Hydroalkylation of Alkynes via Dual Copper-Nickel Catalysis

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A thesis submitted in a partial fulfillment of the requirements for the degree of

Master of Science

University of Washington

2019

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Program Authorized to offer Degree:

Department of Chemistry

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Abstract

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Chapter 1 describes the stereospecific synthesis of E-alkenes through a dual copper and nickel catalysis system involving terminal alkynes and primary and secondary alkyl iodides. This reaction proceeds with excellent anti-Markovnikov and diastereoselectivity and is compatible with a wide range of functional groups. This hydroalkylation reaction allows easy access to a variety of E-alkenes from simple and readily available alkyne precursors.

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List of Abbreviations

Ac:	Acetyl
Ar:	Aryl
BINAP:	2,2'Bis(Diphenylphosphino)-1,1'-binaphthyl
Bn:	Benzyl
Boc:	*tert*-Butyloxycarbonyl
Bz:	Benzoyl
C:	Celsius
C_6D_6:	Benzene-d6
COD:	1,5-cyclooctadiene
CO_2H	Carboxylic Acid
CN:	Cyano
CsF:	Cesium fluoride
Cs_2O_3	Cesium carbonate
Cu:	Copper
Cy:	Cyclohexyl
DCM:	Dichloromethane
DMA:	Dimethylacetamide
DME:	Dimethoxyethane
DMSO:	Dimethyl sulfoxide
dtbpy:	4,4'-di-tert-butyl-2-2'-dipyridyl
Equiv:	Equivalent

EtoAc:	Ethyl Acetate
Et_2O:	Ethyl Ether
ESI-MS:	Electrospray ionization mass spectrometry
Et:	Ethyl
Fe:	Iron
FTIR:	Fourier transform infrared spectroscopy

Abbreviation for IR peaks

s:	Strong
m:	Medium
w:	Weak
b:	broad

GC:	Gas Chromatography
HBpin:	Pinacolborane
h, hr:	Hour
hv:	High energy light
HPLC:	High performance liquid chromatography
HRMS:	High resolution mass spectrometry
Hz:	Hertz
I_2, I:	Iodine, Iodide
IMes:	1,3-Bis-(2,4,6-trimethylphenyl)imidazolium
iPr:	Isopropyl
IPR:	1,3,-Bis-(2,6-

	diisopropylphenyl)imidazolium
i-PrPybox:	2,6-bis[4,5-dihydro-4-(1-methylethyl)-2-oxazolyl]-pyridine
Ir:	Iridium
Isooctane:	2,2,4-Trimethylpentane
Me:	Methyl
Mes:	Mesityl
MHz:	Megahertz
mol:	Mole
Ni:	Nickel
NHC:	N-heterocyclic carbene
NMR:	Nuclear magnetic resonance

Abbreviations for NMR splitting patterns

s:	Single
d:	Doublet
t:	Triplet
q:	Quartet
m:	Multiplet
br:	Broad
dd:	Doublet of doublets
dt:	Doublet of triplets
ddt:	Doublet of doublet of triplets
OTf:	Trifluoromethanesulfonate

OTs:	*p*-Toluenesulfonate
O*t*-Bu:	Tert-butoxide
O*i*-Pr:	Isopropoxide
Ph:	Phenyl
Pin:	Pinacol
Ph_2MeSiH:	Diphenylmethylsilane
Ph_3SiH:	Triphenylsilane
Ph_2SiH_2:	Diphenylsilane
PMHS:	polymethylhydrosiloxane
Ppm:	Parts per million
Pz:	Pyrazole
rt:	Room temperature
SIPr:	1,3-Bis-(2,6-diisopropylphenyl)Imidazolinium
t-Bu, *t*Bu:	*Tert*-butyl
TBS:	*Tert*-butyldimethylsilyl
TBDPS:	*Tert*-butyldiphenylsilyl
TFA:	Trifluoroacetic acid
THF:	Tetrahydrofuran
TIPS:	Triisopropylsilyl
TLC:	Thin layer chromatography
TMB:	1,3,5-trimethoxy benzene
TMS:	Trimethylsilyl

typ:	2,2':6',2''-Terpyridine
typ':	2,2':6',2''-Terpyridine, 4,4',4''-tris(1,1-dimethylethyl)-
Ts:	Tosyl
TEMPO:	(2,2,6,6-Tetramethylpiperidin-1-yl)oxyl
Zn:	Zinc

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Acknowledgement

First and foremost, I would like to express my gratitude to my advisor, Professor Gojko Lalic, for his support and mentorship. He has taught me a lot about chemistry and I am deeply grateful for the patience, endless knowledge and wisdom he has given me.

I would like to acknowledge the assistance of the NMR staff and GC mass spectrometry staff for ensuring the instruments are properly running and functioning.

Furthermore I would like to extend my thanks to the members of the Lalic Lab who have helped me during my time in the group. To the current members, Julia Nguyen, Mitchell Lee, Avijit Hazra, Megan Armstrong, Madison Goodstein and James Baumann, thank you for your guidance and help. During my time in graduate school, I was fortunate to work alongside and become friends with these intelligent and easy-going people.

Finally, I must express my profound gratitude to my parents and family for providing me with their never-ending support and continuous encouragement throughout my years of study and through the process of researching and writing this thesis. Thank you for your support.

Chapter 1: Hydroalkylation of Alkynes via Dual Copper-Nickel Catalysis

1.1 Introduction

Alkenes appear everywhere in organic chemistry. They are used as versatile synthetic intermediates and are common among complex organic molecules with important applications. Due to the importance of alkenes, the field of organic chemistry has been persistent in developing new methods for their synthesis. One method that has emerged from of these efforts has been the hydroalkylation of alkynes. The main benefit of this method has been the availability of simple and ready to use alkynes as precursors to a variety of alkenes.

Current methods for the hydroalkylation of alkynes provide access to several classes of alkenes (Figure 1.1 & 1.2). Z-substituted aryl alkenes can be prepared using a radical hydroalkylation of aryl alkynes that was reported in 2015 by Hu et al (Figure 1.1a).[1] Fu et al. recently developed a selective synthesis of 1,1-disubstituted alkenes through a nickel-catalyzed hydroalkylation of terminal alkynes (Figure 1.1b).[2] A similar transformation of terminal alkynes into 1,1-disubstituted alkenes was subsequently accomplished by MacMillan et al. using a cooperative photoredox/nickel catalysis (Figure 1.1b).[3,4] This approach has also allowed the transformation of sterically differentiated internal alkynes into trisubstituted alkenes with moderate regioselectivity.[3]

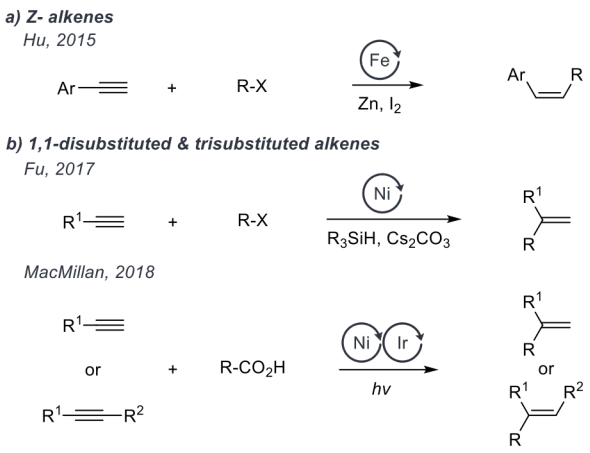


Figure 1.1 Hydroalkylation reactions of alkynes

Surprisingly, there are few hydroalkylation methods that target disubstituted *E*-alkenes. Previously, in 2015, our group reported the copper-catalyzed hydroalkylation of terminal alkynes using alkyl triflates as electrophiles (Figure 1.2).[5,6] While this reaction shows the key usage of hydroalkylation in the synthesis of *E*-alkenes, there were significant limitations. This reaction was highly sensitive to steric properties of the electrophile therefore limiting the types of alkenes that could be synthesized. We could only use linear primary alkyl triflates with no α-branching substituents as viable substrates and both alkyl triflates and the reagents used were highly reactive which further limited the reaction scope and introduced problems relating to preparation, purification and the bench top stability of starting electrophiles.

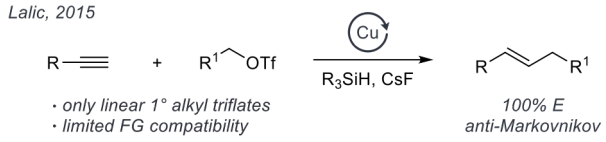


Figure 1.2 Previous work from Lalic lab

This thesis reports the development of our new method for hydroalkylation of terminal alkynes via a dual Cu/Ni catalyst system coupled with primary and secondary iodides for *E*-alkene products with excellent regio- and diastereospecificity (Figure 1.3).

This reaction not only addresses the shortcomings of our original hydroalkylation reaction while maintaining the original benefits, but it also expands upon the scope of coupling partners and products that can be synthesized via this method.

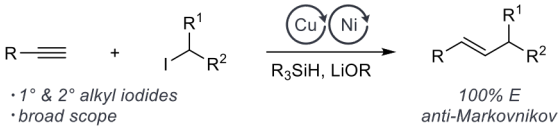


Figure 1.3 Current work: Hydroalkylation of alkynes for synthesis of *E*-alkenes

1.2 Reaction Optimization

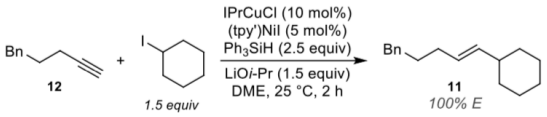
This hydroalkylation of alkynes go through the same general mechanism as other copper hydride based anti-Markovnikov hydrofunctionalization reactions.[7,8] These reactions involve hydrocupration of an alkyne followed by electrophilic functionalization of the alkenyl copper intermediate. The key hydrocupration step is highly regioselective and syn-stereospecific, ultimately resulting in excellent regio- and diastereoselectivity of the overall reaction. The low reactivity of the alkenyl copper complexes make alkylation difficult, to solve this problem we looked at using a dual catalysis system. This approach, based on cooperative catalysis,[9,10,11] was inspired by the pioneering work of Nakao[12,13] and Brown.[14,15,16] In our reaction, the cooperative action of the copper and nickel catalysts would allow us to retain excellent regio- and diastereoselectivity of the hydrocupration, and at the same time, address the current limitations of the hydroalkylation reaction.

To start our investigation, we needed to figure out which catalyst system to use and to ensure that the catalyst systems had orthogonal reactivity that way we would ensure that each substrate or reagent is activated by only one of the catalysts. In our initial stoichiometric experiments we found that the common cross-coupling catalyst

(dtbpy)$NiCl_2$ works. However, in a catalytic hydroalkylation reaction, the same nickel catalyst provided *E*-alkene in only 23% yield. Equally unsuccessful, were reactions with a variety of mono and bidentate phosphine and nitrogen-based ligands. We found that with our nickel(0) complexes we were producing trimerization and tetramerization of alkynes.[17,18]

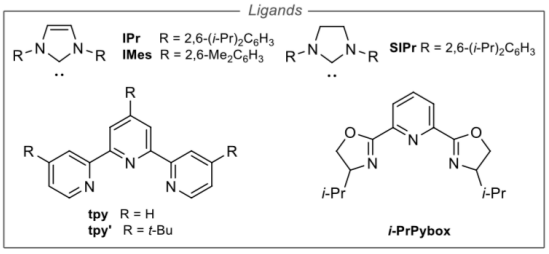
With a better understanding of the inherent reactivities of our reaction system in mind, we turned to the suggestion that tridentate ligands would suppress trimerization. The use of tridentate ligands proved to be a key modification in the development of our reaction as shown in Table 1. The best results in a reaction of a terminal alkyne **12** and cyclohexyl iodide were obtained using IPrCuCl catalyst and a nickel(I) co-catalyst supported by tridentate tpy′ ligand (Table 1.1). Additionally, Ph_3SiH was used as a hydride source and LiO*i*-Pr as a turnover reagent for the copper catalyst. During the development of the reaction we made several observations about reaction parameters (Table 1.1). Alkyl iodides were superior substrates over alkyl bromides. (Table 1.1 Entry 2). As in most other copper-catalyzed hydrofunctionalization reactions of alkynes, catalysts supported by IPr and the closely related SIPr ligands were the only competent catalysts (Table 1.1 Entry 3).

Table 1.1 Reaction optimization of hydroalkylation of E-alkenes with terminal alkynes



entry	*change from standard conditions*	*yield*[a]
1.	none	88%
2.	CyBr *instead of* CyI	2%
3.	SIPrCuCl *instead of* IPrCuCl	87%
4.	IMesCuCl *instead of* IPrCuCl	5%
5.	(tpy)NiI *instead of* (tpy')NiI	48%
6.	(tpy')$NiCl_2$ *instead of* (tpy')NiI	71%
7.	(dtbpy)$NiCl_2$ *instead of* (tpy')NiI	8%
8.	$NiCl_2$(DME) + *i*-PrPybox *instead of* (tpy')NiI	0%
9.	LiO*t*-Bu *instead of* LiO*i*-Pr	3%
10.	NaO*i*-Pr *instead of* LiO*i*-Pr	34%
11.	THF *instead of* DME	78%
12.	Ph_2MeSiH *instead of* Ph_3SiH	51%
13.	PMHS *instead of* Ph_3SiH	8%
14.	Ph_2SiH_2 *instead of* Ph_3SiH	12%

[a] Determined by GC using internal standard.

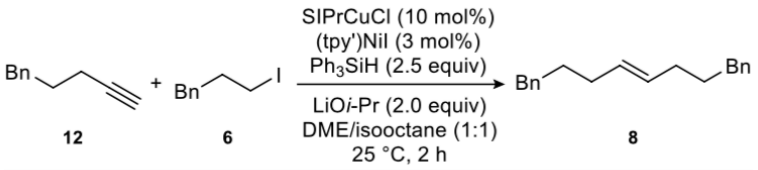


The nickel catalyst was key for the success of the reaction. Using a nickel(II) precatalysts proved to produce a lower yield, while complexes supported by other closely related ligands were inferior (Table 1.1 Entries 5-7). With LiO*t*-Bu instead of LiO*i*-Pr, and changing the alkoxide ion from Li to Na led to lower yield of product (Table 1.1 Entries 9, 10). Among common ethereal solvents, THF was the only solvent other than DME that afforded the desired product in a significant yield (Table 1.1 Entry 11). Finally, PMHS and silanes closely related to Ph_3SiH, were all significantly inferior to Ph_3SiH (Table 1.1 Entries 12-14).

Under our normal optimized conditions for secondary alkyl iodides, our reaction with primary iodides was only achieving yields of 32% with major side products of

reduced alkyl iodide[19] and the semi-reduction of alkyne to alkene. To achieve the optimized reaction of primary alkyl iodides, we had to change the catalyst from IPrCuCl to SIPrCuCl, change the solvent from DME to DME/isooctane(1:1), adjust the stoichiometry of Li-*i*OPr from 1.5 equiv to 2.0 equiv and lower the nickel catalyst loading from 5 mol% to 3 mol% (Table 1.2).

Table 1.2 Reaction optimization for primary alkyl iodides



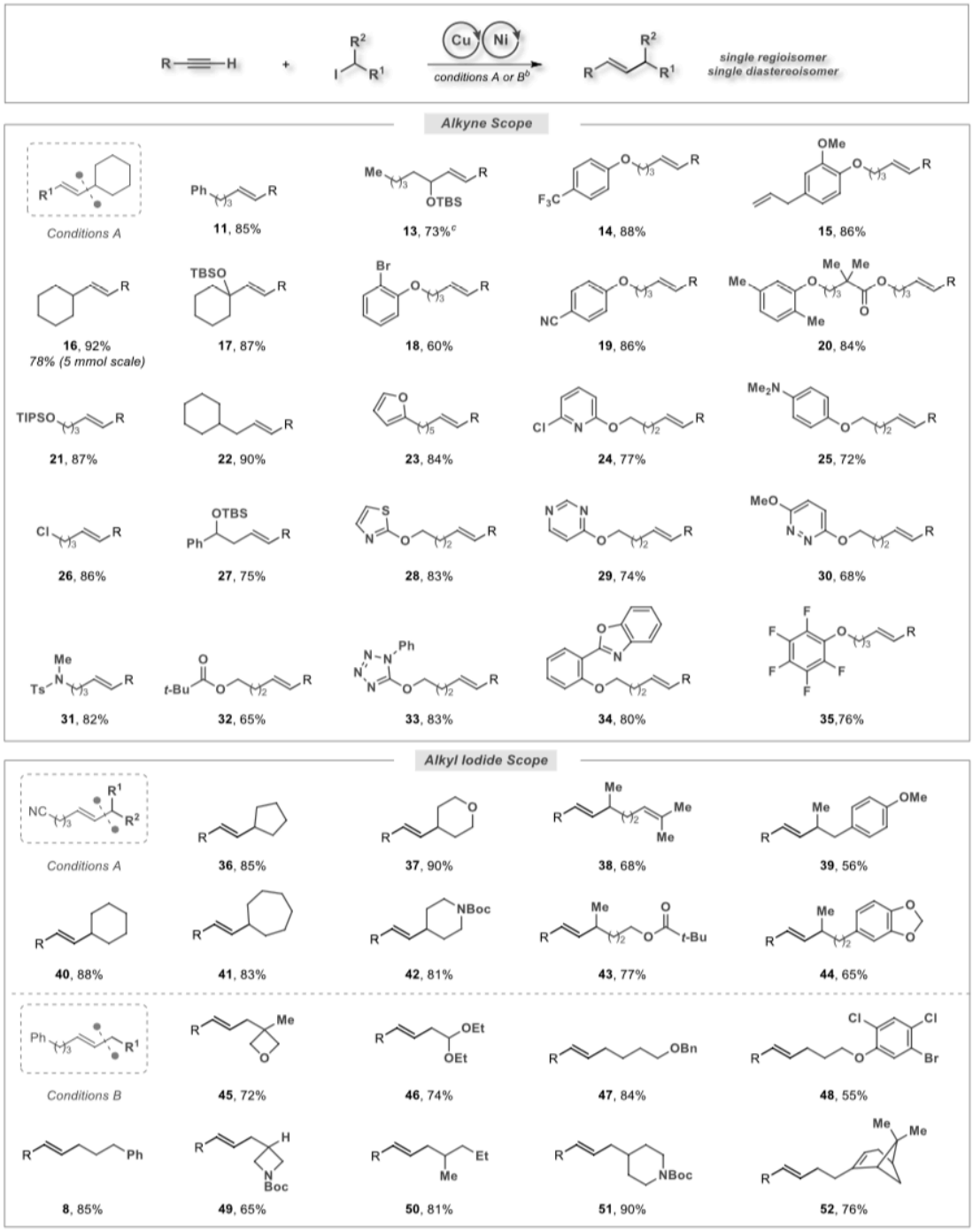
entry	*change from standard conditions*	*yield*
1.	none	90%
2.	IPrCuCl *instead of* SIPrCuCl	43%
3.	DME *instead of* DME/isooctane	58%
4.	1.5 equiv of LiO*i*-Pr *instead of* 2.0 equiv	67%
5.	5 mol% (tpy')NiI *instead of* 3 mol%	68%

1.3 Reaction Scope

Using the optimized reaction conditions, this reaction could be applied to a wide range of terminal alkynes and alkyl iodides. All products were obtained as a single regioisomer and a single diastereoisomer. A wide range of terminal alkynes with various function groups can be successfully used, including nitriles (**19**), esters (**20**), aryl ethers (**15**), silyl ethers (**13**, **17**, **21**, and **27**), alkenes (**15**), alkyl chlorides (**26**), sulfonamides (**31**), dialkyl anilines (**25**), and aryl bromides (**18**). We can also tolerate propargylic(**13**), homopropargylic(**27**) and sterically hindered propargylic(**17**) substituted alkynes. In addition, we were also able to tolerate a wide range of heteroarenes including furans (**23**), 2-chloro-pyridines (**24**), pyridazines (**30**), thiazoles (**28**), pyrimidines (**29**), tetrazoles

(**33**), and benzoxazoles (**34**)(Table 1.3) .We found that heterocycles that were less basic than pyridine were tolerated.

Table 1.3 Substrate scope of alkyne and primary and secondary iodide coupling partners



[a]Yields of isolated products are reported. Reactions performed on 0.5 mmol scale. [b]Conditions A: see Table 1, entry 1. Conditions B: see Table 3, entry 1.[c]The product was isolated as a free alcohol after TBS deprotection.

After examining the terminal alkynes, we then explored the substrate scope of secondary and primary alkyl iodides. We found that 5 through 7 membered cyclic secondary alkyl iodides (**36, 40, 41**) performed well, other acyclic alkyl iodides also worked although the yields were lower. For primary alkyl iodides, we used the re-newly optimized conditions and were able to achieve hydroalkylation using -branched (**46**, **49**, **50**, and **51**), neopentyl-like alkyl iodide (**45**) and electrophiles with heteroatoms in the α-position (**46**)(Table 1.3).

We noticed a few limitations of our hydroalkylation reaction being that protic functional groups such as hydroxyl and amino, reducible groups such as aldehydes and activated alkenes and tertiary alkyl iodides are not compatible with our optimized reaction conditions.

1.4 Conclusion

Using a dual synergistic catalytic system, we have developed a new method for the synthesis of E-alkenes. This reaction produces E-alkene products as a single regio- and diastereoisomer. This reaction has a wide substrate scope and can be used with terminal alkynes in combination with primary and secondary alkyl iodides. The reaction tolerates a wide range of functional groups and can be successfully performed in the presence of nitriles, esters, aryl ethers, silyl ethers, alkenes, alkyl chlorides, sulfonamides, carbamates, dialkyl anilines, aryl bromides, and a wide range of heteroaromatic compounds. Overall, our method provides a significant addition to existing methods for the synthesis of E-alkenes.

1.5 Experimental

1.5.1 General and Materials

General*:* All reactions were performed under a nitrogen atmosphere with flame-dried or oven-dried (120 °C) glassware, using standard Schlenk techniques, or in a glovebox (Nexus II from Vacuum Atmospheres). Column chromatography was performed using a Biotage Iso-1SV flash purification system with silica gel from Agela Technologies Inc. (60Å, 40-60 μm, 230-400 mesh. Infrared (IR) spectra were recorded on a Perkin Elmer Spectrum RX I spectrometer. IR peak absorbencies are represented as follows: s = strong, m = medium, w = weak, br = broad. ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker AV-300 or AV-500 spectrometer. ^{1}H NMR chemical shifts (δ) are reported in parts per million (ppm) downfield of TMS and are referenced relative to residual solvent peak ($CDCl_3$ (7.26 ppm), or C_6D_6 (7.16 ppm)). ^{13}C chemical shifts are reported in parts per million downfield of TMS and are referenced to the carbon resonance of the solvent ($CDCl_3$: δ 77.2 ppm, C_6D_6: δ 128.1 ppm). Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, hept = heptet, m = multiplet), integration, and coupling constants in Hertz (Hz). GC analysis was performed on a Shimadzu GC-2010 instrument with a flame ionization detector and a SHRXI-5MS column (15 m, 0.25 mm inner diameter, 0.25 μm film thickness). The following temperature program was used: 2 min @ 60 °C, 13 °C/min to 160 °C, 30 °C/min to 250 °C, 5.5 min @ 250 °C

Materials*:* THF, CH_2Cl_2, acetonitrile, DME, and toluene were degassed and dried by passing through columns of neutral alumina. 1,4-dioxane was distilled over calcium hydride, degassed, and stored over 3Å (1-2 mm beads) molecular sieves. Isooctane, chlorobenzene, DCE and heptane were degassed and stored over 3Å (1-2 mm beads) molecular sieves. Deuterated solvents were purchased from Cambridge Isotope

Laboratories, Inc. and used as received. Commercial reagents were purchased from Sigma-Aldrich, TCI America, GFS-Chemicals, and AK-Scientific. Nitrogen and phosphine-based ligands were purchased from Sigma Aldrich. NHC ligand was synthesizes from known procedure. Nickel (I) pre-catalyst was synthesized using known literature procedure.[20] Ph_3SiH was purchased from Sigma Aldrich and recrystallized from dry methanol. All commercial alkynes were distilled over $NaBH_4$ and stored over 3Å (1-2 mm beads) molecular sieves. Purchased alkyl iodides (liquid) were distilled over sodium thiosulfate and stored under nitrogen.

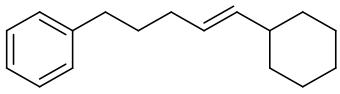
1.5.2 General Procedure for Hydroalkylation of Alkyne with Secondary Iodide

In a nitrogen-filled glovebox, a scintillation vial was charged with a stir bar, Li*O*-*i*-Pr (49.5 mg, 0.75 mmol, 1.5 equiv), IPrCuCl (24.5 mg, 0.050 mmol, 0.10 equiv) and DME (2.0 mL). Ph_3SiH (65.1 mg, 0.25 mmol, 2.5 equiv) and alkyne (0.5 mmol, 1.0 equiv) were added to this solution respectively using 1 mL of DME. The reaction mixture was stirred at 25 °C until the yellow color disappeared. Secondary alkyl iodide (0.75 mmol, 1.5 equiv) and (tpy′)NiI (14.5 mg, 0.025 mmol, 0.05 equiv) were transferred to the reaction mixture by using 2 mL of DME. The reaction mixture was stirred at 25 °C for 2 hours. After 2 hours, 2-Aminoethanol, or ammonium fluoride in methanol were added to quench the unreacted silane (caution: gas evolution). The reaction mixture was filtered through a pad of silica gel and washed with EtOAc and DCM. The filtrate was concentrated under reduced pressure and purified by silica gel chromatography

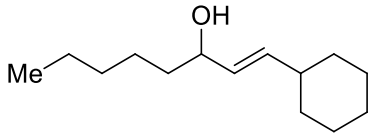
1.5.3 General Procedure for Hydroalkylation of Alkyne with Primary Alkyl Iodide

In a nitrogen-filled glovebox, scintillation vial was charged with a stir bar, LiO*i*-Pr (66.0 mg, 1.0 mmol, 2.0 equiv), SIPrCuCl (24.5 mg, 0.050 mmol, 0.10 equiv) and DME/isooctane (1:1) (2.0 mL). Ph_3SiH (65.1 mg, 0.25 mmol, 2.5 equiv) and alkyne (0.5 mmol, 1.0 equiv) were added to this solution respectively using 1 mL of DME/isooctane. The reaction mixture was stirred at 25 °C until the yellow color disappeared. Primary alkyl iodide (0.75 mmol, 1.5 equiv) and (tpy′)NiI (14.5 mg, 0.015 mmol, 0.03 equiv) were transferred to the reaction mixture by using 2 mL of DME/isoocane. The reaction mixture was stirred at 25 °C for 2 hours. After 2 hours, 2-Aminoethanol, or ammonium fluoride in methanol were added to quench the unreacted silane (caution: gas evolution). The reaction mixture was filtered through a pad of silica gel and washed with EtOAc and DCM. The filtrate was concentrated under reduced pressure and purified by silica gel chromatography

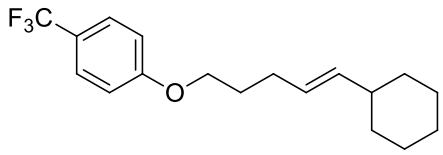
1.5.4 Characterization Data for Products of Hydroalkylation Reaction



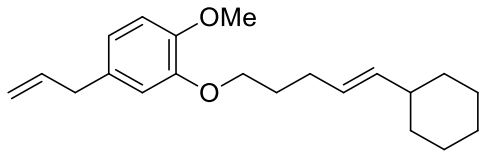
(E)-(5-cyclohexylpent-4-en-1-yl)benzene (11) compound was isolated as a colorless liquid (97.0 mg, 85% yield) ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 – 7.29 (m, 2H), 7.30 – 7.17 (m, 3H), 5.85 – 4.83 (m, 2H), 2.91 – 2.48 (m, 2H), 2.19 – 1.87 (m, 3H), 1.87 – 1.58 (m, 7H), 1.45 – 0.98 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.9, 137.2, 128.6, 128.4, 127.3, 125.7, 40.9, 35.5, 33.5, 32.3. 31.5, 26.4, 26.3. GCMS (EI) calculated for $[M]^+$ 228.19, found 228.20. FTIR (neat, cm-1): 3024 9 (m), 2922 (s), 2850 (s), 1604 (w), 1495 (m), 1448 9m), 1029 (w), 967 (s), 891 (w), 744 (m), 697 (s).



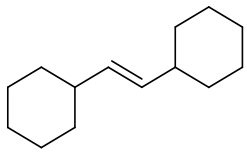
(E)-1-cyclohexyloct-1-en-3-ol (13) compound was isolated as a colorless liquid (76.7 mg, 73% yield) ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.58 (dd, *J* = 15.5, 6.6 Hz, 1H), 5.40 (ddd, *J* = 15.5, 7.0, 1.1 Hz, 1H), 4.02 (q, *J* = 6.6 Hz, 1H), 2.02 – 1.83 (m, 1H), 1.89 – 1.29 (m, 14H), 1.25 –1.00 (5H), 0.88 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.9, 130.7, 73.5, 40.4, 37.5, 33.1, 33.0, 31.9, 26.3, 26.1, 25.3, 22.7, 14.1. GCMS (EI) calculated for $[M]^+$ 210.20, found 210.20. FTIR (neat, cm-1): 3344 (b), 2923 (s), 2851(s), 1666 (w), 1448 (s), 1377 (w), 1302 (w), 1259 (w), 1129 (w), 1021 (m), 967 (s), 916 (w), 892 (w), 842 (w), 725 (w).



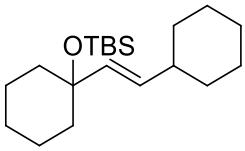
(E)-1-((5-cyclohexylpent-4-en-1-yl)oxy)-4-(trifluoromethyl)benzene (14) compound was isolated as a colorless liquid (137. 4 mg, 88% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.2 Hz, 2H), 6.94 (d, *J* = 8.2 Hz, 2H), 5.53 – 5.28 (m, 2H), 3.99 (t, *J* = 6.1 Hz, 2H), 2.31 – 2.04 (m, 2H), 2.00 – 1.77 (m, 3H), 1.77 – 1.57 (m, 5H), 1.38 – 0.90 (m, 5H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.8, 137.9, 127.0 (q, *J* = 3.6 Hz), 126.3, 124.7 (q, *J* = 270.9 Hz), 122.8 (q, *J* = 32.8 Hz), 114.6, 67.6, 40.8, 33.4, 29.1, 29.0, 26.4, 26.3. ^{19}F NMR (470 MHz, $CDCl_3$) δ -64.39. GCMS (EI) calculated for $[M]^+$ 312.17 , found 312.20. FTIR (neat, cm-1): 3011(w), 2926 (s), 2852 (s), 2361 (w), 1617 (s), 1589 (s), 1519 (s), 1330 (s), 1258 (s0, 1161 (s), 1110 (s), 1068 (s), 1009 (s), 968 (m), 835 (s).



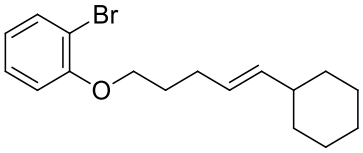
(E)-4-allyl-2-((5-cyclohexylpent-4-en-1-yl)oxy)-1-methoxybenzene (15) compound was isolated as a colorless liquid (135.1mg, 86% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.81 (d, *J* = 8.7 Hz, 1H), 6.76 – 6.67 (m, 2H), 5.96 (ddt, *J* = 16.8, 10.1, 6.7 Hz, 1H), 5.47 – 5.33 (m, 2H), 5.16 – 4.99 (m, 2H), 3.99 (t, *J* = 6.8 Hz, 2H), 3.85 (s, 3H), 3.33 (d, *J* = 6.7 Hz, 2H),2.20 – 2.07 (m, 2H) 1.98 – 1.80 (m, 3H), 1.77 – 1.59 (m, 5H), 1.33 – 0.93 (m, 5H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.5, 147.1, 137.9, 137.5, 132.8, 126.6, 120.6, 115.7, 113.4, 112.5, 68.7, 56.1, 40.8, 39.9, 33.3, 29.2, 29.1, 26.4, 26.2. GCMS (EI) calculated for $[M]^+$ 314.22, found 314.30. FTIR (neat, cm-1): 2999 (w), 2922 (s), 2849 (s), 1638 (m), 1605 (m), 1512 (s), 1465 (s), 1419 (s), 1335 (w), 1260 (s), 1232 (s), 1156 (s), 1139 (s), 1037 (s), 993 (m), 968 (m), 911 (s), 848 (m), 802 (m).



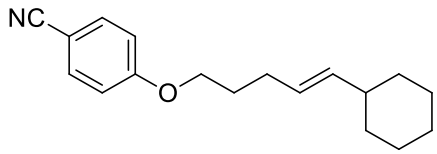
(E)-1,2-dicyclohexylethene (16) compound was isolated as a colorless liquid (88.4 mg, 92% yield) ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.32 (d, *J* = 1.9 Hz, 2H), 1.96 – 1.82 (m, 2H), 1.80 – 1.59 (m, 10H), 1.35 – 0.98 (m, 10H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 133.9, 40.9, 33.6, 26.5, 26.3. GCMS (EI) calculated for $[M]^+$ 192.19, found 192.20. FTIR (neat, cm-1): 3009 (w), 2920 (s), 2850 (s), 1447 (s), 1258 (m), 967 (s), 889 (s), 843 (m).



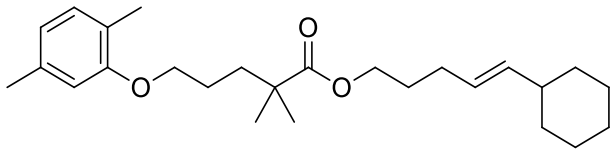
(E)-tert-butyl((1-(2-cyclohexylvinyl)cyclohexyl)oxy)dimethylsilane (17) compound was isolated as a colorless liquid (140.2 mg, 87% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.51 – 5.40 (m, *J* = 4.2 Hz, 2H), 1.74 – 0.98 (m, 21H), 0.88 (s, 9H), 0.02 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.7, 133.9, 73.3, 40.8, 38.6, 33.0, 26.4, 26.3, 26.2, 26.2, 22.4, 18.5, -1.7 GCMS (EI) calculated for $[M]^+$ 322.27, found 322.30. FTIR (neat, cm-1): 2926 (s), 2853 (s), 1640 (w), 1583 (w), 1462 (s), 1449 (s), 1358 (m), 1250 (s), 1148 (m), 1048 (s), 1022 (s), 977 (w), 898 (w), 834 (s), 772 (s).



(E)-1-bromo-2-((5-cyclohexylpent-4-en-1-yl)oxy)benzene (18) compound was isolated as a colorless liquid (96.6 mg, 60% yield) ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 – 7.49 (m, 1H), 7.30 – 7.19 (m, 1H), 6.92 – 6.76 (m, 2H), 5.54 – 5.26 (m, 2H), 4.02 (t, *J* = 6.1 Hz, 2H), 2.32 – 2.09 (m, 2H), 2.03 – 1.82 (m, 3H), 1.80 – 1.58 (m, 5H), 1.38 – 0.90 (m, 5H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.6, 137.7, 133.4, 128.4, 126.4, 121.7, 113.4, 112.4, 68.5, 40.8, 33.3, 29.1, 29.0, 26.3, 26.2. GCMS (EI) calculated for $[M]^+$ 322.09, found 322.10. FTIR (neat, cm-1): 3065 (m), 3035 (m), 2922 (s), 2850 (s), 2361 (w), 2341 (w), 1688 (w), 1589 (s), 1564 (s), 1481 (s), 1443 (s), 138 (m), 1277 (s), 1249 (s), 1161 (m), 1125 (s), 1052 (s), 1031 (s), 969 (s), 926 (w), 892 (w), 745 (s), 677 (s).

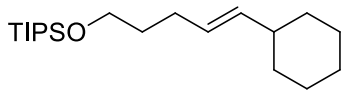


(E)-4-((5-cyclohexylpent-4-en-1-yl)oxy) (19) compound was isolated as a colorless liquid (115.7 mg, 86% yield) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 5.55 – 4.97 (m, 2H), 3.98 (t, *J* = 6.5 Hz, 2H), 2.32 – 1.97 (m, 2H), 1.94 – 1.78 (m, 3H), 1.72 – 1.57 (m, 5H), 1.31 – 0.93 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.5, 137.9, 134.0, 126.0, 119.3, 115.3, 103.8, 67.7, 40.7, 33.3, 28.9, 26.3, 26.1. GCMS (EI) calculated for $[M]^+$ 269.18, found 269.20. FTIR (neat, cm-1): 3115 (w), 2924 (s), 2850 (s), 2225 (s), 1772 (w), 1653 (s), 1600 (s), 1576 (w), 1507 (s), 1473 (w), 1448 (m), 1301 (m), 1264 (s), 1171 (s), 970 (m), 835 (s), 738 (s), 703 (s).

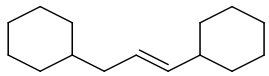


(E)-5-cyclohexylpent-4-en-1-yl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (20) compound was isolated as a colorless liquid (168.1 mg, 84% yield) ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.00 (d, *J* = 7.3 Hz, 1H), 6.65 (d, *J* = 7.3 Hz, 1H), 6.61 (s, 1H), 5.45 – 5.26 (m, 2H), 4.05 (t, *J* = 6.6 Hz, 2H), 3.92 (t, *J* = 4.7 Hz, 2H), 2.30 (s, 3H), 2.17 (s, 3H), 2.10 – 2.00 (m, 2H), 1.97 – 1.80 (m, 1H), 1.80 – 1.57 (m, 11H), 1.36 – 0.90 (m, 11H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.8, 157.1, 137.7, 136.5, 130.4, 126.1, 123.7, 120.8, 112.0, 68.0, 63.9, 42.2, 40.8, 37.2, 33.3, 29.0, 28.7, 26.3, 26.2, 25.3, 21.5, 15.9. GCMS (EI) calculated for $[M]^+$ 400.09, found 400.10. FTIR (neat, cm-1): 3091 (m), 3036 (m), 2924 (s), 2851

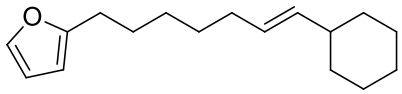
(s), 1958 (w), 1726 (s), 1615 (s), 1586 (s), 1509 (s), 1474 (s), 1448 (s), 1391 (s), 1265 (s), 1192 (s), 1147 (s), 1049 (s), 969 (s), 893 (m), 802 (s), 677 (s).



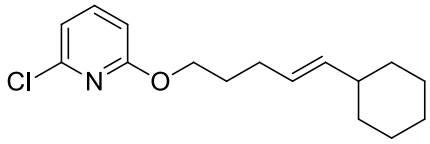
(E)-((5-cyclohexylpent-4-en-1-yl)oxy)triisopropylsilane (21) compound was isolated as a colorless liquid (141.1 mg, 87% yield) ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.46 – 5.16 (m, 2H), 3.67 (t, *J* = 6.5 Hz, 2H), 2.13 – 1.98 (m, 2H), 1.97 – 1.82 (m, 1H), 1.77 – 1.54 (m, 7H), 1.32 – 0.98 (m, 26H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.9, 127.3, 63.0, 40.9, 33.4, 33.1, 29.0, 26.4, 26.3, 18.2, 12.2. GCMS (EI) calculated for $[M]^+$ 324.28, found 324.40. FTIR (neat, cm-1): 3017 (w), 2923 (s), 2864 (s), 1463 (s), 1448 (s), 1382 (m), 1349 (w), 1247 (m), 1108 (s), 1069 (s), 1013 (s), 967 (s), 882 (s), 725 (s), 680 (s).



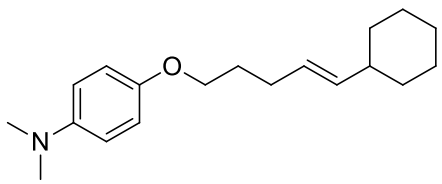
(E)-prop-1-ene-1,3-diyldicyclohexane (22) compound was isolated as a colorless liquid (92.8 mg, 90% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.58 – 5.02 (m, 2H), 1.97 – 1.75 (m, 3H), 1.77 – 1.58 (m, 10H), 1.38 – 0.79 (m, 11H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.6, 126.3, 41.0, 40.9, 38.4, 33.5, 33.3, 26.9, 26.6, 26.5, 26.3. GCMS (EI) calculated for [M]+ 206.20, found 206.20. FTIR (neat, cm-1): 2921 (s), 2850 (s), 1448 (s), 966 (s), 891 (w). 840 (w).



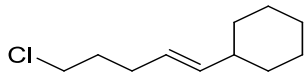
(E)-2-(7-cyclohexylhept-6-en-1-yl)furan (23) compound was isolated as a colorless liquid (103.4 mg, 84% yield) ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29 (d, *J* = 0.8 Hz, 1H), 6.30 – 6.23 (m, 1H), 5.97 (d, *J* = 2.4 Hz, 1H) 5.45 – 5.21 (m, 2H), 2.62 (t, *J* = 7.5 Hz, 2H), 2.07 – 1.83 (m, 3H), 1.77 – 1.55 (m, 7H), 1.47 – 0.93 (m, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.7, 140.8, 136.7, 127.7, 110.2, 104.7, 40.8, 33.5, 32.6, 29.5, 28.8, 28.1, 28.1, 26.4, 26.3. GCMS (EI) calculated for $[M]^+$ 246.20, found 246.20. FTIR (neat, cm-1): 3012 (w), 2923 (s), 2851 (s), 1710 (m), 1596 (m), 1508 (m), 1448 (s), 1349 (w), 1147 (s), 1006 (s), 967 (s), 725 (s).



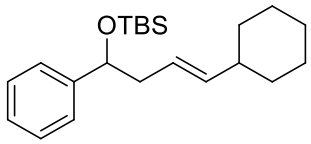
(E)-2-chloro-6-((5-cyclohexylpent-4-en-1-yl)oxy)pyridine (24) compound was isolated as a colorless liquid (107.5 mg, 77% yield) ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (t, *J* = 7.8 Hz, 1H), 6.87 (d, *J* = 7.8 Hz, 1H), 6.63 (d, *J* = 7.8 Hz, 1H), 5.49 – 5.10 (m, 2H), 4.28 (t, *J* = 6.6 Hz, 2H), 2.13 (dd, *J* = 11.7, 7.2 Hz, 2H), 1.96 – 1.55 (m, 8H), 1.41 – 0.94 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.9, 148.5, 140.6, 137.5, 126.5, 116.1, 109.2, 66.2, 40.8, 33.3, 29.1, 29.0, 26.4, 26.2. GCMS (EI) calculated for $[M]^+$ 279.14, found 279.10. FTIR (neat, cm-1): 2922 (s), 1849 (s), 1590 (s), 1559 (s), 1466 (m), 1442 (s), 1407 9s), 1379 (s), 1300 (s), 1262 (s), 1159 (s), 1072 (m), 1011 (m), 948 (s), 787 (s).



(E)-4-((5-cyclohexylpent-4-en-1-yl)oxy)-N,N-dimethylaniline (25) compound was isolated as a colorless liquid (103.4 mg, 72% yield) ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.84 (d, *J* = 9.0 Hz, 2H), 6.74 (d, *J* = 9.0 Hz, 2H), 5.52 – 5.28 (m, 2H), 3.90 (t, *J* = 6.5 Hz, 2H), 2.86 (s, 6H), 2.19 – 2.08 (m, 2H), 1.99 – 1.75 (m, 3H), 1.75 – 1.57 (m, 5H), 1.36 – 0.95 (m, 5H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.6, 145.8, 137.3, 126.6, 115.6, 115.0, 68.0, 41.9, 40.8, 33.3, 29.4, 29.1, 26.3, 26.2. GCMS (EI) calculated for $[M]^+$ 287.22, found 280.10. FTIR (neat, cm-1): 3017 (w), 2922 (s), 2850 (s), 1640 (w), 1514 (s), 1478 (m), 1469 (m), 1244 (s), 1056 (w), 967 (m), 815 (s).

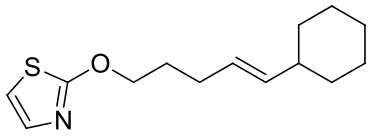


(E)-(5-chloropent-1-en-1-yl)cyclohexane (26) compound was isolated as a colorless liquid (80.0 mg, 86% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.47 – 5.26 (m, 2H), 3.52 (t, *J* = 6.8 Hz, 2H), 2.12 (q, *J* = 6.8 Hz, 2H), 1.95 – 1.86 (m, 1H), 1.81 (p, *J* = 6.8 Hz, 2H), 1.74 – 1.59 (m, 5H), 1.31 – 1.00 (m, 5H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.2, 126.0, 44.5, 40.8, 33.3, 32.6, 29.8, 26.4, 26.2. GCMS (EI) calculated for $[M]^+$ 186.12, found 186.10. FTIR (neat, cm-1): 2989 (m), 2922 (s), 2849 (s), 1447 (s), 1349 (w), 1299 (m), 1288 (m), 969 (s), 892 (m), 842 (m), 726 (m).

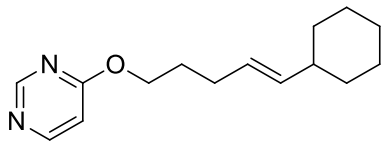


(E)-tert-butyl((4-cyclohexyl-1-phenylbut-3-en-1-yl)oxy)dimethylsilane (27) compound was isolated as a colorless liquid (129.1 mg, 75% yield) ^{1}H NMR (500 MHz,

$CDCl_3$) δ 7.31 – 7.27 (m, 4H), 7.25 – 7.18 (m, 1H), 5.40 – 5.28 (m, 2H), 4.62 (dd, *J* = 7.4, 5.1 Hz, 1H), 2.40 – 2.32 (m, 1H), 2.31 – 2.24 (m, 1H), 1.92 – 1.83 (m, 1H), 1.73 – 1.59 (m, 5H), 1.31 – 1.19 (m, 2H), 1.19 – 1.10 (m, 1H), 1.07 – 0.96 (m, 2H), 0.88 (s, 9H), 0.02 (s, 3H), -0.13 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.6, 139.1, 128.0, 126.9, 126.1, 124.1, 75.7, 44.6, 40.9, 33.2, 26.4, 26.3, 26.0, 18.4, -4.5, -4.7. GCMS (EI) calculated for $[M]^+$ 344.25, found 344.20. FTIR (neat, cm-1): 3028 (m), 2927 (s), 2854 (s), 1602 (w), 1493 (w), 1462 (m), 1450 (s), 1388 (w), 1361 (m), 1256 (s), 1089 (s), 1069 (s), 970 (m), 939 (w), 836 (s), 775 (s), 699 (s).

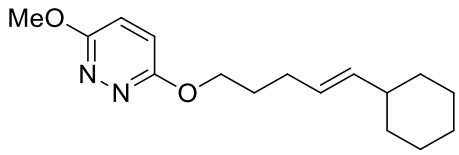


(E)-2-((5-cyclohexylpent-4-en-1-yl)oxy)thiazole (28) compound was isolated as a colorless liquid (104.2 mg, 83% yield) ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.09 (d, *J* = 3.4 Hz, 1H), 6.63 (d, *J* = 3.4 Hz, 1H), 5.58 – 5.11 (m, 2H), 4.37 (t, *J* = 6.4 Hz, 2H), 2.12 (dd, *J* = 12.6, 6.6 Hz, 2H), 1.98 – 1.76 (m, 3H), 1.76 – 1.56 (m, 5H), 1.33 – 0.92 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.4, 137.8, 137.0, 126.0, 110.8, 71.3, 40.7, 33.3, 28.9, 26.3, 26.2. GCMS (EI) calculated for $[M]^+$ 251.13, found 251.20. FTIR (neat, cm-1): 2922 (s), 2849 (s), 1610 (w), 1522 (s), 1482 (m), 1464 (s), 1381 (m). 1308 9s), 1237 (s), 1213 (s), 1162 (s), 968 (s), 700 (s).

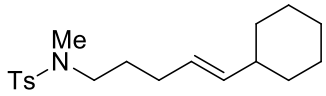


(E)-4-((5-cyclohexylpent-4-en-1-yl)oxy)pyrimidine (29) compound was isolated as a colorless liquid (91.1 mg, 74% yield) ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.76 (s, 1H), 8.41 (d,

J = 5.7 Hz, 1H), 6.71 (d, *J* = 5.7 Hz, 1H), 5.64 – 5.05 (m, 2H), 4.35 (t, *J* = 6.6 Hz, 2H), 2.27 – 1.90 (m, 2H), 2.04 – 1.74 (m, 3H), 1.76 – 1.57 (m, 65), 1.34 – 0.96 (m, 5H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.3, 158.6, 157.1, 137.8, 126.2, 108.8, 66.1, 40.8, 33.3, 29.0, 28.8, 26.4, 26.2. GCMS (EI) calculated for $[M]^+$ 246.17, found 246.20. FTIR (neat, cm-1): 3100 (w), 2956 (s), 2850 (s), 1612 (w), 1582 (s), 1560 (s), 1480 (s), 1464 (s), 1399 (m), 1375 (m), 1264 (s), 986 (s), 835 (s), 742 (s).

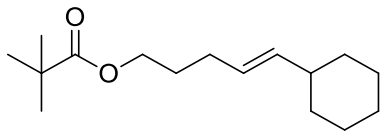


(E)-3-((5-cyclohexylpent-4-en-1-yl)oxy)-6-methoxypyridazine (30) compound was isolated as a colorless liquid (93.9 mg, 68% yield) ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.89 (s, 2H), 5.49 – 5.26 (m, 2H), 4.39 (t, *J* = 6.6 Hz, 2H), 4.03 (s, 3H), 2.22 – 2.01 (m, 2H), 2.01 – 1.73 (m, 3H), 1.73 – 1.51 (m, 5H), 1.35 – 0.87 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.1, 161.9, 137.5, 126.5, 121.6, 121.3, 66.8, 54.6, 40.7, 33.3, 29.1, 29.0, 26.3, 26.2. GCMS (EI) calculated for $[M]^+$ 276.18, found 276.20. FTIR (neat, cm-1): 3064 (m), 2921 (s), 2849 (s), 1613 (w), 1548 (w), 1470 (s), 1449 (s), 1424 (s), 1388 (s), 1339 (w), 1267 (s), 1099 (w), 1015 (s), 969 (s), 846 (s), 790 (m).

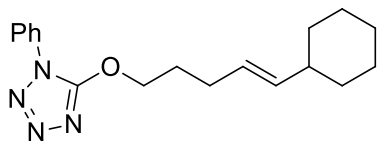


(E)-N-(5-cyclohexylpent-4-en-1-yl)-N,4-dimethylbenzenesulfonamide (31) compound was isolated as a colorless liquid (137.4 mg, 82% yield) ^{1}H NMR (500 MHz, $CDCl_3$) δ

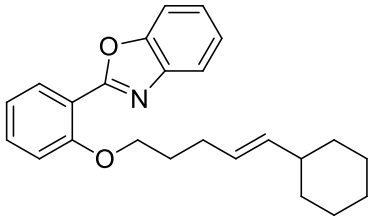
7.66 (d, *J* = 7.9 Hz, 2H), 7.31 (d, *J* = 7.9 Hz, 2H), 5.45 – 5.20 (m, 2H), 2.96 (t, *J* = 7.3 Hz, 2H), 2.70 (s, 3H), 2.43 (s, 3H), 2.10 – 1.92 (m, 2H), 1.94 – 1.76 (m, 1H), 1.73 – 1.51 (m, 7H), 1.30 – 0.88 (m, 5H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.2, 137.6, 134.6, 129.6, 127.4, 126.1, 49.7, 40.7, 34.7, 33.2, 29.6, 27.6, 26.2, 26.1, 21.5. GCMS (EI) calculated for $[M]^+$ 335.19, found 335.10. FTIR (neat, cm-1): 3439 (w), 3064, (w), 3012 (w), 2922 (s), 2849 (s), 1622 (w), 1597 (s), 1493 (m), 1448 (s), 1398 (w), 1374 (w), 1341 (s), 1304 (m), 1161 (s), 1118 (m), 1090 (s), 1019 (m), 968 (s), 801 (s), 739 (s), 715 (s), 700 (s), 652 (s).



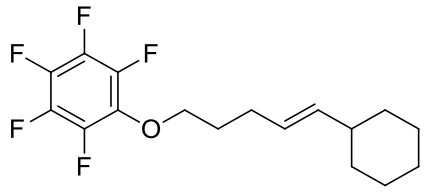
(E)-5-cyclohexylpent-4-en-1-yl pivalate (32) compound was isolated as a colorless liquid (82.0 mg, 65% yield) ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.46 – 5.27 (m, 2H), 4.04 (t, *J* = 6.6 Hz, 2H), 2.14 – 1.97 (m, 2H), 1.98 – 1.80 (m, 1H), 1.79 – 1.59 (m, 7H), 1.34 – 0.95 (m, 14H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.7, 137.7, 126.2, 63.9, 40.8, 38.9, 33.3, 29.0, 28.7, 27.3, 26.3, 26.2. GCMS (EI) calculated for $[M]^+$ 252.21, found 252.20. FTIR (neat, cm-1): 3441 (w), 3092 (w), 3056 (w), 2925 (s), 2851 (s), 1731 (s), 1481 (s), 1448 (s), 1397 (s), 1365 (s), 1283 (s), 1156 (s), 1036 (s), 969 (s), 892 (m), 771 (s), 677 (s).



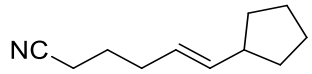
(E)-5-((5-cyclohexylpent-4-en-1-yl)oxy)-1-phenyl-1H-tetrazole (33) compound was isolated as a colorless liquid (129.6 mg, 83% yield) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.1 Hz, 2H), 7.56 – 7.50 (m, 2H), 7.49 – 7.41 (m, 1H), 5.45 – 5.28 (m, 2H), 4.64 (t, *J* = 6.5 Hz, 2H), 2.21 – 2.08 (m, 2H), 2.02 – 1.78 (m, 3H), 1.75 – 1.55 (m, 5H), 1.33 – 0.94 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.3, 138.2, 133.6, 129.6, 128.8, 125.4, 121.5, 73.6, 40.6, 33.1, 28.6, 26.2, 26.1. GCMS (EI) calculated for $[M]^+$ 312.20, found 312.20. FTIR (neat, cm-1): 3065 (w), 3024 (w), 2922 (s), 2849 (s), 1612 (w), 1595 (s), 1560 (s), 1505 (s), 1447 (s), 1381 (s), 1349 (w), 1331 (w), 1294 (s), 1127 (s), 1094 (s), 1071 (s), 1020 (s), 968 (s), 911 (s), 758 (s), 696 (m), 685 (s).



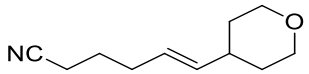
(E)-2-(2-((5-cyclohexylpent-4-en-1-yl)oxy)phenyl)benzo[d]oxazole (34) compound was isolated as a colorless liquid (128.5 mg, 80% yield) ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.80 (dd, *J* = 6.3, 2.8 Hz, 1H), 7.58 (dd, *J* = 6.3, 2.8 Hz, 1H), 7.50 – 7.44 (m, 1H), 7.39 – 7.31 (m, 2H), 7.12 – 7.02 (m, 2H), 5.66 – 5.00 (m, 2H), 4.14 (t, *J* = 6.4 Hz, 2H), 2.40 – 2.08 (m, 2H), 2.08 – 1.76 (m, 3H), 1.78 – 1.59 (m, 5H), 1.36 – 0.92 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.4, 158.2, 150.9, 142.1, 137.7, 132.7, 131.6, 126.5, 124.8, 124.3, 120.7, 120.1, 116.9, 113.6, 110.5, 68.5, 40.7, 33.3, 29.2, 29.0, 26.3, 26.2. GCMS (EI) calculated for $[M]^+$ 361.20, found 361.20. FTIR (neat, cm-1): 2923 (s), 2849(m), 1645(w), 1600(w), 1548(w), 1537(w), 1492(w), 1452(s), 1310(w), 1034(w), 968 (s), 909(s), 749(s).



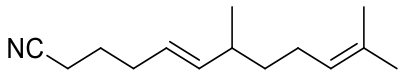
(E)-1-((5-cyclohexylpent-4-en-1-yl)oxy)-2,3,4,5,6-pentafluorobenzene (35) compound was isolated as a colorless liquid (127.0 mg, 76% yield) ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.48 – 5.25 (m, 2H), 4.14 (t, *J* = 6.4 Hz, 2H), 2.22 – 2.10 (m, 2H), 2.00 – 1.76 (m, 3H), 1.76 – 1.59 (m, 5H), 1.37 – 0.93 (m, 5H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.0 (d, *J* = 238.7 Hz), 138.2 (d, *J* = 247.9 Hz), 138.2, 137.4 (d, *J* = 246.7 Hz), 134.1, 125.9, 75.1, 40.9, 33.4, 29.9, 28.6, 26.4, 26.3. ^{19}F NMR (470 MHz, $CDCl_3$) δ -159.81 (d, *J* = 20.3 Hz), -166.56 (t, *J* = 20.5 Hz), -166.93 (t, *J* = 21.8 Hz). GCMS (EI) calculated for $[M]^+$ 334.14, found 334.20. FTIR (neat, cm-1): 3079 (w), 3038 (w), 2925 (s), 2852 (s), 1814 (w), 1638 (w), 1512 (s), 1482 (s), 1449 (s), 1313 (m), 1160 (s), 1031 (s), 996 (s), 893 (w), 677 (s).



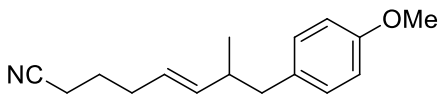
(E)-6-cyclopentylhex-5-enenitrile (36) compound was isolated as a colorless liquid (69.3 mg, 85% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.48 (dd, *J* = 15.3, 7.5 Hz, 1H), 5.38 – 5.19 (m, 1H), 2.47 – 2.23 (m, 3H), 2.14 (q, *J* = 7.0 Hz, 2H), 1.83 – 1.46 (m, 8H), 1.36 – 1.15 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.7, 125.3, 119.8, 43.3, 33.2, 31.2, 25.2, 25.1, 16.3. GCMS (EI) calculated for $[M]^+$ 163.14, found 163.20. FTIR (neat, cm-1): 3020 (w), 2950 (s), 2867 (s), 2245 (m), 1660 (w), 1452 (s), 1425 (m), 1347 (w), 968 (s), 751 (w)



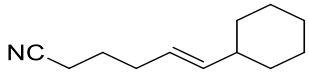
(E)-6-(tetrahydro-2H-pyran-4-yl)hex-5-enenitrile (37) compound was isolated as a colorless liquid (80.6 mg, 90% yield) ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.69 – 5.10 (m, 2H), 3.95 (dd, *J* = 11.4, 2.4 Hz, 2H), 3.40 (td, *J* = 11.6, 2.1 Hz, 2H), 2.32 (t, *J* = 7.2 Hz, 2H), 2.26 – 2.09 (m, 3H), 1.73 (p, *J* = 7.2 Hz, 2H), 1.64 – 1.51 (m, 2H).1.52 – 1.33 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.7, 125.8, 119.5, 67.5, 37.7, 32.6, 31.1, 24.9, 16.1. GCMS (EI) calculated for $[M]^+$ 179.13, found 179.10. FTIR (neat, cm-1): 3008 (w), 2931 (s), 2842 (s), 2755 (w), 2690 (w), 2244 (m), 1620 w), 1441 (s), 1386 (s), 1352 (w), 1236 (s), 1175 (w), 1128 (s), 1093 (s), 1013 (s), 980 (s), 870 (m), 819 (w).



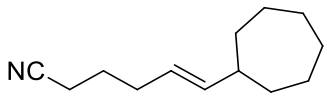
(E)-7,11-dimethyldodeca-5,10-dienenitrile (38) compound was isolated as a colorless liquid (69.8 mg, 68% yield) ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.56 – 5.15 (m, 2H), 5.07 (t, *J* = 7.2 Hz, 1H), 2.31 (t, *J* = 7.2 Hz, 2H), 2.20 – 2.02 (m, 3H), 1.92 (dd, *J* = 15.0, 7.4 Hz, 2H), 1.78 – 1.62 (m, 5H), 1.57 (s, 3H), 1.27 (dd, *J* = 15.0, 7.4 Hz, 2H), 0.95 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.0, 131.3, 125.7, 124.6, 119.7, 37.1, 36.4, 31.3, 25.9, 25.7, 25.2, 20.8, 17.7, 16.3. GCMS (EI) calculated for $[M]^+$ 205.18, found 205.20. FTIR (neat, cm-1): 3024 (w), 2960 (s), 2923 (s), 2867 (s), 2246 (m), 1695 (w), 1675 (w), 1453 (s), 1370 (s), 1111 (w), 970 (s), 829 (m), 739 (m).



(E)-8-(4-methoxyphenyl)-7-methyloct-5-enenitrile (39) compound was isolated as a colorless liquid (68.1 mg, 56% yield) ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.94 (d, *J* = 8.5 Hz, 2H), 6.72 (d, *J* = 8.5 Hz, 2H), 5.30 (dd, *J* = 15.3, 7.5 Hz, 1H), 5.16 – 4.89 (m, 1H), 3.68 (s, 3H), 2.42 (d, *J* = 7.2 Hz, 2H), 2.37 – 2.20 (m, 1H), 2.08 – 1.92 (m, 4H), 1.61 – 1.45 (m, 2H), 0.89 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.8, 138.2, 132.9, 130.1, 126.1, 119.8, 113.5, 55.2, 42.7, 38.9, 31.1, 25.0, 20.3, 15.9. GCMS (EI) calculated for $[M]^+$ 243.16, found 243.20. FTIR (neat, cm-1): 3028(m), 2954(s), 2867 (s), 2836 (m), 2245 (m), 1611 (s), 1582 (m), 1512 (s), 1454 (s), 1441 (s), 1300(s), 1246 (s), 1177 (s), 1112 (m), 1035 (s), 971 (s), 811 (s), 752 (m).

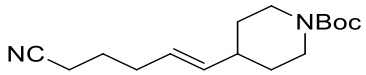


(E)-6-cyclohexylhex-5-enenitrile (40) compound was isolated as a colorless liquid (77.9 mg, 88% yield) ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.45 (dd, *J* = 15.5, 6.6 Hz, 1H), 5.27 (dt, *J* = 15.5, 6.6 Hz, 1H), 2.31 (t, *J* = 7.2 Hz, 2H), 2.13 (q, *J* = 7.2 Hz, 2H), 1.98 – 1.83 (m, 1H), 1.77 – 1.60 (m, 7H), 1.30 – 0.98 (m, 5H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.1, 124.7, 119.8, 40.7, 33.1, 31.4, 26.2, 26.1, 25.2, 16.2. GCMS (EI) calculated for $[M]^+$ 177.15, found 177.20. FTIR (neat, cm-1): 3012 (w), 2923 (s), 2849 (s), 2245 (m), 1624 (w), 1448 (s), 1425 (m), 13478 (w), 1258 (w), 970 (s), 892 (w), 842 (w), 679 (w).

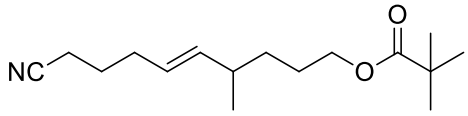


(E)-6-cycloheptylhex-5-enenitrile (41) compound was isolated as a colorless liquid (79.3 mg, 83% yield) ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.49 (ddt, *J* = 15.4, 7.3, 1.1 Hz, 1H),

5.32 – 5.16 (m, 1H), 2.31 (t, *J* = 7.2 Hz, 2H), 2.21 – 2.01 (m, 3H), 1.85 – 1.15 (m, 14H).^{13}C NMR (126 MHz, $CDCl_3$) δ 140.1, 124.1, 119.9, 42.9, 35.0, 31.4, 28.5, 26.4, 25.3, 16.4 GCMS (EI) calculated for $[M]^+$ 191.17, found191.10 . FTIR (neat, cm-1): 2924 (s), 2853 (s), 2361 (m), 2246 (w), 1603 (w), 1460 (s), 1357 (w), 968 (s).

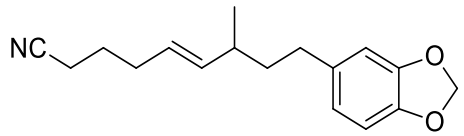


(E)-tert-butyl 4-(5-cyanopent-1-en-1-yl)piperidine-1-carboxylate (42) compound was isolated as a colorless liquid (112.7 mg, 81% yield) ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.57 – 5.12 (m, 2H), 4.03 (d, *J* = 12.2 Hz, 2H), 2.68 (t, *J* = 12.2 Hz, 2H), 2.28 (t, *J* = 7.1 Hz, 2H), 2.23 – 1.92 (m, 3H), 1.83 – 1.45 (m, 4H), 1.41 (s, 9H), 1.31 – 1.06 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.8, 136.7, 126.1, 119.6, 79.2, 44.0, 38.8, 31.8, 31.2, 28.4, 25.0, 16.2. GCMS (EI) calculated for $[M]^+$ 278.20, found 278.10. FTIR (neat, cm-1): 3020 (m), 2973 (s), 2931 (s), 2849 (s), 2245 (m), 1689 (s), 1490 (s), 1481 (s), 1445 (s), 1423 (s), 1365 (s), 1275 (s), 1232 (s), 1165 (s), 970 (s), 868 (m), 769 (m)

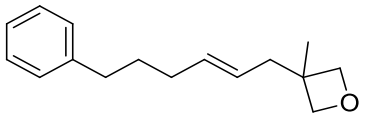


(E)-9-cyano-4-methylnon-5-en-1-yl pivalate (43) compound was isolated as a colorless liquid (102.1 mg, 77% yield) ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.54 – 5.00 (m, 2H), 4.01 (t, *J* = 6.7 Hz, 2H), 2.31 (t, *J* = 7.2 Hz, 2H), 2.23 – 1.98 (m, 3H), 1.71 (p, *J* = 7.2 Hz, 2H), 1.64 – 1.52 (m, 2H), 1.40 – 1.15 (m, 11H), 0.96 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.7, 138.5, 126.1, 119.7, 64.5, 38.8, 36.5, 33.1, 31.3, 27.3, 26.6, 25.2, 20.9, 16.4. GCMS (EI) calculated for $[M]^+$ 265.20, found 265.10. FTIR (neat, cm-1): 3012(w),

2958(s), 2246, (m), 1726 (s), 1543 (w), 1480 (s), 1455 (w), 1398 (w), 1366 (w), 1285 (s), 1159 (s), 972 (s), 771 (w), 732 (w).

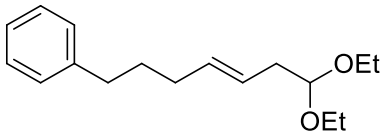


(E)-9-(benzo[d][1,3]dioxol-5-yl)-7-methylnon-5-enenitrile (44) compound was isolated as a colorless liquid (88.1 mg, 65% yield) ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.78 – 6.55 (m, 3H), 5.91 (s, 2H), 5.47 – 5.24 (m, 2H), 2.60 – 2.40 (m, 2H), 2.33 (t, *J* = 7.1 Hz, 2H), 2.22 – 2.05 (m, 3H), 1.73 (p, *J* = 7.2 Hz, 2H), 1.54 (q, *J* = 7.8 Hz, 2H), 1.00 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.6, 145.5, 138.6, 136.5, 126.2, 121.0, 119.7, 108.9, 108.1, 100.8, 39.0, 36.3, 33.5, 31.3, 25.2, 20.8, 16.3. GCMS (EI) calculated for $[M]^+$ 271.16, found 271.20. FTIR (neat, cm-1): 3071 (w), 3035 (m), 2927 (s), 1858 (s), 2776 (m), 2246 (s), 1607 (m), 1509 (s), 1489 (s), 1441 (s), 1363 (m), 1244 (s), 1188 (s), 1244 (s), 1188 (s), 1096 (m), 1039 (s), 979 (s), 937 (s), 857 (m), 810 (s), 756 (w).

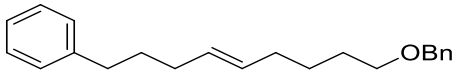


(E)-3-methyl-3-(6-phenylhex-2-en-1-yl)oxetane (45) compound was isolated as a colorless liquid (82.9 mg, 72% yield) ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 – 7.26 (m, 2H), 7.25 – 7.14 (m, 3H), 5.62 – 5.38 (m, 2H), 4.47 (d, *J* = 5.6 Hz, 2H), 4.37 (d, *J* = 5.6 Hz, 2H), 2.71 – 2.60 (m, 2H), 2.35 (d, *J* = 6.9 Hz, 2H), 2.10 (dd, *J* = 14.1, 7.0 Hz, 2H), 1.79 – 1.68 (m, 2H), 1.30 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.5, 133.6, 128.5, 128.3, 125.7, 125.7, 82.2, 42.1, 39.1, 35.4, 32.2, 31.3, 23.6. GCMS (EI) calculated for

$[M]^+$ 230.17, found 230.20. FTIR (neat, cm-1): 3061 (m), 3025 (s), 2959 (s), 2925 (s), 2859 (s), 1603 (m), 1496 (s), 1452 (s), 1436 (s), 1378 (w), 1243 (w), 1077 (w), 1030 (w), 979 (s), 906 (s), 831 (s), 746 (s).

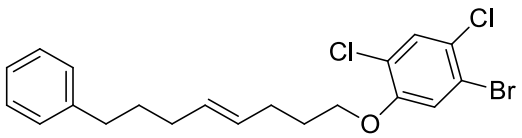


(E)-(7,7-diethoxyhept-4-en-1-yl)benzene (46) compound was isolated as a colorless liquid (97.0 mg, 74% yield) ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23 – 7.11 (m, 2H), 7.12 – 7.00 (m, 3H), 5.64 – 4.99 (m, 2H), 4.39 (t, *J* = 5.8 Hz, 1H), 3.62 – 3.50 (m, 2H), 3.48 – 3.34 (m, 2H), 2.59 – 2.47 (m, 2H), 2.26 (t, *J* = 6.1 Hz, 2H), 1.97 (dd, *J* = 13.9, 6.8 Hz, 2H), 1.68 – 1.53 (m, 2H), 1.12 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.6, 133.0, 128.5, 128.3, 125.7, 125.3, 102.8, 61.1, 37.3, 35.4, 32.2, 31.2, 15.4. GCMS (EI) calculated for $[M]^+$ 262.19, found 262.10. FTIR (neat, cm-1): 3026 (w), 2974 (s), 2927 (s), 1495 (s), 1453 (s), 1371 (s), 1342 (s), 1219 (w), 1126 (s), 1061 (s), 1019 (s), 967 (s), 909 (m), 736 (s), 698 (s).

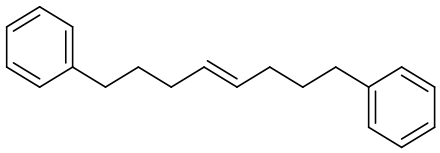


(E)-(9-(benzyloxy)non-4-en-1-yl)benzene (47) compound was isolated as a colorless liquid (129.4 mg, 84% yield) ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 – 7.26 (m, 6H), 7.22 – 7.06 (m, 4H), 5.73 – 5.19 (m, 2H), 4.50 (s, 2H), 3.47 (t, *J* = 6.5 Hz, 2H), 2.81 – 2.41 (m, 2H), 2.19 – 1.87 (m, 4H), 1.74 – 1.57 (m, 4H), 1.51 – 1.36 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.7, 138.8, 130.6, 130.2, 128.6, 128.4, 128.3, 127.7, 127.6, 125.7, 73.0, 70.4, 35.5, 32.5, 32.2, 31.4, 29.4, 26.3 GCMS (EI) calculated for $[M]^+$ 308.21, found 308.20.

FTIR (neat, cm-1): 3084 (m), 3061 (m), 3025 (m), 2930 (s), 2853 (s), 1698 (w), 1603 (m), 1495 (s), 1452 (s), 1361 (s), 1307 (w), 1102 (s), 1028 (m), 967 (s), 733 (s), 696 (s).

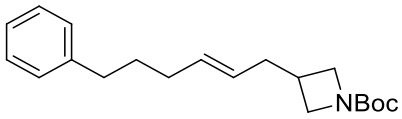


(E)-1-bromo-2,4-dichloro-5-((8-phenyloct-4-en-1-yl)oxy)benzene (48) compound was isolated as a colorless liquid (117.2 mg, 55% yield) ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 (s, 1H), 7.23 – 6.88 (m, 5H), 6.87 (s, 1H), 5.49 – 5.26 (m, 2H), 3.87 (t, *J* = 6.3 Hz, 2H), 2.63 – 2.33 (m, 2H), 2.11 (dd, *J* = 12.7, 6.8 Hz, 2H), 1.95 (dd, *J* = 13.4, 6.3 Hz, 2H), 1.85 – 1.73 (m, 2H), 1.64 – 1.51 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.4, 142.6, 133.9, 133.3, 131.5, 129.2, 128.5, 128.4, 125.8, 122.4, 114.8, 112.6, 69.0, 35.5, 32.2, 31.3, 28.8, 28.8. GCMS (EI) calculated for $[M]^+$ 426.02, found 426.00. FTIR (neat, cm-1): 3024 (m), 2929 (s), 2853 (s), 1578 (s), 1495 (s), 1472 (s), 1465 (s), 1390 (w), 1346 (s), 1281 (s), 1242 (s), 1124 (s), 1075 (s), 1029 9m), 968 (s), 833 (m), 740 (s).

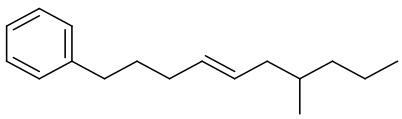


(E)-1,8-diphenyloct-4-ene (8) compound was isolated as a colorless liquid (112.3 mg, 85% yield) ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 – 7.26 (m, 4H), 7.27 – 7.14 (m, 6H), 5.73 – 5.11 (m, 2H), 2.86 – 2.44 (m, 4H), 2.30 – 1.95 (m, 4H), 1.80 – 1.65 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.7, 130.5, 128.6, 128.4, 125.8, 35.5, 32.3, 31.5. GCMS (EI) calculated for [M]+ 264.19, found 264.10. FTIR (neat, cm-1): 3083 (s), 3061 (s), 3024

(s), 2928 (s), 2854 (s), 1603 (m), 1495 (s), 1452 (s), 1075 (w), 1029 (s), 967 (s), 906 (w), 744, (s), 697 (s).

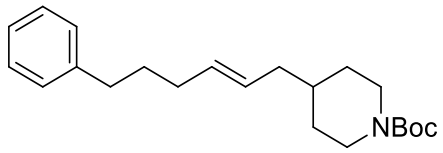


(E)-tert-butyl 3-(6-phenylhex-2-en-1-yl)azetidine-1-carboxylate (49) compound was isolated as a colorless liquid (102.4 mg, 65% yield) ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 2H), 7.24 – 7.12 (m, 3H), 5.54 – 5.39 (m, 1H), 5.38 – 5.27 (m, 1H), 3.97 (t, *J* = 8.4 Hz, 2H), 3.55 (dd, *J* = 8.4, 5.4 Hz, 2H), 2.63 – 2.42 (m, 3H), 2.26 (t, *J* = 6.9 Hz, 2H), 2.03 (dd, *J* = 14.0, 7.0 Hz, 2H), 1.76 – 1.63 (m, 2H), 1.44 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.5, 142.5, 132.3, 128.5, 128.4, 126.9, 125.8, 79.2, 54.0, 37.2, 35.4, 32.2, 31.2, 28.5, 28.4. GCMS (EI) calculated for $[M]^+$ 315.22, found 315.20. FTIR (neat, cm-1): 3024 (m), 2964 (s), 2931 (s), 2877 (s), 1700 (s), 1603 (w), 1496 (m), 1478 (m), 1453 (s), 1399 (s), 1365 (s), 1294 (m), 1135 (s), 1062 (w), 969 (s), 931 (w), 861 (s), 772 (s), 752 (s), 699 (s).

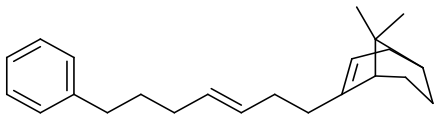


(E)-(7-methyldec-4-en-1-yl)benzene (50) compound was isolated as a colorless liquid (93.2 mg, 81% yield) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.36 (m, 2H), 7.33 – 7.22 (m, 3H), 5.78 – 5.22 (m, 2H), 2.72 (t, *J* = 7.7 Hz, 2H), 2.28 – 2.03 (m, 3H), 2.01 – 1.89 (m, 1H), 1.84 – 1.74 (m, 2H), 1.62 – 1.49 (m, 1H), 1.50 – 1.35 (m, 3H), 1.26 – 1.13 (m, 1H), 1.07 – 0.87 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.8, 131.2, 129.6, 128.6, 128.4,

125.8, 40.3, 39.1, 35.5, 33.1, 32.4, 31.6, 20.3, 19.6, 14.5. GCMS (EI) calculated for $[M]^+$ 230.20, found 230.20. FTIR (neat, cm-1): 3026 (m), 2955 (s), 2926 (s), 2869 (m), 1619 (w), 1495 (s), 1453 (s), 1377 (s), 1030 (m), 967 (s0, 742 (s), 697 (s), 676 (s).



(E)-tert-butyl 4-(6-phenylhex-2-en-1-yl)piperidine-1-carboxylate (51) compound was isolated as a colorless liquid (154.6 mg, 90% yield) ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 – 7.23 (m, 2H), 7.21 – 7.13 (m, 3H), 5.56 – 5.28 (m, 2H), 4.07 (d, J = 12.8 Hz, 2H), 2.76 – 2.53 (m, 4H), 2.09 – 1.97 (m, 2H), 1.94 (t, J = 6.1 Hz, 2H), 1.77 – 1.58 (m, 4H).1.53 – 1.33 (m, 10H), 1.19 – 0.96 (m, 2H) ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.0, 142.6, 131.9, 128.5, 128.3, 128.3, 125.7, 79.2, 44.1, 39.7, 36.4, 35.5, 32.2, 32.0, 31.4, 28.6. GCMS (EI) calculated for $[M]^+$ 343.25, found 343.20. FTIR (neat, cm-1): 3050 (w), 3010 (w), 2977 (m), 2972 (s), 2850 (m), 1687 (s), 1425 (s), 1365 (s), 1265 (s), 1242 (m), 1170 (s), 1123 (w), 966 (m), 864 (w). 738 (s), 700 (s)



(1S)-8,8-dimethyl-2-((E)-7-phenylhept-3-en-1-yl)bicyclo[3.2.1]oct-2-ene(52)

compound was isolated as a colorless liquid (117.1 mg, 76% yield) ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 – 7.28 (m, 2H), 7.29 – 7.19 (m, 3H), 5.60 – 5.45 (m, 2H), 5.28 (s, 1H), 2.76 – 2.58 (m, 2H), 2.49 – 2.24 (m, 3H), 2.23 – 1.99 (m, 8H), 1.85 – 1.68 (m, 2H), 1.36 (s, 3H), 1.25 (d, J = 8.4 Hz, 1H), 0.93 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.2,

142.7, 130.8, 123.0, 128.6, 128.4, 125.7, 116.1, 46.0, 41.0, 38.1, 37.2, 35.4, 32.2, 31.8, 31.4, 30.6, 26.5, 21.4. GCMS (EI) calculated for $[M]^+$ 308.25, found 308.20. FTIR (neat, cm-1): 3061 (m), 3025 (s), 2983 (s), 2916 (s), 2832 (s), 1604 (w), 1495 (s), 1433 (s), 1380 (s), 1363 (s), 1345 (w), 1264 (w), 1219 (w), 1070 (m), 1030 (m), 966 (s), 886 (w), 791 (m), 744 (s), 697 (s).

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