Palladium-Catalyzed Cross-Coupling of *N*-Sulfonylaziridines with Boronic Acids and Synthetic Approaches to Organic Polymer-Supported One-Dimensional Metal Wires

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Abstract

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The development of new reaction methodologies has been the gateway through which chemists have come to understand the world. In pursuit of making something better, faster, or completely novel, the synthetic community has happened upon observations that have had indisputable and far-reaching impact on the way society functions. New drugs are made, materials obtained, and physical and biological interactions revealed through synthesis. Herein, two disparate projects falling under the synthetic umbrella, each with a different end goal, are described.

In Chapter 1, a new method for forming Csp^3-Csp^2 bonds is reported. The products of this reaction are β-phenethylamines, a structural motif that is present in a number of biotransmitters and pharmaceuticals. The reaction uses *N*-sulfonylaziridines as electrophilic coupling partners in a Pd-catalyzed cross-coupling with arylboronic acids. Productive Csp^3-C bond formation is often hampered by β-hydride elimination, an undesirable side reaction presently addressed by bimodal coordination of the aziridine to

Pd and use of a bulky phosphine ligand. The reaction is high yielding, tolerant of a breadth of functionality, and completely regio- and diastereoselective.

Chapter 2 of this work details efforts to develop a synthetic method for the realization of new organic photovoltaic materials. These materials are composed primarily of polymeric organic ligands capable of coordinating transition metal ions such that the ions are organized into one-dimensional metal wires. These 1-D metal wires could function to amplify the polarizability of the organic material and serve as charge-carrying conduits, thereby augmenting solar conversion efficiencies beyond current OPV thresholds. Characterization of these products was complicated by their limited solubilities in organic solvents. Preliminary UV/Vis data indicate red-shifted spectral absorbance profiles for some of the metalated materials; however, absorbance intensities in the visible region are poor, necessitating improvement if these materials are to be used for the originally intended purpose.

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List of Abbreviations

9-BBN:	9-Borabicyclononyl
Ar:	Aryl
bpy:	2,2'-Bipyridine
Bu:	Butyl
cod:	Cyclooctadiene
Cy:	Cyclohexyl
dba:	Dibenzylideneacetone
DG:	Directing group
DMA:	*N,N*-Dimethylacetamide
DME:	Dimethoxyethane
DMSO:	Dimethylsulfoxide
dr:	Diastereomeric ratio
ESI-MS:	Electrospray ionization mass spectrometry
Et:	Ethyl
IR:	Infrared spectroscopy
h:	Hour
Hex:	Hexyl
HFIP:	1,1,1,3,3,3-Hexafluoroisopropanol
Hz:	Hertz
IPV:	Inorganic photovoltaic
J:	NMR coupling constant
J:	Joule
L:	Ligand

M:	Metal
Me:	Methyl
MHz:	Megahertz
mp:	Melting point
M:	Molar
nm:	Nanometer
NMR:	Nuclear Magnetic Resonance

Abbreviations for NMR splitting:

s:	singlet
d:	doublet
t:	triplet
q:	quartet
quin:	quintet
m:	multiplet
br:	broad

NOESY:	Nuclear Overhauser effect spectroscopy
Np:	1-Naphthyl
Ns:	4-Nitrobenzenesulfonyl
$NsNH_2$:	4-Nitrobenzenesulfonamide
OPV:	Organic photovoltaic
PAPy:	Poly(aminopyridine)
Ph:	Phenyl
phen:	1,10-Phenanthroline
ppm:	Parts per million
Pr:	Propyl

PV:	Photovoltaic
Py:	Pyridyl
R:	Alkyl (unspecified)
rt:	Room temperature
THF:	Tetrahydrofuran
TIPS:	Triisopropylsilyl
TLC:	Thin layer chromatography
Tol:	Tolyl
Ts:	*p*-Toluenesulfonyl
$TsNH_2$:	*p*-Toluenesulfonamide
UV/Vis:	Ultraviolet-visible absorption spectroscopy

Acknowledgments

This section of the dissertation tends to serve almost as thank you note for help received throughout life, because getting a Ph.D. often feels like the culmination of all things thus far experienced in the context of one. There are so many people to whom I owe my gratitude, and though I'd love to expound upon their virtues and the reasons I feel indebted to each of them, the amount of time required for such an undertaking is unfortunately prohibitive. This section will therefore be far too abbreviated for my taste, but unabridged devotions relevant to specific individuals may be obtained by verbal or written request.

First, I must thank my advisor, Forrest. He has encouraged me to become a better scientist and logician in all of the precise ways I was lacking at the start of this endeavor. He allowed me to explore new and interesting questions that weren't a sure shot to publication or recognition because he intuited that that was what I needed to remain engaged and excited about my work. Had I been required to focus on a single narrow or largely hashed out synthetic problem, I fear I may not have had the endurance to make it to the academic finish line.

My undergraduate advisor, Hamish Christie, had an enormous impact on my choice to go to graduate school. His curiosity, energy, and gentle manner of molding minds were everything I needed to believe that I could possibly undertake such a thing. He has my profound and unending gratitude for demonstrating his belief in me.

Gojko, AJ, and Mike served on my qualifying and final defense committees and frequently served as my de facto advisors in Forrest's absence. My thanks are due to

them for encouraging me to ask questions, open discussions, and for making me feel supported in my academic career.

Interactions with my labmates were very frequently highlights of my days and weeks in graduate school. Erica and Alicia are both incredibly dear to me. They answered so many questions with patience and kindness, went out of their ways to help me find things, and brought me baked goods and flowers for all of my birthdays. They are lovely human beings, and my intention is to be their friend forever. Richard is another of my amazing labmates. Happiness in his presence is automatic; he is bright and so full of love for the world. Dancing with Richard is a must-do for anyone visiting the L.A. area.

I have several special friends who tread the grad school road and passed the requisite milestones alongside me. Carrie, Jess, and Sam helped me confront anxieties and celebrate victories. Disappointments were equally shared, and every success, whether my own or theirs, felt like a win for the team. I'll miss our 6:30 am group breakfasts, nights out at RPlace, and being around people who are on an overt mission to come up with all possible excuses for donning a costume and asking other people to do it too. Jack is another friend who has added so much depth to my experience of Seattle and of life. Gastronomic adventures with Jack are some of my favorite kind of adventures, and observing his passion for science and family is alternately inspiring and endearing.

My big little brother, Adam, has been a great friend and help throughout this process. My flakiness is no match for his persistence in telling me how much he cares, and my financial life is better off for being his relation. Brother, I promise I'm ready to be a whole adult now. I have a mostly solid career plan and I bought an address book.

My parents—all four of them—are the most supportive, loving folks I could ask for. Their pride in me is palpable, which is such an amazing thing to feel and fall back on when pride in oneself is lacking. If I were to continue to detail the impact of their involvement in my life and the gratitude I feel for the person they've helped me become, the page volume of this dissertation would double. That being what it is, I think I'll only add the following: I love them so much.

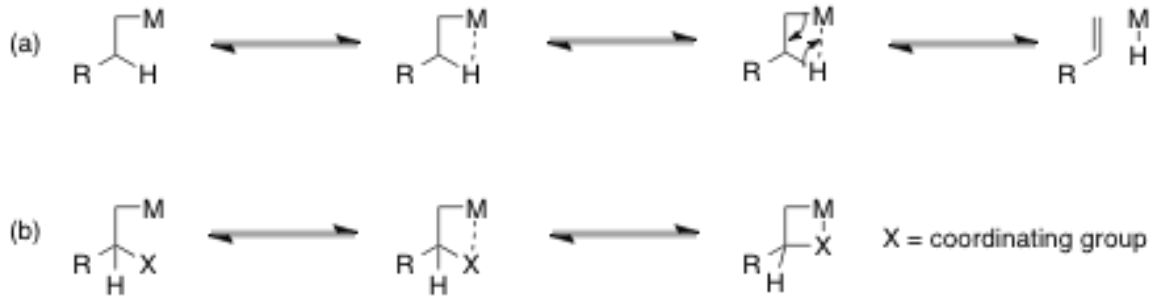
Chapter 1

Palladium-Catalyzed Cross-Coupling of *N*-Sulfonylaziridines With Boronic Acids[1]

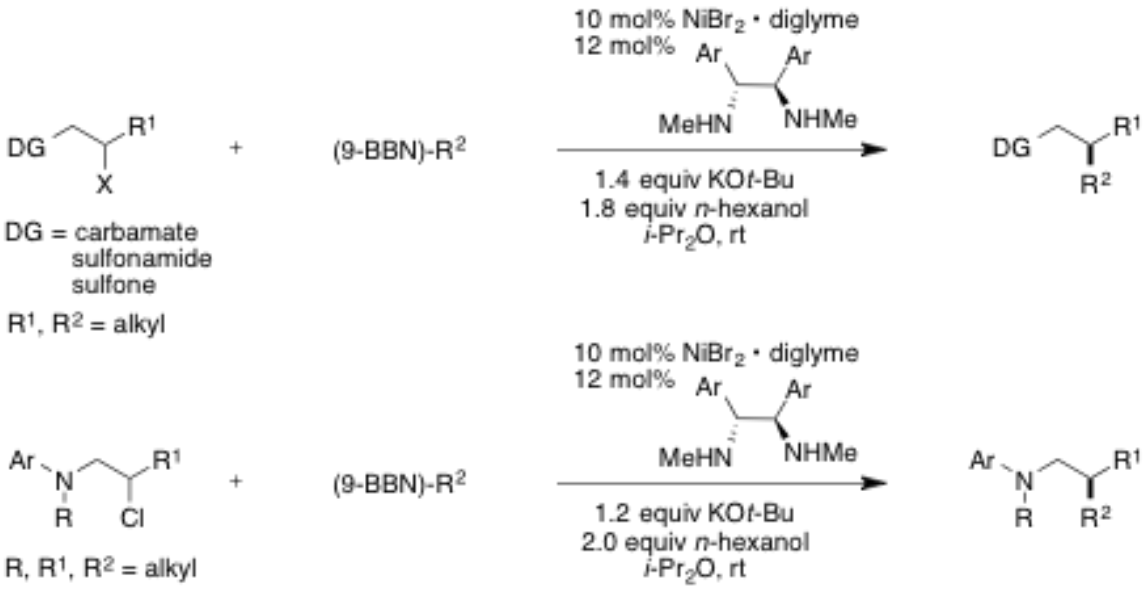
Section 1: Introduction

Transition metal-catalyzed cross-coupling procedures have become some of the most effective and synthetically useful methods for the construction of C-C bonds. Until relatively recently, the formation of Csp^3-C bonds using this method was frequently plagued by facile β-hydride elimination of the alkyl coupling partner (Scheme 1.1), making the achievement of this particular transformation nontrivial.[2] The group of Greg Fu was able to address this problem in part through the use of β-coordinating groups on alkyl halide electrophiles (Scheme 1.2).[3] The possibility for coordination of a group β to the alkyl-metal bond restricts the geometry of the complex such that hydrogens in the β position are sterically inaccessible to the metal and elimination is no longer a favored pathway.

Scheme 1.1. *β-Hydride elimination (a) and β-coordination (b) in alkylmetal complexes.*



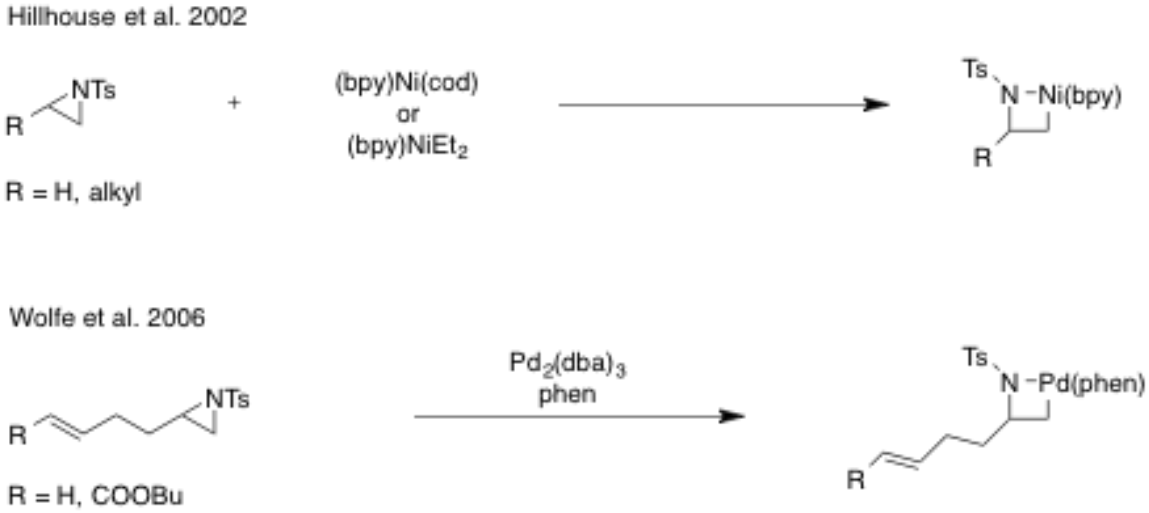
Scheme 1.2. *Ni-catalyzed cross-couplings of alkyl electrophiles using β-coordinating groups by Fu et al.*[3]



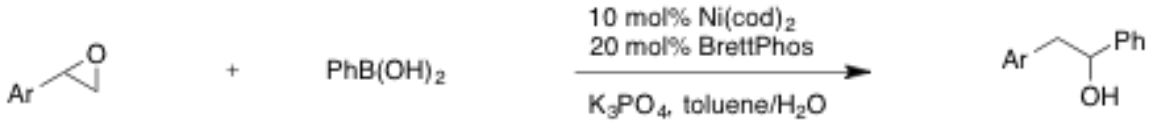
Complexes with analogous structure can also be formed through the oxidative addition of aziridines, a finding published independently by the research groups of Hillhouse[4] and Wolfe[5] (Scheme 1.3). Nickel and palladium azametallacyclobutanes stabilized by diamine ligands were isolated and fully characterized; however, the synthetic utility of these complexes remained largely underexplored in the literature. Recognizing a synthetic opportunity, we planned to exploit this chemistry to effect a metal-catalyzed cross-coupling procedure using a suitable organometallic nucleophile and aziridines as electrophiles.

We were encouraged to seriously examine this possibility upon publication of a Ni-catalyzed coupling of styrenyl epoxides with arylboronic acids by the research group of Abigail Doyle. (Scheme 1.4).[6] The observed regiochemistry of the ring-opened alcohol products suggests β-hydride elimination was not avoided and is in fact probably integral

Scheme 1.3. *Azametallacyclobutane complexes reported by Hillhouse[4] and Wolfe.[5]*

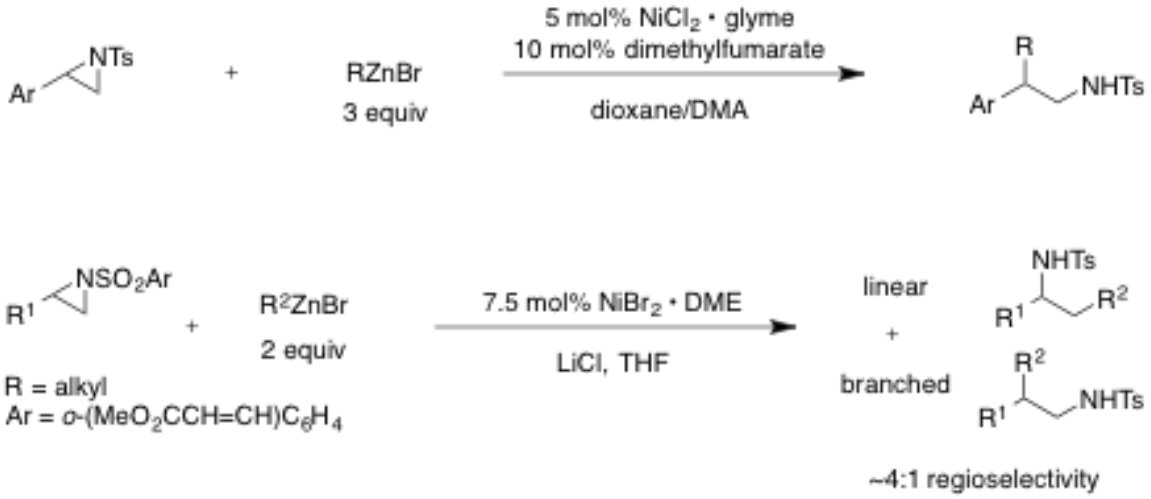


Scheme 1.4. *Doyle's Ni-catalyzed procedure for coupling epoxides with arylboronic acids.[6]*



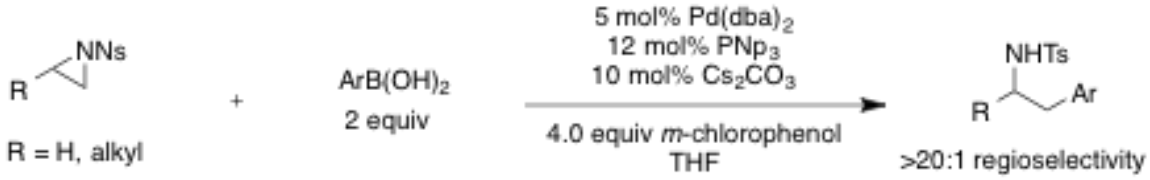
to the catalytic cycle. A mechanism for this transformation is postulated in which a presumed nickellaoxetane complex undergoes β-hydride elimination to produce the corresponding aldehyde intermediate, to which the nucleophilic aryl group is subsequently added. Although the arylboronic acid is not coupled directly to the epoxide, this report is notable in that it is the first transition metal-catalyzed coupling procedure employing three-membered ring electrophiles.

Scheme 1.5. *Doyle's Ni-catalyzed procedures for coupling 2-aryl- and 2-alkyl-substituted aziridines with organozinc bromides.*[7a,b]



During the course of my research on metal-catalyzed additions to aziridines, Doyle's group subsequently published two additional procedures for cross-coupling three-membered ring electrophiles, both using aziridines instead of epoxides (Scheme 1.5). The first of these involved a Ni-catalyzed ring-opening of Ts-protected styrenyl aziridine electrophiles, followed by addition of alkylzinc bromide nucleophiles. Yields ranged from moderate to very good, but stereochemical scrambling in the products was observed.[7a] This suggests that oxidative addition of the aziridine occurs either by a S_N2 mechanism followed by homolysis of the benzylic Ni-C bond or by a single electron transfer (SET) mechanism. The second of Doyle's methods couples alkyl aziridines with organozinc halides, also using a Ni(II) catalyst. The alkyl aziridines require a custom sulfonyl protecting group, and regioselectivity of the transformation is approximately 4:1 in favor of the linear phenethylamine isomers.[7b]

Scheme 1.6. *Our Pd-catalyzed method for coupling 2-alkylaziridines with arylboronic acids.*



Doyle's work in this area represents a significant scientific contribution in that she was the first to report methods for coupling both aryl- and alkyl-substituted aziridines with organometallic nucleophiles under the action of a transition metal catalyst, providing for relatively mild reaction conditions. There are, however, limitations to these methods that we sought to address. To this end, I developed a cross-coupling of *N*-sulfonylaziridines with arylboronic acids, the conditions for which are shown in Scheme 1.6. This procedure is complementary to Doyle's coupling of 2-arylaziridines and offers several notable improvements over constraints inherent to her method for coupling 2-alkylaziridines. Namely, aziridine substrates are protected using a commercially accessible and easily removed 4-nitrobenzenesulfonyl protecting group, couplings are performed using air-stable and readily commercially available boronic acid nucleophiles, and products are consistently obtained with absolute and predictable regio- and stereoselectivities.

In addition to addressing an interesting and technical synthetic problem, our method provides convenient access to an array of functionalized β-phenethylamines, a privileged chemical structure with distinctive and often desirable biological properties. The phenethylamine motif is present in a number of neurotransmitters, such as dopamine and epinephrine, and is frequently a target for pharmaceutical agents used to treat

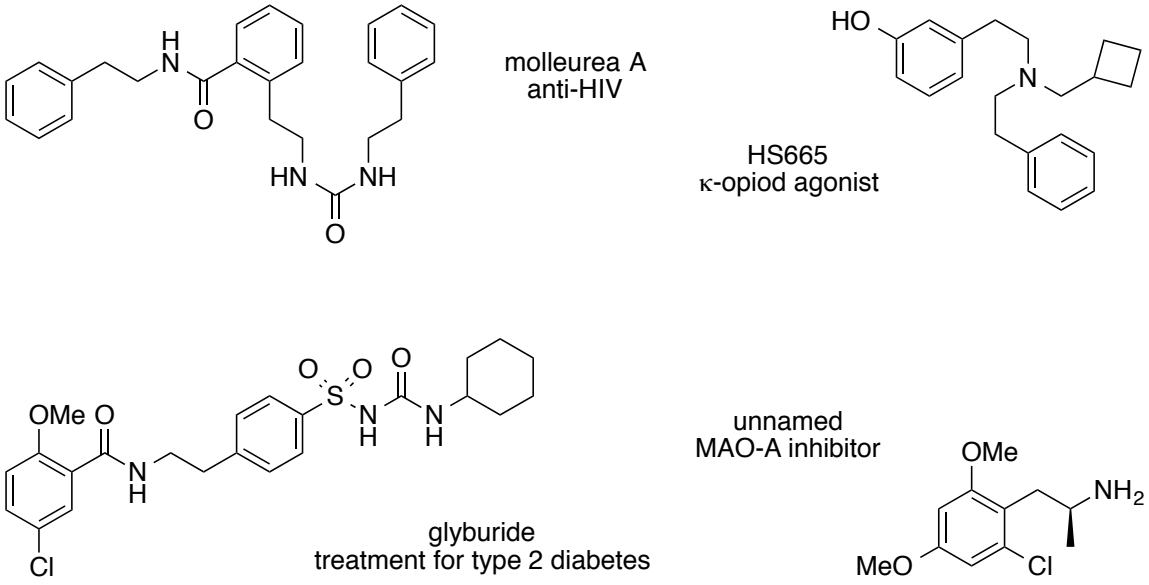


Figure 1.1. A selection of functionalized β-phenethylamines exhibiting interesting biological activities.[8a,9-11]

Parkinson's and Alzheimer's diseases.[8] The β-phenethylamine motif is also found in glyburide, a drug used to treat type II diabetes,[9] and molleurea A, a natural product extracted from the sea sponge *Didemnum molle* that has demonstrated cytoprotective effects against the HIV virus.[10] A selection of biologically relevant β-phenethylamine structures toward which our method may demonstrate utility is shown in *Figure 1.1*.

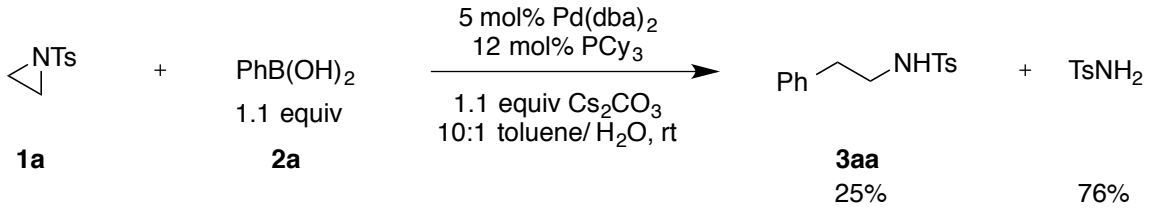
Section 2: Results and Discussion

1.2.1 Initial Results

Initial reaction conditions were selected based on similarity to those reported for existing Csp^3-C couplings with boron-based nucleophiles[12] and are shown in Scheme 1.7. *N*-Tosylaziridine **1a** and phenylboronic acid **2a** were coupled using 5 mol% $Pd(dba)_2$ and 12 mol% PCy_3 under basic conditions in a 10:1 toluene/water solvent mixture to yield the

desired cross-coupled product **3aa** in 25% yield. The remainder of the starting material was converted to *p*-toluenesulfonamide. We suspected this byproduct was the result of β-hydride elimination followed by hydrolysis of the subsequent imine. Interestingly, removal of water from the reaction conditions resulted in no formation of the desired product.

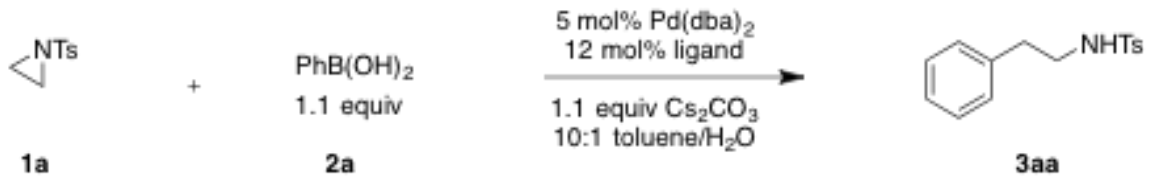
Scheme 1.7. *Initial conditions for cross coupling N-tosylaziridine with phenylboronic acid.*



1.2.2 Reaction Optimization

Following the identification of our initial reaction conditions, early optimizations focused on examining the influence of the ligand on reaction outcome. Substrates **1a** and **2a** were coupled under our established reaction conditions using an array of mono- and bidentate trialkyl- and triarylphosphines (Table 1.1). Unlike the similarly bulky trialkylphosphine PCy_3, use of P(*t*-Bu)$_3$ as supporting ligand (entry 2) resulted in no detectable yield of the desired *N*-tosylphenethylamine coupling product. More promising results were obtained for a number of triarylphosphine ligands, particularly those possessing *ortho* substitution patterns, such as P(*o*-tol)$_3$ and PNp_3 (entries 3, 5). Bidentate phosphine ligands were determined to be largely unsuitable for our reaction, Xantphos being the only one of these ligands that resulted in detectable yield of the product (entry

Table 1.1. Ligand Optimization.

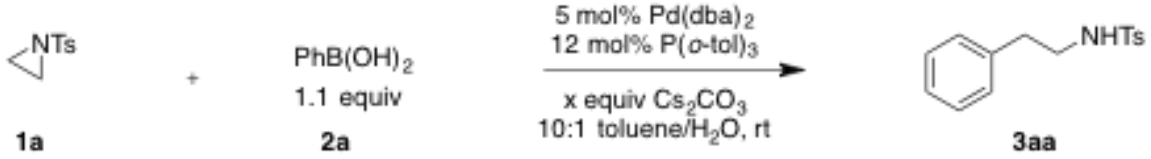


1a **2a** **3aa**

Entry	**Ligand**	**% Yield 3aa[a]**
1	PCy_3	25
2	$P(t\text{-Bu})_3$	0
3	$P(o\text{-tol})_3$	48
4	$P(p\text{-tol})_3$	10
5	PNp_3	35
6	Xantphos	6

[a]NMR yields using 1,3-dinitrobenzene as internal standard.

Table 1.2. Base Optimization.



1a **2a** **3aa**

Entry	**x**	**% Yield 3aa[a]**
1	1.1	48
2	0.5	59
3	0.1	65
4	0.05	64
5	0	43
6	2.0	37

[a]NMR yields using 1,3-dinitrobenzene as internal standard.

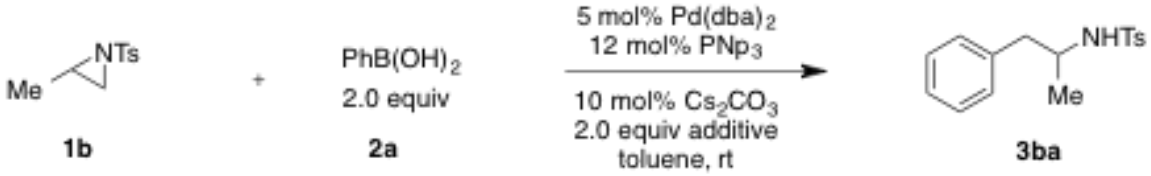
6). Our results suggest that the present reaction is most successfully promoted by the inclusion of sterically bulky monodentate triarylphosphine ligands.

Having adequately addressed optimization of the catalyst ligand, our focus shifted to examining the contribution of the base to reaction outcome. Cesium carbonate was determined to be the optimal base, chosen from a survey of organic and inorganic bases commonly employed in Suzuki-type cross-coupling reactions such as alkali metal carbonates, alkoxides, and trialkylamines. Unlike more traditional cross-couplings characterized by the use of halide or triflate electrophiles, in theory the present reaction does not require the use of stoichiometric base. The presumed base in our reaction, OH^-, would typically function to facilitate transmetalation via coordination to boron. However, the sulfonamide product of the present reaction is anionic and, in the presence of a protic donor such as H_2O, has the potential to regenerate hydroxide ion, providing for a neutral net reaction. As such, we decided to probe the effects of adding substoichiometric base under the conditions listed in Table 1.2. We found that decreasing the concentration of base in the reaction mixture from 1.1 to 0.5 equivalents considerably increased the yield of **3aa** (entries 1, 2). Further reducing the quantity of added base resulted in minor supplementary yield enhancements (entries 3, 4). Addition of two equivalents of cesium carbonate resulted in a diminished yield of 37% (entry 6). Notably, a similar drop in yield was observed upon exclusion of cesium carbonate from the reaction mixture (entry 5). Thus, incorporation of catalytic quantities of base was determined to be optimal for this reaction.

Following optimization of the ligand and base, several additional changes were made to the standard conditions. In order to establish the application of the reaction to

substituted aziridines, the model aziridine was switched from *N*-tosylaziridine **1a** to *N*-tosyl-2-methylaziridine **1b**. I also increased the equivalents of boronic acid from 1.1 to 2.0, doubled the molar concentration of the reaction, and re-optimized the ligand under these new conditions to PNp_3, realizing moderate yield enhancements with each modification. These changes collectively resulted in the achievement of a 74% yield of coupled product **3ba** (Table 1.3, entry 1).

Table 1.3. Additive Optimization.



Entry	**Additive**	**% Yield 3ba**
1	H_2O	74
2	MeOH	67
3	*i*-PrOH	66
4	HFIP	22
5	phenol	82
6	*m*-chlorophenol	77
7	*p*-nitrophenol	30

[a]NMR yields using 1,3-dinitrobenzene as internal standard.

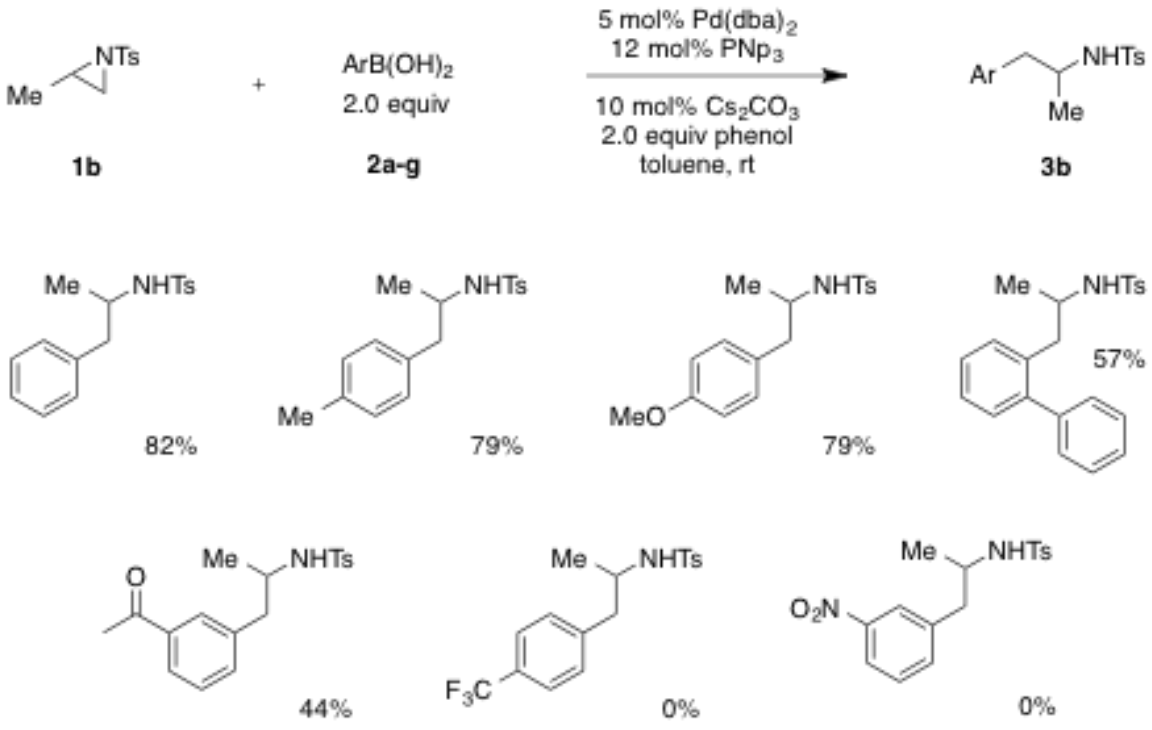
From here, my attention turned to exploring the function of water as an additive in the reaction. As noted previously, none of the desired product was formed when water was omitted from the reaction mixture. I postulated that water, acting as a formal source of both OH^- and H^+, performs a dual role in the catalytic cycle, facilitating transmetalation and serving as a H+ source to neutralize the anionic sulfonamide product.

I reasoned that replacing water with ROH additives of variable acidity might have a quantifiable effect on catalytic turnover, possibly allowing for an increase in yield. Thus, a number of alcohol and phenol additives were screened as potential replacements (Table 1.3). We were surprised to find the reaction was viable in all of the examined cases and gratified that we were able to further augment our yield of **3ba** to 82% using two molar equivalents of phenol (entry 5).

1.2.3 Reaction Scope

The optimized conditions were applied to the coupling of **1b** with an array of differentially substituted arylboronic acids (Table 1.4). It was at this point we discovered

Table 1.4. Initial Exploration of Boronic Acid Scope.[a]

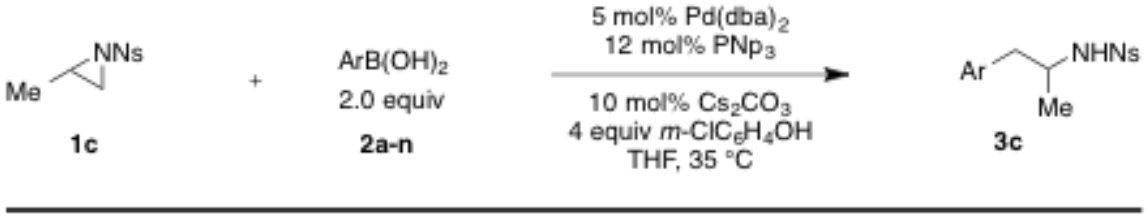


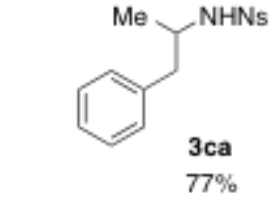
[a]NMR yields using 1,3-dinitrobenzene as internal standard.

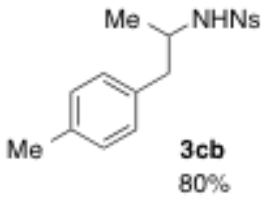
the reaction was remarkably limited in terms of compatible functionality. Reasonable yields were obtained for alkyl-, aryl-, and alkylether-substituted phenylboronic acids, but disappointing or nonexistent yields were achieved when electron-withdrawing groups were present on the aryl ring.

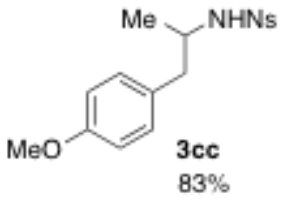
Faced with a reaction that was not applicable to an acceptably broad range of functionalized substrates, we chose to reassess a number of previously optimized parameters. Multiple successive refinements led to an alternative set of conditions that granted access to reasonable product yields for a more generous pool of boronic acid functionality (Table 1.5). The amended reaction parameters are characterized by the use of four molar equivalents of *m*-chlorophenol as proton-donating additive, a change of solvent and minor boost in reaction temperature, and replacement of Ts-protected aziridines with more reactive *N*-nosylaziridine substrates. The greater reactivity of these aziridines may assist in mitigating the low yields observed with boronic acids containing electron-withdrawing functional groups. Additionally, the Ns protecting group is cleaved under milder conditions, making it more synthetically useful than Ts.[13] Using these new parameters, greatly improved yields were obtained for coupling reactions of *N*-nosyl-2-methylaziridine **1c** with arylboronic acids containing electron-withdrawing groups, while products bearing neutral or electron-donating groups were obtained in similarly high yields as before. The reaction is tolerant of ketone, aldehyde, acetal, ether, thioether, and nitro functionalities. It is also tolerant of boronic acids with functional groups bearing acidic hydrogens, such as phenol (**3cj**) and amide (**3ck**). In order to determine whether the method was scalable to larger quantities, reaction of 1c and and 2a was performed on a 2 mmol scale and gave the respective

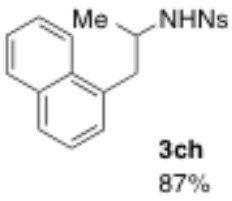
Table 1.5. Boronic Acid Scope of Re-Optimized Reaction.[a]

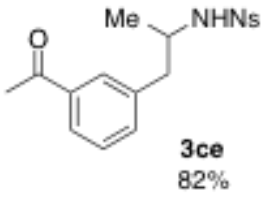


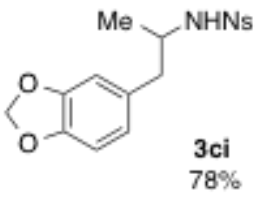


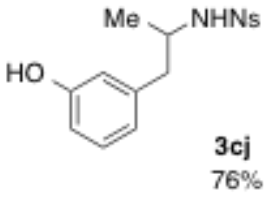


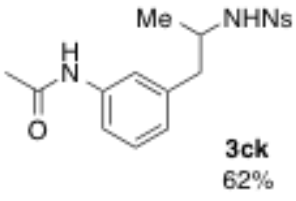


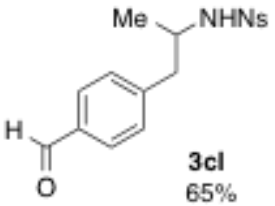


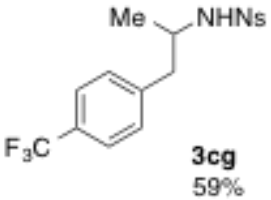


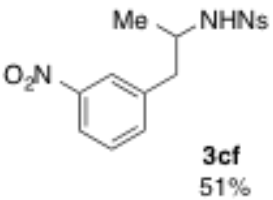


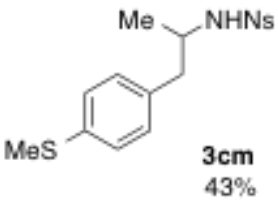


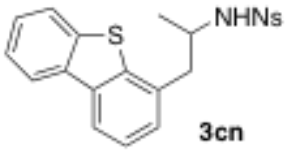


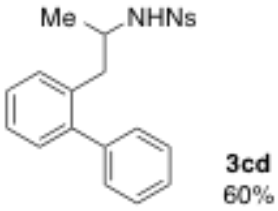






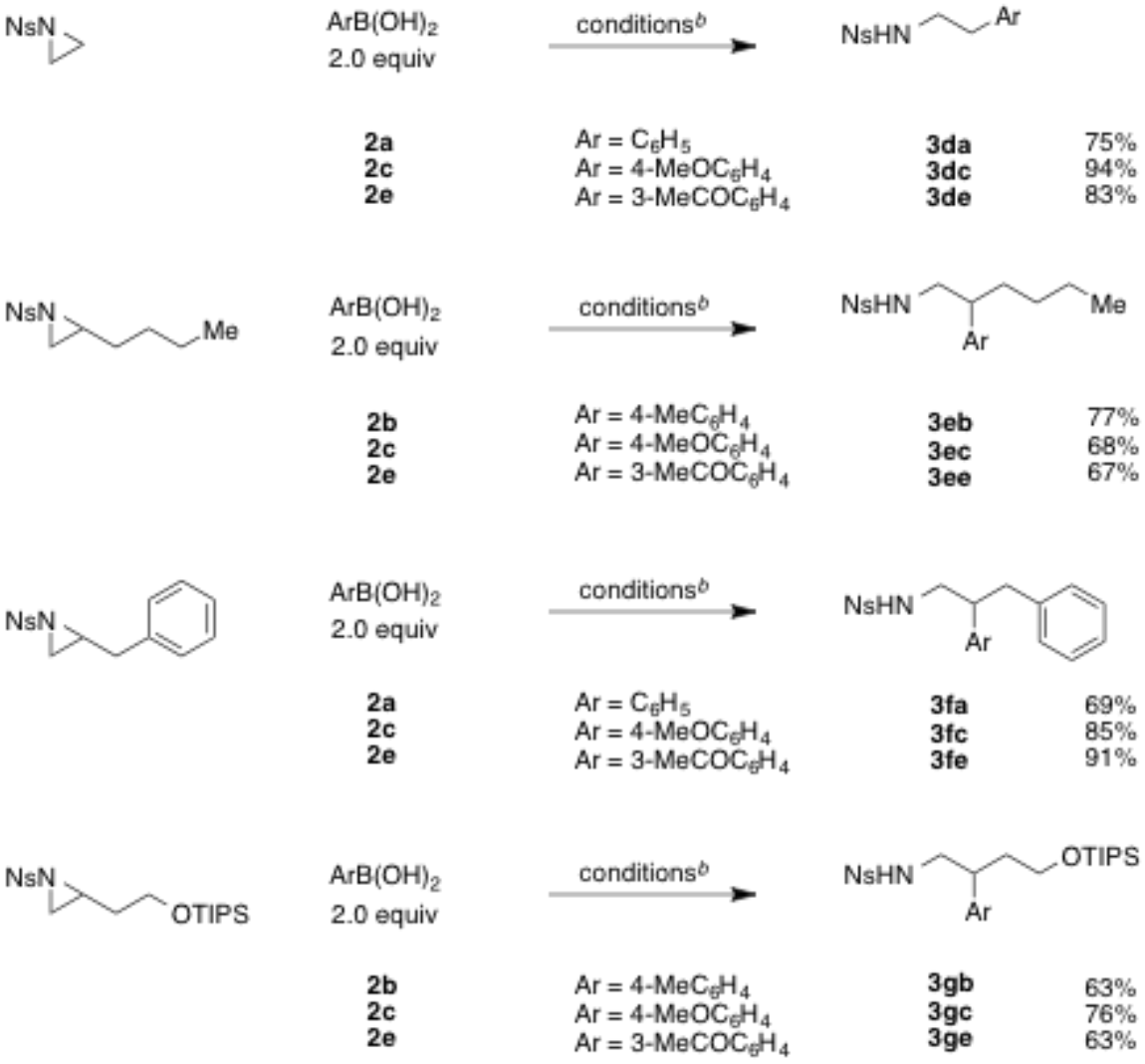






[a]Isolated yields.

Table 1.6. Aziridine Scope.[a]



[a]Isolated yields. [b]Conditions: 5 mol% $Pd(dba)_2$, 12 mol% PNp_3, 10 mol% Cs_2CO_3, 4.0 equiv *m*-ClC_6H_4OH, THF, 35 °C.

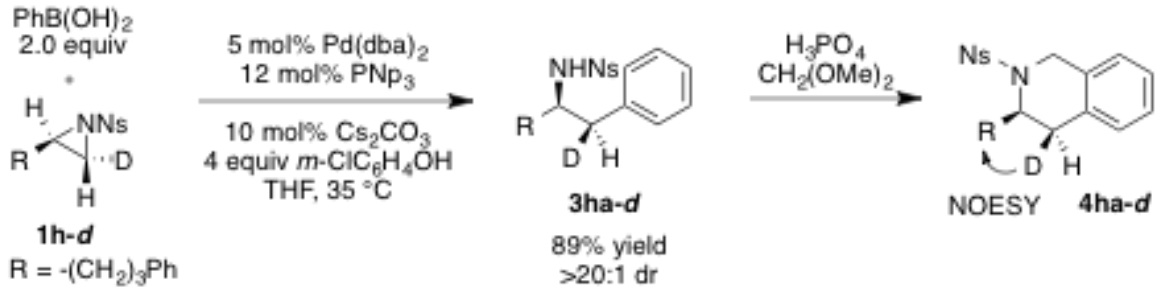
phenethylamine product **3ca** in nearly identical yield (75% vs. 77%). Attempted couplings of alkylboronic acids under these conditions were unsuccessful.

Reaction scope with regard to the aziridine component was next investigated (Table 1.6). We found the reaction could be applied to a number of unsubstituted and 2-alkyl substituted aziridines, with good to excellent yields obtained for couplings of unsubstituted (**1d**), 2-butyl- (**1e**), 2-benzyl- (**1f**), and 2-(2'-triisopropylsiloxyethyl)-*N*-nosylaziridines (**1g**) with arylboronic acids possessing both electron-donating and electron-withdrawing functionalities. In all cases excellent regioselectivity (>20:1) was observed. Unfortunately, the established conditions did not appear to be applicable to 2,2-disubstituted and 2,3-disubstituted aziridines.

1.2.4 Mechanistic Insights

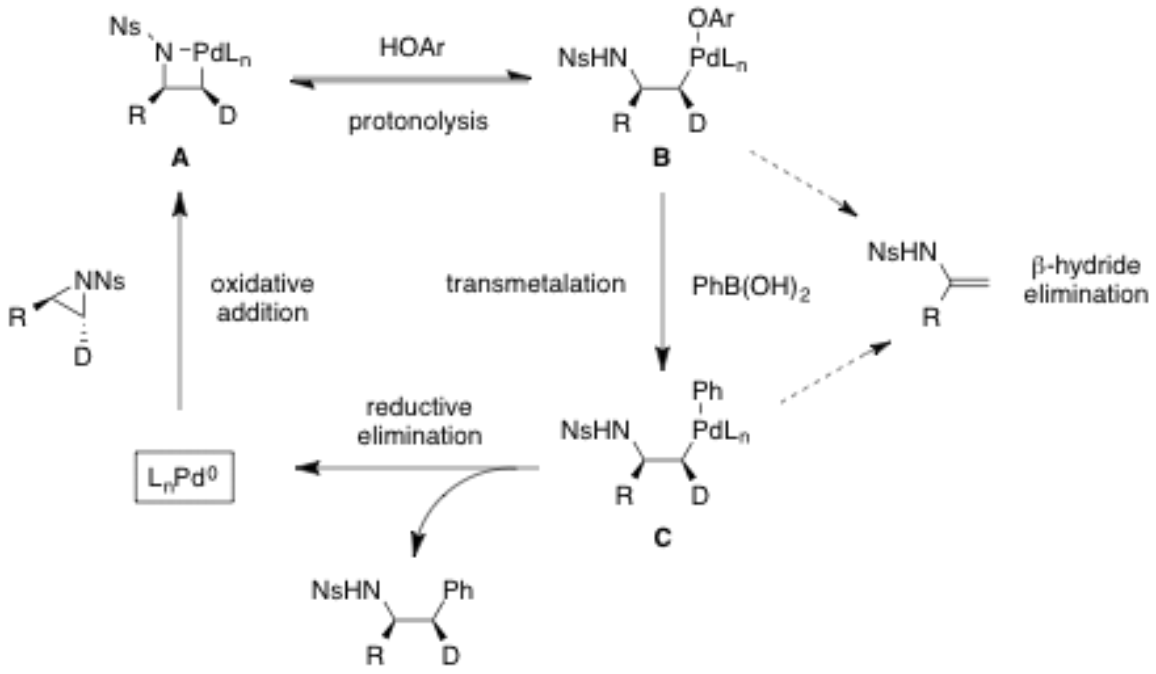
In an effort to probe the mechanism of this reaction, deuterium-labeled aziridine **1h-*d*** was prepared and subjected to the standard reaction conditions (Scheme 1.8). The coupled product, **3ha-*d***, was formed as a single diastereomer in 89% yield. Pictet-Spengler cyclization established that ring opening occurred with 100% inversion of stereochemistry. This is consistent with the stoichiometric studies of Hillhouse and Wolfe establishing that oxidative addition occurs by an S_N2 mechanism and is in contrast to the stereochemical scrambling observed by Doyle.

Scheme 1.8. *Deuterium-labeled substrate coupling and product cyclization.*



A plausible catalytic cycle for this coupling reaction is depicted in Scheme 1.9. Oxidative addition of the aziridine to Pd(0) via an S_N2 mechanism gives the azametallacycle **A**. Subsequent transmetalation of the boronic acid and reductive elimination of the product must occur, but since the coupling largely fails in the absence of additive, direct transmetalation of the boronic acid with the metallacycle does not appear to be viable. Instead, we posit that protonolysis of the metallacycle with ROH gives the Pd alkoxide **B**, which can then undergo transmetalation and reductive elimination to give the product.

Scheme 1.9. *Proposed catalytic cycle.*



One key to the success of this reaction is preventing β-hydride elimination of the alkyl-Pd intermediate. The metallacycle itself is stereoelectronically resistant to β-

hydride elimination but does not undergo direct transmetalation. After protonolysis, however, the ring-opened intermediates **B** and **C** are susceptible to β-hydride elimination. The key role of the *m*-chlorophenol additive is presumably to minimize the lifetime of these two species by careful control of the protonolytic equilibrium and the rate of transmetalation. Interestingly, the pK_a of *m*-chlorophenol (pK_a(DMSO) = 15.8)[14a] is close to that of the sulfonamide product (pK_a(DMSO) = 13.9 for $NsNH_2$),[14b] which supports our initial hypothesis that roughly matching the acidity of the phenol and the sulfonamide may be important.

Section 3: Conclusion

A new palladium-catalyzed procedure for coupling 2-alkyl-substituted *N*-nosylaziridines with arylboronic acid nucleophiles was developed. The reaction is promoted by the use of sterically demanding triarylphosphine ligands, the presence of catalytic base, and addition of a suitable protic additive that presumably plays a role in transmetalation. Furthermore, the reaction is highly regioselective and tolerant of a wide range of functionalities, allowing for quick and efficient synthesis of substituted β-phenethylamine products.

Section 4: Experimental

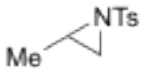
1.4.1 General Procedures and Materials

All reactions were performed under a nitrogen atmosphere using flame-dried glassware unless otherwise indicated. Infrared spectra were acquired using a Perkin Elmer Spectrum RX I spectrometer. Mass spectra were acquired using a Bruker Esquire 1100 Liquid Chromatograph-Ion Trap Mass Spectrometer. Column chromatography was performed using silica gel (Whatman, 60 Å, 230-400 mesh). NMR spectra were recorded

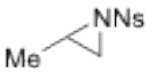
on a Bruker AV-300, AV-301, DRX-499, or AV-500 spectrometer. ^{1}H NMR chemical shifts (δ) are reported in parts per million (ppm) and are referenced relative to residual $CHCl_3$ (7.26 ppm), DMSO (2.50 ppm), or benzene (7.16 ppm). ^{13}C NMR chemical shifts (δ) are reported in parts per million (ppm) relative to the carbon resonance of $CDCl_3$ (77.16 ppm) or DMSO-d_6 (39.52 ppm). Melting points were taken on a MEL-TEMP melting point apparatus and are uncorrected.

Tetrahydrofuran and toluene were degassed and dried by passing through a column of neutral alumina. Deuterated solvents $CDCl_3$, DMSO-d_6, and C_6D_6 were obtained from Cambridge Isotope Laboratories, Inc. and were stored over activated 3Å molecular sieves. Ethyl acetate, hexanes, and dichloromethane were obtained from EMD or Sigma Aldrich and used without further purification. Bis(dibenzylideneacetone)palladium(0) was prepared according to the published procedure,[15] and spectroscopic (^{1}H NMR, ESI-MS) characterization was consistent with reported values. Cesium carbonate was obtained from Sigma Aldrich and stored in a dry box. Phosphine ligands were obtained from Sigma Aldrich or Strem, stored under nitrogen in a glovebox, and used without further purification. Phenol (Mallinckrodt) and *m*-chlorophenol (Aldrich) were purified by recrystallization and distillation, respectively.[16] Boronic acids were obtained from Sigma Aldrich, Frontier Scientific, or Combi-Blocks, Inc. and used without further purification. *N*-(4-toluenesulfonyl)aziridine **(1a)**[17] and *N*-(4-nitrobenzenesulfonyl)-2-benzylaziridine **(1f)**[18] were prepared according to previously published procedures and their respective spectroscopic signatures were found to be consistent with values reported therein.

1.4.2 Synthesis of Aziridines



***N*-(4-toluenesulfonyl)-2-methylaziridine (1b).** 2-Methylaziridine (1.41 mL, 20 mmol, 1 equiv) and triethylamine (5.6 mL, 40 mmol, 2.0 equiv) were dissolved in CH_2Cl_2 (20 mL) in a flame-dried round-bottomed flask charged with a magnetic stirbar. The flask was purged with nitrogen and sealed with a rubber septum equipped with a nitrogen inlet. The solution was cooled to -78 °C, whereupon 4-toluenesulfonyl chloride (4.58 g, 24.0 mmol, 1.2 equiv) was added. The reaction mixture was allowed to stir at -78 °C for 5 minutes and then warmed to 0 °C over a period of 20 minutes, at which point the mixture was diluted with CH_2Cl_2, washed sequentially with 1M HCl and saturated aqueous $NaHCO_3$, dried on Na_2SO_4, concentrated, and chromatographed on silica gel (10% ethyl acetate/ 90% hexanes) to yield the tosyl-protected aziridine as a white crystalline solid (3.66 g, 87%). Spectroscopic values were consistent with those previously reported.[19] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.82 (2H, d, *J* = 8.1 Hz), 7.34 (2H, d, *J* = 8.1 Hz), 2.88-2.79 (1H, m), 2.61 (1H, d, *J* = 6.9 Hz), 2.45 (3H, s), 2.02 (1H, d, *J* = 4.5 Hz), 1.26 (3H, d, *J* = 5.7 Hz).

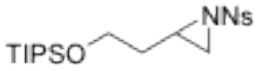


***N*-(4-nitrobenzenesulfonyl)-2-methylaziridine (1c).** 2-Methylaziridine (0.76 mL, 10.0 mmol, 1.0 equiv) and triethylamine (2.8 mL, 20 mmol, 2.0 equiv) were dissolved in CH_2Cl_2 (10 mL) in a flame-dried round-bottomed flask charged with a magnetic stirbar. The flask was purged with nitrogen and sealed with a rubber septum equipped with a nitrogen inlet. The reaction solution was cooled to -78 °C, whereupon 4-nitrobenzenesulfonyl chloride (2.66 g, 12.0 mmol, 1.2 equiv) was added. The reaction mixture was allowed to stir at -78 °C for 5 minutes and then warmed to 0 °C over a period of 20 minutes, at which point the mixture was diluted with CH_2Cl_2, washed sequentially with 1M HCl and saturated aqueous $NaHCO_3$, dried on Na_2SO_4, concentrated, and chromatographed on silica gel (10% ethyl acetate/ 90% hexanes) to yield the nosyl-protected aziridine as a white crystalline solid (2.10 g, 87%). Spectroscopic values were determined to be consistent with those previously reported.[20] ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.40 (2H, d, J = 8.7 Hz), 8.10 (2H, d, J = 8.7 Hz), 3.03-2.94 (1H, m), 2.74 (1H, d, J = 7.9 Hz), 2.13 (1H, d, J = 5.1 Hz), 1.30 (3H, d, J = 5.4 Hz).

***N*-(4-nitrobenzenesulfonyl)aziridine (1d).** Prepared according to a previously reported protocol for the synthesis of *N*-(2-nitrobenzenesulfonyl)aziridine, substituting 4-nitrobenzenesulfonyl chloride for 2-nitrobenzenesulfonyl chloride.[21] *N*-(4-nitrobenzenesulfonyl)aziridine was thus obtained in three steps from ethanolamine in 53% overall yield. Mp: 132-134 °C. IR (thin film): 3101, 3072, 1606, 1528, 1404, 1348, 1329, 1305, 1292, 1238, 1167, 1156, 1096, 909, 859, 818, 800, 752, 742, 688, 662, 616

cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 8.41 (2H, d, J = 9.0 Hz), 8.17 (2H, d, J = 9.0 Hz), 2.49 (4H, s). ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.8, 143.9, 129.4, 124.4, 28.3. MS (ESI, positive mode): $C_8H_8N_2NaO_4S$ $[M + Na]^+$: 251.

***N*-(4-nitrobenzenesulfonyl)-2-*n*-butylaziridine (1e).** Prepared according to the general procedure of Andersson et al.[22] from 1-hexene and obtained in 29% yield. Spectroscopic values were determined to be consistent with those previously reported.[23] ^1H NMR (300 MHz, $CDCl_3$): δ 8.40 (2H, d, *J* = 9.0 Hz), 8.16 (2H, d, *J* = 9.0 Hz), 2.93-2.85 (1H, m), 2.74 (1H, d, *J* = 7.2 Hz), 2.15 (1H, d, *J* = 4.5 Hz), 1.65-1.54 (1H, m), 1.45-1.36 (1H, m), 1.30-1.25 (4H, m), 0.84 (3H, d, *J* = 6.9 Hz).



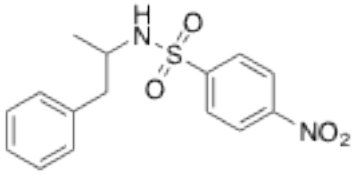
***N*-(4-nitrobenzenesulfonyl)-2-(2-triisopropylsilyloxyethyl)aziridine (1g).** Prepared according to the general procedure of Andersson et al.[22] from 1-triisopropylsilyloxybut-3-ene and obtained in 28% yield. Mp: 69-70 °C. IR (thin film): 3103, 3072, 2944, 2867, 1607, 1531, 1462, 1348, 1337, 1310, 1237, 1168, 1092, 923, 883, 855, 754, 740, 698, 678, 658, 618 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 8.39 (2H, d, J = 9.0 Hz), 8.16 (2H, d, J = 9.0 Hz), 3.70-3.56 (2H, m), 3.10-3.01 (1H, m), 2.79 (1H, d, J = 7.2 Hz), 2.25 (1H, d, J = 4.8 Hz), 1.85-1.74 (1H, m), 1.68-1.58 (1H, m), 1.08-0.97 (21H, m). ^{13}C NMR (125

MHz, $CDCl_3$): δ 150.7, 144.2, 129.4, 124.4, 60.7, 39.3, 34.9, 34.5, 18.1, 12.0. MS (ESI, positive mode): $C_{19}H_{32}KN_2O_5SSi$ $[M + K]^+$: 467.

1.4.3 General Procedure

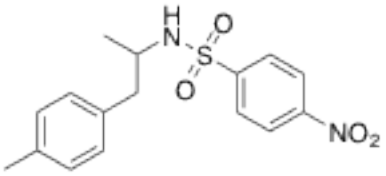
A flame-dried borosilicate glass vial equipped with a magnetic stirbar was charged with bis(dibenzylideneacetone)palladium(0) (5.8 mg, 0.010 mmol, 0.05 equiv), tri-1-naphthylphosphine (9.9 mg, 0.024 mmol, 0.12 equiv), cesium carbonate (6.5 mg, 0.020 mmol, 0.10 equiv), aziridine (0.20 mmol, 1.0 equiv), and arylboronic acid (0.40 mmol, 2.0 equiv). The vial is thoroughly flushed with nitrogen and capped with a Teflon-lined screw cap. A solution of *m*-chlorophenol (102.9 mg, 0.80 mmol, 4.0 equiv) in dry tetrahydrofuran (0.5 mL) was added, and the reaction solution was heated to 35 °C and allowed to stir for 36 h. At this time 1,3-dinitrobenzene (16.8 mg, 0.10 mmol, 0.5 equiv) was added to the reaction mixture as an internal NMR standard, and the mixture was filtered through a silica gel and celite plug, washed with ethyl acetate (5 x 2 mL), and concentrated on a rotary evaporator to afford the crude reaction product.

1.4.4 Characterization of Products

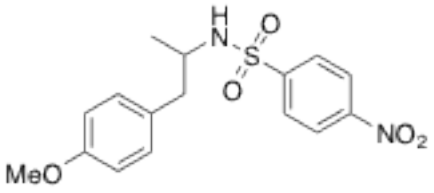


***N*-(4-nitrobenzenesulfonyl)-1-phenylpropan-2-amine (3ca).**[24] Prepared according to the general procedure and purified by silica gel chromatography (15% ethyl acetate/ 85% hexanes) to yield the product as an off-white crystalline solid (49.6 mg, 77% yield). Mp:

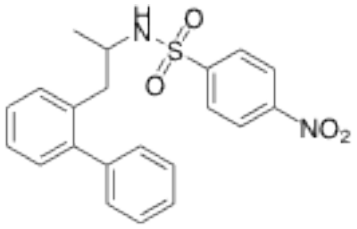
110-112 °C. IR (thin film): 3290, 3103, 3061, 3030, 2978, 2926, 2864, 1607, 1529, 1451, 1420, 1342, 1306, 1161, 1130, 1088, 990, 855, 746, 735, 699, 684, 611 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.17 (2H, d, J = 9.0 Hz), 7.76 (2H, d, J = 8.7 Hz), 7.16 (3H, m), 6.96 (2H, m), 4.44 (1H, d, J = 8.1 Hz), 3.57 (1H, septet, J = 7.5 Hz), 2.78 (1H, dd, J = 5.4, 13.8 Hz), 2.59 (1H, dd, J = 8.1, 13.8 Hz), 1.25 (3H, d, J = 6.3 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 149.8, 146.4, 137.0, 129.3, 128.8, 128.1, 127.1, 124.3, 52.1, 43.6, 22.6. MS (ESI, negative mode): $C_{15}H_{15}N_2O_4S$ $[M - H]^-$: 319.



***N*-(4-nitrobenzenesulfonyl)-1-(4-methylphenyl)propan-2-amine (3cb).** Prepared according to the general procedure and purified by silica gel chromatography (15% ethyl acetate/ 85% hexanes) to yield the product as an off-white crystalline solid (53.3 mg, 80% yield). Mp: 138-139 °C. IR (thin film): 3279, 3103, 3041, 2999, 2926, 2864, 1607, 1524, 1457, 1420, 1348, 1332, 1306, 1166, 1125, 1093, 1062, 990, 917, 850, 829, 803, 746, 735, 678, 616, 549 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.16 (2H, d, J = 9.0 Hz), 7.74 (2H, d, J = 9.0 Hz), 6.93 (2H, d, J = 7.8 Hz), 6.82 (2H, d, J = 8.1 Hz), 4.48 (1H, d, J = 7.5 Hz), 3.52 (1H, septet, J = 7.5 Hz), 2.73 (1H, dd, J = 5.4, 14.1 Hz), 2.51 (1H, dd, J = 8.7, 14.1 Hz), 2.28 (3H, s), 1.26 (3H, d, J = 6.6 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 149.7, 146.3, 136.8, 133.8, 129.4, 129.1, 128.1, 124.1, 52.2, 43.0, 22.7, 21.1. MS (ESI, negative mode): $C_{16}H_{17}N_2O_4S$ $[M – H]^-$: 333.

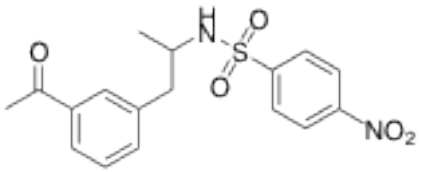


***N*-(4-nitrobenzenesulfonyl)-1-(4-methoxyphenyl)propan-2-amine (3cc).** Prepared according to the general procedure and purified by silica gel chromatography (20% ethyl acetate/ 80% hexanes) to yield the product as a light yellow crystalline solid (57.9 mg, 83% yield). Mp: 153-155 °C. IR (thin film): 3279, 3103, 3041, 2989, 2958, 2926, 2906, 2864, 2833, 1607, 1514, 1457, 1420, 1369, 1343, 1311, 1249, 1161, 1125, 1093, 1062, 1036, 995, 850, 834, 735, 678, 621 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.18 (2H, d, J = 8.4 Hz), 7.75 (2H, d, J = 8.4 Hz), 6.86 (2H, d, J = 8.1 Hz), 6.66 (2H, d, J = 8.1 Hz), 4.41 (1H, d, J = 7.8 Hz), 3.75 (3H, s), 3.52 (1H, septet, J = 6.9 Hz), 2.72 (1H, dd, J = 5.1, 14.1 Hz), 2.49 (1H, dd, J = 8.1, 13.8 Hz), 1.25 (3H, d, J = 6.3 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.7, 149.7, 146.5, 130.2, 128.9, 128.1, 124.2, 114.0, 55.3, 52.4, 42.6, 22.7. MS (ESI, negative mode): $C_{16}H_{17}N_2O_5S$ $[M - H]^-$: 349.



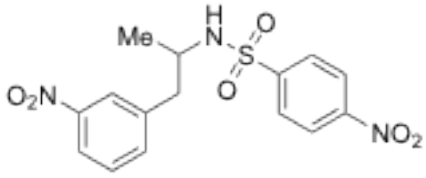
***N*-(4-nitrobenzenesulfonyl)-1-(2-biphenyl)propan-2-amine (3cd).** Prepared according to the general procedure and purified by silica gel chromatography (15% ethyl acetate/

85% hexanes) to yield the product as an off-white amorphous solid (47.6 mg, 60% yield). IR (thin film): 3290, 3103, 3061, 3020, 2968, 2926, 2864, 1607, 1529, 1477, 1451, 1436, 1420, 1400, 1348, 1311, 1161, 1135, 1088, 1052, 990, 912, 855, 829, 777, 735, 704, 684, 616, 569 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.16 (2H, d, J = 8.7 Hz), 7.63 (2H, d, J = 9.0 Hz), 7.40 (3H, m), 7.22 (1H, dd, J = 7.5, 1.5 Hz), 7.11 (5H, m), 4.22 (1H, d, J = 7.8 Hz), 3.30 (1H, septet, J = 7.5 Hz), 2.75 (2H, d, J = 7.2 Hz), 1.04 (3H, d, J = 6.3 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 149.7, 146.4, 142.3, 141.1, 134.8, 130.5, 130.3, 129.1, 128.6, 128.0, 127.7, 127.4, 127.0, 124.2, 52.0, 40.4, 22.7. MS (ESI, negative mode): $C_{21}H_{19}N_2O_4S$ $[M - H]^-$: 395.

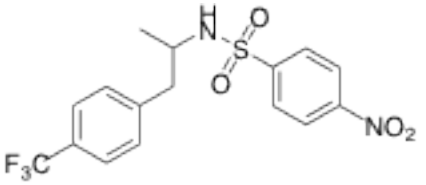


***N*-(4-nitrobenzenesulfonyl)-1-(3-acetylphenyl)propan-2-amine (3ce).** Prepared according to the general procedure and purified by silica gel chromatography (20% ethyl acetate/ 80% hexanes) to yield the product as a light yellow crystalline solid (59.5 mg, 82% yield). Mp: 127-128 °C. IR (thin film): 3279, 3103, 2978, 2926, 2864, 1675, 1602, 1529, 1431, 1348, 1306, 1270, 1161, 1088, 995, 855, 735, 684, 611 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.17 (2H, d, J = 9.0 Hz), 7.80 (2H, d, J = 8.7 Hz), 7.73 (1H, d, J = 7.5 Hz), 7.58 (1H, s), 7.29 (1H, t, J = 7.5 Hz), 7.23 (1H, d, J = 7.8 Hz), 4.51 (1H, d, J = 8.1 Hz), 3.70-3.61 (1H, m), 2.83 (1H, dd, J = 5.7, 13.8 Hz), 2.69 (1H, dd, J = 8.1, 14.1 Hz), 2.56 (3H, s), 1.24 (3H, d, J = 6.6 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.9, 149.8,

146.5, 137.8, 137.5, 134.1, 129.0, 128.8, 128.0, 127.3, 124.3, 52.1, 43.5, 26.7, 22.6. MS (ESI, negative mode): $C_{17}H_{17}N_2O_5S$ $[M - H]^-$: 361.

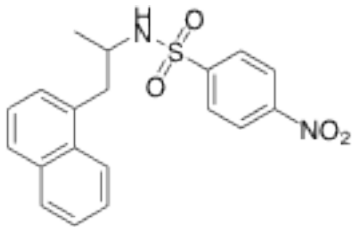


***N*-(4-nitrobenzenesulfonyl)-1-(3-nitrophenyl)propan-2-amine (3cf).** Prepared according to the general procedure and purified by silica gel chromatography (25% ethyl acetate/ 75% hexanes) to yield the product as an off-white crystalline solid (37.0 mg, 51% yield). IR (thin film): 3293, 3103, 2959, 2919, 2875, 1606, 1526, 1459, 1426, 1378, 1351, 1306, 1163, 1135, 1090, 993, 888, 855, 804, 735, 685 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 8.24 (2H, d, J = 9.0 Hz), 8.04 (1H, dt, J = 2.1, 6.9 Hz), 7.90-7.87 (3H, m), 7.45-7.38 (2H, m), 4.48 (1H, d, J = 8.1 Hz), 3.71 (1H, septet, J = 6.9 Hz), 2.89 (1H, dd, J = 6.0, 13.8 Hz), 2.82 (1H, dd, J = 7.2, 13.8 Hz), 1.20 (3H, d, J = 6.6 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.1, 148.4, 146.6, 139.2, 135.6, 129.7, 128.1, 124.4, 124.3, 122.1, 51.8, 43.4, 22.1. MS (ESI, negative mode): $C_{15}H_{14}N_3O_6S$ $[M - H]^-$: 364.



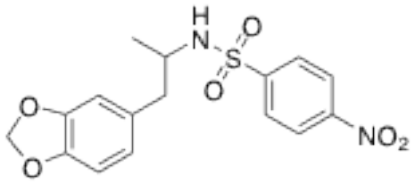
***N*-(4-nitrobenzenesulfonyl)-1-[4-(trifluoromethyl)phenyl]propan-2-amine (3cg).** Prepared according to the general procedure and purified by silica gel chromatography

(15% ethyl acetate/ 85% hexanes) to yield the product as an off-white crystalline solid (45.6 mg, 59% yield). Mp: 149-151 °C. IR (thin film): 3269, 3103, 2978, 2926, 2864, 1618, 1607, 1529, 1420, 1348, 1322, 1161, 1114, 1093, 1062, 1016, 990, 850, 735, 684, 637, 611 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.23 (2H, d, J = 9.0 Hz), 7.84 (2H, d, J = 9.0 Hz), 7.45 (2H, d, J = 7.8 Hz), 7.15 (2H, d, J = 8.1 Hz), 4.42 (1H, d, J = 8.1 Hz), 3.67 (1H, septet, J = 6.6 Hz), 2.85 (1H, dd, J = 6.0, 13.8 Hz), 2.74 (1H, dd, J = 7.5, 13.8 Hz), 1.20 (3H, d, J = 6.6 Hz). ^{13}C NMR (125 MHz, DMSO-d_6): δ 148.9, 147.1, 143.1, 130.0, 127.5, 126.7 (q, $^{2}J_{CF}$ = 31 Hz), 124.7, 124.3 (q, $^{1}J_{CF}$ = 272 Hz), 124.1, 51.4, 42.0, 22.5. MS (ESI, negative mode): $C_{16}H_{15}F_3N_2O_4S$ $[M - H]^-$: 387.

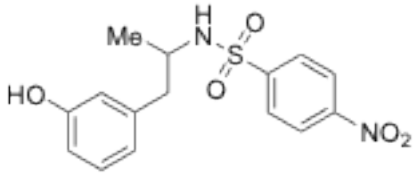


***N*-(4-nitrobenzenesulfonyl)-1-(1-naphthyl)propan-2-amine (3ch).** Prepared according to the general procedure and purified by silica gel chromatography (15% ethyl acetate/ 85% hexanes) to yield the product as a light yellow crystalline solid (64.2 mg, 87% yield). Mp: 147-149 °C. IR (thin film): 3300, 3103, 3061, 2968, 2926, 2864, 1607, 1597, 1519, 1457, 1426, 1400, 1368, 1348, 1327, 1306, 1161, 1135, 1093, 1073, 1016, 1000, 927, 850, 834, 798, 793, 777, 735, 684, 611, 569, 549 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.67-7.59 (5H, m), 7.40-7.34 (2H, m), 7.32-7.25 (3H, m), 7.12 (1H, d, J = 6.6 Hz), 4.45 (1H, d, J = 6.3 Hz), 3.70-3.57 (1H, m), 3.34 (1H, dd, J = 4.2, 14.4 Hz), 2.80 (1H, dd, J = 10.5, 14.1 Hz), 1.50 (3H, d, J = 6.3 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 149.0, 144.6,

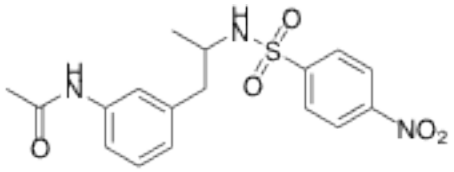
134.0, 133.1, 131.3, 128.9, 128.1, 127.8, 127.1, 126.4, 126.1, 125.5, 123.4, 123.1, 50.8, 41.0, 24.0. MS (ESI, negative mode): $C_{19}H_{18}N_2O_4S$ [M – H]$^-$: 369.



***N*-(4-nitrobenzenesulfonyl)-1-(3,4-methylenedioxyphenyl)propan-2-amine (3ci).** Prepared according to the general procedure and purified by silica gel chromatography (15% ethyl acetate/ 85% hexanes) to yield the product as a bright yellow crystalline solid (57.0 mg, 78% yield). Mp: 173-176 °C. IR (thin film): 3321, 3269, 3103, 2989, 2968, 2926, 2895, 1607, 1524, 1503, 1441, 1420, 1343, 1327, 1311, 1249, 1161, 1119,, 1093, 1062, 1031, 995, 927, 850, 829, 813, 767, 735, 678, 621 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.21 (2H, d, J = 8.7 Hz), 7.75 (2H, d, J = 8.7 Hz), 6.61 (1H, d, J = 7.8 Hz), 6.43 (1H, dd, J = 1.5, 7.8 Hz), 6.23 (1H, d, J = 1.5 Hz), 5.89 (1H, d, J = 1.2 Hz), 5.82 (1H, d, J = 1.2 Hz), 4.38 (1H, d, J = 7.2 Hz), 3.52-3.38 (1H, m), 2.70 (1H, dd, J = 4.8, 14.1 Hz), 2.41 (1H, dd, J = 9.3, 14.1 Hz), 1.30 (3H, d, J = 6.3 Hz). ^{13}C NMR (125 MHz, DMSO-d_6): δ 148.8, 147.2, 146.6, 145.4, 132.0, 127.6, 124.1, 122.2, 109.3, 107.8, 100.6, 51.8, 41.9, 22.5. MS (ESI, negative mode): $C_{16}H_{15}N_2O_6S$ [M – H]$^-$: 363.

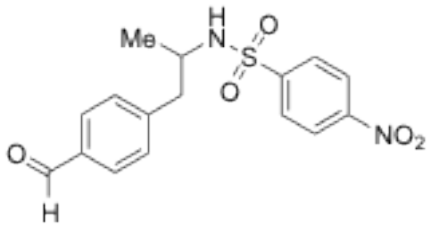


***N*-(4-nitrobenzenesulfonyl)-1-(3-hydroxyphenyl)propan-2-amine (3cj).** Prepared according to the general procedure and purified by silica gel chromatography (10% ethyl acetate/ 90% hexanes) to yield the product as an off-white crystalline solid (51.1 mg, 76% yield). Mp: 134-136 °C. IR (thin film): 3456, 3300, 3103, 2978, 2937, 2864, 1602, 1581, 1528, 1483, 1457, 1426, 1350, 1306, 1162, 1093, 1000, 855, 736, 684 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.18 (2H, d, J = 9.0 Hz), 7.75 (2H, d, J = 9.0 Hz), 7.02 (1H, t, J = 7.8 Hz), 6.61 (1H, dd, J = 2.1, 8.1 Hz), 6.53 (1H, d, J = 7.5 Hz), 6.36 (1H, s), 4.54 (1H, d, J = 7.8 Hz), 3.52 (1H, septet, J = 6.9 Hz), 2.73 (1H, dd, J = 5.1, 13.8 Hz), 2.49 (1H, dd, J = 9.0, 14.1 Hz), 1.28 (3H, d, J = 6.6 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.9, 149.9, 146.0, 138.9, 130.0, 128.0, 124.3, 121.7, 116.0, 114.0, 52.1, 43.3, 22.9. MS (ESI, negative mode): $C_{15}H_{15}N_2O_5S$ $[M - H]^-$: 335.

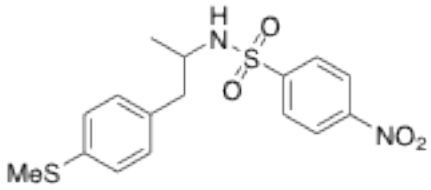


***N*-(4-nitrobenzenesulfonyl)-1-(3-acetamidophenyl)propan-2-amine (3ck).** Prepared according to the general procedure and purified by silica gel chromatography (30% ethyl acetate/ 70% hexanes) to yield the product as an off-white crystalline solid (46.6 mg, 62% yield). Mp: 155-157 °C. IR (thin film): 3362, 3300, 3103, 2978, 2926, 2864, 1664, 1607, 1592, 1529, 1488, 1441, 1420, 1348, 1306, 1161, 1093, 995, 850, 735, 684, 611 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.12 (2H, d, J = 8.7 Hz), 7.72 (2H, d, J = 8.7 Hz), 7.40 (1H, s), 7.10 (1H, t, J = 7.8 Hz), 7.00 (1H, s), 6.95 (1H, dd, J = 1.2, 8.1 Hz), 6.72

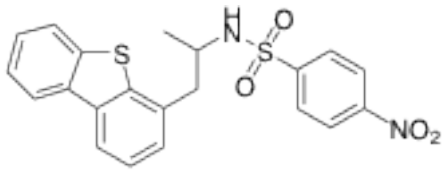
(1H, d, J = 7.8 Hz), 4.54 (1H, d, J = 8.4 Hz), 3.60-3.46 (1H, m), 2.76 (1H, dd, J = 4.8, 14.1 Hz), 2.48 (1H, dd, J = 9.0, 13.8 Hz), 2.14 (3H, s), 1.30 (3H, d, J = 6.6 Hz). ^{13}C NMR (125 MHz, $CDCl_3$ with DMSO-d_6): δ 168.7, 149.1, 146.9, 138.8, 138.5, 128.5, 127.7, 124.5, 123.8, 120.2, 117.5, 52.0, 43.3, 24.3, 22.6. MS (ESI, positive mode): $C_{17}H_{19}N_3NaO_5S$ $[M + Na]^+$: 400; $C_{17}H_{19}N_3KO_5S$ $[M + K]^+$: 416.



***N*-(4-nitrobenzenesulfonyl)-1-(4-formylphenyl)propan-2-amine (3cl).** Prepared according to the general procedure and purified by silica gel chromatography (25% ethyl acetate/ 75% hexanes) to yield the product as an off-white crystalline solid (45.0 mg, 65% yield). Mp: 139-142 °C. IR (thin film): 3276, 3103, 2978, 2926, 2864, 2740, 1692, 1606, 1576, 1528, 1426, 1349, 1307, 1215, 1164, 1130, 1093, 995, 855, 783, 736, 685 cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6): δ 9.86 (1H, s), 8.19-8.16 (3H, m), 7.76 (2H, d, J = 9.0 Hz), 7.62 (2H, d, J = 8.1 Hz), 7.27 (2H, d, J = 7.8 Hz), 3.60-3.45 (1H, m), 2.75 (1H, dd, J = 5.1, 13.2 Hz), 2.63 (1H, dd, J = 8.7, 13.2 Hz), 1.08 (3H, d, J = 6.3 Hz). ^{13}C NMR (125 MHz, DMSO-d_6): δ 192.9, 149.4, 147.6, 146.0, 134.9, 130.4, 129.7, 128.0, 124.7, 51.9, 42.9, 22.8. MS (ESI, negative mode): $C_{16}H_{15}N_2O_5S$ $[M – H]^-$: 347.

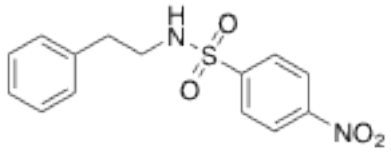


***N*-(4-nitrobenzenesulfonyl)-1-(4-methylthiophenyl)propan-2-amine (3cm).** Prepared according to the general procedure and purified by silica gel chromatography (15% ethyl acetate/ 85% hexanes) to yield the product as a bright yellow crystalline solid (31.2 mg, 43% yield). Mp: 137-144 °C. IR (thin film): 3290, 3103, 2968, 2926, 2854, 1602, 1524, 1493, 1426, 1405, 1348, 1306, 1161, 1130, 1093, 1062, 1010, 995, 855, 839, 803, 735, 684, 616 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.20 (2H, d, J = 9.0 Hz), 7.75 (2H, d, J = 9.0 Hz), 7.00 (2H, d, J = 8.4 Hz), 6.88 (2H, d, J = 8.4 Hz), 4.38 (1H, d, J = 8.1 Hz), 3.62-3.48 (1H, m), 2.74 (1H, dd, J = 5.1, 13.8 Hz), 2.53 (1H, dd, J = 8.1, 13.8 Hz), 2.44 (3H, s), 1.25 (3H, d, J = 6.6 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 149.8, 146.4, 137.6, 133.6, 129.7, 128.1, 126.4, 124.3, 52.3, 43.0, 22.7, 15.6. MS (ESI, negative mode): $C_{16}H_{17}N_2O_4S_2$ $[M - H]^-$: 366.

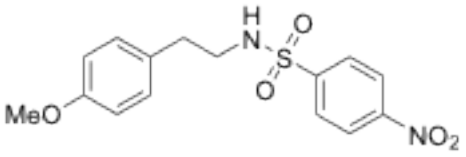


***N*-(4-nitrobenzenesulfonyl)-1-(dibenzo[b,d]thien-4-yl)propan-2-amine (3cn).** Prepared according to the general procedure and purified by silica gel chromatography (15% ethyl acetate/ 85% hexanes) to yield the product as a light yellow crystalline solid (64.6 mg, 76% yield). IR (thin film): 3290, 3103, 3072, 2978, 2926, 2854, 1607, 1524,

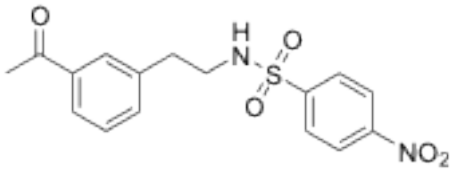
1441, 1420, 1405, 1348, 1306, 1160, 1130, 1088, 1068, 1036, 1016, 990, 912, 850, 829, 756, 730, 684, 611 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 8.01-7.98 (1H, m), 7.86 (1H, d, J = 8.1 Hz), 7.80-7.78 (1H, m), 7.54 (2H, d, J = 8.7 Hz), 7.51-7.48 (2H, m), 7.34 (2H, d, J = 9.0 Hz), 7.29 (1H, d, J = 7.5 Hz), 7.07 (1H, d, J = 6.9 Hz), 4.51 (1H, d, J = 7.5 Hz), 3.95-3.86 (1H, m), 3.05 (1H, dd, J = 3.9, 14.4 Hz), 2.75 (1H, dd, J = 10.8, 14.4 Hz), 1.51 (3H, d, J = 6.3 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 149.0, 145.1, 138.9, 138.3, 136.2, 135.4, 132.0, 127.6, 127.5, 127.2, 125.4, 125.1, 123.2, 122.7, 121.7, 120.4, 50.3, 42.9, 24.3. MS (ESI, negative mode): $C_{21}H_{16}N_2O_4S_2$ $[M - H]^-$: 425.



***N*-(4-nitrobenzenesulfonyl)-2-phenylethylamine (3da).**[25] Prepared according to the general procedure and purified by silica gel chromatography (10% ethyl acetate/ 90% hexanes) to yield the product as a pale yellow crystalline solid (45.8 mg, 75% yield). Mp: 91-93 °C. IR (thin film): 3297, 3106, 3030, 2929, 2864, 1606, 1529, 1454, 1420, 1350, 1310, 1310, 1164, 1094, 1073, 855, 736, 701, 685, 613 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 8.31, (2H, d, J = 9.0 Hz), 7.94 (2H, d, J = 9.0 Hz), 7.30-7.20 (3H, m), 7.07 (2H, dd, J = 2.1, 7.8 Hz), 4.55 (1H, t, J = 6.3 Hz), 3.31 (2H, q, J = 6.9 Hz), 2.80 (2H, t, J = 6.9 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.0, 145.8, 137.1, 128.9, 128.7, 128.2, 127.1, 124.4, 44.4, 35.9. MS (ESI, negative mode): $C_{14}H_{13}N_2O_4S$ $[M - H]^-$: 305.

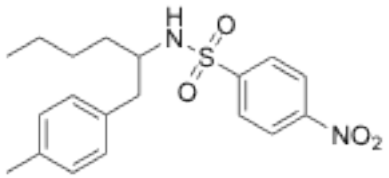


***N*-(4-nitrobenzenesulfonyl)-2-(4-methoxyphenyl)ethylamine (3dc).**[24] Prepared according to the general procedure and purified by silica gel chromatography (15% ethyl acetate/ 85% hexanes) to yield the product as a pale yellow crystalline solid (63.0 mg, 94% yield). Mp: 100-102 °C. IR (thin film): 3293, 3103, 2936, 1610, 1530, 1514, 1462, 1441, 1423, 1350, 1311, 1247, 1162, 1109, 1094, 1073, 1033, 856, 835, 736, 685 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.31, (2H, d, J = 9.0 Hz), 7.93 (2H, d, J = 9.0 Hz), 6.98 (2H, d, J = 8.4 Hz), 6.79 (2H, d, J = 8.7 Hz), 4.46 (1H, t, J = 5.4 Hz), 3.78 (3H, s), 3.27 (2H, q, J = 6.6 Hz), 2.74 (2H, t, J = 6.6 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.8, 150.0, 146.0, 129.8, 129.1, 128.4, 124.5, 114.4, 55.4, 44.7, 35.1. MS (ESI, negative mode): $C_{15}H_{15}N_2O_5S$ $[M - H]^-$: 335.

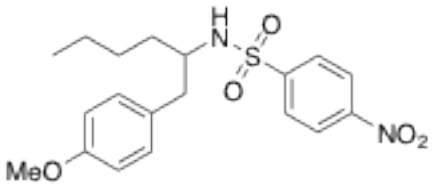


***N*-(4-nitrobenzenesulfonyl)-2-(3-acetylphenyl)ethylamine (3de).** Prepared according to the general procedure and purified by silica gel chromatography (15% ethyl acetate/ 85% hexanes) to yield the product as a white crystalline solid (57.7 mg, 83% yield). Mp: 121 °C. IR (thin film): 3269, 3103, 3072, 2958, 2918, 2875, 2843, 1672, 1604, 1586, 1526, 1460, 1378, 1349, 1308, 1270, 1159, 1092, 1073, 907, 888, 854, 798, 735, 684 cm^{-1}. ^{1}H

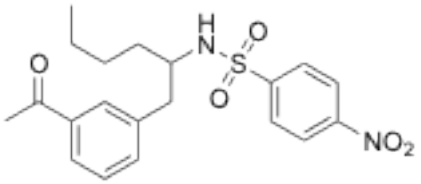
NMR (300 MHz, $CDCl_3$): δ 8.32, (2H, d, J = 8.7 Hz), 7.97 (2H, d, J = 8.7 Hz), 7.80 (1H, d, J = 7.5 Hz), 7.68 (1H, s), 7.39 (1H, t, J = 7.5 Hz), 7.32 (1H, d, J = 7.5 Hz), 4.58 (1H, t, J = 6.6 Hz), 3.35 (2H, q, J = 6.6 Hz), 2.88 (2H, t, J = 6.9 Hz), 2.58 (3H, s). ^{13}C NMR (125 MHz, $CDCl_3$): δ 198.0, 150.2, 146.0, 138.1, 137.8, 133.6, 129.3, 128.3, 128.3, 127.5, 124.6, 44.4, 36.0, 26.8. MS (ESI, negative mode): $C_{16}H_{15}N_2O_5S$ $[M - H]^-$: 347.



***N*-(4-nitrobenzenesulfonyl)-1-(4-methylphenyl)hexan-2-amine (3eb).** Prepared according to the general procedure and purified by silica gel chromatography (5% ethyl acetate/ 95% hexanes) to yield the product as a pale yellow crystalline solid (58.3 mg, 77% yield). Mp: 128 °C. IR (thin film): 3279, 2957, 2917, 2875, 2843, 1607, 1528, 1459, 1378, 1348, 1306, 1162, 1093, 964, 854, 735, 684 cm^{-1}. ^1H NMR (300 MHz, C_6D_6): δ 7.52 (2H, d, J = 9.0 Hz), 7.29 (2H, d, J = 8.7 Hz), 6.66 (2H, d, J = 7.8 Hz), 6.53 (2H, d, J = 8.1 Hz), 3.88 (1H, d, J = 8.4 Hz), 3.25 (1H, sextet, J = 6.9 Hz), 2.37 (1H, dd, J = 5.1, 13.5 Hz), 2.05 (3H, s), 2.03 (1H, dd, J = 8.1, 13.5 Hz), 1.35-1.18 (2H, m), 1.13-0.99 (4H, m), 0.78 (3H, t, J = 6.6 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 149.6, 146.6, 136.7, 133.9, 129.4, 129.2, 128.1, 124.1, 56.5, 40.9, 35.7, 27.8, 22.6, 21.1, 14.1. MS (ESI, negative mode): $C_{19}H_{23}N_2O_4S$ $[M - H]^-$: 375.

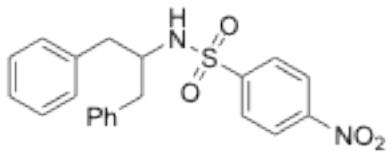


***N*-(4-nitrobenzenesulfonyl)-1-(4-methoxyphenyl)hexan-2-amine (3ec).** Prepared according to the general procedure and purified by silica gel chromatography (10% ethyl acetate/ 90% hexanes) to yield the product as a pale yellow crystalline solid (53.1 mg, 68% yield). Mp: 110-111 °C. IR (thin film): 3291, 3105, 2934, 2861, 1610, 1529, 1513, 1459, 1422, 1349, 1305, 1248, 1162, 1094, 1034, 963, 854, 736, 685, 616 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.17 (2H, d, J = 9.0 Hz), 7.75 (2H, d, J = 9.0 Hz), 6.85 (2H, d, J = 8.4 Hz), 6.63 (2H, d, J = 8.4 Hz), 4.42 (1H, d, J = 8.4 Hz), 3.50-3.39 (1H, m), 2.75 (2H, dd, J = 5.1, 14.1 Hz), 2.47 (2H, dd, J = 8.1, 14.1 Hz), 1.62-1.44 (2H, m), 1.35-1.23 (4H, m), 0.85 (3H, t, J = 6.6 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.5, 149.5, 146.6, 130.2, 128.9, 127.9, 124.0, 113.9, 56.6, 55.1, 40.4, 35.5, 27.7, 22.4, 13.9. MS (ESI, negative mode): $C_{19}H_{23}N_2O_5S$ $[M - H]^-$: 392.

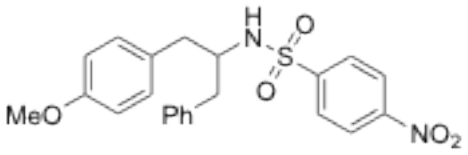


***N*-(4-nitrobenzenesulfonyl)-1-(3-acetylphenyl)hexan-2-amine (3ee).** Prepared according to the general procedure and purified by silica gel chromatography (15% ethyl acetate/ 85% hexanes) to yield the product as a white crystalline solid (53.8 mg, 67%

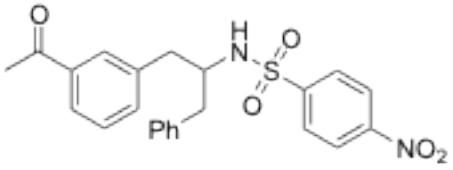
yield). Mp: 116-118°C. IR (thin film): 3279, 3072, 2959, 2918, 2875, 1680, 1607, 1586, 1529, 1463, 1379, 1353, 1306, 1270, 1161, 1093, 969, 888, 735, 684 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.16 (2H, d, J = 9.0 Hz), 7.79 (2H, d, J = 8.7 Hz), 7.71 (1H, dt, J = 1.5, 7.5 Hz), 7.57 (1H, s), 7.30-7.21 (2H, m), 4.47 (1H, d, J = 9.0 Hz), 3.56 (1H, sextet, J = 6.3 Hz), 2.87 (2H, dd, J = 5.4, 13.8 Hz), 2.65 (2H, dd, J = 7.8, 14.1 Hz), 2.55 (3H, s), 1.63-1.42 (2H, m), 1.33-1.19 (4H, m), 0.83 (3H, t, J = 6.6 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.9, 149.8, 146.7, 138.0, 137.4, 134.2, 129.0, 128.0, 127.2, 124.2, 56.4, 41.6, 35.6, 27.8, 26.7, 22.5, 14.0. MS (ESI, negative mode): $C_{20}H_{23}N_2O_5S$ $[M - H]^-$: 403.



***N*-(4-nitrobenzenesulfonyl)-1,3-diphenylpropan-2-amine (3fa).** Prepared according to the general procedure and purified by silica gel chromatography (10% ethyl acetate/ 90% hexanes) to yield the product as a yellow crystalline solid (54.4 mg, 69% yield). Mp: 138-139 °C. IR (thin film): 3293, 3103, 3061, 3030, 2926, 2854, 1606, 1528, 1496, 1454, 1420, 1349, 1310, 1163, 1084, 1052, 971, 855, 736, 701, 685 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.01, (2H, d, J = 9.0 Hz), 7.52 (2H, d, J = 9.0 Hz), 7.21-7.14 (6H, m), 7.04-7.01 (4H, m), 4.45 (1H, d, J = 8.1 Hz), 3.71-3.56 (1H, m), 2.91 (2H, dd, J = 5.7, 13.8 Hz), 2.73 (2H, dd, J = 7.2, 13.8 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 149.5, 145.5, 136.8, 129.4, 128.7, 127.7, 126.9, 124.0, 57.5, 41.5. MS (ESI, negative mode): $C_{21}H_{19}N_2O_4S$ $[M - H]^-$: 395.

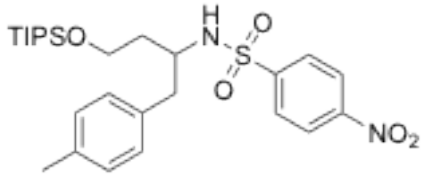


***N*-(4-nitrobenzenesulfonyl)-1-(4-methoxyphenyl)-3-phenylpropan-2-amine (3fc).** Prepared according to the general procedure and purified by silica gel chromatography (15% ethyl acetate/ 85% hexanes) to yield the product as a bright yellow crystalline solid (72.1 mg, 85% yield). Mp: 97-100 °C. IR (thin film): 3295, 3103, 3061, 3030, 2926, 2833, 1610, 1528, 1513, 1454, 1422, 1349, 1307, 1248, 1162, 1110, 1094, 1057, 1034, 972, 854, 824, 736, 702, 684, 615 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.02 (2H, d, J = 9.0 Hz), 7.53 (2H, d, J = 9.0 Hz), 7.20-7.18 (3H, m), 7.05-7.02 (2H, m), 6.91 (2H, d, J = 8.7 Hz), 6.68 (2H, d, J = 8.4 Hz), 4.43 (1H, d, J = 8.1 Hz), 3.67-3.55 (1H, m), 2.91 (1H, dd, J = 6.0, 13.8 Hz), 2.85 (1H, dd, J = 5.1, 13.8 Hz), 2.74 (1H, dd, J = 6.9, 13.5 Hz), 2.62 (1H, dd, J = 7.5, 14.1 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.6, 149.4, 145.7, 136.9, 130.3, 129.5, 128.7, 128.7, 127.8, 126.9, 123.9, 113.9, 57.7, 55.2, 41.7, 40.5. MS (ESI, negative mode): $C_{21}H_{21}N_2O_5S$ $[M - H]^-$: 426.



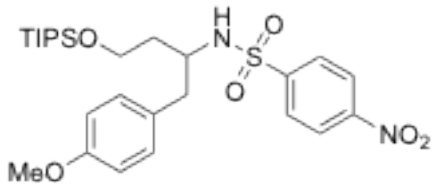
***N*-(4-nitrobenzenesulfonyl)-1-(3-acetylphenyl)-3-phenylpropan-2-amine (3fe).** Prepared according to the general procedure and purified by silica gel chromatography (15% ethyl acetate/ 85% hexanes) to yield the product as a white crystalline solid (79.9

mg, 91% yield). Mp: 113-114 °C. IR (thin film): 3276, 3103, 3030, 2958, 2924, 1678, 1604, 1586, 1528, 1451, 1431, 1349, 1309, 1273, 1162, 1086, 974, 909, 855, 798, 736, 699, 685 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.00 (2H, d, J = 8.7 Hz), 7.75 (1H, d, J = 6.6 Hz), 7.63 (1H, s), 7.54 (2H, d, J = 8.7 Hz), 7.34-7.26 (2H, m), 7.20-7.18 (3H, m), 7.02-6.99 (2H, m), 4.44 (1H, d, J = 8.4 Hz), 3.71 (1H, sextet, J = 7.5 Hz), 2.99 (1H, dd, J = 5.4, 13.5 Hz), 2.91 (1H, dd, J = 5.7, 13.8 Hz), 2.81 (1H, dd, J = 7.5, 14.1 Hz), 2.70 (1H, dd, J = 7.2, 13.5 Hz), 2.57 (3H, s). ^{13}C NMR (125 MHz, $CDCl_3$): δ 198.0, 149.6, 145.7, 137.8, 137.5, 136.6, 134.3, 129.5, 129.1, 129.0, 128.9, 127.8, 127.2, 127.2, 124.1, 57.5, 41.7, 41.6, 26.8. MS (ESI, negative mode): $C_{21}H_{21}N_2O_5S$ $[M - H]^-$: 437.

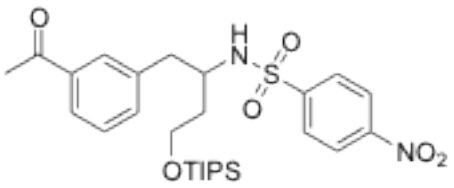


***N*-(4-nitrobenzenesulfonyl)-1-(4-methylphenyl)-4-(triisopropylsiloxy)butan-2-amine (3gb).** Prepared according to the general procedure and purified by silica gel chromatography (5% ethyl acetate/ 95% hexanes) to yield the product as a white solid (65.3 mg, 63% yield). Mp: 103-104 °C. IR (thin film): 3287, 2957, 2924, 2867, 1607, 1531, 1461, 1378, 1348, 1310, 1164, 1093, 1013, 883, 853, 736, 684 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.20 (2H, d, J = 8.7 Hz), 7.84 (2H, d, J = 8.7 Hz), 6.96 (2H, d, J = 7.8 Hz), 6.89 (2H, d, J = 8.1 Hz), 5.86 (1H, d, J = 6.9 Hz), 3.94-3.87 (1H, m), 3.76-3.64 (2H, m), 2.85 (2H, dd, J = 6.9, 14.1 Hz), 2.76 (2H, dd, J = 7.5, 13.8 Hz), 2.27 (3H, s), 1.82-1.72 (1H, m), 1.68-1.55 (1H, m), 1.19-1.03 (21H, m). ^{13}C NMR (125 MHz, $CDCl_3$): δ

149.7, 146.9, 136.5, 134.5, 129.3, 129.2, 128.2, 124.1, 60.9, 55.4, 40.6, 35.9, 21.1, 18.2, 11.9. MS (ESI, negative mode): $C_{26}H_{39}N_2O_5SSi$ $[M - H]^-$: 519.

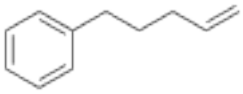


***N*-(4-nitrobenzenesulfonyl)-1-(4-methoxyphenyl)-4-(triisopropylsiloxy)butan-2-amine (3gc).** Prepared according to the general procedure and purified by silica gel chromatography (10% ethyl acetate/ 90% hexanes) to yield the product as an off white solid (81.2 mg, 76% yield). IR (thin film): 3291, 3103, 2943, 2866, 1611, 1531, 1514, 1464, 1349, 1304, 1249, 1163, 1093, 1036, 1016, 883, 854, 736, 684 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 8.20 (2H, d, J = 9.0 Hz), 7.84 (2H, d, J = 9.0 Hz), 6.92 (2H, d, J = 8.7 Hz), 6.68 (2H, d, J = 8.7 Hz), 5.87 (1H, d, J = 7.2 Hz), 3.93-3.86 (1H, m), 3.74 (3H, s), 3.76-3.60 (2H, m), 2.82 (2H, dd, J = 6.9, 13.8 Hz), 2.75 (2H, dd, J = 7.5, 14.1 Hz), 1.81-1.73 (1H, m), 1.69-1.60 (1H, m), 1.15-1.02 (21H, m). ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.5, 149.7, 146.9, 130.3, 129.5, 128.2, 124.1, 114.0, 60.9, 55.5, 55.3, 40.1, 35.8, 18.2, 11.9. MS (ESI, negative mode): $C_{26}H_{39}N_2O_5SSi$ $[M - H]^-$: 536.



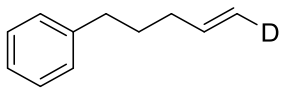
***N*-(4-nitrobenzenesulfonyl)-1-(3-acetylphenyl)-4-(triisopropylsiloxy)butan-2-amine (3ge).** Prepared according to the general procedure and purified by silica gel chromatography (15% ethyl acetate/ 85% hexanes) to yield the product as a white crystalline solid (68.6 mg, 63% yield). Mp: 108-109 °C. IR (thin film): 3276, 2954, 2926, 2867, 1685, 1605, 1586, 1531, 1462, 1436, 1349, 1309, 1272, 1164, 1093, 1013, 995, 883, 854, 736, 685 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.21 (2H, d, J = 9.0 Hz), 7.89 (2H, d, J = 8.7 Hz), 7.75-7.72 (1H, m), 7.65 (1H, s), 7.31 (2H, d, J = 4.2 Hz), 6.05 (1H, d, J = 6.9 Hz), 3.94-3.86 (1H, m), 3.77-3.67 (2H, m), 3.01 (2H, dd, J = 6.6, 13.5 Hz), 2.88 (2H, dd, J = 6.9, 13.8 Hz), 2.56 (3H, s), 1.82-1.68 (1H, m), 1.64-1.56 (1H, m), 1.18-1.04 (21H, m). ^{13}C NMR (125 MHz, $CDCl_3$): δ 198.0, 149.8, 146.9, 138.4, 137.5, 134.2, 129.0, 128.2, 127.1, 124.3, 61.0, 55.4, 41.1, 35.5, 26.7, 18.1, 11.9. MS (ESI, negative mode): $C_{27}H_{39}N_2O_6SSi$ $[M - H]^-$: 547.

1.4.5 Experimental Procedures for Deuteration Studies

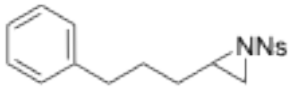


5-Phenylprop-1-ene. To Cp_2ZrCl_2 (6.40 g, 21.9 mmol, 1.5 equiv) in THF (33mL) was added $LiAlH_4$ (220 mg, 5.9 mmol, 0.4 equiv) in THF (8 mL). The reaction mixture was stirred at room temperature for 1.5 h and 5-phenyl-1-propyne (2.16 g, 15.0 mmol, 1.0 equiv) was added. The solution was stirred for an additional 2.5 h, at which point it was quenched with H_2O and allowed to stir overnight. The mixture was diluted with ether, washed sequentially with 1M HCl (aq.), saturated $NaHCO_3$ (aq.), and brine, and dried on Na_2SO_4. The dried solution was decanted and concentrated on a rotary evaporator.

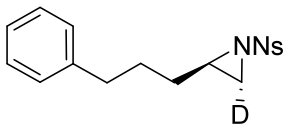
Filtration of the crude mixture through a short silica gel column eluting with pentane provided the crude alkene as a clear colorless liquid, which was carried on to the next step without further purification. Spectroscopic data were determined to be consistent with reported values.[26] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.31-7.17 (5H, m), 5.91-5.78 (1H, m), 5.07-4.96 (2H, m), 2.63 (2H, t, *J* = 7.5 Hz), 2.10 (2H, quartet, *J* = 7.5 Hz), 1.73 (2H, quintet, *J* = 7.5 Hz).



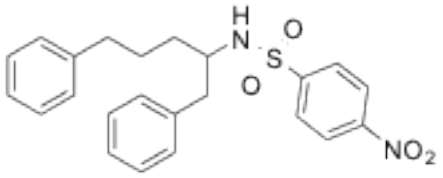
(*E*)-1-deuterio-5-phenylprop-1-ene. To Cp_2ZrCl_2 (6.40 g, 21.9 mmol, 1.5 equiv) in THF (33mL) was added $LiAlH_4$ (220 mg, 5.9 mmol, 0.4 equiv) in THF (8 mL). The reaction mixture was stirred at room temperature for 1.5 h and 5-phenyl-1-propyne (2.16 g, 15.0 mmol, 1.0 equiv) was added. The solution was stirred for an additional 2.5 h, at which point it was quenched with D_2O and allowed to stir overnight. The mixture was diluted with ether, washed sequentially with 1M HCl (aq.), saturated $NaHCO_3$ (aq.), and brine, and dried on Na_2SO_4. The dried solution was decanted and concentrated on a rotary evaporator. Filtration of the crude mixture through a short silica gel column eluting with pentane provided the crude (*E*)-alkene as a clear colorless liquid, which was carried on to the next step without further purification. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.31-7.17 (5H, m), 5.84 (1H, dt, *J* = 6.6, 17.1 Hz), 5.02 (1H, d, *J* = 17.1 Hz), 2.63 (2H, t, *J* = 7.5 Hz), 2.10 (2H, quartet, *J* = 7.5 Hz), 1.73 (2H, quintet, *J* = 7.5 Hz).



***N*-(4-nitrobenzenesulfonyl)-2-(3-phenylpropyl)aziridine (1h).** Rhodium(II) octanoate dimer (62.3 mg, 0.08 mmol, 0.02 equiv) was added to a stirred solution of **5-phenylprop-1-ene** (581 mg, 4.0 mmol, 1.0 equiv) in CH_2Cl_2 (8 mL). The reaction mixture was cooled to -5 °C and PhI=NNs was added in one portion. The reaction mixture was permitted to slowly warm to room temperature over a period of 2 h and then stirred overnight. Filtering through celite and eluting with CH_2Cl_2 afforded the crude product, which was purified using column chromatography (gradient 100% hexanes to 15% ethyl acetate/ 85% hexanes) and recrystallized from ethyl acetate/ hexanes to obtain the title compound as a white crystalline solid (261 mg, 19% yield). Mp: 79-81 °C. IR (thin film): 2958, 2921, 2873, 2847, 1607, 1533, 1462, 1455, 1379, 1298, 1230, 1161, 1011, 972, 929, 887, 854, 747, 739, 697 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 8.36 (2H, d, J = 9.0 Hz), 8.14 (2H, d, J = 9.0 Hz), 7.28-7.15 (3H, m), 7.08 (2H, d, J = 6.9 Hz), 2.94-2.86 (1H, m), 2.74 (1H, d, J = 6.9 Hz), 2.59 (2H, t, J = 7.5 Hz), 2.15 (1H, d, J = 4.5 Hz), 1.72-1.57 (3H, m), 1.44-1.34 (1H, m). ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.7, 144.2, 141.5, 129.4, 128.5, 128.4, 126.2, 124.4, 41.2, 35.1, 34.8, 30.8. 28.6. MS (ESI, positive mode): $C_{17}H_{18}N_2NaO_4S$ $[M + Na]^+$: 369.

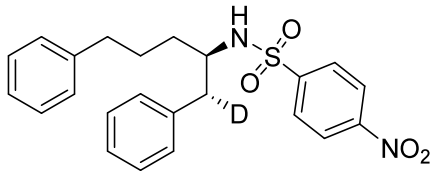


***(trans)-N*-(4-nitrobenzenesulfonyl)-2-deuterio-3-(3-phenylpropyl)aziridine (1h-*d*).** Rhodium(II) octanoate dimer (62.3 mg, 0.08 mmol, 0.02 equiv) was added to a stirred solution of **(*E*)-1-deuterio-5-phenylprop-1-ene** (585 mg, 4.0 mmol, 1.0 equiv) in CH_2Cl_2 (8 mL). The reaction mixture was cooled to -5 °C and PhI=NNs was added in one portion. The reaction mixture was permitted to slowly warm to room temperature over a period of 2 h and then stirred overnight. Filtering through celite and eluting with CH_2Cl_2 afforded the crude product, which was purified using column chromatography (gradient 100% hexanes to 15% ethyl acetate/ 85% hexanes) and recrystallized from ethyl acetate/ hexanes to obtain the title compound as a white crystalline solid (368 mg, 26% yield). Mp: 81-82 °C. IR (thin film): 2957, 2922, 2873, 2845, 1608, 1530, 1460, 1379, 1351, 1327, 1306, 1218, 1161, 1091, 1010, 968, 933, 887, 852, 789, 740, 693 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 8.36 (2H, d, J = 9.0 Hz), 8.14 (2H, d, J = 8.7 Hz), 7.28-7.15 (3H, m), 7.08 (2H, d, J = 6.9 Hz), 2.92-2.87 (1H, m), 2.59 (2H, t, J = 7.2 Hz), 2.14 (1H, d, J = 4.8 Hz), 1.72-1.54 (3H, m), 1.44-1.35 (1H, m). ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.7, 144.2, 141.5, 129.4, 128.5, 128.4, 126.2, 124.4, 41.1, 35.1, 34.6 (t, $^1J_{CD}$ = 26 Hz), 30.7, 28.6. MS (ESI, positive mode): $C_{17}H_{17}DN_2NaO_4S$ $[M + Na]^+$: 370.



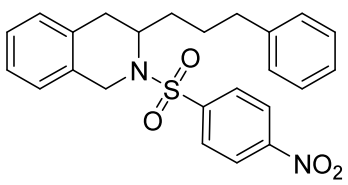
***N*-(4-nitrobenzenesulfonyl)-1,5-diphenylpentan-2-amine (3ha).** A flame-dried borosilicate glass vial equipped with an egg-shaped magnetic stirbar was charged with bis(dibenzylideneacetone)palladium(0) (14.4 mg, 0.025 mmol, 0.05 equiv), tri-1-

naphthylphosphine (24.8 mg, 0.060 mmol, 0.12 equiv), cesium carbonate (16.3 mg, 0.050 mmol, 0.10 equiv), ***N*-(4-nitrobenzenesulfonyl)-2-(3-phenylpropyl)aziridine** (166 mg, 0.48 mmol, 1.0 equiv), and phenylboronic acid (122 mg, 1.0 mmol, 2.0 equiv). The vial was thoroughly flushed with nitrogen and capped with a Teflon-lined screw cap. A solution of *m*-chlorophenol (260 mg, 2.0 mmol, 4.0 equiv) in dry tetrahydrofuran (1.25 mL) was added, and the reaction solution was heated to 35 °C and allowed to stir for 36 h. The mixture was filtered through a silica gel and celite plug, washed with ethyl acetate (5 x 5 mL), and concentrated on a rotary evaporator. The crude product was purified using silica gel chromatography (10% ethyl acetate/ 90% hexanes) to afford the title compound as an off white solid (172 mg, 85 % yield). Mp: 90 °C. IR (thin film): 3285, 3106, 3072, 3028, 2958, 2871, 1607, 1528, 1497, 1456, 1424, 1379, 1350, 1312, 1163, 1090, 1012, 888, 853, 746, 735, 701, 686 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.13 (2H, d, J = 9.0 Hz), 7.74 (2H, d, J = 9.0 Hz), 7.29-7.10 (6H, m), 7.07 (2H, d, J = 6.9 Hz), 6.95-6.91 (2H, m), 4.35 (1H, d, J = 8.4 Hz), 3.59-3.48 (1H, m), 2.79 (1H, dd, J = 5.4, 13.8 Hz), 2.60-2.52 (3H, m), 1.63-1.46 (4H, m). ^{13}C NMR (125 MHz, $CDCl_3$): δ 149.7, 146.6, 141.7, 136.9, 129.4, 128.8, 128.5, 128.4, 128.0, 127.0, 126.2, 124.3, 56.2, 41.6, 35.5, 35.2, 27.6. MS (ESI, negative mode): $C_{23}H_{23}N_2O_4S$ [M - H]$^-$: 423.

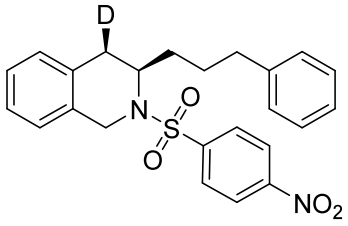


***N*-(4-nitrobenzenesulfonyl)-1-deuterio-1,5-diphenylpentan-2-amine (3ha-*d*).** A flame-dried borosilicate glass vial equipped with an egg-shaped magnetic stirbar was charged

with bis(dibenzylideneacetone)palladium(0) (14.4 mg, 0.025 mmol, 0.05 equiv), tri-1-naphthylphosphine (24.8 mg, 0.060 mmol, 0.12 equiv), cesium carbonate (16.3 mg, 0.050 mmol, 0.10 equiv), ***trans-N*-(4-nitrobenzenesulfonyl)-2-deuterio-3-(3-phenylpropyl)aziridine** (174 mg, 0.50 mmol, 1.0 equiv), and phenylboronic acid (122 mg, 1.0 mmol, 2.0 equiv). The vial was thoroughly flushed with nitrogen and capped with a Teflon-lined screw cap. A solution of *m*-chlorophenol (260 mg, 2.0 mmol, 4.0 equiv) in dry tetrahydrofuran (1.25 mL) was added, and the reaction solution was heated to 35 °C and allowed to stir for 36 h. The mixture was filtered through a silica gel and celite plug, washed with ethyl acetate (5 x 5 mL), and concentrated on a rotary evaporator. The crude product was purified using silica gel chromatography (10% ethyl acetate/ 90% hexanes) to afford the title compound as an off white solid (189 mg, 89 % yield). Mp: 89-90 °C. IR (thin film): 3284, 3105, 3064, 3026, 2960, 2927, 2873, 1607, 1527, 1498, 1452, 1428, 1378, 1349, 1311, 1162, 1091, 1016, 971, 854, 745, 738, 701, 685 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.13 (2H, d, J = 8.7 Hz), 7.74 (2H, d, J = 9.0 Hz), 7.28-7.10 (6H, m), 7.07 (2H, d, J = 6.6 Hz), 6.95-6.92 (2H, m), 4.35 (1H, d, J = 8.4 Hz), 3.57-3.48 (1H, m), 2.77 (1H, d, J = 5.4 Hz), 2.60-2.50 (2H, m), 1.65-1.47 (4H, m). ^{13}C NMR (125 MHz, $CDCl_3$): δ 149.8, 146.7, 141.7, 136.9, 129.4, 128.8, 128.5, 128.4, 128.0, 127.0, 126.2, 124.3, 56.2, 41.2 (t, $^{1}J_{CD}$ = 20 Hz), 35.5, 35.2, 27.5. MS (ESI, negative mode): $C_{23}H_{22}DN_2O_4S$ $[M - H]^-$: 424.



2-(4-nitrobenzenesulfonyl)-3-(3-phenylpropyl)-1,2,3,4-tetrahydroisoquinoline (4ha). To a solution of ***N*-(4-nitrobenzenesulfonyl)-1,5-diphenylpentan-2-amine** (85 mg, 0.20 mmol, 1.0 equiv) and dimethoxymethane (0.32 mL, 3.6 mmol, 18 equiv) in toluene (0.32 mL) in a Teflon-capped borosilicate glass vial purged with nitrogen is added 85 wt. % H_3PO_4 (0.7 mL, 2.4 mmol, 12 equiv). The reaction mixture is heated to 75 °C and allowed to stir at this temperature for 3 days. The reaction mixture is diluted with ether (2 mL), extracted with water (2 x 2 mL), saturated aqueous $NaHCO_3$ (2 x 2 mL), and brine (1 x 2 mL), dried over Na_2SO_4, and concentrated to yield the crude product mixture. Purification of the mixture using silica gel chromatography (5% ethyl acetate/ 95% hexanes) yielded the product as a white crystalline solid (10 mg, 12% yield) and recovered starting material (76 mg, 89% recovery). Mp: 105-108 °C. IR (thin film): 3106, 3068, 3030, 2959, 2925, 2866, 1607, 1531, 1497, 1456, 1378, 1350, 1313, 1165, 1120, 1095, 1042, 1014, 965, 902, 855, 749, 739, 702, 688, 651 cm^{-1}. ^1H NMR (500 MHz, C_6D_6): δ 7.45 (2H, d, J = 9.0 Hz), 7.37 (2H, d, J = 8.5 Hz), 7.16-7.07 (3H, m), 6.97 (2H, d, J = 7.0 Hz), 6.88-6.84 (2H, m), 6.64-6.61 (2H, m), 4.62 (1H, d, J = 17.0 Hz), 4.10-4.06 (1H, m), 3.94 (1H, d, J = 16.5 Hz), 2.43 (1H, dd, J = 5.5, 16.0 Hz), 2.40-2.27 (2H, m), 2.01 (1H, d, J = 16.5 Hz), 1.49-1.43 (2H, m), 1.29-1.21 (1H, m), 1.07-1.00 (1H, m). ^{13}C NMR (125 MHz, $CDCl_3$): δ 149.8, 146.4, 141.8, 131.8, 130.9, 129.7, 128.5, 128.4, 128.1, 127.4, 126.6, 126.1, 126.0, 124.3, 52.4, 43.3, 35.4, 32.3, 31.3, 28.0. MS (ESI, positive mode): $C_{24}H_{24}N_2NaO_4S$ $[M + Na]^+$: 459.



(*cis*)-4-deuterio-2-(4-nitrobenzenesulfonyl)-3-(3-phenylpropyl)-1,2,3,4-tetrahydroisoquinoline (4ha-*d*). To a solution of ***N*-(4-nitrobenzenesulfonyl)-1-deuterio-1,5-diphenylpentan-2-amine** (85 mg, 0.20 mmol, 1.0 equiv) and dimethoxymethane (0.32 mL, 3.6 mmol, 18 equiv) in toluene (0.32 mL) in a Teflon-capped borosilicate glass vial purged with nitrogen is added 85 wt. % H_3PO_4 (0.7 mL, 2.4 mmol, 12 equiv). The reaction mixture is heated to 75 °C and allowed to stir at this temperature for 5 days. The reaction mixture is diluted with ether (2 mL), extracted with water (2 x 2 mL), saturated aqueous $NaHCO_3$ (2 x 2 mL), and brine (1 x 2 mL), dried over Na_2SO_4, and concentrated to yield the crude product mixture. Purification of the mixture using silica gel chromatography (5% ethyl acetate/ 95% hexanes) yielded the product as a white crystalline solid (32 mg, 37% yield) and recovered starting material (49 mg, 58% recovery). Mp: 102-105 °C. IR (thin film): 3104, 3067, 3029, 2958, 2928, 2871, 1606, 1531, 1497, 1456, 1379, 1351, 1312, 1165, 1115, 1107, 1090, 1028, 1013, 954, 855, 738, 701, 687, 651, 646 cm^{-1}. ^1H NMR (500 MHz, C_6D_6): δ 7.44 (2H, d, J = 9.0 Hz), 7.36 (2H, d, J = 8.5 Hz), 7.16-7.07 (3H, m), 6.97 (2H, d, J = 7.0 Hz), 6.89-6.84 (2H, m), 6.63-6.61 (2H, m), 4.62 (1H, d, J = 17.0 Hz), 4.07 (1H, dt, J = 6.5, 8.0 Hz), 3.94 (1H, d, J = 17.0 Hz), 2.40 (1H, d, J = 6.5 Hz), 2.38-2.26 (2H, m), 1.48-1.42 (2H, m), 1.29-1.21 (1H, m), 1.06-0.99 (1H, m). ^{13}C NMR (125 MHz, $CDCl_3$): δ 149.8, 146.4, 141.8, 131.8, 130.9, 129.6, 128.5, 128.4, 128.1, 127.4, 126.6, 126.1, 126.0, 124.3, 52.4, 43.3, 35.3, 31.9

(t, $^{1}J_{CD}$ = 19.5 Hz), 31.3, 28.0. MS (ESI, positive mode): $C_{24}H_{23}DN_2NaO_4S$ $[M + Na]^+$: 460.

References and Notes for Chapter 1

[1] A majority of the results reported in this chapter have been published. Duda, M. L. Michael, F. E. *J. Am. Chem. Soc*. **2013**, *135*, 18347-18349.

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Chapter 2

Synthetic Approaches to Organic Polymer-Supported One-Dimensional Metal Wires

Section 1: Introduction

Nearly 200 worldwide scientific organizations, including the American Association for the Advancement of Science, the American Chemical Society, and the American Meteorological Society, hold the position that climate change is caused by human activity, in particular the release of greenhouse gas emissions into the earth's atmosphere.[1] Accumulation of these gases, composed primarily of carbon dioxide, with lesser amounts of methane, nitrous oxide, and chlorofluorocarbons, is principally linked with consumption of fossil fuels for energy generation.[2] Sustainable and environmentally friendly substitutions such as wind, geothermal, and solar energy-capturing technologies are thus being actively explored as alternative energy sources. Of these, solar energy is of particular interest, due to its vast abundance and availability. It has been established that more energy from sunlight strikes the earth in one hour (4.3×10^{20} J) than all the energy currently consumed on the planet in one year (4.1×10^{20} J).[3]

Harvesting of solar energy is accomplished through use of photovoltaics, materials that convert solar power to electrical current. Photovoltaics, or PVs, are frequently classified according to their chemical composition, with the majority of materials falling into one of two major categories: inorganic (IPV) and organic (OPV) photovoltaics. IPVs very efficiently convert sunlight to chemical energy, and they have thus achieved widespread use in commercial products; however, economic viability is hampered by substantial costs of production associated with raw materials and

manufacturing conditions. Organic photovoltaics, on the other hand, suffer for efficiency but have nonetheless managed to hold the attention of the scientific and clean energy communities since their introduction due in part to the following factors: (a) materials for making OPVs are widely available and inexpensive, (b) methods of processing are amenable to industrial scale up, and (c) the materials themselves are physically flexible, allowing for practical installation on a range of surfaces.

Attempts have been made to address low efficiencies in OPVs, the remediation of which would open a rich field of scientific research to practical utilization in the quest to secure sustainable energy. When electron-hole pairs are formed in IPVs, separation of the two charged particles is immediate due to the high polarizability of the materials, leading to a productive electrical current. When electron-hole pairs are formed in OPVs, however, the electron and hole travel through the material as a pair, held together by electrostatic force. Many attempts to increase solar conversion efficiencies in OPVs have been employed, most notably the fabrication of the bulk heterojunction solar cell, but because the polarizability of organic materials is not enough to separate the two charges the electron-hole pairs recombine frequently, resulting in low quantum conversions. It stands to reason that quantum efficiencies in OPVs could well be augmented by the selective incorporation of an inorganic component, while retaining many of the properties that have sustained their appeal as targets of research.

One possible synthetic solution is to incorporate a one-dimensional metal wire via coordination to an organic polymer. Bulk metals, while highly polarizable, are insoluble in organic media and therefore not readily integrated into organic materials. By limiting metal-metal bonding to a singular dimension, however, one could theoretically preserve

the desirable electronic properties of the bulk inorganic material that are dependent upon metal-metal bonding while providing for its solubility and incorporation into an organic medium. Metal-metal bonds are often weak and easily cleaved, but by coordinating the wire to an organic polymer, we anticipated that covalent bonding in the backbone would reinforce the metal-metal bonds, preserving the integrity of the wire and its ability to conduct electronic charge. Possible examples of these structures are shown in *Figure 2.1*.

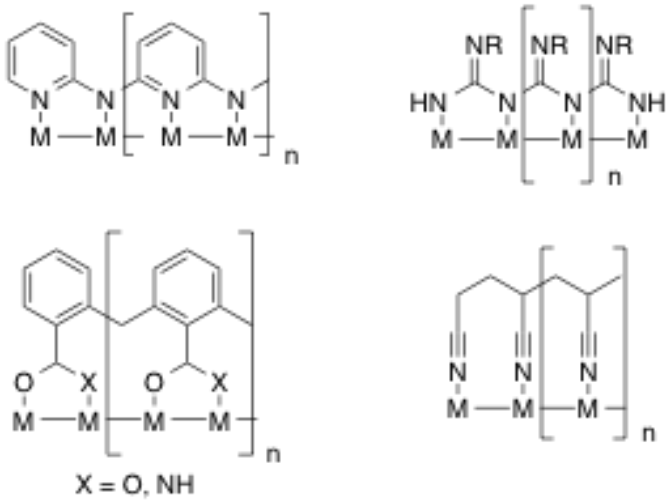


Figure 2.1. Possible modes of transition metal coordination to various organic polymers.

One-dimensional metal polymers have been known since the late 1960s, when Krogmann first published his finding that partially oxidized square planar tetracyanoplatinate units interact via dz^2 orbitals to form Pt-Pt bonds (*Figure 2.2*).[4] Since

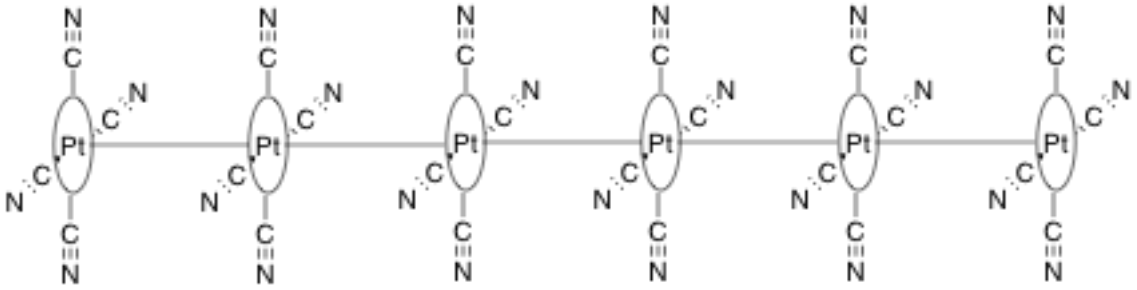
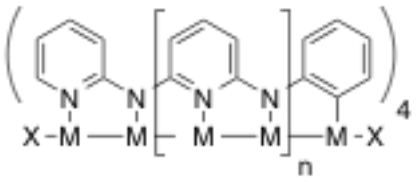


Figure 2.2. Krogmann's salt.

that time, a number of 1-D metallopolymers have been synthesized, but their utility went underexplored and efforts to produce and characterize iterations petered out. Recent scientific attention to the unique properties of materials constructed on the nanoscale has revived interest in these molecular wires, and efforts to systematically explore the relationship between structure and electronic properties have been undertaken in many cases.[5]

Table 2.1. Previously Synthesized Metal String Complexes Supported by Oligo-α-pyridylamine Ligands.[6,7,8,9]



n	**M**
0	Cr^{II}, Ru^{II}, Co^{II}, Rh^{II}, Ni^{II}, Cu^{II}
1	Cr^{II}, Co^{II}, Ni^{II}
2	Cr^{II}, Ni^{II}
3	Cr^{II}, Ni^{II}

Of particular interest to us were a group of published syntheses of several structures possessing an oligo-α-pyridylamine backbone and 3-9 nuclear transition metal atoms (Table 2.1). Reported by the independent research groups of Cotton,[6a,b,d] Peng,[6c,g] Hathaway,[6f] and Pinkerton,[6e] trinuclear compounds of the type $[M_3(\mu^3\text{-dpa})_4X_2]$ (dpa = *syn-syn*-bis(2-pyridyl)amido) were synthesized, with M taking the form of transition metals as varied as Cu, Ni, Cr, Co, Rh, and Ru. Cotton and Peng have additionally prepared M_5 chains (n = 1) with Cr, Co, and Ni[7a,b,c] and M_7 (n = 2) and M_9 (n = 3) chains with Cr and Ni.[8a,b,9a,b] Similar complexes with higher numbers of metal atoms have not yet been characterized, presumably as a consequence of decreasing solubility of the metal wire complex with added molecular weight. The Peng group, however, has performed computational calculations that suggest the infinite Ni and Cr metal string complexes should serve as semiconducting and conducting materials, respectively.[9a] Should these polymeric metal wire complexes be realized, there exists obvious potential for practical application to PV devices and other clean energy solutions.

Having extensive experience with organometallic complexes, our lab sought to address the question of whether polymeric forms of these supported metal wires might be accessed and characterized in order to determine their usefulness as photovoltaics. Our initial assessment of the synthetic problem led us to conclude that a more soluble organic polymeric backbone would be a necessity. We planned to install solubilizing alkyl groups at the 4-positions of the pyridyl rings to accomplish this. We also saw the need for a simple, streamlined synthesis of these materials. The oligomeric pyridylamido complexes were purified using recrystallization, but if polymeric analogs were to be viable they would need to be prepared relatively cleanly such that purification was minimized and

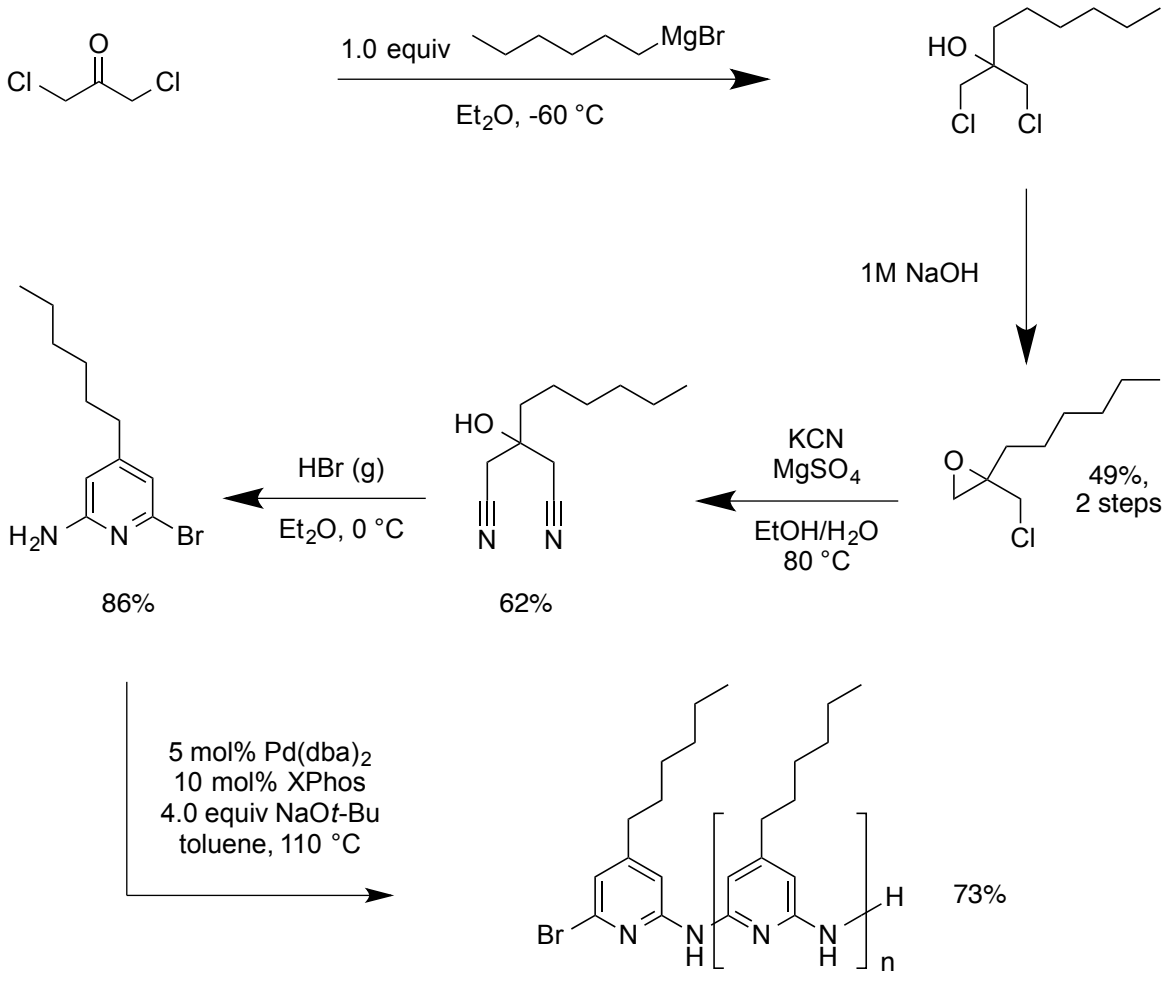
Scheme 2.1. *Proposed synthetic approach to polypyridylamine-supported 1-D metal wires.*

limited to processes such as extraction and precipitation. We envisioned using a salt metathesis to metallate the polymer, deprotonating the amino groups in an initial step followed by introduction of a metal dihalide to the reaction mixture (Scheme 2.1). The metal ions could then coordinate both the pyridyl and amido functionalities with concomitant formation of lithium chloride, a reaction byproduct that is readily removed during an aqueous workup or extraction with various organic solvents[10] provided the metal wires are stable under such conditions. The metals, existing in an oxidation state of +2 and positioned within bonding distance of one another, would thus be primed for formation of the desired one-dimensional wire. Upon successful synthesis of these organometallic materials, our aim was to probe their physical properties to evaluate their potential utility in photovoltaic devices.

Section 2: Results and Discussion

The novel polymer poly(4-hexyl-2,6-pyridinediylimine), or 4-Hex-2,6-PAPy, was synthesized in 19% overall yield from 1,3-dichloroacetone based on modified literature procedures (Scheme 2.2) and characterized by ^{1}H NMR spectroscopy. The polymer was determined to be reasonably soluble in dichloromethane, chloroform, and tetrahydrofuran, and fully insoluble in hexane and methanol.

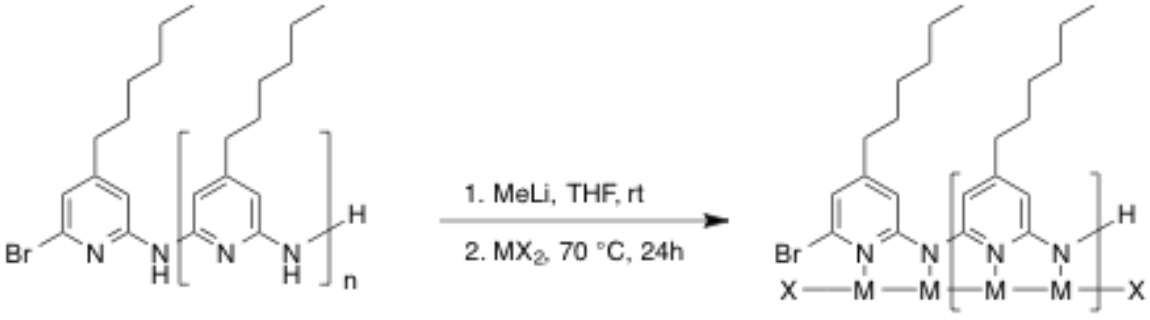
Scheme 2.2. *Synthesis of 4-Hex-2,6-PAPy.*



Tetrahydrofuran was selected as the medium for our proposed metallation reaction. Frequently used to facilitate organometallic reactions, THF is capable of stabilizing ionic intermediates through oxygen lone pair coordination and should therefore assist in facilitating the desired salt metathesis reaction. Methyllithium was deemed an appropriate base for the reaction, as an immediate exotherm and evolution of gas were observed upon addition of MeLi to a THF solution of 4-hexyl-2,6-PAPy during

an initial qualitative base screen. Furthermore, facile removal of methane from the reaction medium would simplify purification of the metallopolymers.

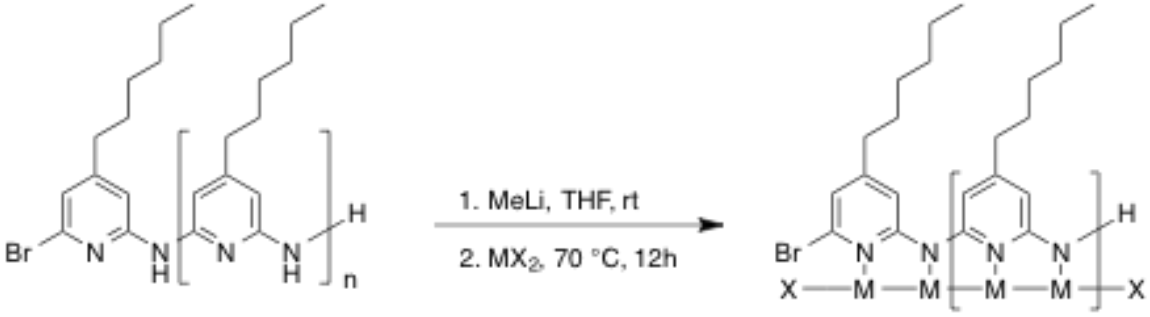
Table 2.2. Initial Metalation Conditions.



Entry	**MX_2**	**Solubility in Organic Solvents[11]**
1	$NiCl_2$	insoluble
2	$CoCl_2$	insoluble
3	$CuCl_2$	insoluble
4	$CrCl_2$	insoluble
5	$PdCl_2$	insoluble

Salt metathesis reactions were conducted by reacting transition metal dichloride complexes MCl_2 with lithiated 4-Hex-2,6-PAPy in THF at 70 °C for 24 hours (Table 2.2). During this time, thick brown-black gelatinous precipitates began to accumulate on the sides of the glass vials, presumably an indicator of product formation. No such accumulation was observed for reactions with $PdCl_2$ and $NiCl_2$ at room temperature. Unfortunately, all metallation reaction products were largely insoluble in multiple organic solvents, including chloroform and dichloromethane, and could not be characterized.

Table 2.3. Results of Applying Reduced Reaction Time to Polymer Metalation.



Entry	**MX_2**	**Solubility in Organic Solvents[11]**
1	$NiCl_2$	partial solubility (THF, $CHCl_3$)
2	$CoCl_2$	partial solubility (THF, $CHCl_3$)
3	$CuCl_2$	insoluble
4	$CrCl_2$	insoluble

In an effort to examine the effect of time of reaction on product solubilities, reactions were conducted at 70 °C for a reduced period of 12 hours (Table 2.3). Solubilities of Ni, Cu, Cr, and Co metallopolymers obtained after 12 and 24 hours were compared. Reduced reaction time increased the solubilities of the Ni and Co metallopolymers, such that they displayed reasonable solubility in both THF and chloroform (entries 1, 2). No such effect was observed for the Cr metallopolymer, and Cu metallopolymer appeared to exhibit an overall decrease in solubility in organic solvents with reduced time of reaction (entries 3, 4).

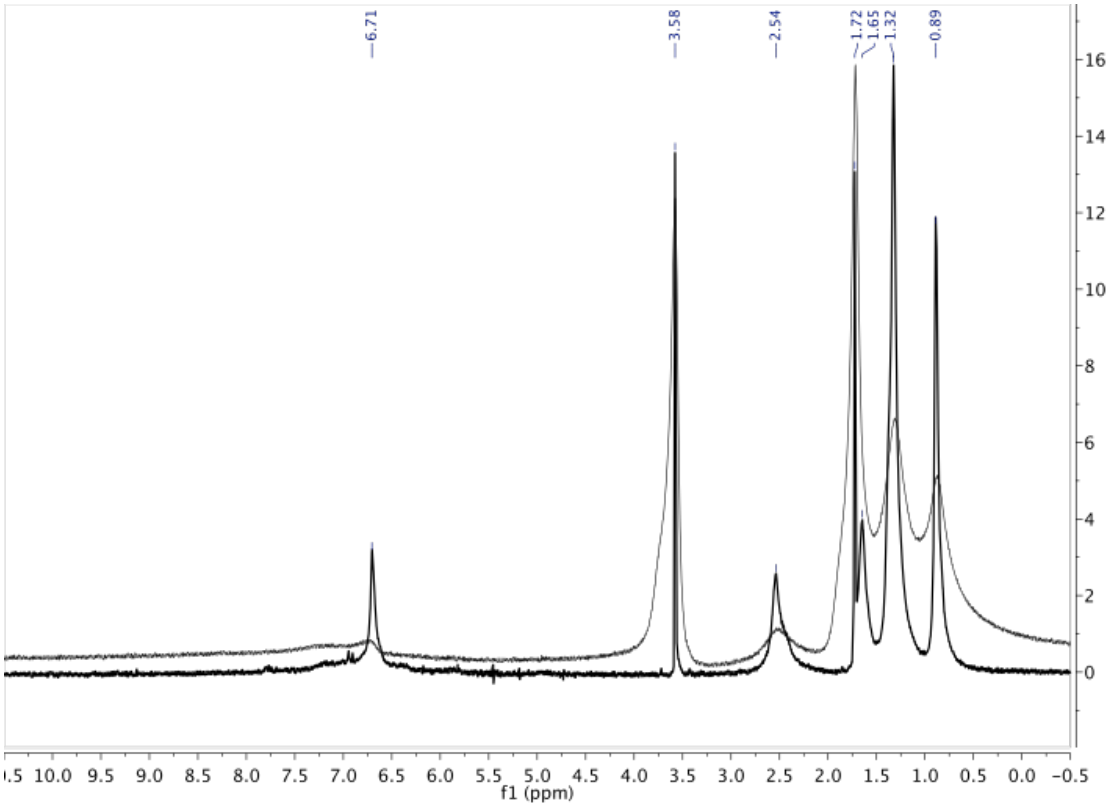


Figure 2.3. Superimposed ^{1}H NMR spectra of unmetalated (black) and nickelated (gray) 4-Hex-2,6-PAPy.

Nickelated metallopolymer obtained after a 12h reaction period (Table 2.2, entry 1) was soluble enough in THF-d_8 to acquire a ^{1}H NMR spectrum for comparison with that of the unmetalated polymer (*Figure 2.3*). The signals are significantly broader for the Ni metallopolymer, suggesting it may have partial paramagnetic character. In fact, Peng et al. have established via magnetic measurements that the terminal Ni atoms in the Ni_3 to Ni_9 metal string series are paramagnetic, while the internal Ni ions are low spin.[9a] A ^{1}H NMR spectrum of the partially soluble Co metallopolymer (Table 2.2, entry 2) in THF-d_8 was also obtained, but broadening of the signals was extremely exaggerated, such

that many barely registered above the baseline. We surmised that this was likely due to the paramagnetic nature of Co^{II}.

Both Ni and Co metallopolymers were examined by UV/Vis spectroscopy alongside the unmetallated polymer (*Figure 2.4*). Unmetallated 4-Hex-2,6-PAPy exhibited two maxima in the spectrum, both in the UV region: a major absorption at 357 nm and a secondary absorption occurring at 271 nm. These absorptions were absent in the spectrum of the Ni metallopolymer. Two new local maxima were observed, at 285 and 335 nm, with the tail of the latter trailing well into the visible light region of the spectrum. A minor absorption at 357 nm appeared in the spectrum of the Co metallopolymer, suggesting unmetallated 4-Hex-2,6-PAPy may have been present. Additional absorptions were observed at 285 and 395 nm, and similar to the Ni species, the Co metallopolymer demonstrated enhanced absorption in the near-UV compared to 4-

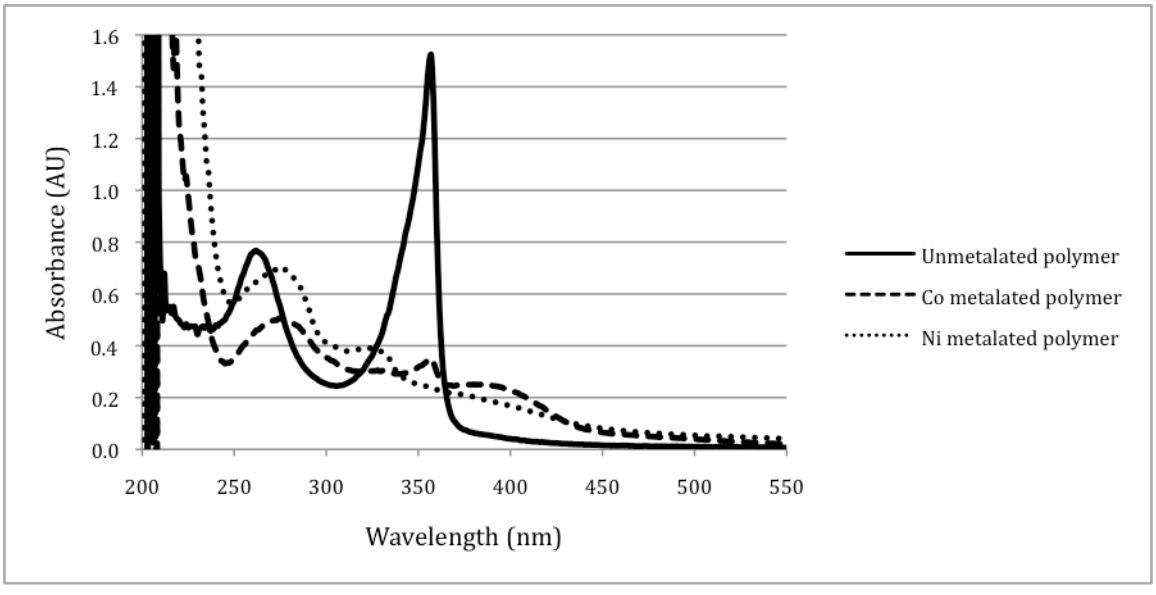


Figure 2.4. UV/Vis absorbance spectra of unmetalated, Co-, and Ni-metalated 4-Hex-2,6-PAPy in THF.

Hex-2,6-PAPy. The UV/Vis spectral signatures of the metallopolymers suggest new materials were indeed obtained, and increased absorptions in the visible spectral region are promising. However, absorbance intensities in this region are poor, making the usefulness of these particular materials in PV devices questionable until further research is undertaken.

Section 3: Conclusion

New polymeric materials were synthesized and partially characterized by ^{1}H NMR and UV/Vis spectroscopies. Characterizable species were limited to Ni and Co metallopolymers, which displayed limited solubility in organic solvents. Both species are thought to be at least partially paramagnetic in character, consistent with previous findings. Both metallopolymers display red-shifted spectral absorbance comparative to the unmetallated polymer, 4-Hex-2,6-PAPy, but the absorbance intensities are less than ideal for practical application in PV devices.

Section 4: Experimental

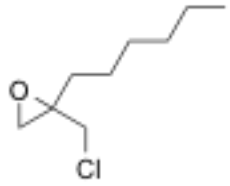
2.4.1 General Procedures and Materials

All reactions were performed under a nitrogen atmosphere using flame-dried glassware unless otherwise indicated. NMR spectra were recorded on a Bruker AV-300, AV-301, DRX-499, or AV-500 spectrometer. ^{1}H NMR chemical shifts (δ) are reported in parts per million (ppm) and are referenced relative to residual $CHCl_3$ (7.26 ppm) or THF (3.58 ppm). UV/Vis spectra were recorded on a Varian Cary 50 spectrophotometer equipped with a fiber optic cable connected to a "dip" ATR probe.

Tetrahydrofuran, diethyl ether, and dichloromethane were degassed and dried by passing through a column of neutral alumina. Deuterated solvents $CDCl_3$ and THF-d_8

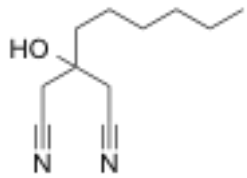
were obtained from Cambridge Isotope Laboratories, Inc. and were stored over activated 3Å molecular sieves. $PdCl_2$ was obtained from Pressure Chemical Company and used without further purification. $NiCl_2$, $CuCl_2$, $CoCl_2$, and $CrCl_2$ were obtained from Strem Chemicals, Inc. and used without further purification. Ethyl acetate, hexanes, acetic acid, 1,3-dichloroacetone, dry gaseous HBr, XPhos, NaOt-Bu, and MeLi (1.6M in diethyl ether) were obtained from Sigma Aldrich and used without further purification. Bis(dibenzylideneacetone)palladium(0) was prepared according to the published procedure,[12] and spectroscopic (^{1}H NMR, ESI-MS) characterization was consistent with reported values. Hexylmagnesium bromide in diethyl ether was synthesized just prior to use from distilled 1-bromohexane and granular Mg metal according to the well-known procedure.

2.4.2 Synthesis of 4-Hex-2,6-PAPy Polymer



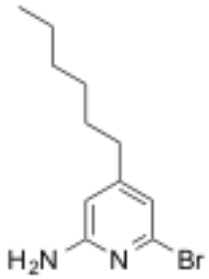
2-(Chloromethyl)-2-hexyloxirane.[13] 1,3-Dichloroacetone (22.9 mL, 0.25 mol) was dissolved in anhydrous ether (120 mL) and the solution cooled to -60 °C. A solution of hexylmagnesium bromide (0.26 mol, 1.05 equiv) in ether (240 mL) was added over a period of 2 hours with vigorous stirring. Ten minutes after the addition was complete, the heterogeneous reaction mixture was treated with acetic acid (25.6 g) in ether (40 mL), followed by water (20 mL). With continued stirring, the temperature was allowed to rise

to 0 °C and a clear biphasic mixture was obtained, from which the ether layer was separated. The aqueous phase was washed once with ether and the organic extracts combined, washed with water, and evaporated down to yield crude 1-chloro-2-hydroxy-2-chloromethyloctane. Aqueous 1M NaOH solution (0.29 mol, 1.15 equiv) was added dropwise to the neat crude material while stirring at ambient temperature over a period of 1 hour. Stirring was continued overnight. Subsequently, the biphasic mixture extracted with ether (4 x 75 mL). The combined organic solutions were dried over Na_2SO_4 and concentrated to yield the epoxide as a clear oil (21.5 g, 49% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.59 (1H, d, *J* = 11.4 Hz), 3.51 (1H, d, *J* = 11.7 Hz), 2.76 (2H, s), 1.78-1.88 (1H, m), 1.62-1.74 (1H, m), 1.26-1.40 (8H, m), 0.88 (3H, t, *J* = 6.9 Hz).

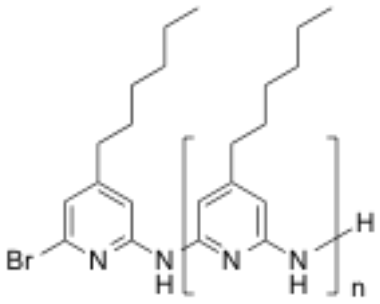


3-Hexyl-3-hydroxyglutaronitrile.[13] 2-(Chloromethyl)-2-hexyloxirane (3.0 g, 17 mmol) was added to a round-bottomed reaction flask equipped with a magnetic stirbar and reflux condenser and suspended in a 1:1 mixture of ethanol and water (20 mL). $MgSO_4 \cdot 7H_2O$ (7.5 g, 1.8 equiv) was added, followed by KCN (2.2 g, 2.0 equiv), and the reaction mixture was heated to 85 ^{o}C and stirred overnight. Upon cooling to room temperature, the reaction mixture was diluted with dichloromethane and washed sequentially with water and saturated aqueous $NaHCO_3$. The organic layer was dried over Na_2SO_4 and concentrated. The resulting dark brown oil was distilled under reduced pressure (0.2 torr, 158 °C) to yield the product as a clear oil (2.0 g, 62% yield). ^{1}H NMR (300 MHz,

$CDCl_3$): δ 2.74 (2H, d, *J* = 16.8 Hz), 2.68 (2H, d, *J* = 16.8 Hz), 2.44 (1H, br s), 1.78-1.84 (2H, m), 1.30-1.37 (8H, m), 0.90 (3H, t, *J* = 6.9 Hz).



2-Amino-6-bromo-4-hexylpyridine.[14] 3-Hexyl-3-hydroxyglutaronitrile (1.28 g, 6.6 mmol) was dissolved in dry diethyl ether (15 mL) and the solution was cooled in an ice water bath. Gaseous HBr was bubbled through the reaction mixture for 1 h. The mixture was poured into excess saturated $NaHCO_3$ solution and diluted with ether. The organic phase was separated, washed with a small amount of water and dried over Na_2SO_4. Evaporation gave the crude product, which was purified using column chromatography (ethyl acetate/hexanes) to give the product as a white solid in 86% yield (1.45 g). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.68 (1H, s), 6.27 (1H, s), 4.76 (2H, br s), 2.45 (2H, t, *J* = 7.8 Hz), 1.51-1.58 (2H, m), 1.28-1.35 (6H, m), 0.88 (3H, t, *J* = 6.9 Hz).



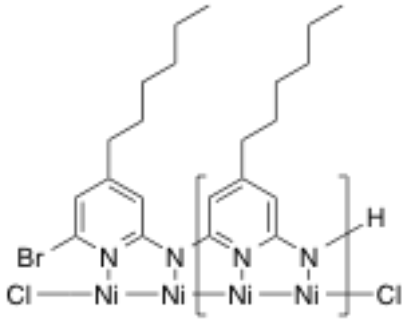
Poly(4-hexyl-2,6-pyridinediylimine) (4-Hex-2,6-PAPy).[15] 2-Amino-6-bromo-4-hexylpyridine (2.57 g, 10.0 mmol), $Pd(dba)_2$ (290 mg, 0.5 mmol, 0.05 equiv), XPhos (480 mg, 1.0 mmol, 0.10 equiv), and NaO*t*-Bu (3.8 g, 40 mmol, 4.0 equiv) were combined in a flame dried round bottom flask fitted with a magnetic stirbar and water condenser and dissolved in toluene (20 mL). The reaction mixture was stirred at reflux for 18 h. After cooling to room temperature, the solution was neutralized with 1M HCl (30 mL). Aqueous 0.1M EDTA tetrasodium salt (30 mL) was added and the heterogeneous mixture was permitted to stir overnight. The mixture was diluted with dichloromethane, and the organic and aqueous layers were separated. The aqueous layer was washed with a small amount of CH_2Cl_2, and the organics combined and dried over Na_2SO_4, filtered, and concentrated. The resulting residue was redissolved in a minimal amount of CH_2Cl_2 and the polymeric product precipitated with hexane. The product was collected by vacuum filtration and washed sequentially with hexane and methanol until the filtrates ran clear. The collected brown solid was dried under vacuum to produce the desired polymer in 73% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.63 (2H, br s), 2.47 (2H, br s), 1.59 (2H, br s), 1.28 (6H, br s), 0.88 (3H, br s). ^{1}H NMR (500 MHz, THF-d_8): 6.71 (2H, br s), 2.54 (2H, br s), 1.65 (2H, br s), 1.33 (6H, br s), 0.89 (3H, br s). UV/Vis: λmax 357 nm.

2.4.3 General Procedure

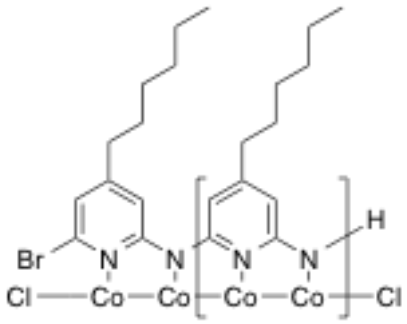
Poly(4-hexyl-2,6-pyridinediylimine) (35 mg) was partially dissolved in dry THF (1 mL) within a flame dried 1 dram glass vial equipped with a magnetic stirbar, rubber septum, and a nitrogen line. MeLi (125 µL, 1.6 M in diethyl ether, 1.0 equiv) was added and the reaction mixture was stirred for 10 minutes at ambient temperature. Metal chloride (0.1

mmol, 0.5 equiv), suspended in dry THF (0.5 mL), was syringed into the polymer solution, followed by a 0.5 mL dry THF rinse. The reaction vial was sealed with a fluoropolymer-lined screwcap and heated to 70 °C for a period of 12 hours. Upon cooling to ambient temperature, solvent was removed in vacuo to yield the crude metallopolymer product.

2.4.4 Characterization of Products



Nickelated 4-Hex-2,6-PAPy. Prepared according to the general procedure to yield a dark brown solid that demonstrated limited solubility in THF, chloroform, and dichloromethane. ^{1}H NMR (500 MHz, THF-d_8): δ 6.74 (2H, br s), 2.54 (2H, br s), 1.72 (2H, br s), 1.31 (6H, br s), 0.88 (3H, br s). UV/Vis (THF): λmax 285, 335 nm.



Cobaltalated 4-Hex-2,6-PAPy. Prepared according to the general procedure to yield a dark brown solid that demonstrated limited solubility in THF, chloroform, and dichloromethane. UV/Vis (THF): λmax 285, 395 nm.

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