2, 2.5 Hz, 1H), 2.42 (s, 3H), 2.24-2.14 (m, 2H), 1.97 (td, *J* = 7.1, 3.2 Hz, 1H), 1.84 (ddd, *J* = 9.6, 7.1, 4.4 Hz, 1H), 1.74-1.70 (m, 1H), 1.42 (dddd, *J* = 12.9, 10.2, 7.6, 2.7 Hz, 1H), 1.08 (t, *J* = 7.9 Hz, 9H), 0.78 (q, *J* = 8.0 Hz, 6H).
^{13}C NMR (126 MHz; $CDCl_3$)
δ 152.0, 145.1, 135.4, 130.3, 127.7, 126.03, 125.90, 107.6, 37.2, 30.5, 29.9, 21.6, 19.3, 6.9, 5.3
IR:
1663 cm^{-1} (C=C), 1184 cm^{-1} (C-O)
LRMS *m/z* (%relative intensity, ion): (EI+, 30 eV)
302.25 (9.71, M^+), 273.20 (50.82, M^+ - C_2H_5), 211.10 (6.09, M^+ - $PhCH_3$), 171.10 (8.93, M^+ - $C_6H_{15}OSi$), 131.10 (6.00, M^+ - $C_{13}H_{15}$)
HRMS (EI+):
Calc. for $C_{19}H_{30}OSi$ $[M]^+$: 302.2066; Found: 302.2062

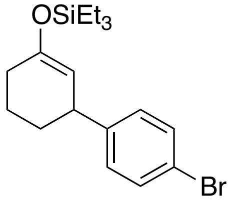
((4'-chloro-1,4,5,6-tetrahydro-[1,1'-biphenyl]-3-yl)oxy)triethylsilane (19) (Scheme 4)



General procedure **(III)(B)** was followed with 2-cyclohexen-1-one (96.8 μL, 1.00 mmol, 1.00 equiv), 1-chloro-4-iodobenzene (239 mg, 1.00 mmol, 1.00 equiv) and chlorotriethylsilane (185 μL, 1.10 mmol, 1.10 equiv). After 1 h, the reaction mixture was purified by silica gel column chromatography to afford faint yellow oil.

Data for **19**, **Scheme 4**
TLC: R_f 0.3 (1% EtOAc in hexanes) [silica gel treated with 0.1% Et_3N, UV and $KMnO_4$ stain]
GC Method: A
Yield: Run 1 (247 mg, 77%)
Yield: Run 2 (239 mg, 74%)
Average Yield: 76%
^{1}H NMR (500 MHz, $CDCl_3$)
δ 7.26-7.25 (m, 2H), 7.16-7.14 (m, 2H), 4.88-4.87 (m, 1H), 3.47-3.43 (m, 1H), 2.19-2.04 (m, 2H), 1.94-1.88 (m, 1H), 1.79-1.73 (m, 1H), 1.68-1.60 (m, 1H), 1.41-1.34 (m, 1H), 1.00 (t, *J* = 7.9 Hz, 9H), 0.69 (q, *J* = 7.9 Hz, 6H).
^{13}C NMR (126 MHz; $CDCl_3$)
δ 152.5, 146.0, 131.7, 129.1, 128.5, 106.9, 41.1, 32.7, 29.9, 21.6, 6.9, 5.3
LRMS *m/z* (%relative intensity, ion): (EI+, 30 eV)
322.15 (<1.00, M^+), 115.05 (100.00, M^+ - $C_{12}H_{12}ClO$), 110.90 (2.73, M^+ - $C_{12}H_{23}OSi$)
HRMS (EI+):
Calc. for $C_{18}H_{27}ClOSi$ $[M]^+$: 322.1520; Found: 322.1508

((4'-bromo-1,4,5,6-tetrahydro-[1,1'-biphenyl]-3-yl)oxy)triethylsilane (20) (Scheme 4)

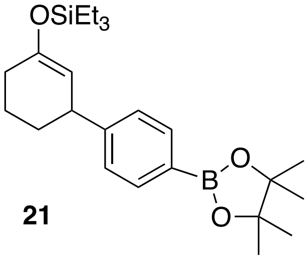


General procedure **(III)(B)** was followed with 2-cyclohexen-1-one (96.8 μL, 1.00 mmol, 1.00 equiv), 1-bromo-4-iodobenzene (283 mg, 1.00 mmol, 1.00 equiv) and chlorotriethylsilane (185 μL, 1.10 mmol, 1.10 equiv). After 1 h, the reaction mixture was purified by silica gel column chromatography to afford faint yellow oil.

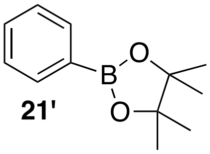
Data for **20**, **Scheme 4**
TLC: R_f 0.3 (1% EtOAc in hexanes) [silica gel treated with 0.1% Et_3N, UV and $KMnO_4$ stain]
GC Method: A
Yield: Run 1 (246 mg, 67%)
Yield: Run 2 (273 mg, 74%)
Average Yield: 71%
^{1}H NMR (400 MHz, $CDCl_3$)
δ 7.41 (d, *J* = 8.3 Hz, 2H), 7.10 (d, *J* = 8.4 Hz, 2H), 4.871-4.865 (m, 1H), 3.46-3.41 (m, 1H), 2.19-2.03 (m, 2H), 1.94-1.80 (m, 1H), 1.72-1.58 (m, 2H), 1.41-1.33 (m, 1H), 1.00 (t, *J* = 7.9 Hz, 9H), 0.69 (q, *J* = 7.9 Hz, 6H).

^{13}C NMR (101 MHz; $CDCl_3$)
δ 152.5, 146.5, 131.4, 129.6, 119.7, 106.8, 41.1, 32.7, 29.8, 21.6, 6.9, 5.3
LRMS *m/z* (%relative intensity, ion): (EI+, 30 eV)
366.5 (39.34, M^+), 337.10 (100.00, M^+ - C_2H_5), 287.15 (18.39, M^+ - Br), 211.05 (6.10, M^+ - C_6H_4Br), 155.05 (31.66, M^+ - $C_{12}H_{23}OSi$), 115.05 (52.30, M^+ - $C_{12}H_{12}BrO$)
HRMS (EI+):
Calc. for $C_{18}H_{27}BrOSi$ $[M]^+$: 366.1015; Found: 366.1021

triethyl((4'-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4,5,6-tetrahydro-[1,1'-biphenyl]-3-yl)oxy)silane (21) (Scheme 4)



21



21'

General procedure **(III)(B)** was followed with 2-cyclohexen-1-one (96.8 μL, 1.00 mmol, 1.00 equiv), 2-(4-iodophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (330 mg, 1.00 mmol, 1.00 equiv) and chlorotriethylsilane (185 μL, 1.10 mmol, 1.10 equiv). After 1 h, the reaction mixture was purified by silica gel column chromatography to afford a faint yellow oil which was an inseparable mixture of **21** and phenylboronic acid pinacol ester (**21'**).[9]

NOTE: Employing 396 mg (1.20 mmol, 1.20 equiv) of 2-(4-iodophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane instead of 1.00 equiv provided 310 mg of a 85:15 mixture of **21**:**21'** by ^{1}H NMR analysis, which corresponds to 285 mg of **21** (69% yield) and 25 mg of **21'**.[9]

Data for **21, Scheme 4**
TLC: R_f 0.3 (2% EtOAc in hexanes) [silica gel treated with 0.1% Et_3N, UV and $KMnO_4$ stain]
GC Method: B
Yield: Run 1 (261 mg of a 87:13 mixture of **21**:**21'** by ^{1}H NMR analysis, which corresponds to 245 mg of **21** (59% yield) and 16 mg of **21'**).
Yield: Run 2 (275 mg of a 84:16 mixture of **21**:**21'** by ^{1}H NMR analysis, which corresponds to 252 mg of **21** (61% yield) and 23 mg of **21'**).
Average Yield: 60%
^{1}H NMR (400 MHz, $CDCl_3$)
δ 7.76 (d, *J* = 7.8 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 4.92-4.91 (m, 1H), 3.50-3.46 (m, 1H), 2.20-2.03 (m, 2H), 1.96-1.82 (m, 1H), 1.79-1.74 (m, 1H), 1.68-1.59 (m, 1H), 1.45-1.39 (m, 1H), 1.34 (s, 12H), 1.00 (t, *J* = 7.9 Hz, 9H), 0.69 (q, *J* = 7.9 Hz, 6H).
^{13}C NMR (101 MHz; $CDCl_3$)
δ 152.2, 151.0, 135.0, 127.3, 107.2, 83.8, 41.9, 32.7, 29.9, 25.0, 24.8, 21.7, 6.9, 5.3
LRMS *m/z* (%relative intensity, ion): (EI+, 30 eV)
414.30 (44.27, M^+), 385.25 (12.58, M^+ - C_2H_5), 283.20 (25.74, M^+ - $C_6H_{15}OSi$), 211.10 (17.48, M^+ - $C_{12}H_{16}BO_2$), 131.05 (18.15, M^+ - $C_{18}H_{24}BO_2$), 115.05 (30.38, M^+ - $C_{18}H_{24}BO_3$)
HRMS (EI+):
Calc. for $C_{24}H_{39}O_3BSi$ $[M]^+$: 414.2762; Found: 414.2755

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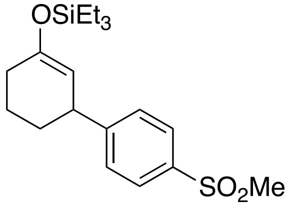
[9] NMR data for phenylboronic acid pinacol ester: Zhu, W.; Ma, D. *Org. Lett.* **2006**, *8*, 261.

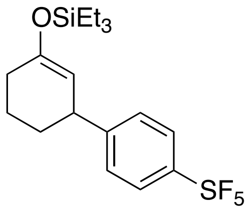
triethyl((4'-(methylsulfonyl)-1,4,5,6-tetrahydro-[1,1'-biphenyl]-3-yl)oxy)silane (22) (Scheme 4)



General procedure **(III)(B)** was followed with 2-cyclohexen-1-one (96.8 μL, 1.00 mmol, 1.00 equiv), 1-bromo-4-(methylsulfonyl)benzene (282 mg, 1.00 mmol, 1.00 equiv) and chlorotriethylsilane (185 μL, 1.10 mmol, 1.10 equiv). After 1 h, the reaction mixture was purified by silica gel column chromatography to afford faint yellow oil.

Data for **22**, **Scheme 4**
TLC: R_f 0.3 (25% EtOAc in hexanes) [silica gel treated with 0.1% Et_3N, UV and $KMnO_4$ stain]
GC Method: B
Yield: Run 1 (200 mg, 55%)
Yield: Run 2 (191 mg, 52%)
Average Yield: 54%
^{1}H NMR (400 MHz, $CDCl_3$)
δ 7.86 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 4.872-4.865 (m, 1H), 3.59-3.55 (m, 1H), 3.05 (s, 3H), 2.22-1.92 (m, 3H), 1.81-1.61 (m, 2H), 1.44-1.36 (m, 1H), 1.00 (t, *J* = 7.9 Hz, 9H), 0.70 (q, *J* = 7.9 Hz, 6H).
^{13}C NMR (101 MHz; $CDCl_3$)
δ 154.2, 153.2, 138.3, 128.8, 127.6, 105.9, 44.7, 41.7, 32.5, 29.8, 21.5, 6.9, 5.3
LRMS *m/z* (%relative intensity, ion): (EI+, 30 eV)
366.20 (34.81, M^+), 337.15 (100.00, M^+ - C_2H_5), 287.20 (16.58, M^+ - CH_3O_2S), 155.10 (32.19, M^+ - $C_{12}H_{23}OSi$), 115.10 (59.85, M^+ - $C_{13}H_{15}O_3S$)
HRMS (EI+):
Calc. for $C_{19}H_{30}O_3SSi$ $[M]^+$: 366.1685; Found: 366.1678

triethyl((3-(*p*-phenylpentafluorosulfur)cyclohex-1-en-1-yl)oxy)silane (23) (Scheme 4)



General procedure **(III)(B)** was followed with 2-cyclohexen-1-one (96.8 μL, 1.00 mmol, 1.00 equiv), (4-iodophenyl)sulfurpentafluoride (330 mg, 1.00 mmol, 1.00 equiv) and chlorotriethylsilane (185 μL, 1.10 mmol, 1.10 equiv). After 1 h, the reaction mixture was purified by silica gel column chromatography to afford faint yellow oil.

NOTE: Employing 396 mg (1.20 mmol, 1.20 equiv) of (4-iodophenyl)sulfurpentafluoride instead of 1.00 equiv provided 293 mg, 71% of the desired product.

Data for **23**, **Scheme 4**
TLC: R_f 0.3 (3% EtOAc in hexanes) [silica gel treated with 0.1% Et_3N, UV and $KMnO_4$ stain]
GC Method: B
Yield: Run 1 (242 mg, 58%)
Yield: Run 2 (227 mg, 55%)
Average Yield: 57%

^{1}H NMR (400 MHz, $CDCl_3$)

δ 7.67 (d, *J* = 8.7 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 4.88-4.87 (m, 1H), 3.55-3.51 (m, 1H), 2.21-2.05 (m, 2H), 1.97-1.90 (m, 1H), 1.81-1.61 (m, 2H), 1.44-1.35 (m, 1H), 1.01 (t, *J* = 7.9 Hz, 9H), 0.70 (q, *J* = 7.9 Hz, 6H).

^{13}C NMR (101 MHz; $CDCl_3$)

δ 154.8, 153.1, 151.5, 128.0, 126.0 (t), 106.0, 41.3, 32.5, 29.8, 21.5, 6.9, 5.3

^{19}F NMR (376 MHz; $CDCl_3$)

δ 147.8 (quintet, *J* = 151.2 Hz, 1 F_{axial}), 125.6 (d, *J* = 49.6 Hz, 4 $F_{equatorial}$)

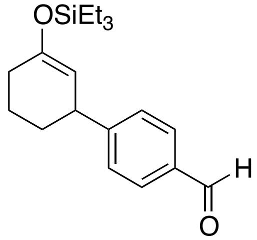
LRMS *m/z* (%relative intensity, ion): (EI+, 30 eV)

414.15 (38.00, M^+), 385.15 (13.58, $M^+ - C_2H_5$), 287.20 (17.22, $M^+ - SF_5$), 127.05 (12.61, $M^+ - C_{18}H_{27}OSi$), 115.05 (65.51, $M^+ - C_{12}H_{12}F_5OS$)

HRMS (EI+):

Calc. for $C_{18}H_{27}OF_5SiS$ $[M]^+$: 414.1472; Found: 414.1490

5'-((triethylsilyl)oxy)-1',2',3',4'-tetrahydro-[1,1'-biphenyl]-4-carbaldehyde (24) (Scheme 4)



General procedure **(III)(B)** was followed with 2-cyclohexen-1-one (96.8 μL, 1.00 mmol, 1.00 equiv), 4-iodobenzaldehyde (278 mg, 1.20 mmol, 1.20 equiv) and chlorotriethylsilane (185 μL, 1.10 mmol, 1.10 equiv). After 1 h, the reaction mixture was purified by silica gel column chromatography to afford faint yellow oil.

NOTE: Employing 232 mg (1.00 mmol, 1.00 equiv) of 4-iodobenzaldehyde instead of 1.20 equiv provided 158 mg, 50% of the desired product.

Data for **24**, **Scheme 4**

TLC: R_f 0.3 (5% EtOAc in hexanes) [silica gel treated with 0.1% Et_3N, UV and $KMnO_4$ stain]

GC Method: A

Yield: Run 1 (199 mg, 63%)

Yield: Run 2 (198 mg, 63%)

Average Yield: 63%

^{1}H NMR (400 MHz, $CDCl_3$)

δ 9.98 (s, 1H), 7.81 (d, *J* = 8.1 Hz, 2H), 7.39 (d, *J* = 8.1 Hz, 2H), 4.90-4.89 (m, 1H), 3.58-3.53 (m, 1H), 2.22-2.05 (m, 2H), 1.99-1.92 (m, 1H), 1.83-1.62 (m, 2H), 1.46-1.38 (m, 1H), 1.00 (t, *J* = 7.9 Hz, 9H), 0.70 (q, *J* = 7.9 Hz, 6H).

^{13}C NMR (101 MHz; $CDCl_3$)

δ 192.1, 155.0, 152.9, 134.8, 130.0, 128.5, 106.2, 41.9, 32.5, 29.8, 21.6, 6.9, 5.3

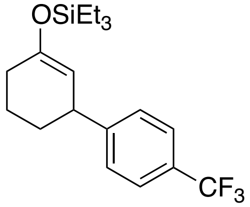
LRMS *m/z* (%relative intensity, ion): (EI+, 30 eV)

316.20 (38.45, M^+), 287.15 (90.97, $M^+ - CHO$), 115.10 (49.98, $M^+ - C_{13}H_{13}O_2$)

HRMS (EI+):

Calc. for $C_{19}H_{28}O_2Si$ $[M]^+$: 316.1859; Found: 316.1846

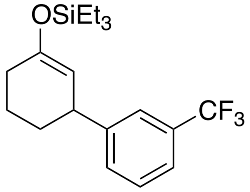
triethyl((4'-(trifluoromethyl)-1,4,5,6-tetrahydro-[1,1'-biphenyl]-3-yl)oxy)silane (25) (Scheme 4)



General procedure **(III)(B)** was followed with 2-cyclohexen-1-one (96.8 μL, 1.00 mmol, 1.00 equiv), 1-bromo-4-(trifluoromethyl)benzene (141 μL, 1.00 mmol, 1.00 equiv) and chlorotriethylsilane (185 μL, 1.10 mmol, 1.10 equiv). After 1 h, the reaction mixture was purified by silica gel column chromatography to afford faint yellow oil.

Data for **25**, **Scheme 4**
TLC: R_f 0.2 (2% EtOAc in hexanes) [silica gel treated with 0.1% Et_3N, UV and $KMnO_4$ stain]
GC Method: A
Yield: Run 1 (215 mg, 60%)
Yield: Run 2 (186 mg, 52%)
Average Yield: 56%
^{1}H NMR (400 MHz, $CDCl_3$)
δ 7.55 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 4.89-4.89 (m, 1H), 3.56-3.53 (m, 1H), 2.21-2.05 (m, 2H), 1.97-1.91 (m, 1H), 1.82-1.61 (m, 2H), 1.45-1.36 (m, 1H), 1.00 (t, *J* = 7.9 Hz, 9H), 0.70 (q, *J* = 8.0 Hz, 6H).
^{13}C NMR (101 MHz; $CDCl_3$)
δ 152.8, 151.6, 127.8, 126.3 (q, *J* = 3.6 Hz), 125.9 (q, *J* = 271.9 Hz), 125.3 (q, *J* = 3.5 Hz), 106.4, 41.6, 32.6, 29.9, 21.6, 6.9, 5.3
^{19}F NMR (376 MHz; $CDCl_3$)
δ 0.17
LRMS *m/z* (%relative intensity, ion): (EI+, 30 eV)
356.15 (33.98, M^+), 327.15 (34.34, $M^+ - C_2H_5$), 115.05 (43.27, $M^+ - C_{13}H_{12}F_3O$)
HRMS (EI+):
Calc. for $C_{19}H_{27}F_3OSi$ $[M]^+$: 356.1783; Found: 356.1796

triethyl((3'-(trifluoromethyl)-1,4,5,6-tetrahydro-[1,1'-biphenyl]-3-yl)oxy)silane (26) (Scheme 4)

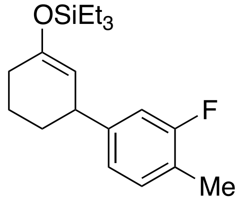


General procedure **(III)(B)** was followed with 2-cyclohexen-1-one (96.8 μL, 1.00 mmol, 1.00 equiv), 1-iodo-3-(trifluoromethyl)benzene (144 μL, 1.00 mmol, 1.00 equiv) and chlorotriethylsilane (185 μL, 1.10 mmol, 1.10 equiv). After 1 h, the reaction mixture was purified by silica gel column chromatography to afford faint yellow oil.

Data for **26**, **Scheme 4**
TLC: R_f 0.3 (2% EtOAc in hexanes) [silica gel treated with 0.1% Et_3N, UV and $KMnO_4$ stain]
GC Method: A
Yield: Run 1 (295 mg, 83%)
Yield: Run 2 (281 mg, 79%)
Average Yield: 81%

<u>^{1}H NMR (400 MHz, CDCl$_3$)</u>
δ 7.49-7.39 (m, 4H), 4.90-4.89 (dd, *J* = 2.0, 1.0 Hz, 1H), 3.56-3.52 (m, 1H), 2.21-2.05 (m, 2H), 1.99-1.92 (m, 1H), 1.82-1.61 (m, 2H), 1.45-1.36 (m, 1H), 1.01 (t, *J* = 7.9 Hz, 9H), 0.71 (q, *J* = 7.9 Hz, 6H).
<u>^{13}C NMR (101 MHz; CDCl$_3$)</u>
δ 152.9, 148.5, 131.3, 130.7 (q, *J* = 31.7 Hz), 128.8, 124.53 (q, *J* = 272.7 Hz), 124.51 (q, *J* = 4.06 Hz), 122.96 (q, *J* = 3.6 Hz), 106.4, 41.6, 32.7, 29.9, 21.6, 6.8, 5.3
<u>^{19}F NMR (376 MHz; CDCl$_3$)</u>
δ -0.14
<u>LRMS *m/z* (%relative intensity, ion)</u>: (EI+, 30 eV)
356.15 (24.78, M$^+$), 337.15 (34.15, M$^+$ - F), 327.10 (28.64, M$^+$ - C$_2$H$_5$), 211.05 (7.33, M$^+$ - C$_7$H$_4$F$_3$), 115.05 (30.63, M$^+$ - C$_{13}$H$_{12}$F$_3$O)
<u>HRMS (EI+)</u>:
Calc. for C$_{19}$H$_{27}$F$_3$OSi [M]$^+$: 356.1783; Found: 356.1790

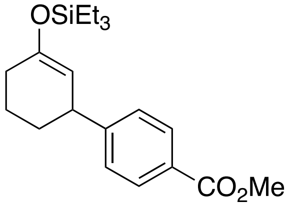
triethyl((3'-fluoro-4'-methyl-1,4,5,6-tetrahydro-[1,1'-biphenyl]-3-yl)oxy)silane (27) (Scheme 4)



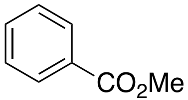
General procedure **(III)(B)** was followed with 2-cyclohexen-1-one (96.8 μL, 1.00 mmol, 1.00 equiv), 2-fluoro-4-iodo-1-methylbenzene (236 mg, 1.00 mmol, 1.00 equiv) and chlorotriethylsilane (185 μL, 1.10 mmol, 1.10 equiv). After 1 h, the reaction mixture was purified by silica gel column chromatography to afford faint yellow oil.

<u>Data for **27**, **Scheme 4**</u>
<u>TLC</u>: R$_f$ 0.3 (1% EtOAc in hexanes) [silica gel treated with 0.1% Et$_3$N, UV and KMnO$_4$ stain]
<u>GC Method</u>: A
<u>Yield</u>: Run 1 (258 mg, 80%)
<u>Yield</u>: Run 2 (239 mg, 75%)
<u>Average Yield</u>: 78%
<u>^{1}H NMR (400 MHz, CDCl$_3$)</u>
δ 7.09 (t, *J* = 8.0 Hz, 1H), 6.90-6.86 (m, 2H), 4.89-4.88 (m, 1H), 3.46-3.42 (m, 1H), 2.24 (s, 3H), 2.19-2.03 (m, 2H), 1.94-1.87 (m, 1H), 1.81-1.73 (m, 1H), 1.68-1.58 (m, 1H), 1.44-1.35 (m, 1H), 1.01 (t, *J* = 7.9 Hz, 9H), 0.70 (q, *J* = 7.9 Hz, 6H).
<u>^{13}C NMR (101 MHz; CDCl$_3$)</u>
δ 152.3, 147.4, 131.2 (d, *J* = 5.3 Hz), 123.0 (d, *J* = 2.7 Hz), 122.2 (d, *J* = 8.1 Hz), 114.2 (d, *J* = 22.2 Hz), 107.0, 41.1, 32.6, 29.9, 21.6, 14.32, 14.29, 6.9, 5.3
<u>^{19}F NMR (376 MHz; CDCl$_3$)</u>
δ 40.35
<u>LRMS *m/z* (%relative intensity, ion)</u>: (EI+, 30 eV)
320.15 (81.58, M$^+$), 291.15 (35.73, M$^+$ - C$_2$H$_5$), 211.05 (11.73, M$^+$ - C$_7$H$_6$F), 189.05 (33.51, M$^+$ - C$_6$H$_{15}$OSi), 131.15 (M$^+$ - C$_{13}$H$_{14}$F), 115.05 (17.47, M$^+$ - C$_{13}$H$_{14}$FO), 109.00 (13.32, M$^+$ - C$_{12}$H$_{23}$OSi)
<u>HRMS (EI+)</u>:
Calc. for C$_{19}$H$_{29}$FOSi [M]$^+$: 320.1972; Found: 320.1985

methyl 5'-((triethylsilyl)oxy)-1',2',3',4'-tetrahydro-[1,1'-biphenyl]-4-carboxylate (28) (Scheme 4)



28

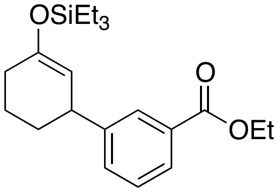


28'

General procedure **(III)(B)** was followed with 2-cyclohexen-1-one (96.8 μL, 1.00 mmol, 1.00 equiv), methyl-4-bromobenzoate (215 mg, 1.00 mmol, 1.00 equiv) and chlorotriethylsilane (185 μL, 1.10 mmol, 1.10 equiv). After 1 h, the reaction mixture was purified by silica gel column chromatography to afford faint yellow oil which was an inseparable mixture of **28** and methyl benzoate (**28'**).[10]

Data for **28, Scheme 4**
TLC: R_f 0.3 (3% EtOAc in hexanes) [silica gel treated with 0.1% Et_3N, UV and $KMnO_4$ stain]
GC Method: A
Yield: Run 1 (227 mg of a 92:8 mixture of **28**:**28'** by ^{1}H NMR analysis, which corresponds to 219 mg of **28** (63% yield) and 8 mg of **28'**).
Yield: Run 2 (209 mg of a 92:8 mixture of **28**:**28'** by ^{1}H NMR analysis, which corresponds to 202 mg of **28** (58% yield) and 7 mg of **28'**).
Average Yield: 61%
^{1}H NMR (400 MHz, $CDCl_3$)
δ 7.96 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 8.3 Hz, 2H), 4.90-4.89 (m, 1H), 3.90 (s, 3H), 3.56-3.51 (m, 1H), 2.21-2.04 (m, 2H), 1.97-1.90 (m, 1H), 1.82-1.60 (m, 2H), 1.45-1.37 (m, 1H), 1.00 (t, *J* = 7.9 Hz, 9H), 0.70 (q, *J* = 7.9 Hz, 6H).
^{13}C NMR (101 MHz; $CDCl_3$)
δ 167.3, 153.0, 152.6, 129.8, 128.1, 127.8, 106.6, 52.1, 41.7, 32.5, 29.9, 21.6, 6.9, 5.3
LRMS *m/z* (%relative intensity, ion): (EI+, 30 eV)
346.20 (47.13, M^+), 317.15 (34.37, $M^+ - C_2H_5$), 287.15 (20.72, $M^+ - C_2H_3O_2$), 115.05 (29.43, $M^+ - C_{14}H_{15}O_3$) 59.00 (43.04, $M^+ - C_{18}H_{27}OSi$)
HRMS (EI+):
Calc. for $C_{20}H_{30}O_3Si$ $[M]^+$: 346.1964; Found: 346.1974

ethyl 5'-((triethylsilyl)oxy)-1',2',3',4'-tetrahydro-[1,1'-biphenyl]-3-carboxylate (29) (Scheme 4)



General procedure **(III)(B)** was followed with 2-cyclohexen-1-one (96.8 μL, 1.00 mmol, 1.00 equiv), ethyl-3-iodobenzoate (200 μL, 1.20 mmol, 1.20 equiv) and chlorotriethylsilane (185 μL, 1.10 mmol, 1.10 equiv). After 1 h, the reaction mixture was purified by silica gel column chromatography to afford faint yellow oil.

NOTE: Employing 166 μL (1.00 mmol, 1.00 equiv) of ethyl-3-iodobenzoate instead of 1.20 equiv provided 179 mg, 50% of the desired product.

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(10) NMR data for methyl benzoate: Hirashima, S.; Nobuta, T.; Tada, N.; Miura, T.; Ito, A. *Org. Lett.* **2010**, *12*, 3645.

Data for **29, Scheme 4**

TLC: R_f 0.3 (5% EtOAc in hexanes) [silica gel treated with 0.1% Et_3N, UV and $KMnO_4$ stain]

GC Method: A

Yield: Run 1 (305 mg, 84%)

Yield: Run 2 (292 mg, 81%)

Average Yield: 83%

^{1}H NMR (400 MHz, $CDCl_3$)

δ 7.90-7.87 (m, 2H), 7.43-7.34 (m, 2H), 4.92-4.91 (m, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 3.56-3.52 (m, 1H), 2.20-2.05 (m, 2H), 1.98-1.91 (m, 1H), 1.83-1.74 (m, 1H), 1.71-1.62 (m, 1H), 1.46-1.37 (m, 4H), 1.01 (t, *J* = 7.9 Hz, 9H), 0.71 (q, *J* = 7.8 Hz, 6H).

^{13}C NMR (101 MHz; $CDCl_3$)

δ 167.0, 152.6, 147.8, 132.3, 130.7, 128.8, 128.4, 127.5, 106.9, 61.0, 41.6, 32.8, 29.9, 21.7, 14.5, 6.9, 5.3

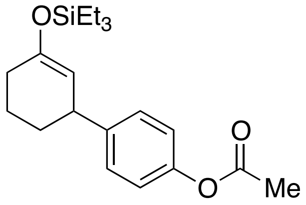
LRMS *m/z* (%relative intensity, ion): (EI+, 30 eV)

360.21 (<1.00, M^+), 245.15 (3.72, M^+ - $C_6H_{15}Si$), 148.90 (1.67, M^+ - $C_{12}H_{23}OSi$), 131.02 (2.20, M^+ - $C_{15}H_{17}O_2$), 115.05 (98.71, M^+ - $C_{15}H_{17}O_3$), 73.10 (9.47, M^+ - $C_{18}H_{27}OSi$)

HRMS (EI+):

Calc. for $C_{21}H_{32}O_3Si$ $[M]^+$: 360.2121; Found: 360.2133

5'-((triethylsilyl)oxy)-1',2',3',4'-tetrahydro-[1,1'-biphenyl]-4-yl (30) (Scheme 4)



General procedure **(III)(B)** was followed with 2-cyclohexen-1-one (96.8 μL, 1.00 mmol, 1.00 equiv), 4-iodophenyl acetate (262 mg, 1.00 mmol, 1.00 equiv) and chlorotriethylsilane (185 μL, 1.10 mmol, 1.10 equiv). After 1 h, the reaction mixture was purified by silica gel column chromatography to afford faint yellow oil.

NOTE: Employing 314 mg (1.20 mmol, 1.20 equiv) of 4-iodophenyl acetate instead of 1.00 equiv provided 304 mg, 88% of the desired product.

Data for **30, Scheme 4**

TLC: R_f 0.3 (5% EtOAc in hexanes) [silica gel treated with 0.1% Et_3N, UV and $KMnO_4$ stain]

GC Method: A

Yield: Run 1 (214 mg, 62%)

Yield: Run 2 (223 mg, 64%)

Average Yield: 63%

^{1}H NMR (500 MHz, $CDCl_3$)

δ 7.24-7.20 (m, 2H), 7.02-6.98 (m, 2H), 4.912-4.905 (m, 1H), 3.50-3.45 (m, 1H), 2.29 (s, 3H), 2.19-2.03 (m, 2H), 1.94-1.88 (m, 1H), 1.81-1.73 (m, 1H), 1.68-1.58 (m, 1H), 1.44-1.35 (m, 1H), 1.00 (t, *J* = 7.9 Hz, 9H), 0.69 (q, *J* = 8.0 Hz, 6H).

^{13}C NMR (126 MHz; $CDCl_3$)

δ 169.9, 152.3, 148.9, 145.0, 128.7, 121.3, 107.2, 41.1, 32.8, 29.9, 21.6, 21.3, 6.9, 5.2

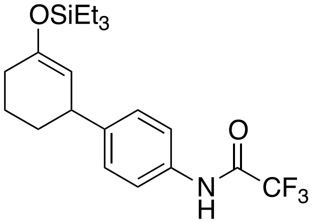
LRMS *m/z* (%relative intensity, ion): (EI+, 30 eV)

346.15 (40.26, M^+), 317.10 (31.07, M^+ - C_2H_5), 303.10 (25.64, M^+ - C_2H_3O), 287.10 (19.34, M^+ - $C_2H_3O_2$), 215.00 (7.04, M^+ - $C_6H_{15}OSi$), 211.05 (7.53, M^+ - $C_8H_7O_2$), 131.05 (8.31, M^+ - $C_{14}H_{15}O_2$), 115.00 (29.68, M^+ - $C_{14}H_{15}O_3$), 59.00 (43.41, M^+ - $C_{18}H_{27}OSi$),

HRMS (EI+):

Calc. for $C_{20}H_{30}O_3Si$ $[M]^+$: 346.1964; Found: 346.1953

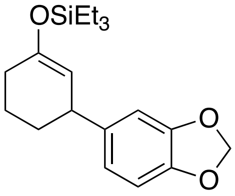
2,2,2-trifluoro-*N*-(5'-((triethylsilyl)oxy)-1',2',3',4'-tetrahydro-[1,1'-biphenyl]-4-yl)acetamide (31) (Scheme 4)



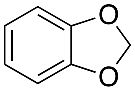
General procedure **(III)(B)** was followed with 2-cyclohexen-1-one (96.8 μL, 1.00 mmol, 1.00 equiv), 2,2,2-trifluoro-*N*-(4-iodophenyl)acetamide (315 mg, 1.00 mmol, 1.00 equiv) and chlorotriethylsilane (185 μL, 1.10 mmol, 1.10 equiv). After 1 h, the reaction mixture was purified by silica gel column chromatography to afford faint yellow oil.

Data for **31**, **Scheme 4**
TLC: R_f 0.3 (10% EtOAc in hexanes) [silica gel treated with 0.1% Et_3N, UV and $KMnO_4$ stain]
GC Method: B
Yield: Run 1 (284 mg, 71%)
Yield: Run 2 (299 mg, 75%)
Average Yield: 73%
^{1}H NMR (400 MHz, $CDCl_3$)
δ 7.76 (s, br, 1H), 7.46 (d, *J* = 8.5 Hz, 2H), 7.23 (d, *J* = 8.6 Hz, 2H), 4.87-4.86 (m, 1H), 3.49-3.44 (m, 1H), 2.16-2.03 (m, 2H), 1.93-1.86 (m, 1H), 1.79-1.57 (m, 2H), 1.41-1.33 (m, 1H), 0.98 (t, *J* = 7.9 Hz, 9H), 0.67 (q, *J* = 7.9 Hz, 6H).
^{13}C NMR (101 MHz; $CDCl_3$)
δ 155.2 (q, *J* = 37.1 Hz), 152.4, 145.8, 133.2, 128.4, 120.9, 116.9 (q, *J* = 287.6 Hz), 106.9, 41.1, 32.6, 29.8, 21.5, 6.7, 5.2
^{19}F NMR (376 MHz; $CDCl_3$)
δ -160.96
LRMS *m/z* (%relative intensity, ion): (EI+, 30 eV)
399.20 (60.10, M^+), 370.15 (52.93, M^+ - C_2H_5), 268.10 (32.86, M^+ - $C_6H_{15}OSi$), 211.00 (10.83, M^+ - $C_8H_5F_3NO$), 115.10 (53.61, M^+ - $C_{14}H_{13}F_3NO_2$)
HRMS (EI+):
Calc. for $C_{20}H_{28}F_3NO_2Si$ $[M]^+$: 399.1841; Found: 399.1845

((3-(benzo[*d*][1,3]dioxol-5-yl)cyclohex-1-en-1-yl)oxy)triethylsilane (32) (Scheme 4)



32



32'

General procedure **(III)(B)** was followed with 2-cyclohexen-1-one (96.8 μL, 1.00 mmol, 1.00 equiv), 5-iodobenzo[*d*][1,3]dioxole (127 μL, 1.00 mmol, 1.00 equiv) and chlorotriethylsilane (185 μL, 1.10 mmol, 1.10 equiv). After 1 h, the reaction mixture was purified by silica gel column chromatography to afford faint yellow oil which was an inseparable mixture of **32** and benzo[1,3]dioxole (**32'**).[11]

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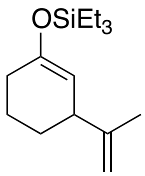
(11) NMR data for benzo[1,3]dioxole: Castillo, P.; Rodriguez-Ubis, J. C.; Rodriguez, F. *Synthesis*, **1986**, 839.

Data for **32**, **Scheme 4**
TLC: R$_f$ 0.3 (3% EtOAc in hexanes) [silica gel treated with 0.1% Et$_3$N, UV and KMnO$_4$ stain]
GC Method: B
Yield: Run 1 (258 mg of a 95:5 mixture of **32**:**32'** by ^{1}H NMR analysis, which corresponds to 253 mg of **32** (76% yield) and 5 mg of **32'**).
Yield: Run 2 (253 mg of a 96:4 mixture of **32**:**32'** by ^{1}H NMR analysis, which corresponds to 249 mg of **32** (75% yield) and 4 mg of **32'**).
Average Yield: 76%
^{1}H NMR (500 MHz, CDCl$_3$)
δ 6.74-6.67 (m, 3H), 5.92 (q, *J* = 1.9 Hz, 2H), 4.89-4.88 (m, 1H), 3.42-3.38 (m, 1H), 2.17-2.02 (m, 2H), 1.92-1.86 (m, 1H), 1.80-1.73 (m, 1H), 1.66-1.58 (m, 1H), 1.41-1.34 (m, 1H), 1.00 (t, *J* = 7.9 Hz, 9H), 0.69 (q, *J* = 7.9 Hz, 6H).
^{13}C NMR (126 MHz; CDCl$_3$)
δ 152.1, 147.6, 145.8, 141.6, 120.5, 108.3, 108.1, 107.6, 100.9, 41.4, 33.0, 29.9, 21.6, 6.9, 5.3
LRMS *m/z* (%relative intensity, ion): (EI+, 30 eV)
332.15 (100.00, M$^+$), 304.10 (27.69, M$^+$ - C$_2$H$_5$), 216.95 (5.95, M$^+$ - C$_6$H$_{15}$Si), 211.05 (5.78, M$^+$ - C$_7$H$_5$O$_2$), 115.05 (42.22, M$^+$ - C$_{13}$H$_{13}$O$_3$)
HRMS (EI+):
Calc. for C$_{19}$H$_{28}$O$_3$Si [M]$^+$: 332.1808; Found: 332.1810

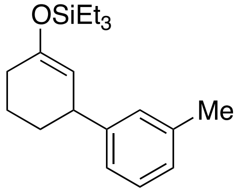
triethyl((3-(prop-1-en-2-yl)cyclohex-1-en-1-yl)oxy)silane (33) (Scheme 4)



General procedure **(III)(B)** was followed with 2-cyclohexen-1-one (96.8 μL, 1.00 mmol, 1.00 equiv), 2-bromopropene (89 μL, 1.00 mmol, 1.00 equiv) and chlorotriethylsilane (185 μL, 1.10 mmol, 1.10 equiv). After 1 h, the reaction mixture was purified by silica gel column chromatography to afford faint yellow oil.

Data for **33**, **Scheme 4**
TLC: R$_f$ 0.3 (1% EtOAc in hexanes) [silica gel treated with 0.1% Et$_3$N, UV and KMnO$_4$ stain]
GC Method: A
Yield: Run 1 (167 mg, 66%)
Yield: Run 2 (168 mg, 66%)
Average Yield: 66%
^{1}H NMR (400 MHz, CDCl$_3$)
δ 4.77-4.76 (m, 1H), 4.74 (s, 2H), 2.85-2.79 (m, 1H), 2.08-1.95 (m, 2H), 1.79-1.66 (m, 5H), 1.62-1.52 (m, 1H), 1.39-1.31 (m, 1H), 0.98 (t, *J* = 7.9 Hz, 9H), 0.67 (q, *J* = 7.9 Hz, 6H).
^{13}C NMR (101 MHz; CDCl$_3$)
δ 151.5, 150.0, 110.3, 107.3, 42.8, 30.0, 27.9, 21.6, 20.8, 6.9, 5.2
LRMS *m/z* (%relative intensity, ion): (EI+, 30 eV)
252.15 (90.70, M$^+$), 237.10 (79.61, M$^+$ - CH$_3$), 211.10 (32.76, M$^+$ - C$_3$H$_5$), 115.10 (52.99, M$^+$ - C$_9$H$_{13}$O)
HRMS (EI+):
Calc. for C$_{15}$H$_{28}$OSi [M]$^+$: 252.1909; Found: 252.1915

triethyl((3'-methyl-1,4,5,6-tetrahydro-[1,1'-biphenyl]-3-yl)oxy)silane (34) (Scheme 4)



General procedure **(III)(B)** was followed with 2-cyclohexen-1-one (96.8 μL, 1.00 mmol, 1.00 equiv), 1-iodo-3-methylbenzene (128 μL, 1.00 mmol, 1.00 equiv) and chlorotriethylsilane (185 μL, 1.10 mmol, 1.10 equiv). After 1 h, the reaction mixture was purified by silica gel column chromatography to afford faint yellow oil.

Data for **34**, **Scheme 4**
TLC: R_f 0.3 (1% EtOAc in hexanes) [silica gel treated with 0.1% Et_3N, UV and $KMnO_4$ stain]
GC Method: A
Yield: Run 1 (238 mg, 79%)
Yield: Run 2 (242 mg, 80%)
Average Yield: 80%
^{1}H NMR (400 MHz, $CDCl_3$)
δ 7.21-7.18 (m, 1H), 7.06-7.01 (m, 3H), 4.94 (d, *J* = 1.4 Hz, 1H), 3.46-3.42 (m, 1H), 2.34 (s, 3H), 2.21-2.04 (m, 2H), 1.96-1.89 (m, 1H), 1.83-1.75 (m, 1H), 1.70-1.60 (m, 1H), 1.46-1.37 (m, 1H), 1.01 (t, *J* = 8.0 Hz, 9H), 0.71 (q, *J* = 8.0 Hz, 6H).
^{13}C NMR (101 MHz; $CDCl_3$)
δ 152.0, 147.5, 137.9, 128.6, 128.3, 126.8, 124.9, 107.7, 41.6, 32.9, 29.9, 21.8, 21.6, 6.9, 5.3
LRMS *m/z* (%relative intensity, ion): (EI+, 30 eV)
302.20 (34.09, M^+), 287.15 (M^+ - CH_3), 211.05 (M^+ - C_7H_7), 171.10 (33.35, M^+ - $C_6H_{15}OSi$), 131.05 (12.32, M^+ - $C_{13}H_{15}$), 115.05 (27.62, M^+ - $C_{13}H_{15}O$), 91.00 (8.42, M^+ - $C_{12}H_{23}OSi$)
HRMS (EI+):
Calc. for $C_{19}H_{30}OSi$ $[M]^+$: 302.2066; Found: 302.2059

VI. Mechanistic Studies.

(A) General Procedure

In a nitrogen-filled glove box, the required amount of desired reagents were added directly into an oven-dried 1-dram vial containing a teflon-coated stir bar (10 mm × 3 mm). The reaction vials were capped with a PTFE-faced silicone septum, removed from the glove box and stirred at 1200 rpm in a reaction block at 20 °C. After 5 min reaction time, 10 μL aliquots of the reaction mixture were removed with a 50-μL gas-tight syringe and quenched with 10 μL of 1 M aqueous $NaHSO_4$, diluted with diethyl ether (1 mL), and filtered through a short silica gel pad (1.5 cm) in a pipette. The filtrate was analyzed by gas chromatography and the reported percent yield was calculated versus the internal standard (dodecane).

(B) In Situ Formation of (neocuproine)Ni(Ph)I (Complex IA) (Section 3.6, equation 5)

In a nitrogen filled glove box, $Ni(COD)_2$ (14.0 mg, 0.050 mmol, 1.00 equiv) and neocuproine (11.0 mg, 0.050 mmol, 1.00 equiv) were weighed directly into an oven-dried 20-mL scintillation vial equipped with a teflon-coated stir bar. DMA (20 mL) was added to the vial with an automatic pipet. The vial was capped with a polyseal cap and stirred at 20 °C inside the glove box until complete dissociation of 1 equiv of cyclooctadiene was observed by GC (~30 mins). During the course of the reaction the solution changed color from colorless to deep blue-purple. Next, iodobenzene (5.6 μL, 0.050 mmol, 1.0 equiv) was added to afford a deep red brown colored solution of desired (neocuproine)Ni(Ph)I complex[12] which was used immediately for stoichiometric studies in **Table 3, Entries 1-5**, **eq 7** and kinetic study in **Figure S8**. When a 10 μL sample of (neocuproine)Ni(Ph)I solution was quenched with 10 μL of aq. $NaHSO_4$, GC showed mostly benzene and 10-15% biphenyl. For NMR analysis of the same complex formed in DMF-*d*$_7$, see **Figure S6** below.

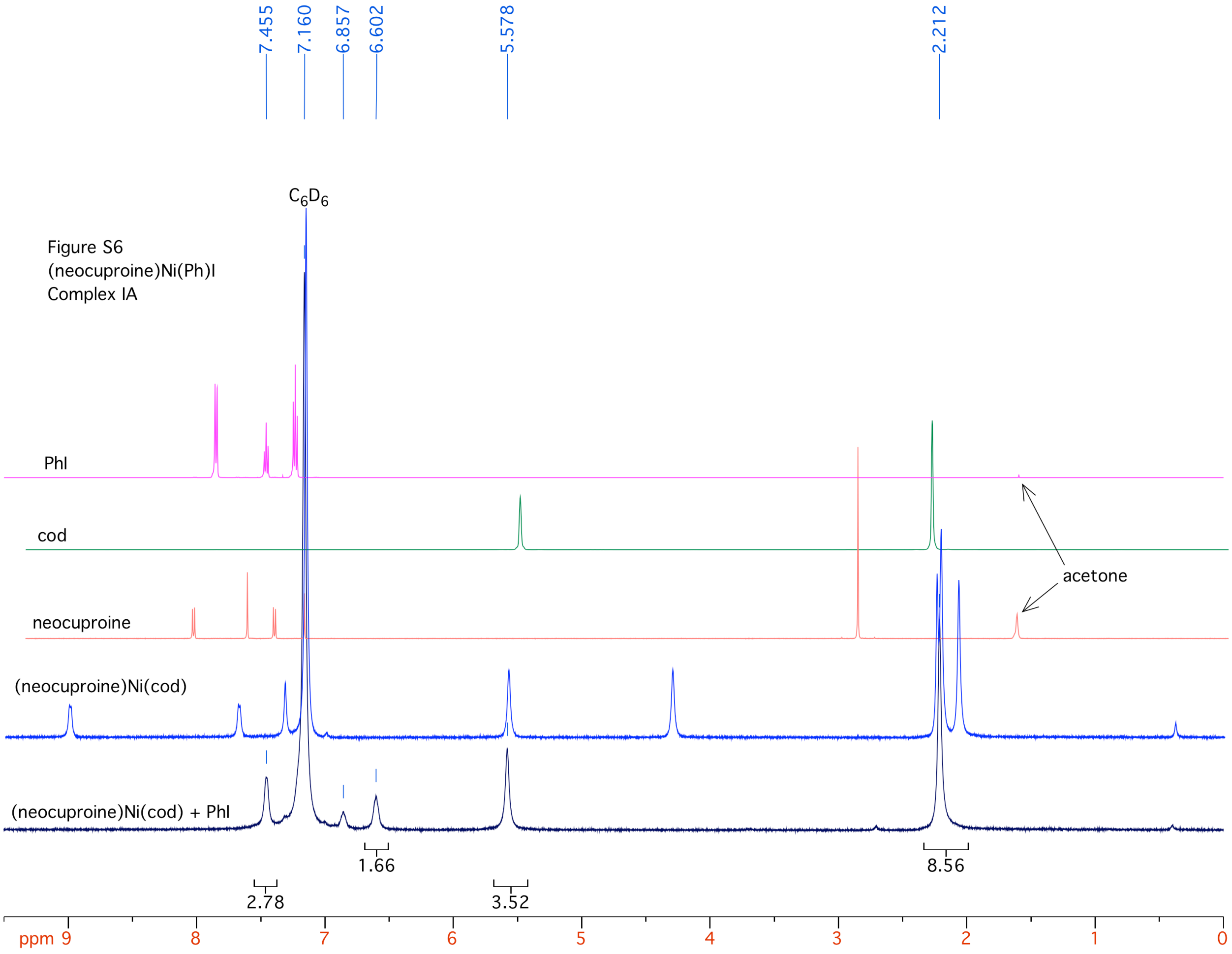


Figure S6. ^{1}H NMR Analysis of the product mixture from the combination of (**L10**)Ni(cod) with PhI. The analysis is consistent with formation of (**L10**)Ni(Ph)I (Complex **IA**). **L10** = 2,9-dimethyl-1,10-phenanthroline.

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[12] Yamamoto, T.; Wakabayashi, S.; Osakada, K. *J. Organomet. Chem.* **1992**, *428*, 223

(C) In Situ Formation of (neocuproine)Ni(η^3-1-triethylsilyloxycyclohexenyl)Cl (Complex IIA) (Section 3.6, equation 6)

In a nitrogen filled glove box, (pyridine)Ni(η^3-1-triethylsilyloxycyclohexenyl)Cl[13,14] (18.0 mg, 0.050 mmol, 1.00 equiv), and neocuproine (11.0 mg, 0.050 mmol, 1.00 equiv) were weighed directly into an oven-dried scintillation vial equipped with a teflon-coated stir bar. DMA (20 mL) was added to the vial with an automatic pipet. The vial was capped with a polyseal cap and stirred at 20 °C in a reaction block inside the glove box. The brick-red colored (pyridine)Ni(η^3-1-triethylsilyloxycyclohexenyl)Cl rapidly changed to a deep blue-purple solution. NMR analysis of the ligand exchange reaction in DMF-d_7 showed consumption of the starting Ni-pyridine complex and new peaks attributable to the Ni-neocuproine complex were visible. The *in-situ* formed (neocuproine)Ni(η^3-1-triethylsilyloxycyclohexenyl)Cl was used immediately for the stoichiometric studies in **Table 4, Entries 1-6**, **eq 7** and kinetic study in **Figure S8**. For NMR analysis, see **Figure S7** below.

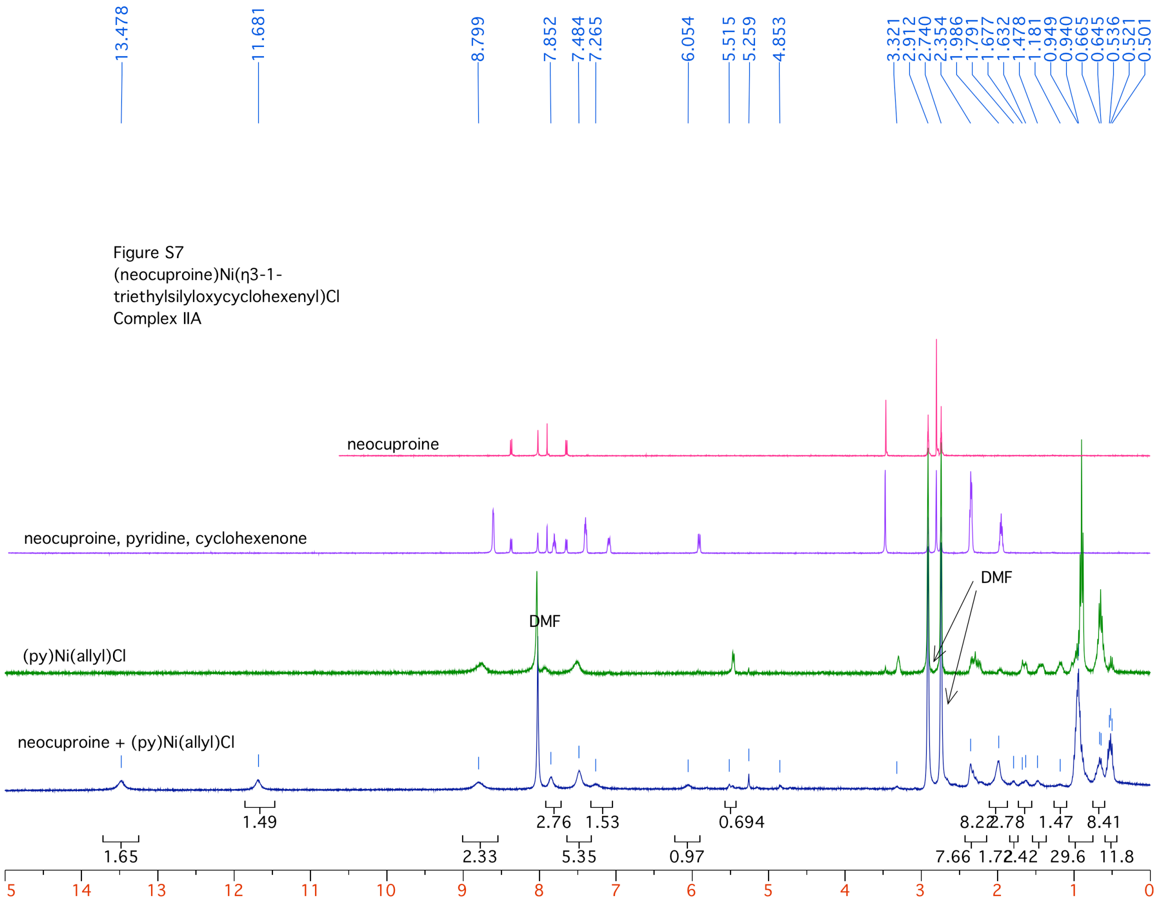

Figure S7. ^{1}H NMR analysis of the product mixture from the reaction of (py)Ni(η^3-1-triethylsilyloxycyclohexenyl)Cl with **L10**. Spectra are consistent with (**L10**)Ni(η^3-1-triethylsilyloxycyclohexenyl)Cl (Complex **IIA**). **L10** = 2,9-dimethyl-1,10-phenanthroline (neocuproine).

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(13) Shrestha, R.; Weix, D. J. *Org. Lett.* **2011**, *13*, 2766 and unpublished studies.

(14) Johnson, J. R.; Tully, P. S.; Mackenzie, P. B.; Sabat, M. *J. Am. Chem. Soc.* **1991**, *113*, 6172.

(D) Reactions of (L10)Ni(Ph)I (IA) and (L10)Ni(η^3-1-triethylsilyloxycyclohexenyl)Cl (IIA) (Tables 3 and 4 in Section 3.7)

Table 3 Entry 1

General procedure (VI)(A) was followed with (neocuproine)Ni(Ph)I (2 mL of 2.5 mM stock solution, 0.005 mmol, 1.00 equiv).

Table 3 Entry 2: XS enone and XS Et_3SiCl

General procedure (VI)(A) was followed with 2-cyclohexen-1-one (48.0 µL, 0.50 mmol, 100 equiv), chlorotriethylsilane (92.0 µL, 0.55 mmol, 110 equiv) and (neocuproine)Ni(Ph)I (2 mL of 2.5 mM stock solution, 0.005 mmol, 1.00 equiv).

Table 3 Entry 3: XS enone and XS Et_3SiCl and XS Mn^0

General procedure (VI)(A) was followed with 2-cyclohexen-1-one (48.0 µL, 0.50 mmol, 100 equiv), chlorotriethylsilane (92.0 µL, 0.55 mmol, 110 equiv), (neocuproine)Ni(Ph)I (2 mL of 2.5 mM stock solution, 0.005 mmol, 1.00 equiv) and Mn^0 (110 mg, 1.0 mmol, 200 equiv).

Table 3 Entry 4: EQ enone, EQ Et_3SiCl, EQ PhI and XS Mn^0

General procedure (VI)(A) was followed with 2-cyclohexen-1-one (0.48 µL, 0.005 mmol, 1.00 equiv), chlorotriethylsilane (0.92 µL, 0.0055 mmol, 1.10 equiv), iodobenzene (0.56 µL, 0.005 mmol, 1.00 equiv), (neocuproine)Ni(Ph)I (2 mL of 2.5 mM stock solution, 0.005 mmol, 1.00 equiv) and Mn^0 (55.0 mg, 1.0 mmol, 200 equiv).

Table 3 Entry 5 at 20 minutes

After 20 minutes, a 10 µL aliquot of the solution from **Table 3 Entry 4** was removed with a 50 µL gas-tight syringe and quenched with 10 µL of 1 M aqueous $NaHSO_4$, diluted with ethyl ether (1 mL), and filtered through a short silica pad (1.5 cm) in a pipette packed with glass wool. The filtrate was analyzed by gas chromatography and the percent yield was calculated versus the dodecane internal standard.

Table 4 Entry 1

General procedure (VI)(A) was followed with (neocuproine)Ni(η^3-1-triethylsilyloxycyclohexenyl)Cl (2 mL of 2.5 mM stock solution, 0.005 mmol, 1.00 equiv).

Table 4 Entry 2: XS PhI

General procedure (VI)(A) was followed with iodobenzene (56.0 µL, 0.50 mmol, 100 equiv) and (neocuproine)Ni(η^3-1-triethylsilyloxycyclohexenyl)Cl (2 mL of 2.5 mM stock solution, 0.005 mmol, 1.00 equiv).

Table 4 Entry 3: XS Et_3SiCl and XS PhI

General procedure (VI)(A) was followed with iodobenzene (56.0 µL, 0.50 mmol, 100 equiv), chlorotriethylsilane (92.0 µL, 0.55 mmol, 110 equiv) and (neocuproine)Ni(η^3-1-triethylsilyloxycyclohexenyl)Cl (2 mL of 2.5 mM stock solution, 0.005 mmol, 1.00 equiv).

Table 4 Entry 4: XS Et_3SiCl and XS PhI and XS Mn^0

General procedure (VI)(A) was followed with iodobenzene (56.0 µL, 0.50 mmol, 100 equiv), chlorotriethylsilane (92.0 µL, 0.55 mmol, 110 equiv) (neocuproine)Ni(η^3-1-triethylsilyloxycyclohexenyl)Cl (2 mL of 2.5 mM stock solution, 0.005 mmol, 1.00 equiv) and Mn^0 (110 mg, 1.0 mmol, 200 equiv).

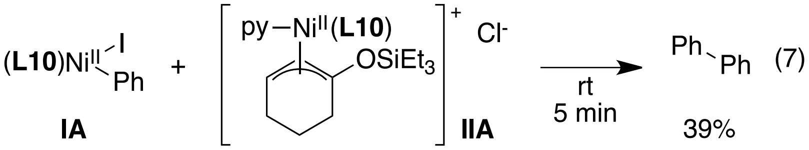
Table 4 Entry 5: XS Et_3SiCl and EQ PhI and XS Mn^0

General procedure (VI)(A) was followed with iodobenzene (0.56 μL, 0.005 mmol, 1.00 equiv), chlorotriethylsilane (92.0 μL, 0.55 mmol, 110 equiv), (neocuproine)Ni(η^3-1-triethylsilyloxycyclohexenyl)Cl (2 mL of 2.5 mM stock solution, 0.005 mmol, 1.00 equiv) and Mn^0 (55.0 mg, 1.00 mmol, 200 equiv).

Table 4 Entry 6: XS PhI and EQ TDAE

General procedure (VI)(A) was followed with iodobenzene (56.0 μL, 0.50 mmol, 100 equiv), tetrakis(dimethylamino)ethylene (23.3 μL, 0.10 mmol, 20.0 equiv) and (neocuproine)Ni(η^3-1-triethylsilyloxycyclohexenyl)Cl (2 mL of 2.5 mM stock solution, 0.005 mmol, 1.00 equiv).

Equation 7 (Section 3.7). Transmetalation Mechanism.



General procedure (VI)(A) was followed with (neocuproine)Ni(η^3-1-triethylsilyloxycyclohexenyl)Cl (2 mL of 2.5 mM stock solution, 0.005 mmol, 1.00 equiv) and (neocuproine)Ni(Ph)I (2 mL of 2.5 mM stock solution, 0.005 mmol, 1.00 equiv).

(E) Reactions (L1)Ni(η^3-1-triethylsilyloxycyclohexenyl)Cl with 2-bromoheptane (Scheme 5, Section 3.11)

In a nitrogen filled glove box, (pyridine)Ni(η^3-1-triethylsilyloxycyclohexenyl)Cl[15,16] (7.0 mg, 0.02 mmol, 1.00 equiv) and **L1** (8.1 mg, 0.02 mmol, 1.00 equiv) were weighed directly into an oven-dried 1 dram vial equipped with a teflon-coated stir bar. DMF (2 mL) and the appropriate reagents were added to the reaction vial as desired (details in **a**-**c** below). The reaction vial was capped with a PTFE-faced silicone septum, removed from the glovebox and the mixture was stirred at 40 °C at 1200 rpm for 1 h. After 1 h, a 10 µL aliquot of the solution was removed with a 50 µL gas-tight syringe and quenched with 10 µL of 1 M aqueous $NaHSO_4$. This mixture was diluted with ethyl ether (1 mL) and filtered through a short silica pad (1.5 cm) in a pipette packed with glass wool. The filtrate was analyzed by gas chromatography and the percent yield was calculated versus the dodecane internal standard.

a) Without Mn^0

2-bromoheptane (94 µL, 0.5 mmol, 25 equiv), and dodecane (10 µL). GC analysis showed exclusively enone dimer formation (94% yield).

b) With activated Mn^0:

2-bromoheptane (94 µL, 0.5 mmol, 25 equiv), chlorotriethylsilane (109 µL, 0.65 mmol, 32 equiv), manganese powder (55 mg, 1.0 mmol, 50 equiv), and dodecane (10 µL). GC analysis showed a 17% yield of cross-product and no observable enone dimer.

c) Catalytic Reaction:

To an oven-dried 1-dram vial, equipped with a teflon-coated stir bar, was added $Ni(acac)_2$ (5.1 mg, 0.02 mmol, 0.04 equiv), **L1** (8.1 mg, 0.02 mmol, 0.04 equiv), DMF (2 mL), 2-bromoheptane (94 µL, 0.5 mmol, 1 equiv), 2-cyclohexen-1-one (78 µL, 0.8 mmol, 1.6 equiv), chlorotriethylsilane (109 µL, 0.65 mmol, 1.3 equiv), manganese (55 mg, 1.0 mmol, 2.0 equiv), and dodecane (10.0 µL, internal standard). The reaction vial was capped with a PTFE-faced silicone septum, removed from the glovebox, and the mixture was stirred at 40 °C at 1200 rpm. After 24 h, a 10 µL aliquot was removed and quenched with 10 µL of 1 M aqueous $NaHSO_4$, diluted with diethyl ether (1 mL), and filtered through a short pad of silica (1 cm) in a glass pipette packed with glass wool. The filtrate was analyzed by gas chromatography and percent yield was calculated versus the dodecane internal standard.

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(15) Shrestha, R.; Weix, D. J. *Org. Lett.* **2011**, *13*, 2766 and unpublished studies.

(16) Johnson, J. R.; Tully, P. S.; Mackenzie, P. B.; Sabat, M. *J. Am. Chem. Soc.* **1991**, *113*, 6172.

(F) Kinetic competency experiments of IA and IIA (see Section 3.8 in manuscript).

In a nitrogen-filled glove box, the appropriate catalyst solution (2 mL of 2.5 mM stock solution, 0.005 mmol, 0.001 equiv), 2-cyclohexen-1-one (48.0 µL, 0.50 mmol, 1.00 equiv), iodobenzene (56.0 µL, 0.50 mmol, 1.00 equiv), chlorotriethylsilane (92.0 µL, 0.55 mmol, 1.10 equiv), Mn^0 (55.0 mg, 1.00 mmol, 2.00 equiv), and dodecane internal standard (10.0 µL, 0.044 mmol) were added directly into an oven-dried 1-dram vial containing a teflon-coated stir bar (10 mm × 3 mm). The reaction vial was capped with a PTFE-faced silicone septum, and stirred at 1200 rpm in a reaction block at 20 °C. Every three minutes, a 10 µL aliquot of the reaction mixture were removed with a 50-µL gas-tight syringe. This aliquot was quenched with 10 µL of 1 M aqueous $NaHSO_4$, diluted with diethyl ether (1 mL), and filtered through a short silica gel pad (1.5 cm) in a pipette. The filtrate was analyzed by gas chromatography and the reported percent yield was calculated versus the internal standard (dodecane).

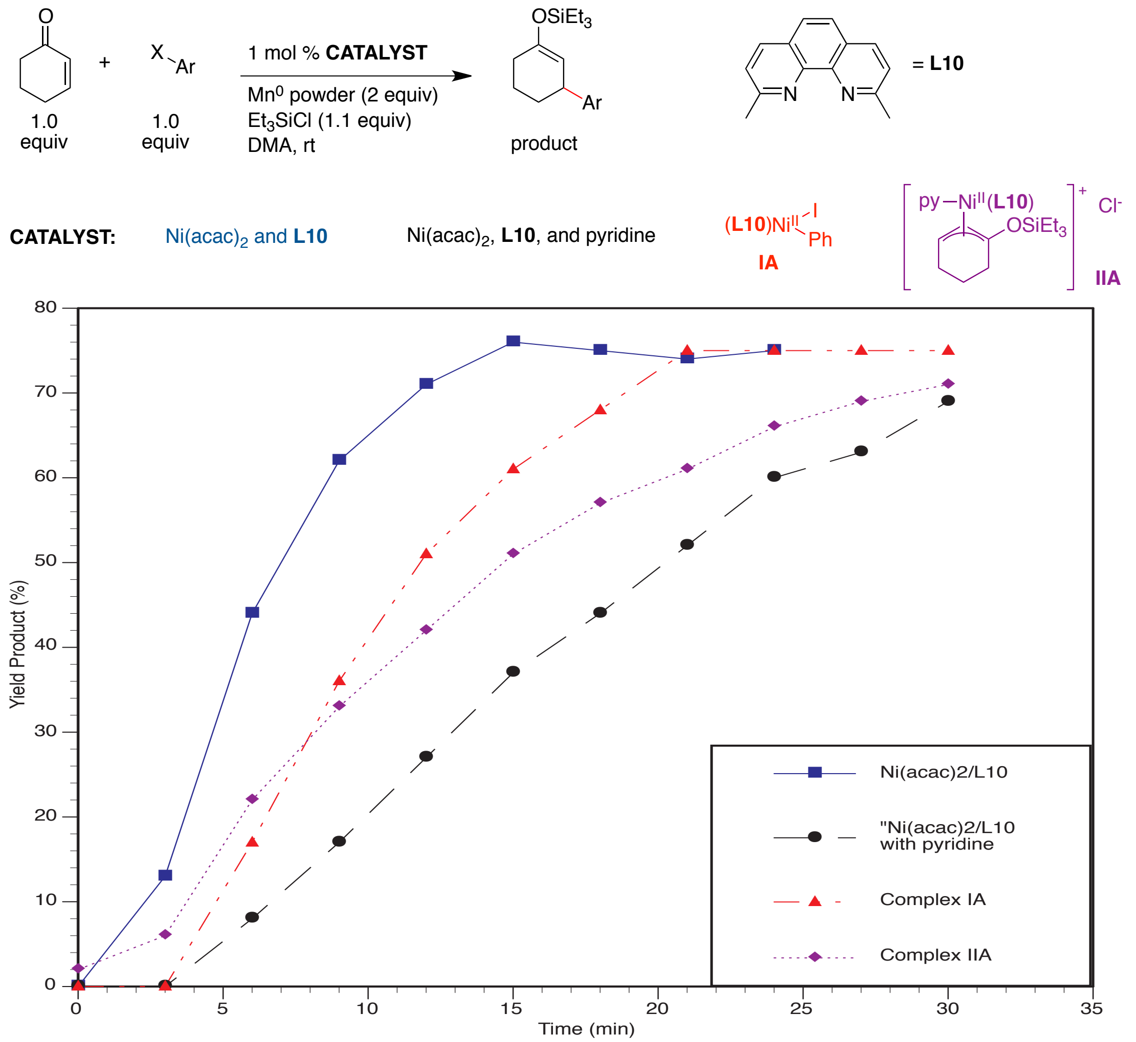
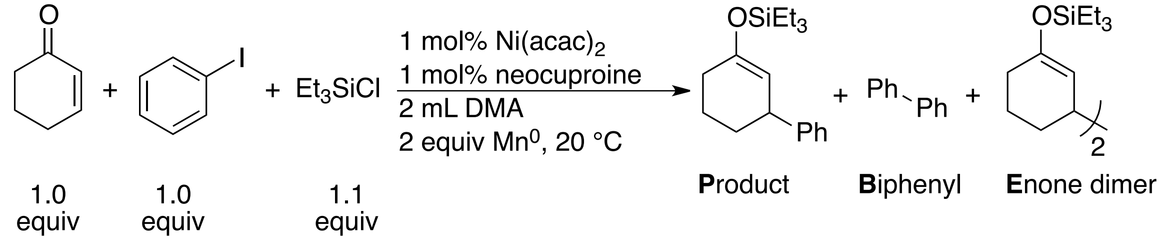


Figure S8. Product formation vs. time for reactions catalyzed by $Ni(acac)_2$/**L10**, $Ni(acac)_2$/**L10** + pyridine (1 equiv), **IA**, and **IIA**. Yield refers to GC yields vs. internal standard, corrected. Note that **IIA** contains 1 equiv pyridine.

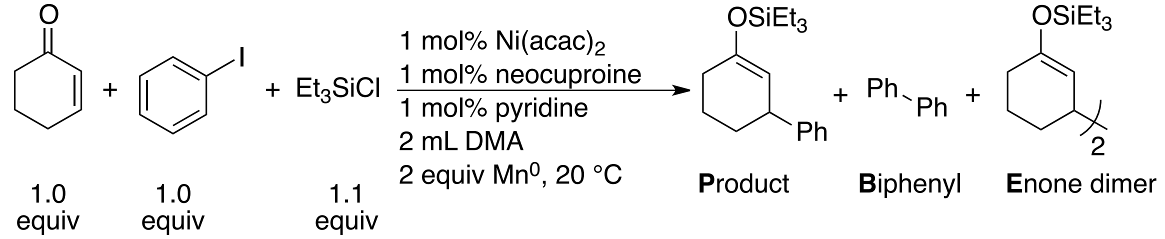
(a) Table S3. Product distribution for reaction catalyzed by Ni(acac)$_2$/**L10** in Figure S8.



Entry	time (mins)	% **P**^{b}	% **B**^{b}	% **E**^{c}
1	0	0	0	0
2	3	13	0	0
3	6	44	0	2
4	9	62	0	3
5	12	71	0	10
6	15	76	0	9
7	18	75	4	9
8	21	74	5	9
9	24	75	6	9

[a] Product distribution vs. time for reactions catalyzed by Ni(acac)$_2$/**L1**. [b]Corrected GC yields vs. dodecane standard. [c]Uncorrected GC yields vs dodecane standard.

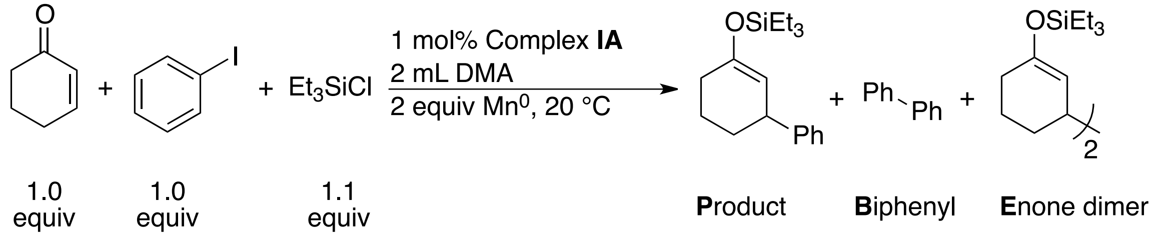
(b) Table S4. Product distribution for reaction catalyzed by Ni(acac)$_2$/**L10**/py in Figure S8



Entry	time (mins)	% **P**^{b}	% **B**^{b}	% **E**^{c}
1	0	0	0	0
2	3	0	0	0
3	6	8	0	10
4	9	17	0	14
5	12	27	0	14
6	15	37	0	14
7	18	44	0	14
8	21	52	0	14
9	24	60	0	14
10	27	63	0	14
11	30	69	0	14

[a] Product distribution vs. time for reactions catalyzed by Ni(acac)$_2$/**L1** with pyridine. [b]Corrected GC yields vs. dodecane standard. [c]Uncorrected GC yields vs dodecane standard.

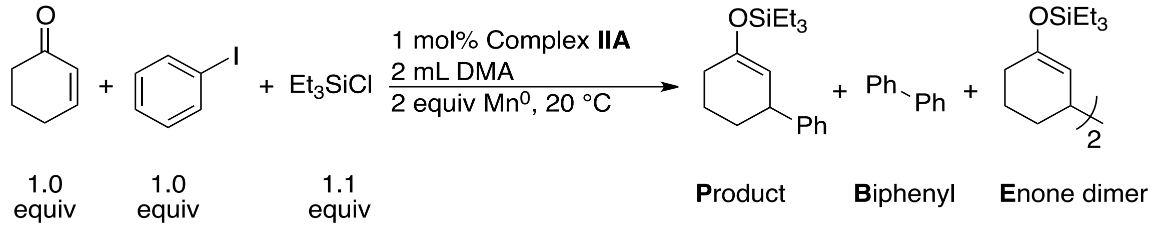
(c) Table S5. Product distribution for reaction catalyzed by complex **IA** in Figure S8.



Entry	time (mins)	% **P**[b]	% **B**[b,c]	% **E**[d]
1	0	0	1(67)	0
2	3	0	1(100)	5
3	6	17	1	4
4	9	36	1	4
5	12	51	1	4
6	15	61	1	7
7	18	68	1	7
8	21	75	1	7
9	24	75	1	7
10	27	75	1	7
11	30	75	1	7

[a] Product distribution vs. time for reactions catalyzed by Complex **IA**. [b]Corrected GC yields vs dodecane standard. [c] Yield in parentheses is with respect to [Ni]. [d]Uncorrected GC yields vs dodecane standard.

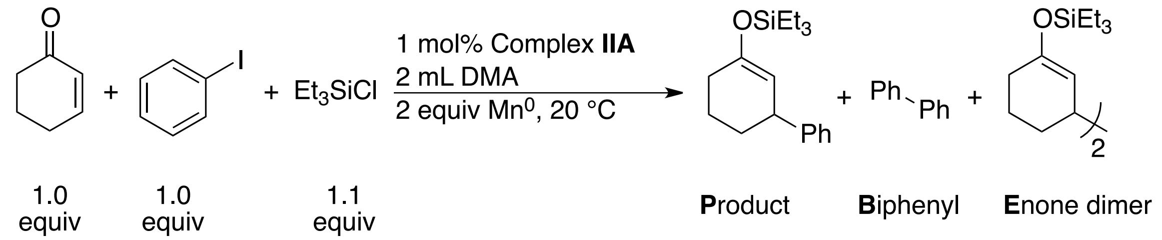
(d) Table S6. Product distribution for reaction catalyzed by complex **IIA** in Figure S8.



Entry	time (mins)	% **P**[b]	% **B**[b]	% **E**[c]
1	0	2	0	0
2	3	6	0	0
3	6	22	0	4
4	9	33	0	6
5	12	42	0	6
6	15	51	0	5
7	18	57	1	5
8	21	61	1	5
9	24	66	1	6
10	27	69	1	6
11	30	71	1	6

[a] Product distribution vs. time for reactions catalyzed by Complex **IIA**. [b]Corrected GC yields vs. dodecane standard. [c]Uncorrected GC yields vs dodecane standard.

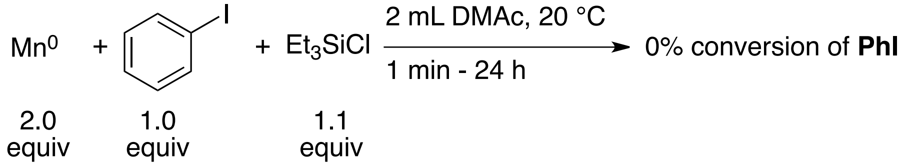
(e) Table S7. Product distribution for reaction catalyzed by Complex **IIA** with pre-activated Mn^0



Entry	time (mins)	% **P**	% **B**	% **E**
1	0	2	0	3
2	3	13	0	7
3	6	24	0	14
4	9	35	0	19
5	12	45	0	19
6	15	53	0	19
7	18	57	0	19
8	21	63	0	19
9	24	68	0	19
10	27	71	0	19
11	30	71	0	19

[a] Product distribution vs. time for reactions catalyzed by Complex **IIA**. [b]Corrected GC yields vs. dodecane standard. [c]Uncorrected GC yields vs dodecane standard.

(G) Figure S9. Direct Insertion of Mn^0 into Iodobenzene **(Section 3.10)**



General procedure (III)(A) was followed with iodobenzene (56.0 μL, 0.50 mmol, 1.00 equiv), chlorotriethylsilane (92.3 μL, 0.55 mmol, 1.10 equiv), Mn^0 (55.0 mg, 1.00 mmol, 2.00 equiv) and DMA (2 mL).

(H) Figure S10. Reduction of Iodobenzene with (tetrakis)dimethylamino ethylene (TDAE). **(Section 3.10)**

General procedure (III)(A) was followed with iodobenzene (5.6 μL, 0.05 mmol, 1.00 equiv), TDAE (23.3 μL, 0.10 mmol, 2.00 equiv) and C_6D_6 (1 mL). 1,2-dichloroethane (39 μL, 0.50 mmol, 10.0 equiv) was used and the mixture was monitored by ^1H NMR. No significant change was observed for iodobenzene or TDAE over the course of 1 h.

(I) Reactions of (neocuproine)Ni(cod) and Et_3SiCl (Section 3.5)

In a nitrogen-filled glove box, $Ni(COD)_2$ (20.7 mg, 0.075 mmol, 1.0 equiv), neocuproine (16.0 mg, 0.075 mmol, 1.0 equiv), and THF-*d₈* (1 mL, sparged with nitrogen) were added directly into an oven-dried 1-dram vial containing a teflon-coated stir bar (10 mm × 3 mm). The reaction vial was capped with a PTFE-faced silicone septum, and stirred at rt for 24 h. The next day, 40 μL of the solution was added to a screw cap NMR tube with additional THF-d_8 (0.6 mL) and capped with a PTFE-faced silicone septum. After ^1H NMR analysis, Et_3SiCl was added (13 μL of a solution of 0.225 mmol Et_3SiCl in 1 mL THF-d_8) through the septum. The color immediately changed from dark purple to yellow. A ^1H NMR spectrum was obtained using both normal and paramagnetic parameters (**Figures S4** and **S5** on next page)

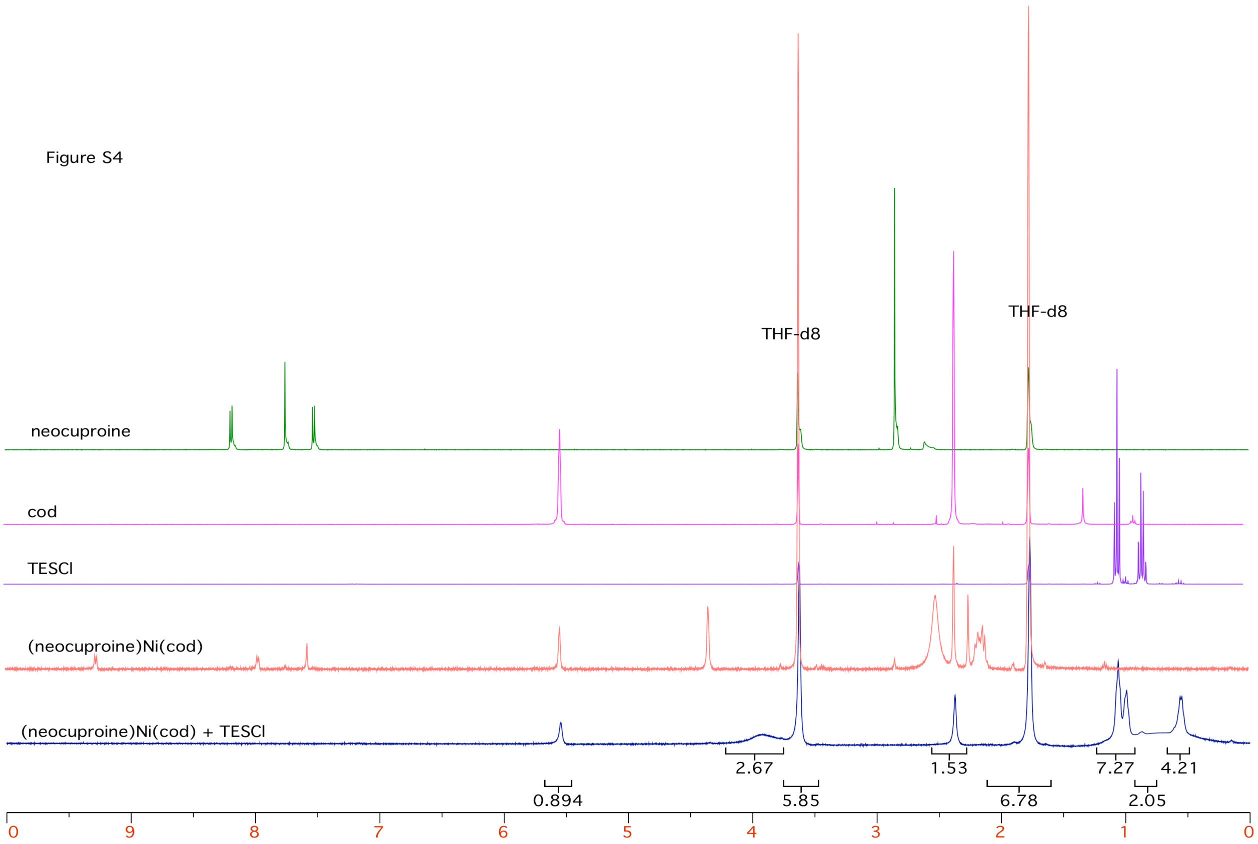


Figure S4. ^{1}H NMR analysis for the reaction of (**L10**)Ni(cod) with Et_3SiCl in DMF-d_7. Spectra of starting materials appear above to aid interpretation of new peaks.

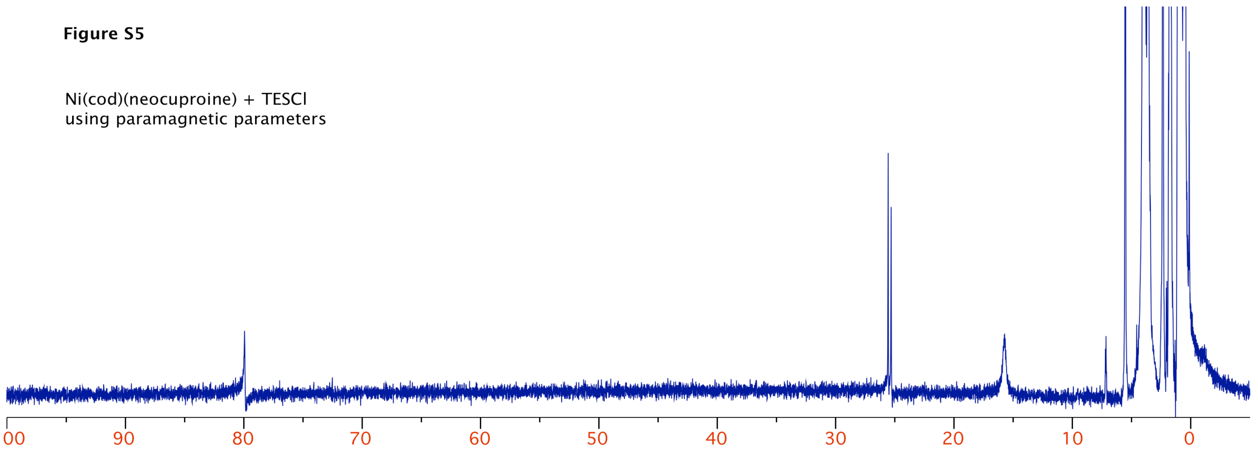
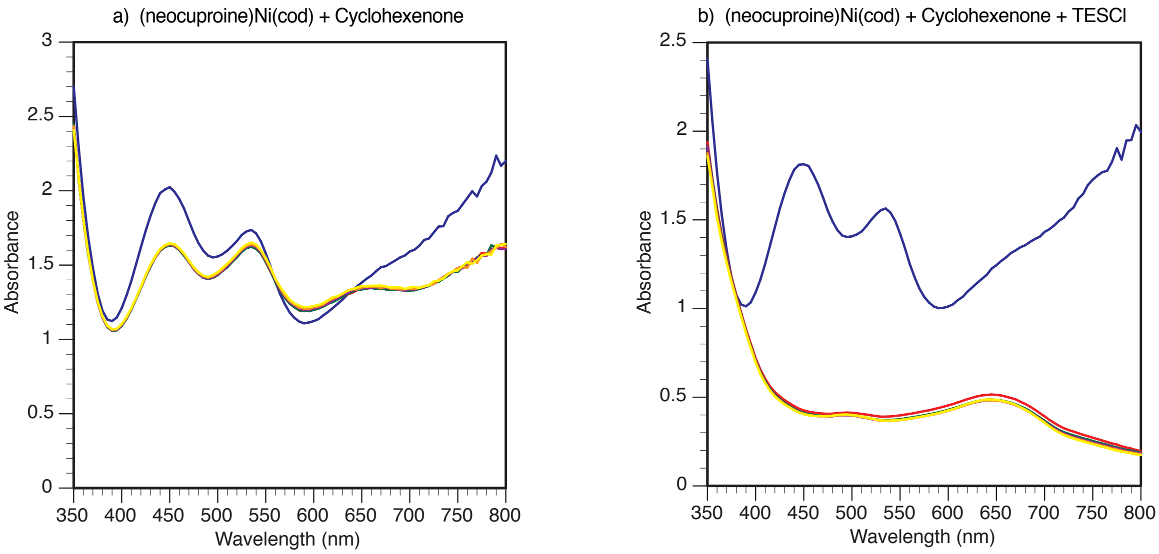


Figure S5. Paramagnetic ^{1}H NMR spectrum of the product mixture for the reaction of (**L10**)Ni(cod) and Et_3SiCl.

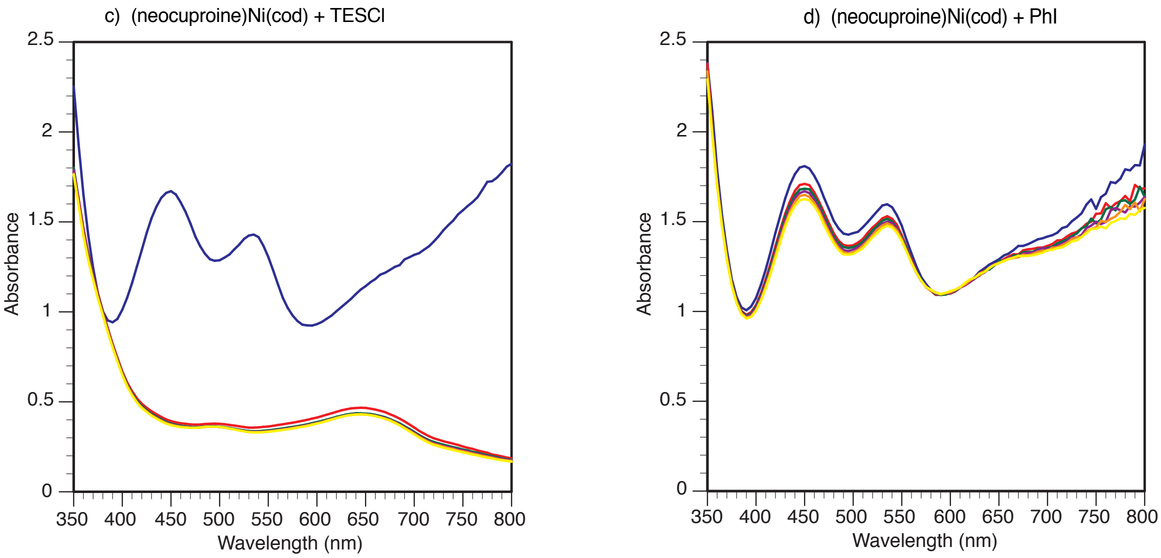
(J) Reactions of (L10)Ni(cod) with different electrophiles (Section 3.5)

In a nitrogen-filled glove box, Ni(COD)$_2$ (41.3 mg, 0.15 mmol, 1.0 equiv), neocuproine (31.2 mg, 0.15 mmol, 1.0 equiv), and DMA (2 mL) were added directly into an oven-dried 1-dram vial containing a teflon-coated stir bar (10 mm × 3 mm). The reaction vial was capped with a PTFE-faced silicone septum, and stirred at rt for 24 h. The next day, 25 μL of the solution and 2975 μL of DMA were added to a quartz cuvette, which was capped with a PTFE-faced silicone septum and a screw cap. After an initial UV-Vis spectrum was taken, the other reagent(s) were added through the septum. UV-Vis spectra were taken for 500 scans every 6 sec (**Figures S1a-d**, Plots derived from UV-Vis data: **Figures S2,** and **S3**).

a) Enone Only: 12 μL cyclohexenone (.225 mmol in 1 mL DMA) were added to the cuvette.
b) Enone and Et$_3$SiCl: 12 μL cyclohexenone (.225 mmol in 1 mL DMA) and 12 μL Et$_3$SiCl (.225 mmol in 1 mL DMA) were added to the cuvette simultaneously.
c) Et$_3$SiCl Only: 12 μL Et$_3$SiCl (.225 mmol in 1 mL DMA) was added to the cuvette
d) PhI Only: 12 μL PhI (.225 mmol in 1 mL DMA) was added to the cuvette


a) (neocuproine)Ni(cod) + Cyclohexenone

b) (neocuproine)Ni(cod) + Cyclohexenone + TESCl


c) (neocuproine)Ni(cod) + TESCl

d) (neocuproine)Ni(cod) + PhI

Figure S1. UV-Vis spectra of a mixture of (**L10**)Ni(cod) and an electrophile over time. Blue ■ = 0 min, Red ● = 1 min, Green ▲= 2 min, Purple ◆= 3 min, Orange ☐ = 4 min, Yellow ○,5 min. **L10** = 2,9-dimethyl-1,10-phenanthroline (neocuproine).

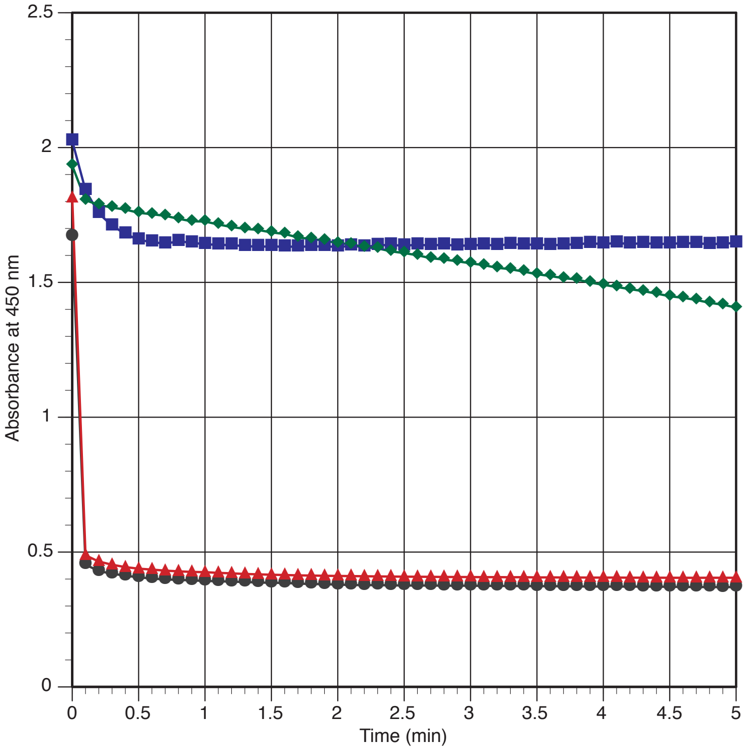


Figure S2. Absorbance at 450 nm vs. time plotted from data in Figure S1. a) Enone only (Blue ■), b) Enone and TESCl (Red ▲), c) TESCl only (Black ●), d) PhI only (Green ◆).

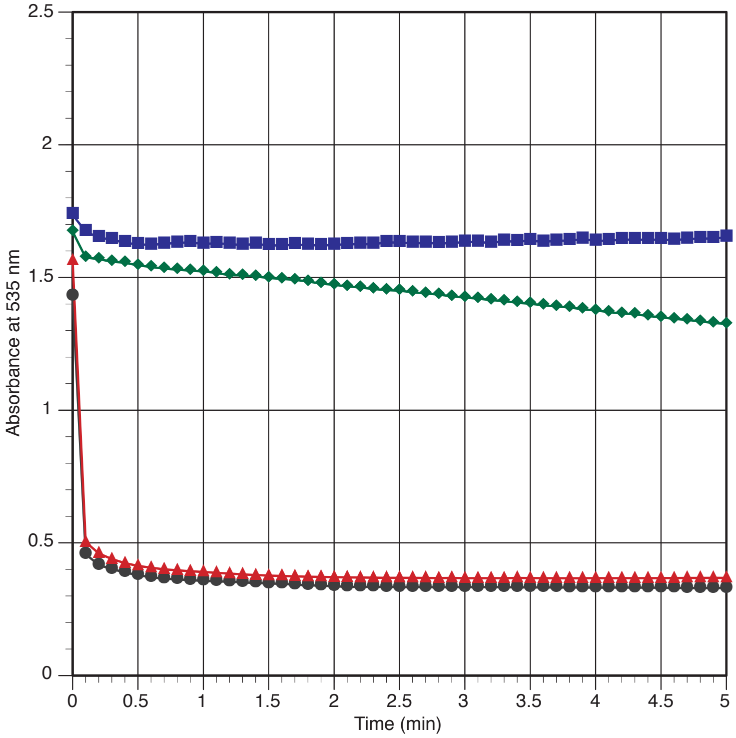
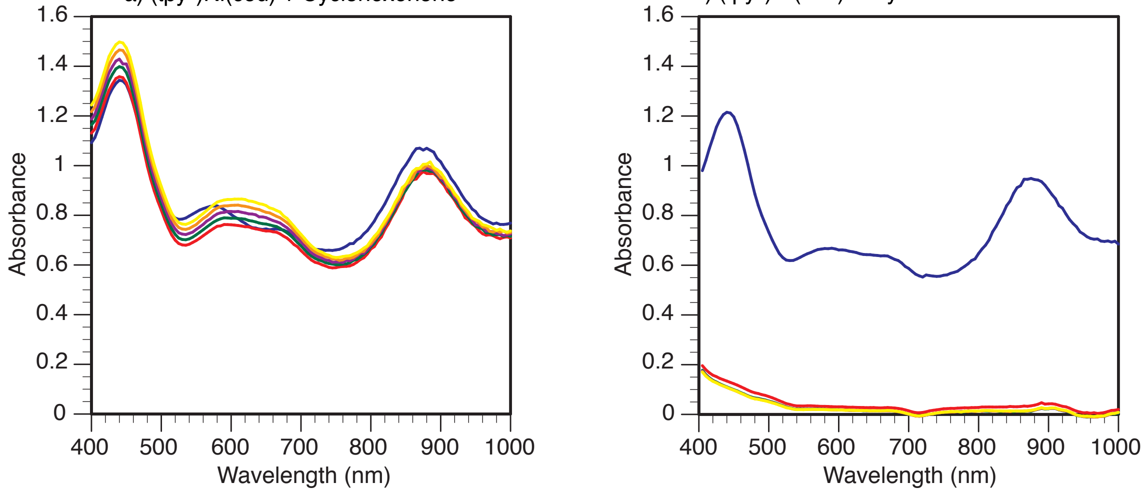


Figure S3. Absorbance at 535 nm vs. time plotted from data in Figure S1. a) Enone only (Blue ■), b) Enone and TESCl (Red ▲), c) TESCl only (Black ●), d) PhI only (Green ◆).

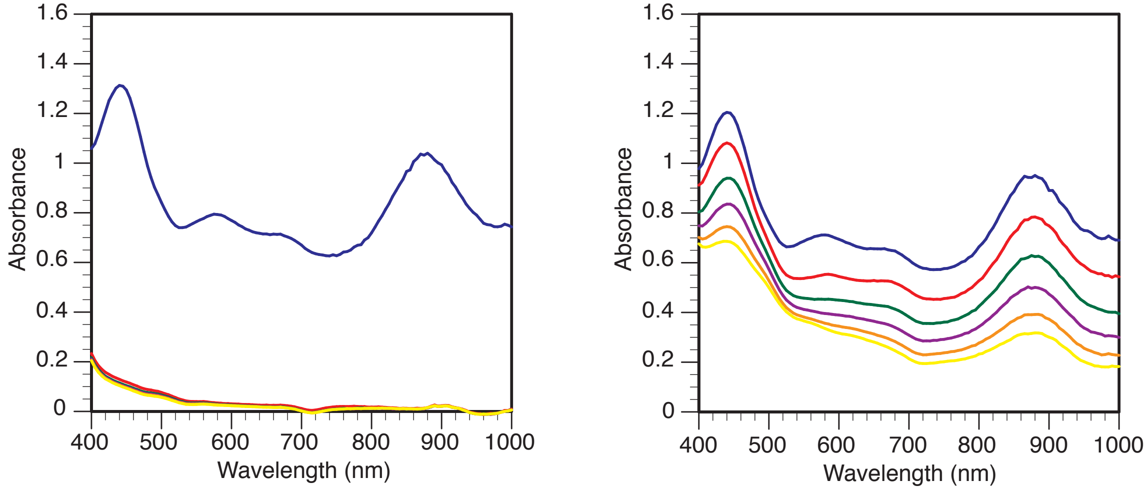
(K) Reactions of (L1)Ni(cod) with different electrophiles (Section 3.11)

In a nitrogen-filled glove box, Ni(COD)$_2$ (10.3 mg, 0.0375 mmol, 1.0 equiv), 4,4',4"-tri-*tert*-butyl-2,2':6',2"-terpyridine (15.1 mg, 0.0375 mmol, 1.0 equiv), and DMA (0.5 mL) were added directly into an oven-dried 1-dram vial containing a teflon-coated stir bar (10 mm × 3 mm). The reaction vial was capped with a PTFE-faced silicone septum, and stirred at rt for 24 h. The next day, 25 μL of the solution and 2975 μL of DMA was added to a quartz cuvette, which was capped with a screw cap with a PTFE-faced silicone septum. After an initial spectra was acquired (t = 0), the other reagent(s) were added through the septum. UV-Vis spectra were taken for 1000 scans every 12 sec (**Figures S11a-d**, Plot derived from UV-Vis data: **Figure S12**).

(a) Enone Only: 12 μL cyclohexenone (.225 mmol in 1 mL DMA) were added to the cuvette.
(b) Enone and Et$_3$SiCl : 12 μL cyclohexenone (.225 mmol in 1 mL DMA) and 12 μL Et$_3$SiCl (.225 mmol in 1 mL DMA) were added to the cuvette simultaneously.
(c) Et$_3$SiCl Only: 12 μL Et$_3$SiCl (.225 mmol in 1 mL DMA) was added to the cuvette
(d) 2-bromoheptane Only: 12 μL 2-bromoheptane (.225 mmol in 1 mL DMA) was added to the cuvette


a) (tpy*)Ni(cod) + Cyclohexenone

b) (tpy*)Ni(cod) + Cyclohexenone + TESCl


c) (tpy*)Ni(cod) + TESCl

d) (tpy*)Ni(cod) + 2-bromoheptane

Figure S11. UV-Vis spectra of a mixture of (**L1**)Ni(cod) and an electrophile over time. Blue ■ = 0 min, Red ● = 1 min, Green ▲= 2 min, Purple ◆= 3 min, Orange ☐ = 4 min, Yellow ○ = 5 min. **L1** = 4,4',4''-tri-*tert*-butyl-2,2':6',2''-terpyridine

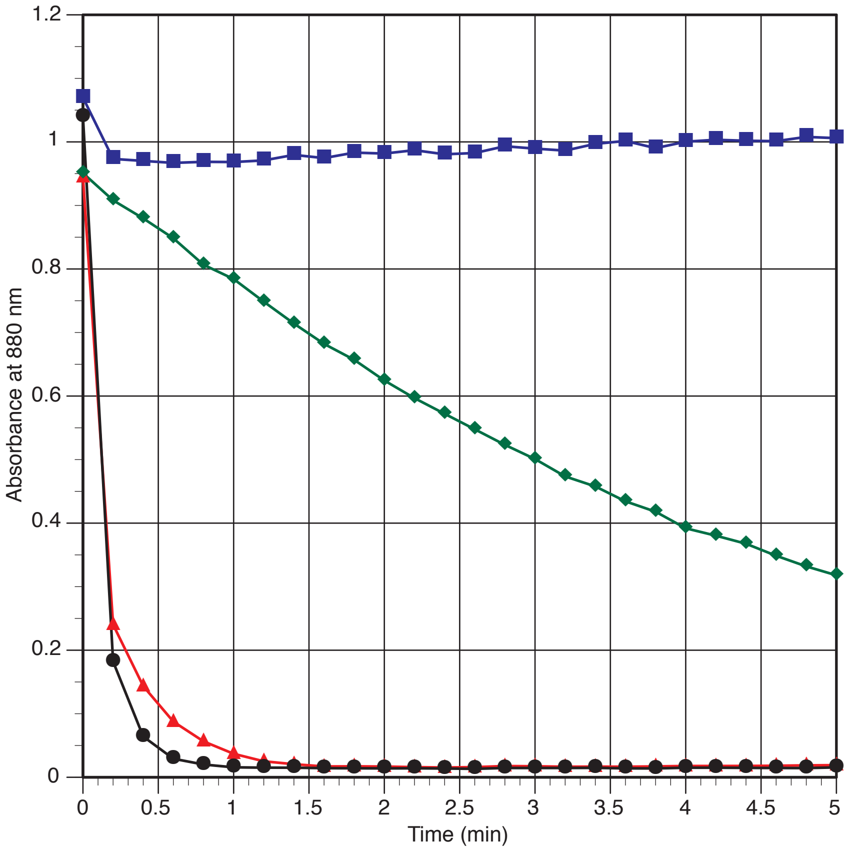


Figure S12. Absorbance at 880 nm vs. time for the spectra in Figure S11. a) Enone only (Blue ■), b) Enone and TESCl (Red ▲), c) TESCl only (Black ●), d) Bromoheptane only (Green ◆).