C–N Bond Formation from Allylic Alcohols Via Cooperative Nickel and Titanium Catalysis

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Supporting Information Placeholder

ABSTRACT: Amination of allylic alcohols is facilitated via cooperative catalysis. Catalytic Ti(O*i*-Pr)$_4$ is shown to dramatically increase the rate of nickel-catalyzed allylic amination and mechanistic experiments confirm activation of the allylic alcohol by titanium. Aminations of primary and secondary allylic alcohols are demonstrated with a variety of amine nucleophiles. Diene-containing substrates also cyclize onto the nickel allyl intermediate prior to amination, generating carbocyclic amine products. This tandem process is only achieved under our cooperative catalytic system.

Cooperative catalysis is a strategy for reaction engineering that involves the simultaneous use of multiple catalysts to improve reaction efficiency or facilitate different reaction mechanisms.[1] This approach provides unique opportunities for substrate activation that can enable catalysis under much milder conditions and enable new selectivity not observed in single catalyst systems. In addition, the catalytic activation of multiple reacting partners[2] can preclude the need for stoichiometric substrate activation, which is a common strategy in single catalyst systems. One application of cooperative catalysis is the *in situ* activation of alcohol electrophiles by Lewis acids for cross coupling reactions.[3] This approach enables the use of readily available allylic alcohols as electrophilic partners for cross couplings without the need for stoichiometric activation of the alcohol as a carbonate, halide, or ester. Our group is interested in the discovery and development of cooperative catalysis systems, including those with heterobimetallic complexes.[4,5] Our results presented herein demonstrate that catalytic activation of the allylic alcohol is a viable strategy for rapid allylic amination under nickel catalysis and that this approach provides unique substrate reactivity not observed in single catalyst systems.

Metal-catalyzed allylic functionalization reactions, including allylic aminations, are widely employed in modern catalysis due to the ability of these reactions to proceed with high product selectivity.[6] The use of unactivated allylic alcohols in this transformation is attractive because it precludes the need for stoichiometric activation of the alcohol, but the acidity of the OH bond and the poor leaving group ability of alcohols makes this transformation difficult to achieve.[7] Our previous studies have shown that bidentate NHC phosphine ligands enable selective nickel-catalyzed Suzuki-Miyaura cross couplings with allylic alcohols and boronic esters.[8] Nickel-catalyzed allylic amination reactions with unprotected alcohols have also previously been demonstrated,[9] including in work by Mashima and coworkers using nickel catalysts and acetate additives (Figure 1a).[10] Kimura and Onodera[11] also recently reported allylic aminations with allylic alcohols under palladium catalysis with boronic ester-containing phosphine ligands, which activate the allylic alcohol (Figure 1b). In this report, we show that the *in situ* activation of allylic alcohols with catalytic amounts of titanium Lewis acids enables highly efficient nickel-catalyzed allylic aminations with a broad range of primary and secondary allylic alcohols and various primary and secondary amine nucleophiles. In addition, we demonstrate that diene-containing

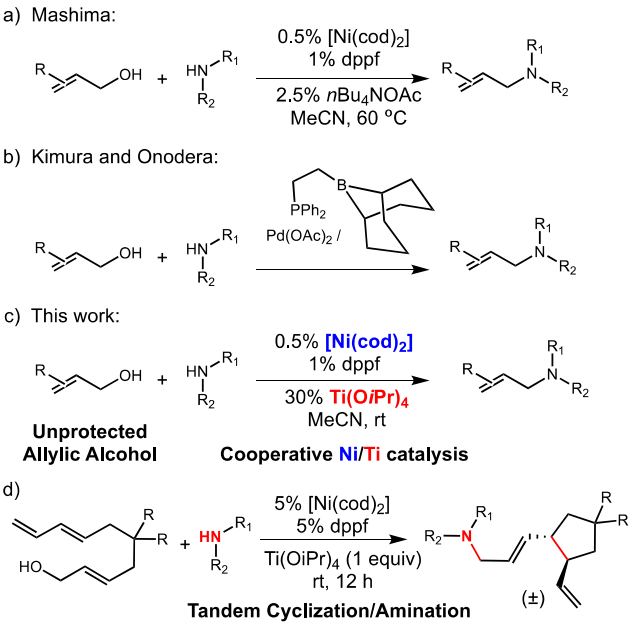
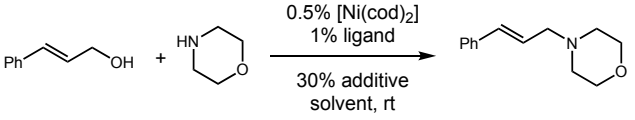


Figure 1. Allylic amination under mild conditions via cooperative Ni/Ti catalysis.

substrates readily cyclize prior to amination only under our cooperative catalysis conditions, generating carbocyclic allylic amine products with good diastereoselectivity (Figure 1d).

During the course of our studies in C–C bond forming Suzuki-Miyaura couplings with allylic alcohols,[8] we wondered whether the nickel allyl intermediate generated in the reaction could be trapped with amine nucleophiles to generate the allyl amine product. To begin our optimization studies, we found that addition of $Ni(cod)_2$ and bis-(diphenylphosphino)ferrocene (dppf) to the reaction of morpholine with cinnamyl alcohol resulted in very low yield of the amination product (Table 1, entry 1). However, the addition of a catalytic amount of titanium isopropoxide (30%) to the reaction dramatically improved the rate of product formation, presumably via alcohol activation (entry 2). Similar Lewis acid effects have been observed in allylic aminations with noble metal catalysts.[12] Importantly, this allylic amination occurs under very mild conditions at room temperature with inexpensive nickel catalysts. No conversion was observed in the absence of nickel and in the presence of titanium (entry 3) and lower amounts of titanium led to slower reactions (entry 4). Under conditions previously reported for nickel-catalyzed allylic aminations using tetrabutylammonium acetate (TBAA) as additive,[10] only 12% yield was observed under the same conditions (Entry 5). Catalytic amounts of alternative Lewis acids also accelerated the transformation (entries 6–8),

Table 1. Optimization of cooperative catalysis system.



entry[a]	ligand	additive	solvent	time (h)	conv.[b] (yield)
1	dppf	-	MeCN	24	3
2	dppf	Ti(O*i*-Pr)$_4$	MeCN	12	90(85)
3	-	Ti(O*i*-Pr)$_4$	MeCN	20	-
4[c]	dppf	Ti(O*i*-Pr)$_4$	MeCN	20	36
5	dppf	TBAA	MeCN	12	14
6	dppf	$TiCl_4$	MeCN	12	22
7	dppf	BF_3	MeCN	12	45
8	dppf	$AlCl_3$	MeCN	12	65
9	PPh_3	Ti(O*i*-Pr)$_4$	MeCN	12	46
10	dppe	Ti(O*i*-Pr)$_4$	MeCN	12	21
11	dppp	Ti(O*i*-Pr)$_4$	MeCN	12	41
12	dppb	Ti(O*i*-Pr)$_4$	MeCN	12	86
13	BINAP	Ti(O*i*-Pr)$_4$	MeCN	12	67
14	dppf	Ti(O*i*-Pr)$_4$	toluene	12	9
15	dppf	Ti(O*i*-Pr)$_4$	THF	12	6
16	dppf	Ti(O*i*-Pr)$_4$	dioxane	12	6
17	dppf	Ti(O*i*-Pr)$_4$	DMF	12	1
18[d]	dppf	Ti(O*i*-Pr)$_4$	MeCN	4	96
19[e]	dppf	Ti(O*i*-Pr)$_4$	MeCN	2	99 (96)

a) Reaction run with 1.6 mmol alcohol, 2.4 mmol amine (1.5 equiv) in solvent (4 M). b) Conversion measured by ^{1}H NMR analysis of the crude reaction. c) With 10% Ti(O*i*-Pr)$_4$. d) With 50% Ti(O*i*-Pr)$_4$. e) With 100% Ti(O*i*-Pr)$_4$

but not to the same degree as with titanium isopropoxide. We also investigated the impact of phosphine ligand structure on the rate of catalysis and found that various phosphines could be employed, but dppf provided the highest yield in the reaction (entries 9–13). Acetonitrile as solvent was also found to be important to obtaining good conversions (entries 14–17).

In order to further investigate the role of titanium, we also conducted the reaction with 0.5 and 1.0 equivalents of the Lewis acid and found that the rate increased as the amount of titanium increased (Table 1, entries 18–19). This supports our hypothesis that titanium activates the alcohol toward oxidative addition by the nickel catalyst, presumably via formation of the Ti(O-allyl)$_4$ species. Indeed, when titanium isopropoxide is mixed with cinnamyl alcohol in the presence or absence of morpholine, shifts in the ^{1}H NMR spectrum indicate coordination of the alcohol with the Lewis acid. However, when titanium isopropoxide was added to the preformed nickel dppf catalyst, no change in the ^{1}H NMR spectrum was observed (see supporting information). This final result suggests that the titanium does not impact the structure of the nickel catalyst.

Our next goal was to demonstrate that our catalytic system performed well across a wide variety of substrates. To this end, we screened a variety of allylic alcohol substrates and found that the reaction tolerates various substitutions at the alkene and alcohol carbons (Figure 2). For example, simple allyl alcohols that are unsubstituted or monosubstituted on the alkene react in high yield (**2a**–**2c**). Electron rich and electron poor cinnamyl alcohols also provide high yield of the allyl amine product (**2d**–**2h**). Secondary allylic alcohols are also well-tolerated and provide high yields of the secondary amine products (**2i**–**2m**). Substrates containing the thiophene heterocycle also react in high yield (**2n**). However, while trisubstituted alkenes do react (**2o**), including Baylis-Hillman adducts (**2p**), they provide only modest yield of the product. For the majority of substrates, catalytic amounts of titanium are sufficient to obtain high yields. In certain cases much better yields were obtained with stoichiometric titanium Lewis acid, such as with secondary allylic alcohols (**2i**–**k**, **2m**) and with other sensitive functional groups (**2n**–**2p**).

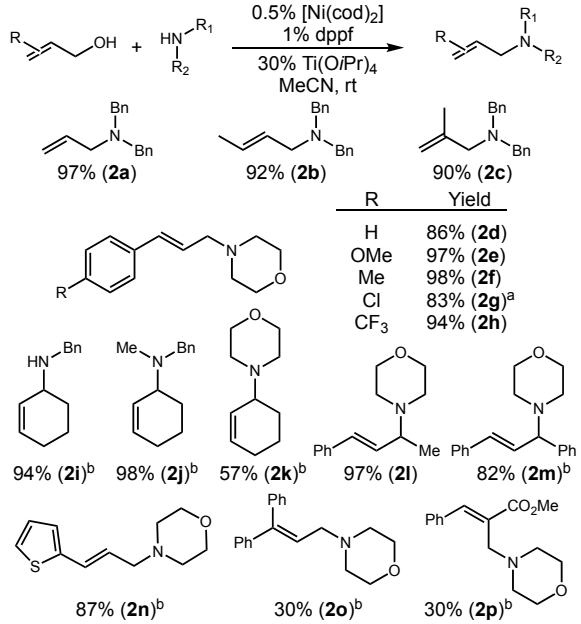


Figure 2. Amination of various primary and secondary alcohol substrates. a) Reaction run with 2 mol% Ni and 0.5 equiv Ti(O*i*-Pr)4. b) Reaction run with 5 mol% Ni and 1 equiv Ti(O*i*-Pr)4.

Our attention next turned to exploring the substrate scope with respect to the amine nucleophile (Figure 3). Secondary amines are excellent substrates for the allylic amination (**3a**–**3i**), including cyclic amines (**3g**–**3i**) and heterocyclic amine **3i**. Primary amines are also acceptable substrates and give mono-allylated products (**3j**–**3k**), but slightly reduced yields are observed due to the formation of overalkylated products. Alpha-branched primary amines, however, provide high yields with primary alcohols (**3l**), and monosubstituted primary amines provide higher yields with secondary allylic alcohols (**3m**). In these last cases, steric hindrance around the amine product is essential for obtaining high yield of the mono-alkylated product. Very sterically hindered amines, on the other hand (**3n**), only provide modest yield in the reaction.

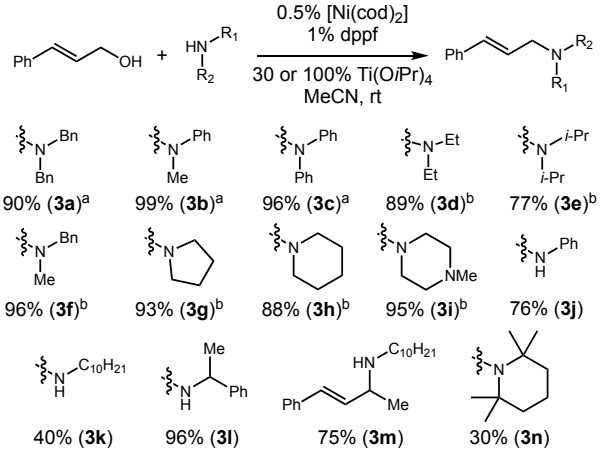


Figure 3. Substrate scope for the amine nucleophile. a) reaction run with 2 mol% nickel and 100% Ti(O*i*-Pr)4. b) reaction run with 100% Ti(O*i*-Pr)4.

Tandem processes are attractive synthetically because they enable the formation of multiple bonds in the same transformation, leading to rapid construction of complex molecules. In this vein, we investigated the tandem oxidative addition, cyclization, and amination reaction shown in Figure 4. When our cooperative catalysis system was employed, the cyclized products (**4**) were observed as the major product and in good yield when 5% nickel catalyst and 100% titanium isopropoxide were used. In contrast, under the catalytic conditions developed by Mashima (see Figure 1a),[10] only amination was observed and no cyclization. To the best of our knowledge, this is the first example of an insertion of a nickel allyl intermediate into a pendant diene to generate a cyclized amination product. This new transformation generates a multifunctional cyclopentane product containing two stereocenters with moderate to good diastereoselectivity. The reaction proceeds in moderate to high yield with a variety of amine nucleophiles, including acyclic (**4a**, **4b**, **4c**), cyclic (**4d**, **4e**), and heterocyclic amines (**4f**, **4g**). These new amine products could be valuable intermediates in the synthesis of complex alkaloids due to the dense arrangement of reactive functional groups.

In conclusion, we have developed a cooperative catalytic system for the amination of unactivated allylic alcohols under mild conditions. These conditions rely on the Ti-mediated activation of the allylic alcohol to facilitate efficient catalysis. A broad range of amines and alcohol substrates react in high yield in this transformation. In addition, this catalytic system enables tandem cyclization amination reactions for the first time via insertion of the nickel allyl intermediate into a pendent diene func

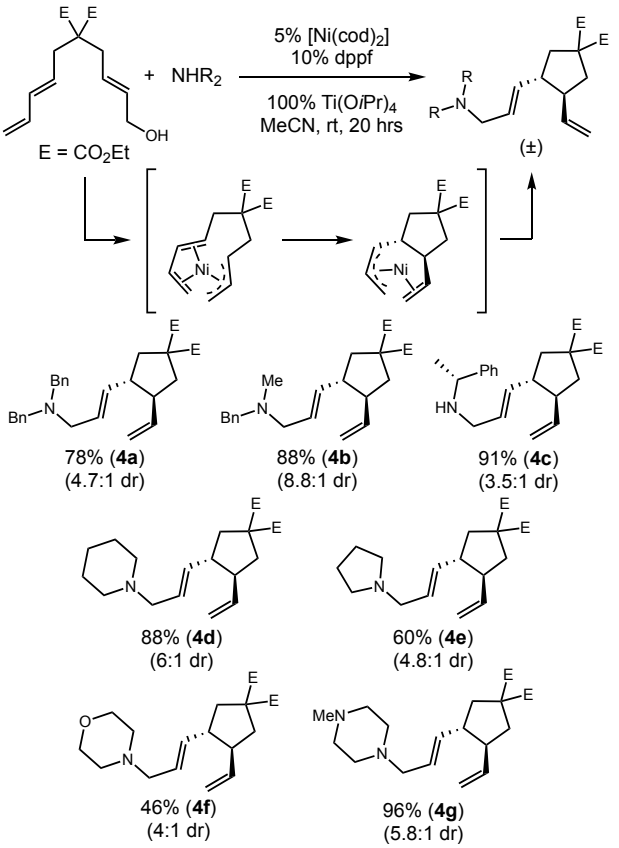


Figure 4. Tandem cyclization/amination of diene-containing substrates.

tional group. These results provide access to synthetically valuable allylic amine products in high yield as potential building blocks for alkaloid synthesis.

Experimental Section

General Information: All reactions were carried out under an atmosphere of nitrogen or argon in oven-dried glassware with magnetic stirring, unless otherwise indicated. Solvents were dried by J. C. Meyer's Solvent Purification System. The substrates were prepared by literature procedures or as described below. All other reagents were used as obtained unless otherwise noted. Flash chromatogaphy was performed with EM Science silica gel (0.040-0.063μm grade). Analytical thin-layer chromatography was performed with 0.25 mm coated commercial silica gel plates (E. Merck, DC-Plastikfolien, kieselgel 60 F254). Proton nuclear magnetic resonance (^{1}H-NMR) data were acquired on an Inova 300 MHz, an Inova 500 MHz, or an NMR-S 500 MHz spectrometer. Chemical shifts are reported in delta (δ) units relative to the 2H signal of the $CDCl_3$ solvent. Signals are reported as follows: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), qd (quartet of doublets), bs (broad singlet), m (multiplet), rot (rotamers). Coupling constants are reported in hertz (Hz). Carbon-13 nuclear magnetic resonance (^{13}C-NMR) data were acquired on an Inova at 75 MHz or Inova or NMR-S spectrometer at 125 MHz. Chemical shifts are reported in ppm. All NMR spectra were collected at 298 K. Mass spectral data were obtained using

ESI techniques (Agilent, 6210 TOF). Infrared (IR) data were recorded as films on sodium chloride plates on a Thermo Scientific Nicolet IR100 FT-IR spectrometer. Absorbance frequencies are reported in reciprocal centimeters (cm^{-1}).

Substrates **2i-2k** were synthesized according to previously reported procedures[13].

diethyl 2-((*E*)-4-hydroxybut-2-en-1-yl)-2-((E)-penta-2,4-dien-1-yl)malonate (4): To a solution of diethyl (E)-2-(penta-2,4-dien-1-yl)malonate[14a] (L_1, 550 mg, 2.43 mmol, 1eq) in THF was added sodium hydride (60% dispersion in mineral oil, 146 mg, 3.64 mmol, 1.5 eq) at 0 °C and stirred at room temperature for 30 minutes. A solution of (*E*)-tert-butyl((4-chlorobut-2-en-1-yl)oxy)dimethylsilane[14b] (L_2, 642 mg, 2.91 mmol, 1.2 eq) in DMSO (2mL) was added and the mixture stirred overnight. The reaction mixture diluted with ethyl acetate and washed with $NaHCO_3$ (aq), dried over magnesium sulfate, and concentrated in vacuum. Purification on column using EtOAc/hexanes(1% to 2.5%) gave the product as a yellowish liquid (900 mg, 76%).[1] ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.19-6.35 (m, 1H), 6.02-6.13 (m, 1H), 5.41-5.68 (m, 3H), 5.08 (d, J = 16.91 Hz, 1H), 5.0 (d, J = 10.55 Hz,1H), 4.17 (q, J = 14.23 Hz, 4H), 4.10 (d, J = 4.66 Hz, 2H), 2.63 (t, J = 7.82 Hz, 4H), 1.23 (t, J = 7.12 Hz, 6H), 0.9 (s, 9H), 0.055 (s, 6H) ; ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.8, 136.7, 135.0, 134.1, 128.0, 123.9, 116.3, 63.6, 61.3, 57.7, 35.8, 35.5, 26.0, 14.2, -5.1; IR (film)νmax 2929, 2856, 1736, 1462, 1256, 1133; HRMS(ESI) calcd. for $C_{30}H_{29}N_3P$, $[M+H]^+$, 463.2172; found, 463.2175.

To a solution of the product from above (1 g, 2.5 mmol, 1eq) in THF was added tetrabutylammonium fluoride (1M in THF, 6 mL, 6 mmol, 2 eq) at 0°C. The reaction mixture warmed up and stirred at room temperature overnight. The mixture was diluted with EtOAc and washed with water. Organics were dried on sodium sulfate, concentrated, and purified on column chromatography using hexanes/EtOAc (0 to 25%) gave the product as a colorless liquid (600 mg, 82%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.22-6.32 (m, 1H), 6.05-6.13 (m, 1H), 5.68-5.77 (m, 1H), 5.47-5.59 (m, 2H), 5.12 (d, J = 17.34 Hz, 1H), 5.01 (d, J = 10.42 Hz, 1H), 4.18 (q, J = 14.31 Hz, 4H), 4.08 (t, J = 5.39 Hz, 2H), 2.64 (dd, J = 7.96,11.23 Hz, 4H), 1.24 (t, J = 7.18 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.7, 136.6, 135.1, 133.8, 127.9, 126.1, 116.5, 63.4, 61.4, 57.6, 35.8, 35.4, 14.2; IR (film) νmax 3465, 2980, 1732, 1456, 1202,; HRMS (ESI) calcd. for $C_{30}H_{29}N_3P$, $[M+H]^+$, 463.2172; found, 463.2175.

General procedure for nickel-catalyzed cross coupling of allylic alcohols with amines: Inside a glove box and in a 3 mL dram vial were placed $Ni(COD)_2$ (2.2 mg, 0.008 mmL, 0.005eq) and dppf (9 mg, 0.016 mmol, 0.01eq) in acetonitrile (300 µL). the mixture stirred for 5 minutes, and after addition of the allylic alcohol (1.6 mmol, 1 eq), the amine (2.4 mmol, 1.5 eq), and $Ti(O\textit{i}\text{-}Pr)_4$ (0.1 mL, 0.3 eq, 4.879 M solution in toluene), the vial was sealed and the reaction mixture stirred for 12 hours. All the volatiles were removed on the rotovap, and the crude mixture was purified on column using EtOAc/hexanes as eluent.

***N,N*-dibenzylprop-2-en-1-amine (2a):** Prepared following the general procedure using $Ni(COD)_2$ (2.2 mg, 0.008 mmL, 0.005 eq), dppf (9 mg, 0.016 mmol, 0.01eq), allyl alcohol (93 mg, 1.6 mmol, 1 eq), dibenzyl amine (473 mg, 2.4 mmol, 1.5 eq), and $Ti(O\textit{i}\text{-}Pr)_4$ (0.1 mL, 0.3 eq, 4.879 M solution in toluene) in acetonitrile (300 µL). Product was purified on column using pure hexanes to 50% EtOAc/hexanes as eluent (368 mg, 97%). Spectral data is in accordance with the reported values[15a].

***(E)*-*N,N*-dibenzylbut-2-en-1-amine (2b):** Prepared following the general procedure using $Ni(COD)_2$ (2.2 mg, 0.008 mmL, 0.005eq), dppf (9 mg, 0.016 mmol, 0.01 eq), (E)-2-butene-1-ol (115 mg, 1.6 mmol, 1 eq), dibenzylamine (473 mg, 2.4 mmol, 1.5 eq), and $Ti(O\textit{i}\text{-}Pr)_4$ (0.1 mL, 0.3 eq, 4.879 M solution in toluene) in acetonitrile (300 µL). Product was purified on column using pure hexanes to 50% EtOAc/hexanes as eluent (369 mg, 92%). Spectral data is in accordance with the reported values[15a].

***N,N*-dibenzyl-2-methylprop-2-en-1-amine (2c):** Prepared following the general procedure using $Ni(COD)_2$ (2.2 mg, 0.008 mmL, 0.005eq), dppf (9 mg, 0.016 mmol, 0.01 eq), 2-methyl-2-propene-1-ol (115 mg, 1.6 mmol, 1 eq), dibenzylamine (473 mg, 2.4 mmol, 1.5 eq), and $Ti(O\textit{i}\text{-}Pr)_4$ (0.1 mL, 0.3 eq, 4.879 M solution in toluene) in acetonitrile (300 µL). Product was purified on column using pure hexanes to 50% EtOAc/hexanes as eluent (361 mg, 90%). Spectral data is in accordance with the reported values[15b].

4-cinnamylmorpholine (2d): Prepared following the general procedure using $Ni(COD)_2$ (2.2 mg, 0.008 mmL, 0.005 eq), dppf (9 mg, 0.016 mmol, 0.01 eq), cinnamyl alcohol (214 mg, 1.6 mmol, 1 eq), morpholine (236 mg, 2.4 mmol, 1.5 eq), and $Ti(O\textit{i}\text{-}Pr)_4$ (0.1 mL, 0.3 eq, 4.879 M solution in toluene) in acetonitrile (300 µL). Product was purified on column using pure hexanes to 50% EtOAc/hexanes as eluent (277 mg, 86%). Spectral data is in accordance with the reported values[15b].

***(E)*-4-(3-(4-methoxyphenyl)allyl)morpholine (2e):** prepared following the general procedure using $Ni(COD)_2$ (1.1 mg, 0.004 mmol, 0.005 eq), dppf (9 mg, 0.008 mmol, 0.01 eq), (E)-3-(4-methoxyphenyl)prop-2-en-1-ol (132mg, 0.8 mmol, 1 eq), morpholine (140 mg, 1.2 mmol, 1.5 eq), and $Ti(O\textit{i}\text{-}Pr)_4$ (0.05 mL, 0.3 eq, 4.879 M solution in toluene) in acetonitrile (100 µL). Product was purified on column using pure hexanes to 50% EtOAc/hexanes as eluent (90.5 mg, 97%). Spectral data is in accordance with the reported values[15b].

***(E)*-4-(3-(p-Tolyl)allyl)morpholine (2f):** Prepared following the general procedure using $Ni(COD)_2$ (1.1 mg, 0.008 mmol, 0.005 eq), dppf (9 mg, 0.008 mmol, 0.01 eq), (*E*)-3-(p-tolyl)prop-2-en-1-ol (120 mg, 0.8 mmol, 1 eq), morpholine (140 mg, 1.2 mmol, 1.5 eq), and $Ti(O\textit{i}\text{-}Pr)_4$ (0.05 mL, 0.3 eq, 4.879 M solution in toluene) in acetonitrile (100 µL). Product was purified on column using pure hexanes to 50% EtOAc/hexanes as eluent (85 mg, 98%). Spectral data is in accordance with the reported values[15c].

***(E)*-4-(3-(4-chlorophenyl)allyl)morpholine (2g):** Prepared following the general procedure using $Ni(COD)_2$ (2.2 mg, 0.008 mmol, 0.02 eq), dppf (9 mg, 0.016 mmol, 0.04 eq), (*E*)-3-(4-chlorophenyl)prop-2-en-1-ol (68 mg, 0.4 mmol, 1 eq), morpholine (70 mg, 0.6 mmol, 1.5 eq), and $Ti(O\textit{i}\text{-}Pr)_4$ (0.05 mL, 0.5 eq, 4.879 M solution in toluene) in acetonitrile (100 µL). Product was purified on column using pure hexanes to 50% EtOAc/hexanes as eluent (79 mg, 83%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22-7.36 (m, 4H), 6.48 (d, J = 16.33 Hz, 1H), 6.16-6.28 (m, 1H), 3.73 (t, J = 4.62 Hz, 4H), 3.13 (dd, J = 1.38, 6.74 Hz, 2H), 2.49 (t, J = 4.64 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 132.1, 128.7, 127.5, 126.9, 67.0, 61.4, 53.7; IR (film) νmax 2856, 2464, 1492, 1452, 1119; HRMS (ESI) calcd. for $C_{13}H_{16}ClNO$, $[M+H]^+$, 239.0891; found, 239.0897.

***(E)*-4-(3-(4-(trifluoromethyl)phenyl)allyl)morpholine (2h):** Prepared following the general procedure using $Ni(COD)_2$ (2.2

mg, 0.008 mmol, 0.02 eq), dppf (9 mg, 0.016 mmol, 0.04 eq), (*E*)-3-(4-(trifluoromethyl)phenyl)prop-2-en-1-ol (80 mg, 0.4 mmol, 1 eq), morpholine (70 mg, 0.6 mmol, 1.5 eq), and Ti(O*i*-Pr)$_4$ (0.05 mL, 0.5 eq, 4.879 M solution in toluene) in acetonitrile (100 µL). Product was purified on column using pure hexanes to 50% EtOAc/hexanes as eluent (101.5 mg, 94%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38-7.63 (m, 4H), 6.57 (d, J = 15.68 Hz, 1H), 6.27-6.45 (m, 1H), 3.73 (t, J = 4.62 Hz, 4H), 3.13 (dd, J = 1.38, 6.74 Hz, 2H), 2.49 (t, J = 4.64 Hz,4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 131.9, 129.1, 126.5, 125.6, 67.0, 61.3, 53.7; IR (film) νmax 2958, 2806, 1615, 1325, 1117; HRMS (ESI) calcd. for $C_{14}H_{16}F_3NO$, $[M+H]^+$, 272.1218; found, 272.1212.

***N*-benzylcyclohex-2-en-1-amine (2i):** Prepared following the general procedure using Ni(COD)$_2$ (5.5 mg, 0.02 mmol, 0.05 eq), dppf (18 mg, 0.04 mmol, 0.1eq), cyclohex-2-en-1-ol (40 mg, 0.4 mmol, 1 eq), benzylamine (64 mg, 0.6 mmol, 1.5 eq), and Ti(O*i*-Pr)$_4$ (0.08 mL, 1 eq, 4.879 M solution in toluene) in acetonitrile (100 µL). Product was purified on column using pure hexanes to 50% EtOAc/hexanes as eluent (101.5 mg, 94%). Spectral data is in accordance with the reported values[15c].

***N*-benzyl-*N*-methylcyclohex-2-en-1-amine (2j):** Prepared following the general procedure using Ni(COD)$_2$ (5 mg, 0.016 mmol, 0.04 eq), dppf (18 mg, 0.320 mmol, 0.08 eq), cyclohex-2en-1-ol (100 mg, 1 mmol, 1 eq), *N*-methylbenzylamine (250 mg, 2 mmol, 2 eq), and Ti(O*i*-Pr)$_4$ (284 mg, 1 mmol, 1 eq) in acetonitrile (500 µL). Product was purified on column using pure hexanes to 10% ethylacetate/hexanes as eluent (197 mg, 98%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18-7.33 (m, 5H), 5.79-5.85 (m, 1H), 5.70-5.74 (m, 1H), 3.62-3.66 (d, J = 13.5 Hz, 1H), 3.43-3.47 (d, J=13.5 Hz, 1H), 3.32-3.37 (m, 1H), 2.20 (s, 3H), 1.94-1.99 (m, 2H), 1.76-1.85 (m, 2H), 1.50-1.56 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.4, 130.5, 129.9, 128.8, 128.3, 126.8, 59.5, 57.4, 37.9, 25.4, 22.9, 21.8; IR (film) νmax 2911, 2931, 2859, 2836, 2787, 1494, 1452, 1043; HRMS (ESI) calcd. for $C_{14}H_{19}N$ $[M+H]^+$, 202.1596; found, [M+H]+, 202.1590.

4-(cyclohex-2-en-1-yl)morpholine (2k): Prepared following the general procedure using Ni(COD)$_2$ (5 mg, 0.016 mmol, 0.04 eq), dppf (18 mg, 0.320 mmol, 0.08 eq), cyclohex-2en-1-ol (100 mg, 1 mmol, 1 eq), morpholine (300 mg, 3 mmol, 3eq), and Ti(O*i*-Pr)$_4$ (284 mg, 1 mmol, 1 eq) in acetonitrile (500 µL). Product was purified on column using pure pentane to 20% ether/pentane as eluent (96 mg, 57%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.82-5.85 (m, 1H), 5.65-5.67 (m, 1H), 3.71-3.73 (m, 4H), 3.15-3.17 (m, 1H), 2.54-2.6 (m, 4H), 1.98-1.99 (m, 2H), 1.78-1.81 (m, 2H), 1.53-1.57 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 133.5, 133.3, 130.4, 128.8, 128., 128.1, 69.9, 67.5, 60.4, 25.3, 23.1, 21.4; IR (film) νmax 2911, 2930.26, 2853.28, 1450.28, 1249.41, 1117.06; HRMS (ESI) calcd. for $C_{10}H_{17}NO$, $[M+H]^+$, 168.1388; found, [M+H]+, 168.1382

***(E)*-4-(4-phenylbut-3-en-2-yl)morpholine (2l):** Prepared following the general procedure using Ni(COD)$_2$ (2.2 mg, 0.008 mmol, 0.02eq), dppf (9 mg, 0.016 mmol, 0.04 eq), (*E*)-4-phenylbut-3-en-2-ol (60 mg, 0.4 mmol, 1 eq), morpholine (64 mg, 0.6 mmol, 1.5 eq), and Ti(O*i*-Pr)$_4$ (0.05 mL, 0.5 eq, 4.879 M solution in toluene) in acetonitrile (100 µL). Product was purified on column using pure hexanes to 50% EtOAc/hexanes as eluent (84.2 mg, 97%). Spectral data is in accordance with the reported values[15d].

***(E)*-4-(1,3-diphenylallyl)morpholine (2m):** Prepared following the general procedure using Ni(COD)$_2$ (5.5mg, 0.02 mmol, 0.05eq), dppf (18 mg, 0.04 mmol, 0.1 eq), (*E*)-1,3-diphenylprop-2-en-1-ol (84 mg, 0.4 mmol, 1 eq), morpholine (64 mg, 0.6 mmol, 1.5 eq), and Ti(O*i*-Pr)$_4$ (0.08 mL, 1 eq, 4.879 M solution in toluene) in acetonitrile (100 µL). Product was purified on column using pure hexanes to 50% EtOAc/hexanes as eluent (91 mg, 82%). Spectral data is in accordance with the reported values[15e].

***(E)*-4-(3-(thiophen-2-yl)allyl)morpholine (2n):** Prepared following the general procedure using Ni(COD)$_2$ (5.5 mg, 0.02 mmol, 0.05 eq), dppf (18mg, 0.04 mmol, 0.1 eq), (*E*)-3-(thiophen-2-yl)prop-2-en-1-ol (56 mg, 0.4mmol, 1 eq), morpholine (64 mg, 0.6 mmol, 1.5 eq), and Ti(O*i*-Pr)$_4$ (0.08 mL, 1 eq, 4.879 M solution in toluene) in acetonitrile (100 µL). Product was purified on column using pure hexanes to 50% EtOAc/hexanes as eluent (73 mg, 87%). Spectral data is in accordance with the reported values[15g].

4-(3,3-diphenylallyl)morpholine (2o): Prepared following the general procedure using Ni(COD)$_2$ (5.5 mg, 0.02 mmol, 0.05 eq), dppf (18mg, 0.04 mmol, 0.1eq), 3,3-diphenylprop-2-en-1-ol (84 mg, 0.4mmol, 1 eq), morpholine (64 mg, 0.6 mmol, 1.5 eq), and Ti(O*i*-Pr)$_4$ (0.08 mL, 1 eq, 4.879 M solution in toluene) in acetonitrile (100 µL). Product was purified on column using pure hexanes to 50% EtOAc/hexanes as eluent (33 mg, 30%). Spectral data is in accordance with the reported values[15f].

Methyl (*E*)-2-(morpholinomethyl)-3-phenylacrylate (2p): Prepared following the general procedure using Ni(COD)$_2$ (5.5 mg, 0.02 mmol, 0.05 eq), dppf (18 mg, 0.04 mmol, 0.1eq), methyl 2-(hydroxy(phenyl)methyl)acrylate (77 mg, 0.4mmol, 1 eq), morpholine (64 mg, 0.6 mmol, 1.5 eq), and Ti(O*i*-Pr)$_4$ (0.08 mL, 1 eq, 4.879 M solution in toluene) in acetonitrile (100 µL). Product was purified on column using pure hexanes to 50% EtOAc/hexanes as eluent (23mg, 30%). Spectral data is in accordance with the reported values[15h].

***(E)*-*N*,*N*-dibenzyl-3-phenylprop-2-en-1-amine (3a):** prepared following the general procedure using Ni(COD)$_2$ (2.2 mg, 0.008 mmol, 0.02 eq), dppf (9 mg, 0.016 mmol, 0.04eq), cinnamyl alcohol (54 mg, 0.4 mmol, 1 eq), dibenzylamine (118 mg, 0.6 mmol, 1.5 eq), and Ti(O*i*-Pr)$_4$ (0.08 mL, 1 eq, 4.879 M solution in toluene) in acetonitrile (100 µL). Product was purified on column using pure hexanes to 50% EtOAc/hexanes as eluent (112.5 mg, 90%). Spectral data is in accordance with the reported values[16a].

***N*-cinnamyl-*N*-methylaniline (3b):** Prepared following the general procedure using Ni(COD)$_2$ (2.2 mg, 0.008 mmol, 0.02 eq), dppf (9 mg, 0.016 mmol, 0.04 eq), cinnamyl alcohol (54 mg, 0.4 mmol, 1 eq), N-methyl aniline (64 mg, 0.6 mmol, 1.5 eq), and Ti(O*i*-Pr)$_4$ (0.08 mL, 1eq, 4.879 M solution in toluene) in acetonitrile (100 µL). Product was purified on column using pure hexanes to 50% EtOAc/hexanes as eluent (88.5 mg, 99%). Spectral data is in accordance with the reported values[16b].

***N*-cinnamyl-*N*-phenylaniline (3c):** Prepared following the general procedure using Ni(COD)$_2$ (2.2 mg, 0.008 mmol, 0.02eq), dppf (9 mg, 0.016 mmol, 0.04 eq), cinnamyl alcohol (54 mg, 0.4 mmol, 1 eq), diphenyl amine (100 mg, 0.6 mmol, 1.5 eq), and Ti(O*i*-Pr)$_4$ (0.08 mL, 1eq, 4.879 M solution in toluene) in acetonitrile (100 µL). Product was purified on column using pure hexanes to 50% EtOAc/hexanes as eluent (109 mg, 96%). Spectral data is in accordance with the reported values[16c].

***(E)*-*N*,*N*-diethyl-3-phenylprop-2-en-1-amine (3d):** Prepared following the general procedure using Ni(COD)$_2$ (1.1 mg, 0.008 mmol, 0.005eq), dppf (9 mg, 0.008 mmol, 0.01eq), cinnamyl alcohol (54 mg, 0.4 mmol, 1 eq), diethylamine (44mg, 0.6

mmol, 1.5 eq), and Ti(O*i*-Pr)$_4$ (0.05 mL, 0.5 eq, 4.879 M solution in toluene) in acetonitrile (100 µL). Product was purified on column using pure hexanes to 50% EtOAc/Hexanes as eluent (67 mg, 89%). Spectral data is in accordance with the reported values[16d].

***(E)*-*N*,*N*-diisopropyl-3-phenylprop-2-en-1-amine (3e):** Prepared following the general procedure using Ni(COD)$_2$ (2.2 mg, 0.008 mmol, 0.02eq), dppf (9 mg, 0.016 mmol, 0.04 eq), cinnamyl alcohol (54 mg, 0.4 mmol, 1 eq), diisopropylamine (60 mg, 0.6 mmol, 1.5 eq), and Ti(O*i*-Pr)$_4$ (0.05 mL, 0.5 eq, 4.879 M solution in toluene) in acetonitrile (100 µL). Product was purified on column using pure hexanes to 50% EtOAc/hexanes as eluent (67 mg, 77%). Spectral data is in accordance with the reported values[16e].

***(E)*-*N*-benzyl-*N*-methyl-3-phenylprop-2-en-1-amine (3f):** Prepared following the general procedure using Ni(COD)$_2$ (2.2 mg, 0.008 mmol, 0.02eq), dppf (9 mg, 0.016 mmol, 0.04 eq), cinnamyl alcohol (54 mg, 0.4 mmol, 1 eq), *N*-methyl-1-phenylmethanamine (73 mg, 0.6 mmol, 1.5 eq), and Ti(O*i*-Pr)$_4$ (0.05 mL, 0.5 eq, 4.879 M solution in toluene) in acetonitrile (100 µL). Product was purified on column using pure hexanes to 50% EtOAc/hexanes as eluent (91 mg, 96%). Spectral data is in accordance with the reported values[16f].

1-cinnamylpyrrolidine (3g): Prepared following the general procedure using Ni(COD)$_2$ (2.2 mg, 0.008 mmol, 0.02eq), dppf (9 mg, 0.016 mmol, 0.04 eq), cinnamyl alcohol (54 mg, 0.4 mmol, 1 eq), pyrrolidine (43 mg, 0.6 mmol, 1.5 eq), and Ti(O*i*-Pr)$_4$ (0.05 mL, 0.5 eq, 4.879 M solution in toluene) in acetonitrile (100 µL). Product was purified on column using pure hexanes to 50% EtOAc/hexanes as eluent (69.6 mg, 93%). Spectral data is in accordance with the reported values[16g].

1-cinnamylpiperidine (3h): Prepared following the general procedure using Ni(COD)$_2$ (2.2 mg, 0.008 mmol, 0.02eq), dppf (9 mg, 0.016 mmol, 0.04eq), cinnamyl alcohol (54 mg, 0.4 mmol, 1 eq), piperidine (51 mg, 0.6 mmol, 1.5 eq), and Ti(O*i*-Pr)$_4$ (0.05 mL, 0.5 eq, 4.879 M solution in toluene) in acetonitrile (100 µL). Product was purified on column using pure hexanes to 50% EtOAc/hexanes as eluent (70.4 mg, 88%). Spectral data is in accordance with the reported values[16h].

1-cinnamyl-4-methylpiperazine (3i): Prepared following the general procedure using Ni(COD)$_2$ (2.2 mg, 0.008 mmol, 0.02 eq), dppf (9 mg, 0.016 mmol, 0.04eq), cinnamyl alcohol (54 mg, 0.4 mmol, 1 eq), N-methyl piperazine (60 mg, 0.6 mmol, 1.5 eq), and Ti(O*i*-Pr)$_4$ (0.05 mL, 0.5 eq, 4.879 M solution in toluene) in acetonitrile (100 µL). Product was purified on column using pure hexanes to 50% EtOAc/hexanes as eluent (82 mg, 95%). Spectral data is in accordance with the reported values[16i].

***N*-cinnamylaniline (3j):** Prepared following the general procedure using Ni(COD)$_2$ (2.2 mg, 0.008 mmol, 0.02eq), dppf (9 mg, 0.016 mmol, 0.04 eq), cinnamyl alcohol (54 mg, 0.4 mmol, 1 eq), aniline (56 mg, 0.6 mmol, 1.5 eq), and Ti(O*i*-Pr)$_4$ (0.05 mL, 0.5 eq, 4.879 M solution in toluene) in acetonitrile (100 µL). Product was purified on column using pure hexanes to 50% EtOAc/hexanes as eluent (63 mg, 76%). Spectral data is in accordance with the reported values[16j].

***(E)*-*N*-(4-phenylbut-3-en-2-yl)decan-1-amine (3k):** Prepared following the general procedure using Ni(COD)$_2$ (1.1 mg, 0.008 mmol, 0.005eq), dppf (9 mg, 0.008 mmol, 0.01 eq), cinnamyl alcohol (54 mg, 0.4 mmol, 1 eq), decylamine (94 mg, 0.6 mmol, 1.5 eq), and Ti(O*i*-Pr)$_4$ (0.05 mL, 0.5 eq, 4.879 M solution in toluene) in acetonitrile (100 µL). Product was purified on column using pure hexanes to 20% Methanol/EtOAc as eluent (46 mg, 40%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, J = 4.04 Hz, 2H), 7.31 (t, J =7.45 Hz, 2H), 7.20-7.25 (m, 1H), 6.52 (d, J = 7.45 Hz, 1H), 6.26-6.35 (m, 1H), 3.29 (d, J = 3.19, 2H), 2.51 (t, J = 7.55 Hz, 1H), 1.48-1.57 (m,1H), 1.19-1.33 (m, 8H), 0.85-0.95 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.2, 134.6, 129.7, 128.5, 127.3, 136.2, 56.4, 47.7, 31.9, 30.4, 29.6, 29.6, 29.3, 27.5, 22.7, 22.1, 14.1; IR (film) νmax 2924, 2359, 1733, 1456, 1273; HRMS (ESI) calcd. for $C_{19}H_{31}N$, $[M+H]^+$, 274.2535; found, 274.2530.

***(E)*-3-phenyl-*N*-(1-phenylethyl)prop-2-en-1-amine (3l):** Prepared following the general procedure using Ni(COD)$_2$ (1.1 mg, 0.008 mmol, 0.005 eq), dppf (9 mg, 0.008 mmol, 0.01eq), cinnamyl alcohol (54 mg, 0.4 mmol, 1 eq), 1-phenylethan-1-amine (73 mg, 0.6 mmol, 1.5 eq), and Ti(O*i*-Pr)$_4$ (0.05 mL, 0.5 eq, 4.879 M solution in toluene) in acetonitrile (100 µL). Product was purified on column using pure hexanes to 50% EtOAc/hexanes as eluent (91 mg, 96%). Spectral data is in accordance with the reported values[16m].

(*E*)-*N*-(4-phenylbut-3-en-2-yl)decan-1-amine (3m): Prepared following the general procedure using Ni(COD)$_2$ (2.2 mg, 0.008 mmol, 0.02eq), dppf (9 mg, 0.016 mmol, 0.04eq), (*E*)-4-phenylbut-3-en-2-ol (60 mg, 0.4mmol, 1 eq), decylamine (94 mg, 0.6 mmol, 1.5 eq), and Ti(O*i*-Pr)$_4$ (0.05 ml, 0.5 eq, 4.879 M solution in toluene) in acetonitrile (100 µl). Product was purified on a column of silica gel using 20% methanol/EtOAc as eluent (86mg, 75%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, J = 3.7 Hz, 2H), 7.31 (t, J = 7.64 Hz, 2H), 7.20-7.25 (m, 1H), 6.47 (d, J = 7.96 Hz, 1H), 6.09 (q, J = 7.89 Hz, 1H), 3.36 (quin, J = 6.68, 1H), 2.61-2.68 (m, 1H), 2.53-2.60 (m, 1H), 1.45-1.55 (m, 2H), 1.23-1.34 (m, 18H), 0.89 (t, J = 6.68 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.2, 134.6, 129.7, 128.5, 127.3, 136.3, 56.4, 47.7, 31.9, 30.4, 29.6, 29.6, 29.3, 27.5, 22.7, 22.1, 14.1; IR (film) νmax 2924, 2359, 1465, 1136, 964; HRMS (ESI) calcd. for $C_{20}H_{33}N$, [M+H]+, 288.2691; found, 288.2698.

1-cinnamyl-2,2,6,6-tetramethylpiperidine (3n): prepared following the general procedure using Ni(COD)$_2$ (5.5mg, 0.02 mmol, 0.05 eq), dppf (18mg, 0.04 mmol, 0.1eq), cinnamyl alcohol (54 mg, 0.4 mmol, 1 eq), 2,2,6,6-tetramethylpiperidine (85 mg, 0.6 mmol, 1.5 eq), and Ti(O*i*-Pr)$_4$ (0.08 mL, 1 eq, 4.879 M solution in toluene) in acetonitrile (100 µL). Product was purified on column using pure hexanes to 50% EtOAc/hexanes as eluent (31 mg, 30%). Spectral data is in accordance with the reported values[16n].

diethyl (*E*)-3-(3-(dibenzylamino)prop-1-en-1-yl)-4-vinylcyclopentane-1,1-dicarboxylate (4a): Prepared following the general procedure using Ni(COD)$_2$ (1.5 mg, 0.005 mmol, 0.05eq), dppf (5.5 mg, 0.01 mmol, 0.1 eq), diethyl 2-((*E*)-4-hydroxybut-2-en-1-yl)-2-((*E*)-penta-2,4-dien-1-yl)malonate (30 mg, 0.1 mmol, 1 eq), dibenzylamine (24 mg, 0.12 mmol, 1.2 eq), and Ti(O*i*-Pr)$_4$ (0.03 mL, 1 eq, 4.879 M solution in toluene) in acetonitrile (50 µL). The product was obtained as an unseparable mixture of two diastereomers (4.7:1) after purification on column using pure hexanes to 70% EtOAc/hexanes as eluent (37 mg, 78%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21-7.39 (m, 10H) 5.62-5.78 (m, 1H), 5.48-5.58 (m, 2H), 4.94-5.03 (m, 2H), 4.16-4.24 (m, 4H), 3.56 (s, 4H), 3.01 (2,2H), 2.74-2.84 (m, 2H), 2.44-2.58 (m, 2H), 2.14-2.26 (m, 2H), 1.20-1.31 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.7, 139.8, 138.7, 133.5, 128.8, 128.3, 128.2, 126.8, 115.2, 61.6, 61.5, 59.1, 57.6, 55.3, 50.1, 48.8, 47.3, 46.1, 39.2, 38.7, 14.1; IR (film) νmax 2979, 2793, 1729, 1254, 1104; HRMS (ESI) calcd. for $C_{30}H_{37}NO_4$, 476.2756; found, $[M+H]^+$, 476.2753.

diethyl (*E*)-3-(3-(benzyl(methyl)amino)prop-1-en-1-yl)-4-vinylcyclopentane-1,1-dicarboxylate (4b): Prepared following the general procedure using $Ni(COD)_2$ (1.5 mg, 0.005 mmol, 0.05 eq), dppf (5.5 mg, 0.01 mmol, 0.1 eq), diethyl 2-((*E*)-4-hydroxybut-2-en-1-yl)-2-((*E*)-penta-2,4-dien-1-yl)malonate (30 mg, 0.1 mmol, 1 eq), *N*-methyl-1-phenylmethanamine (15mg, 0.12 mmol, 1.2 eq), and Ti(O*i*-Pr)$_4$ (0.03 mL, 1 eq, 4.879 M solution in toluene) in acetonitrile (50 µL). The product was obtained as an unseparable mixture of two diastereomers (8.8:1) after purification on column using pure hexanes to 70% EtOAc/hexanes as eluent (35 mg, 88%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.63-5.78 (m, 1H), 5.45-5.55 (m, 2H), 4.94-5.00 (m, 2H), 4.19 (dq, J = 7.15, 7.03 Hz, 4H), 3.46 (d, J = 2.85 Hz, 2H), 2.94-2.97 (m, 2H), 2.72-2.84 (m, 2H), 2.47 (dd, J = 13.89, 13.89 2H), 2.16-2.24 (m, 2H), 2.15 (s, 3H), 1.20-1.28 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.7, 172.4, 139.1, 138.6, 133.7, 129.1, 128.2, 126.9, 115.2, 61.5, 61.5, 59.5, 59.1, 47.3, 46.1, 42.0, 39.2, 38.7, 29.7, 14.1; IR (film) νmax 2925, 2359, 1730, 1453, 1254,; HRMS (ESI) calcd. for $C_{24}H_{33}NO_4$, $[M+H]^+$, 400.2443; found, 400.2447.

diethyl (*E*)-3-(3-((1-phenylethyl)amino)prop-1-en-1-yl)-4-vinylcyclopentane-1,1-dicarboxylate (4c): Prepared following the general procedure using $Ni(COD)_2$ (1.5 mg, 0.005 mmol, 0.05 eq), dppf (5.5 mg, 0.01 mmol, 0.1 eq), diethyl 2-((*E*)-4-hydroxybut-2-en-1-yl)-2-((*E*)-penta-2,4-dien-1-yl)malonate (30 mg, 0.1 mmol, 1 eq), 1-phenylethan-1-amine (15 mg, 0.12 mmol, 1.2 eq), and Ti(O*i*-Pr)$_4$ (0.03 mL, 1 eq, 4.879 M solution in toluene) in acetonitrile (50 µL). The product was obtained as an unseparable mixture of two diastereomers (3.5:1) after purification on column using pure hexanes to 70% EtOAc/hexanes as eluent (36.3 mg, 91%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20-7.36 (m, 5H), 5.59-5.75 (m, 1H), 5.29-5.55 (m, 2H), 4.92-5.08 (m, 2H), 4.12-4.23 (m, 4H), 3.78 (q, J = 6.24 Hz,1H), 2.97-3.09 (m, 2H), 2.70-2.79 (m, 2H), 2.37-2.56 (m,2H), 2.10-2.23(m, 2H), 1.34 (d, J = 6.44, 3H), 1.24 (q, J = 6.85, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.7, 172.4, 145.5, 138.6, 138.5, 132.1, 129.5, 129.4, 128.4, 126.9, 126.7, 126.6, 115.3, 61.5, 59.1, 57.2, 49.8, 49.3, 48.4, 47.2, 45.9, 40.3, 40.0, 39.1, 39.0, 38.7, 24.2, 21.8, 21.5, 14.0; IR (film) νmax 2924, 1728, 1254, 1178; HRMS (ESI) calcd. for $C_{24}H_{33}NO_4$, $[M+H]^+$, 400.2443; found, 400.2448.

diethyl (*E*)-3-(3-(piperidin-1-yl)prop-1-en-1-yl)-4-vinylcyclopentane-1,1-dicarboxylate (4d): Prepared following the general procedure using $Ni(COD)_2$ (1.5 mg, 0.005 mmol, 0.05 eq), dppf (5.5 mg, 0.01 mmol, 0.1eq), diethyl 2-((*E*)-4-hydroxybut-2-en-1-yl)-2-((*E*)-penta-2,4-dien-1-yl)malonate (30 mg, 0.1 mmol, 1 eq), piperidine (11 mg, 0.12 mmol, 1.2 eq), and Ti(O*i*-Pr)$_4$ (0.03 mL, 1 eq, 4.879 M solution in toluene) in acetonitrile (50 µL). The product was obtained as an unseparable mixture of two diastereomers (6:1) after purification on column using pure hexanes to 70% EtOAc/hexanes as eluent (35 mg, 88%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.65-5.76 (m, 1H), 5.43-5.54 (m, 2H), 4.93-5.03 (m, 2H), 4.19 (q, J = 8.02, 4H), 2.89-2.93 (m, 2H), 2.71-2.83 (m, 2H), 2.46 (q, J = 7.14 Hz, 2H), 2.27-2.40 (s, 4H), 2.13-2.24(m, 2H), 1.58 (t, J=5.28, 4H), 1.42 (s, 2H), 1.24 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.7, 172.4, 138.6, 133.8, 127.6, 115.1, 114.4, 67.5, 61.5, 59.1, 54.3, 47.7, 47.2, 46.0 48.4, 47.2, 45.9, 39.0, 38.7, 24.2, 21.5, 14.0; IR (film) νmax 2933, 2795, 1730, 1443, 1254,; HRMS (ESI) calcd. for $C_{21}H_{33}NO_4$, $[M+H]^+$, 364.2443; found, 364.2449.

diethyl (*E*)-3-(3-(pyrrolidin-1-yl)prop-1-en-1-yl)-4-vinylcyclopentane-1,1-dicarboxylate (4e): Prepared following the general procedure using $Ni(COD)_2$ (1.5 mg, 0.005 mmol, 0.05 eq), dppf (5.5 mg, 0.01 mmol, 0.1 eq), diethyl 2-((*E*)-4-hydroxybut-2-en-1-yl)-2-((*E*)-penta-2,4-dien-1-yl)malonate (30 mg, 0.1mmol, 1 eq), pyrrolidine (11 mg, 0.12 mmol, 1.2 eq), and Ti(O*i*-Pr)$_4$ (0.03 mL, 1 eq, 4.879 M solution in toluene) in acetonitrile (50 µL). The product was obtained as an unseparable mixture of two diastereomers (4.8:1) after purification on column using pure hexanes to 70% EtOAc/hexanes as eluent (21 mg, 60%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.63-5.76 (m, 1H), 5.47-5.60 (m, 2H), 4.94-5.07 (m, 2H), 4.19 (q, J = 7.19 Hz, 4H), 3.06-3.15 (m, 2H), 2.71-2.82 (m, 2H), 2.44 (s, 4H), 2.47 (q, J = 7.10 Hz, 2H), 2.14-2.24 (m, 2H), 1.78-1.83 (m, 4H), 1.21-1.28 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.4, 138.5, 115.2, 61.6, 59.1, 58.0, 53.7, 47.2, 46.0, 39.1, 38.7, 23.4, 14.0; IR (film) νmax 2925, 2359, 1729, 1255, 1178; HRMS (ESI) calcd. for $C_{20}H_{31}NO_4$, 350.2287; found, [M+H]+, 350.2281.

diethyl (*E*)-3-(3-morpholinoprop-1-en-1-yl)-4-vinylcyclopentane-1,1-dicarboxylate (4f): Prepared following the general procedure using $Ni(COD)_2$ (3 mg, 0.01 mmol, 0.05 eq), dppf (11 mg, 0.02 mmol, 0.1 eq), diethyl 2-((*E*)-4-hydroxybut-2-en-1-yl)-2-((*E*)-penta-2,4-dien-1-yl)malonate (60 mg, 0.2 mmol, 1 eq), morpholine (30 mg, 0.3 mmol, 1.5 eq), and Ti(O*i*-Pr)$_4$ (0.05 mL, 1 eq, 4.879 M solution in toluene) in acetonitrile (50 µL). The product was obtained as an unseparable mixture of two diastereomers (4:1) after purification on column using pure hexanes to 70% EtOAc/hexanes as eluent (33 mg, 46%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.60-5.74 (m, 1H), 5.40-5.55 (m, 2H), 4.93-5.08 (m, 2H), 4.19 (q, J = 7.13 Hz, 4H), 3.70 (t, J= 4.64 Hz, 4H), 2.88-3.02 (m, 2H), 2.71-2.83 (m, 2H), 2.43-2.50 (m,2H), 2.33-2.54 (m, 6H), 2.11-2.24 (m, 2H), 1.19-1.29 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.6, 172.3, 139.3, 138.5, 134.6, 126.8, 115.5, 115.2, 67.0, 61.6, 59.1, 53.7, 53.5, 49.9, 48.5, 47.2, 46.0, 40.2, 39.9, 39.1, 38.7, 29.7, 14.0; IR (film) νmax 2926, 2806, 1729, 1453, 1257, 1118; HRMS (ESI) calcd. for $C_{20}H_{31}NO_5$, $[M+H]^+$, 366.2236; found, 366.2231. Diethyl 2-((E)-4-morpholinobut-2-en-1-yl)-2-((E)-4-morpholinopent-2-en-1-yl)malonate (**4h**) was isolated as the main byproduct of the reaction as a brown liquid (30 mg, 40%) using Methanol/EtOAc as eluent. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.52-5.65 (m, 1H), 5.41-5.52 (m, 2H), 5.29-5.41 (m, 2H), 4.16 (q, J = 7.18 Hz, 4H), 3.70 (s, 8H), 2.93 (d, J = 6.33, 2H), 2.75-2.85 (m, 2H) 2.53-2.65 (m, 4H), 2.30-2.52 (m, 8H), 1.20-1.30 (m, 6H), 1.12 (d, J = 6.47, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.7, 170.7, 136.9, 131.0, 127.9, 125.5, 67.1, 66.9, 62.7, 61.3, 61.1, 57.6, 53.5, 50.6, 35.4, 17.9, 14.1; IR (film) νmax 2958, 2807, 1731, 1453, 1265, 1200; HRMS (EI) calcd. for $C_{30}H_{29}N_3P$, [M+H]+, 463.2172; found, 463.2175.

diethyl (*E*)-3-(3-(4-methylpiperazin-1-yl)prop-1-en-1-yl)-4-vinylcyclopentane-1,1-dicarboxylate (4g): Prepared following the general procedure using $Ni(COD)_2$ (1.5 mg, 0.005 mmol, 0.05 eq), dppf (5.5 mg, 0.01 mmol, 0.1 eq), diethyl 2-((*E*)-4-hydroxybut-2-en-1-yl)-2-((*E*)-penta-2,4-dien-1-yl)malonate (30 mg, 0.1 mmol, 1 eq), *N*-methylpiperazine (15 mg, 0.12 mmol, 1.2 eq), and Ti(O*i*-Pr)$_4$ (0.03 mL, 1 eq, 4.879 M solution in toluene) in acetonitrile (50 µL). The product was obtained as an unseparable mixture of two diastereomers (5.8:1) after purification on column using 10% MeOH/EtOAC as eluent (36.5 mg, 96.5%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.60-5.78 (m, 1H), 5.46-5.55 (m, 2H), 4.90-5.06 (m, 2H), 4.19 (q, J = 7.10 Hz, 4H), 2.91-2.98 (m, 2H), 2.71-2.85 (m, 2H), 2.37-2.59 (m, 10H), 2.29 (s, 3H), 2.15-2.24 (m, 2H), 1.19-1.30 (m, 6H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 172.4, 138.6, 134.3,

127.3, 115.2, 61.6, 61.5, 60.1, 59.1, 55.1, 53.2, 52.9, 47.2, 46.1, 39.1, 38.7, 14.1; IR (film) vmax 2934, 2794, 2359, 1730, 1456, 1256, 1178; HRMS (ESI) calcd. for $C_{21}H_{34}N_2O_4$, 379.2553; found, [M+H]+, 379.2557.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:
Spectral images for all compounds (PDF)

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Abstract Graphic: