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Liquid Triarylamines: The Scope and Limitations of Piers–Rubinsztajn Conditions for Obtaining Triarylamine–Siloxane Hybrid Materials

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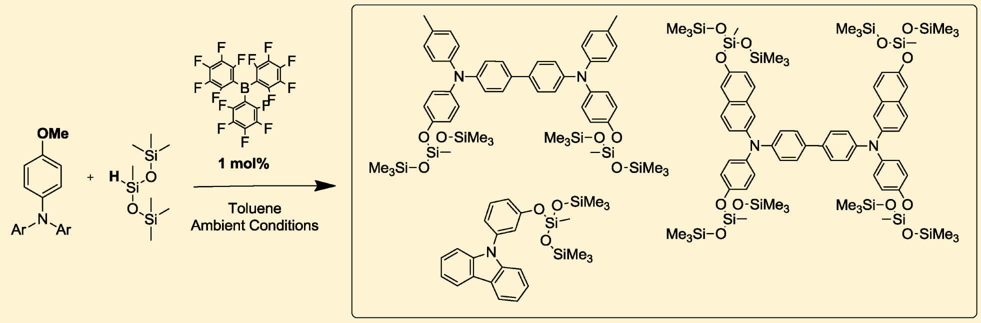
Supporting Information



Liquid Organic Semiconductors

ABSTRACT: New liquid triarylamine–siloxane hybrid materials are produced using the Piers–Rubinsztajn reaction. Under mild conditions, liquid analogues of conventional and commonly crystalline triarylamines are easily synthesized from readily available or accessible intermediates. Using a diverse selection of triarylamines, we explored the effects of siloxane group and substitution pattern on the physical properties of these materials, and we have demonstrated that relatively large molecular liquids with desirable electrochemical properties can be produced. The interactions between the strongly Lewis acidic catalyst used for this transformation, tris(pentafluorophenyl)borane (BCF), and the Lewis basic triarylamine substrates were studied. Through UV–vis–NIR and ^{19}F NMR spectroscopy, we have proposed that the catalyst undergoes a reversible redox reaction with the substrates to produce a charge transfer complex. The formation of this charge transfer complex is sensitive to the oxidation potential of the triarylamine and can greatly affect the kinetics of the Piers–Rubinsztajn reaction.

INTRODUCTION

The study of organic electronic devices such as organic light emitting diodes (OLEDs),[1] organic photovoltaics (OPVs),[2] organic field effect transistors (OFETs),[3] and photoreceptors[4] has resulted in the synthesis and characterization of a multitude of novel semiconducting materials specifically designed for these devices. A considerable range of useful electronic and photonic properties has been achieved through changes in the molecular structure of the semiconductor. However, considering only the physical state of the semiconducting material, the vast majority are designed to be amorphous, crystalline, or semicrystalline solids with varying degrees of solubility in organic solvents.[5] Recently, there have been examples of organic electronic devices incorporating organic semiconductors, which replace conventional materials with free-flowing liquids.[6,7] The incorporation of liquid semiconductors has a number of *potential* advantages such as good interfacial contact with rough surfaces and the possibility of solvent-free (or solvent-minimal) device processing. To our knowledge, there are only two organic semiconducting materials that are free-flowing liquids at room temperature *and* have been applied in devices: tris(4-methoxyethoxyphenyl)amine (TMEPA)[6] and *N*-(2-ethylhexyl)carbazole.[7] These have been successfully used as charge-transporting materials in dye-sensitized solar cells (DSSCs) and OLEDs, respectively. However, the further exploration of this unique class of materials has been hampered by the lack of a general synthetic strategy to produce them.

One strategy to produce new liquid organic semiconductors is the modification of known solid organic semiconductors with functionalities that can alter their physical properties while not affecting their electronic and photophysical properties. Using

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this general strategy, we have shown that the incorporation of simple silyl ethers into the structure of triarylamines results in some derivatives that are liquids. The nature of the silyl ether group as well as the overall symmetry and structure of the triarylamine was found to dictate whether or not these well-known organic semiconductors are liquids, waxes, or crystalline solids.[8]

Building upon this idea, we have recently shown that the incorporation of short, discrete disiloxane units around the periphery of triarylamines is a potentially more versatile strategy to produce liquid triarylamines (Figure 1).[9] Central to this synthetic strategy is the use of the Piers−Rubinsztajn reaction,[10] which uses tris(pentafluorophenyl)borane (BCF) as a catalyst (1 mol %, Figure 1). The reaction is performed under very mild and ambient conditions and requires low catalyst loadings. The only byproduct of the reaction is methane, and the substitution proceeds without metathesis or redistribution of the siloxane component, which commonly occur for many types of siloxane chemistries and limit the ability to construct discrete structures. Rapid conversion was observed despite the use of the strongly Lewis acidic catalyst, which on first examination may have been assumed to complex with the Lewis basic triarylamine substrate, preventing the reaction from proceeding. An investigation using UV−vis spectroscopy into the potential complexation showed a small amount of charge transfer between BCF and the triarylamine indicated by the presence of an absorption, which could be directly attributed to the oxidized arylamine (radical cation). Despite the detectable presence of this absorption, the relatively weak signal observed coupled with the known high extinction coefficient for radical cations of triarylamines suggests that the equilibrium between the charge transfer/interaction state and the freely dissociated state lies far toward dissociation.

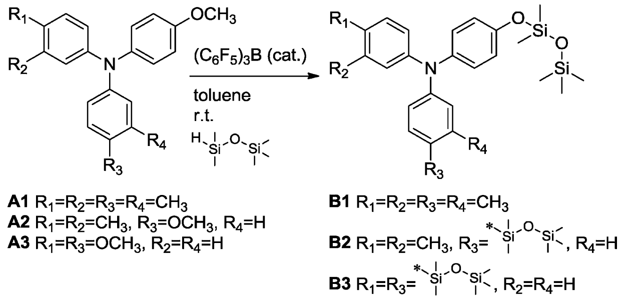


Figure 1. Previous work on the synthesis of siloxane-functionalized triarylamines (reproduced with slight modifications with permission (© 2011 American Chemical Society)).[9]

Piers−Rubinsztajn conditions have previously been shown to enable the reaction of silanes with a number of different coupling partners including carbonyl groups,[11] aryl hydroxyl/alkoxy groups,[12] alkyl hydroxyl groups,[13] siloxy groups, and silanols.[14] Piers−Rubinsztajn conditions have been shown to have a wide scope and have been used for the synthesis of structured and functional materials such as siloxane dendrimers,[15] polysiloxanes and copolymers thereof,[16] and surface active siloxane ambiphiles.[17] While this chemistry has good functional group tolerance,[18] there are cases where Lewis basic substrates react poorly because of competitive catalyst binding to these Lewis basic functionalities.[19] The strength of the Lewis basic functionality is thus an important factor in the reaction kinetics and whether the reaction can proceed at all.

Our original study was limited to performing this reaction on simple triarylamines with a single nitrogen center. Those in the field will recognize that simple triarylamines have a limited range of electrochemical oxidation potentials and applications in functional devices.[20] We report herein our efforts to broaden the scope of the Piers−Rubinsztajn process and its intersection with triarylamine−siloxane hybrid materials with an aim at producing a larger number of liquid triarylamines. We have focused our attention on multinitrogen centered triarylamines as well as molecules containing the related carbazole moeity. Triarylamines containing multiple conjugated nitrogen centers are known to possess a wider range of electrochemical properties and can exhibit better stability upon oxidation (better radical cation stability), leading to improved device performance. Conversely, they also have the potential to be significantly more Lewis basic than simple triarylamines because of their multiple nitrogen centers. Therefore, these substrates provide an opportunity to probe the scope and limitation of the reaction of methoxy-functionalized triarylamines with discrete silanes under Piers−Rubinsztajn conditions. The limitation of most interest is whether the increase in Lewis basicity on moving to triarylamines with multiple centers will result in a significant shift in charge transfer equilibrium between BCF and the triarylamine substrate, thus inhibiting the reaction.

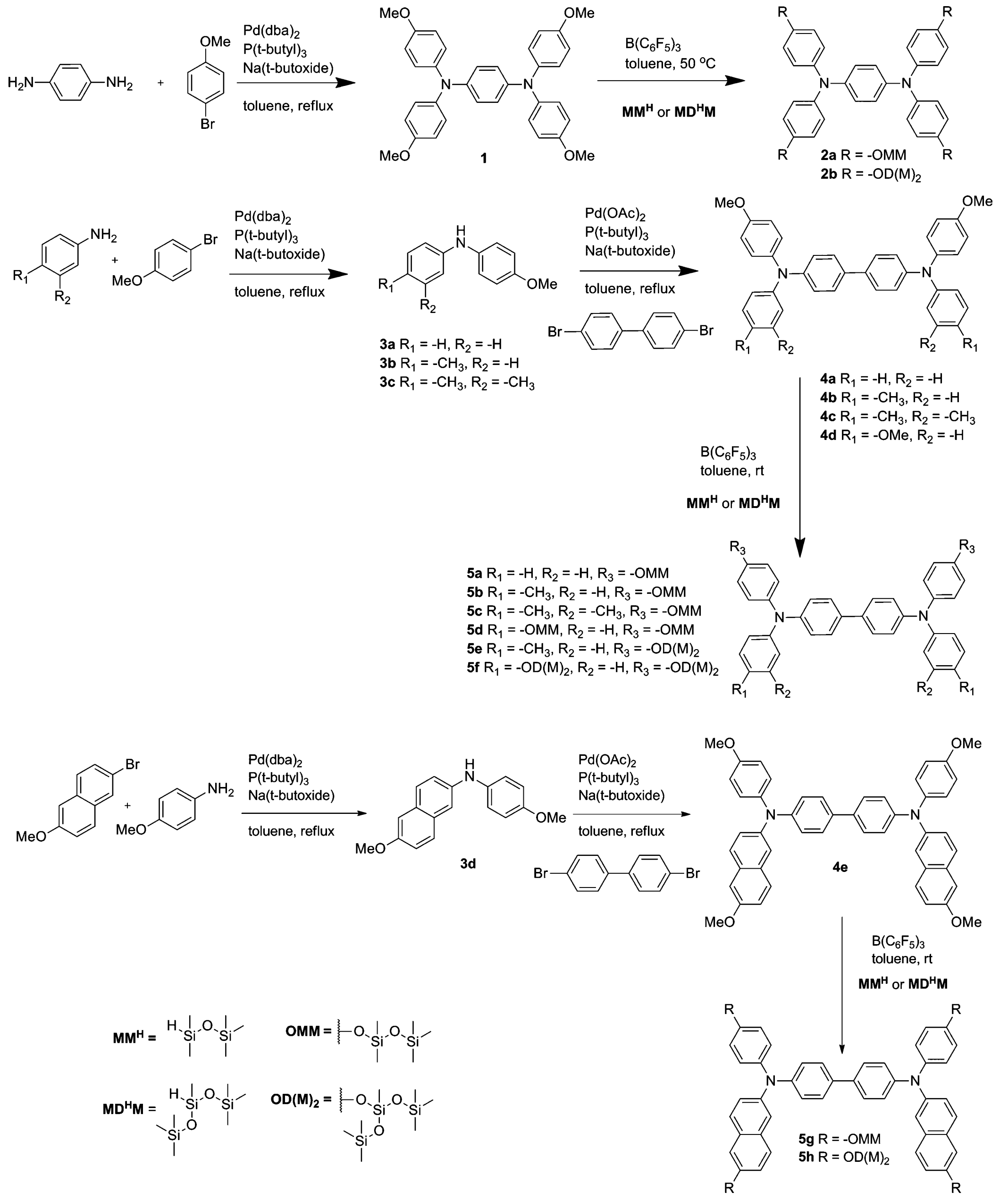
■ RESULTS AND DISCUSSION

While there are many different triarylamine structures from which to choose for this study, we began by choosing two of the more common motifs: triarylamines with a phenylene diamine core and those with a benzidine core (Scheme 1). Several variants on these backbones were synthesized so as to understand the effect of molecular symmetry and degree of siloxane functionalization on the physical and electrochemical properties of the resulting materials. Furthermore, the structural changes in each variant are also accompanied by inherent electronic variations affecting the Lewis basicity of the molecule.

Triarylamines based on a phenylene diamine core (compounds **2a−b**) were synthesized in two steps (Scheme 1). 1,4-Phenylene diamine was first reacted with 4-bromoanisole under standard Buchwald−Hartwig amination conditions[21] to yield an intermediate triarylamine **1**.[22] This aryl-methoxy-substituted triarylamine was then functionalized with discrete siloxane groups (1,1,1,3,3-pentamethyldisiloxane (MM^H) or 1,1,1,3,5,5,5-heptamethyltrisiloxane (MD^HM)) by a reaction with the corresponding silanes in the presence of a catalytic amount of tris(pentafluorophenyl)borane (BCF, the so-called Piers−Rubinsztajn conditions) under ambient and open air conditions. In our previous work,[9] we found that the functionalization of methoxy-containing triarylamines with MM^H under these conditions proceeded rapidly. However, in this case, complete conversion took approximately 7 h to achieve. Gentle heating (50 °C) was found to speed up the process considerably. ***Caution****: As the temperature in the flask increased, the reaction would proceed rapidly with the rapid evolution of methane gas.*

Triarylamines with a benzidine core (**5a−h**) were synthesized in three steps (Scheme 1). Diarylamines were first prepared by Buchwald−Hartwig coupling of the corresponding aryl bromides with an excess of the appropriate aniline. Diarylamines **3a**,[23] **3b**,[24] and **3c**[25] have been previously described in the literature, although their synthesis was

Scheme 1. Synthesis of Siloxane-Functionalized Arylamines



achieved using other means with differing yields. In our case, each diarylamine was easily purified by an acidic aqueous extraction followed by recrystallization from nonpolar solvents. They were then reacted with 4,4′-dibromobiphenyl to achieve the methoxy-functionalized triarylamines (**4a**−**e**), of which **4a**[26] and **4d**[22] have been previously described in the literature. Finally, the triarylamines were functionalized with discrete siloxane chains by reaction with the corresponding silane and catalytic amounts of BCF to give compounds **5a**−**h**. Unlike the reaction with the 1,4-phenylene-based materials (**2a**−**b**), the introduction of the siloxane groups proceeded quickly at room temperature, requiring up to a minute of induction time before reacting rapidly.

Generally speaking, all reactions proceeded to high conversion, and we did not see any correlation between triarylamine molecular structure and crude yields. We also did not see a correlation between the equivalent amount of silane used (in some cases we used 2 equiv and in others 5 equiv) and the crude yields. NMR analysis of the crude reaction mixtures does suggest that the reaction generates small amounts of polymeric silicone species as evidenced by a corresponding and characteristic CH_3 resonance in the ^1H NMR spectrum. The generation of this byproduct is likely due to the reaction of ambient water with silane in the reaction mixture moderated by BCF.[27] Column chromatography was found to be effective in removing this byproduct. Clearly, conducting the P−R process under anhydrous conditions would preclude the formation of the silicone species. However, as column chromatography is generally necessary to produce triarylamine suitable for study in organic electronic devices, its use to remove the produced silicones is balanced against the ease of operating under ambient vs anhydrous conditions.

All of the final triarylamine−siloxane hybrid materials were isolated by column chromatography (SiO_2, toluene/cyclohexane) as viscous liquids (compounds **2b**, **5a−c**, **e−f,h**) or as crystalline solids (compounds **2a**, **5d**, and **5g**), and their structure and purity (and those of the intermediates) were unambiguously confirmed by high resolution mass spectrometry (HRMS) and NMR analysis. Yields for the complete unoptimized process ranged significantly between 48 and 90% after column chromatography. Overall, compounds with the bulkier −OD(M)$_2$ group gave higher isolated yields than those with the less bulky −OMM group.

Each compound was characterized by differential scanning calorimetry (DSC) to determine the effect of silicone substitution and molecular symmetry on the melting point and/or glass transition temperatures of the materials (Table 1).

Table 1. DSC and CV Results from Silicone-Hybridized Triarylamines[a]

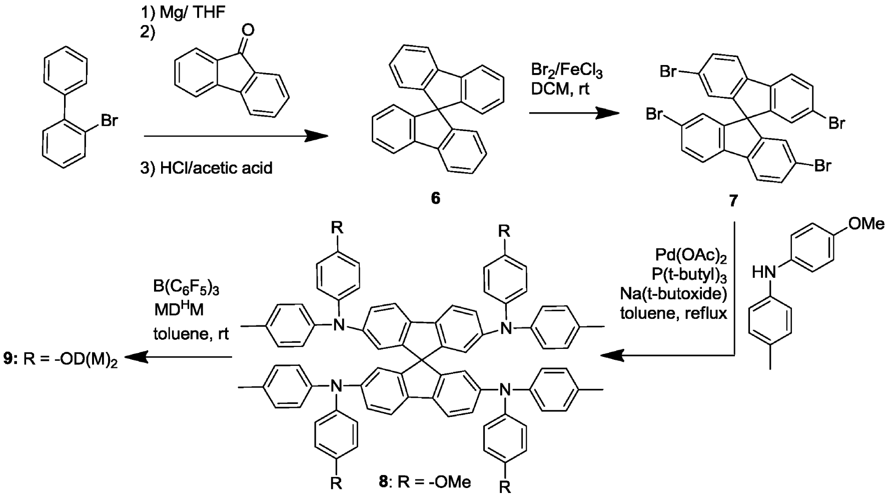
compound	appearance	T_m (°C)	T_g (°C)	$E_{ox\ 1}$ (mV vs Ag/AgCl)	$E_{ox\ 2}$ (mV vs Ag/AgCl)
2a	crystalline	87	−49[b]	443	902
2b	oil		−47	436	906
5a	oil		6	749	994
5b	oil		11	725	942
5c	oil		14	673	935
5d	crystalline	52, 58	−23[b]	661	892
5e	oil		−4	699	942
5f	oil		−31	682	921
5g	crystalline	88	−1	701	907
5h	oil		−9	704	929
9	crystalline	150	28	616	772
11	crystalline	131	20	366	696
15a	oil		−44	1495[c]	
15b	oil		−50	1320[c]	
15c	crystalline	47	−48[b]	1485[c]	
15d	oil		−48	1510[c]	

[a] T_m, melting temperature; T_g, glass transition temperature; $E_{ox\ 1}$, first half wave oxidation potential; $E_{ox\ 2}$, second half wave oxidation potential. [b] Detected on second heating cycle. [c] Irreversible, peak potential on first scan reported.

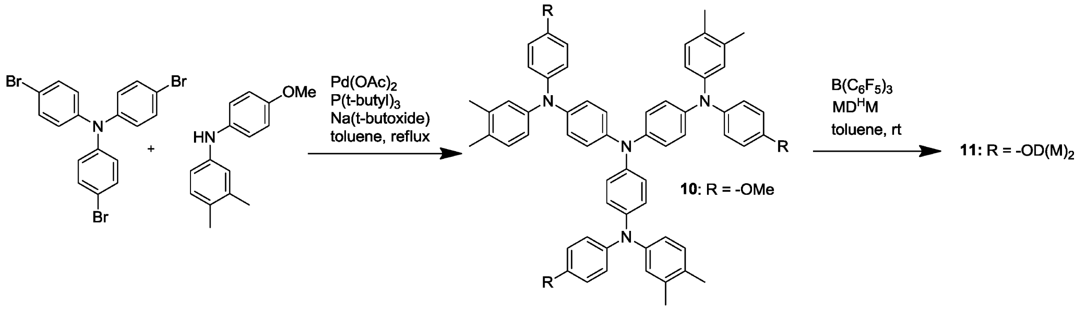
Consistent with our observations regarding the analogous single nitrogen centered triarylamine−siloxane hybrids,[9] the effect of adding discrete silicone groups to the arylamine cores had a significant effect on the glass transition temperature (T_g) and the presence of a crystalline state. Using pentamethyldisiloxane (−OMM) as a siloxane, the most symmetrically substituted arylamines (**2b**, **5d**, **5g**) were isolated as crystalline solids and exhibited well-defined and sharp melting points by DSC. Upon heating, compound **5d** exhibited two exothermic transitions at 52 and 58 °C, possibly indicating polymorphism. For each compound that showed a melting transition on the first DSC scan, a glass transition temperature well below room temperature was detected on the second heating cycle. These low glass transition temperatures suggested that if crystallization could be inhibited, the materials would behave as liquids at room temperature. This hypothesis was tested by utilizing the bulkier and branched 1,1,1,3,5,5,5-heptamethyltrisiloxane (−OD(M)$_2$) group in place of the linear −OMM group. The resulting compounds (**2b**, **5f**, **5h**) were isolated as free-flowing oils, and no detectable crystallization was observed over several months of storage at ambient conditions. The bulkier siloxane groups appear to prevent the π−π stacking interactions that are found in the crystal structures of these molecules.[28] Additionally, we found that the presence of asymmetry in the substitution pattern of the triarylamine along the axis bisecting the two nitrogen atoms resulted in compounds that were isolated as highly viscous oils at room temperature (**5a**, **5b**, **5c**, **5e**). For example, compounds **5a−c** containing two −OMM groups and various methyl group substituents on the adjacent phenyl ring are liquids, whereas their symmetric counterparts are not. Increasing the number of methyl groups raised the glass transition temperature, whereas replacing the linear −OMM siloxane with a branched −OD(M)$_2$ siloxane (**5e**) lowered the glass transition temperature by 15 °C as compared to its structural counterpart (**5b**).

From these observations, along with those in our previous study,[9] we can make several conclusions about the effect of siloxane substitution on the physical state of arylamines. We find that the incorporation of larger siloxane chains lowers the glass transition temperature of the material. Furthermore, as the base molecule increases in size, the number of siloxane chains needed to achieve a room temperature liquid arylamine−silicone hybrid increases. A secondary consideration is the addition of asymmetry to the molecule, which is shown to decrease the chances of crystallization in the molecule.

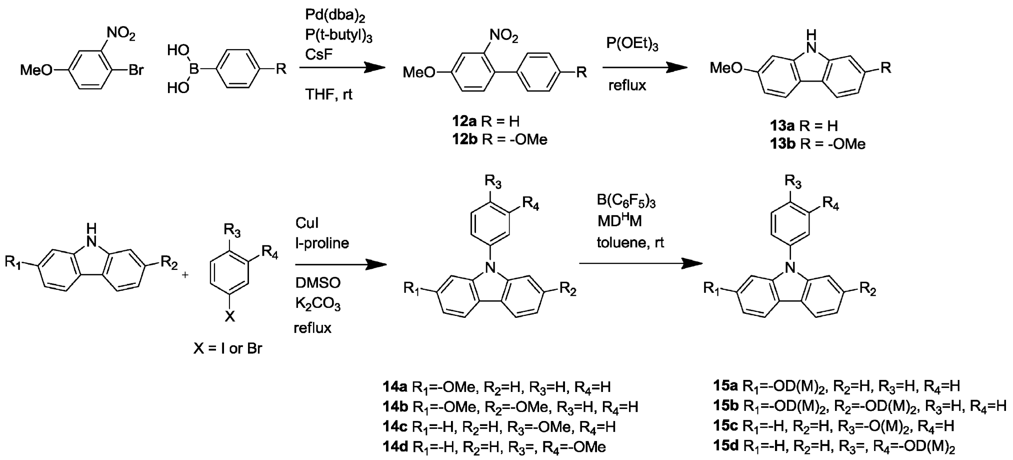
Scheme 2. Synthesis of Spiro Core Triarylamine 9



Scheme 3. Synthesis of Triarylamine 11



Scheme 4. Synthesis of Siloxane-Functionalized Carbazoles



The electrochemical behavior of this initial group of triarylamine−siloxane hybrids was studied using solution cyclic voltammetry in dichloromethane with 0.1 M tetrabutylammonium perchlorate as a supporting electrolyte. A small amount of decamethylferrocene was added to all solutions and used as an internal standard.[29] The results of the electrochemical analysis are included in Table 1. All of the compounds underwent two reversible 1-electron oxidation events, which is characteristic of triarylamines containing two nitrogen centers. This demonstrates that the siloxane functionalization of arylamines does not have an undesirable impact on their electrochemical behavior. Variations in the position of the oxidation potentials can be explained by number and strength of electron-donating silicone groups as well as degree of conjugation between each arylamine redox center. There does not seem to be a consistent difference in the electron-donating potential of the −OD(M$_2$) versus the −OMM group. Voltammograms for all compounds are included in the Supporting Information (Figures S1−S12).

Encouraged by the success of this chemistry on phenylene diamine and benzidine-based substrates, we further extended this study to larger (higher molecular weight) multinitrogen centered triarylamines. Two well-known triarylamine structures were chosen as model compounds: one based on the spiro-TAD core[30] and one based on the TDATA motif,[5] each containing four nitrogen centers (Schemes 2 and 3, respectively). The spiro-TAD derivative (**9**) was synthesized using a slightly modified literature procedure,[31] resulting in a structure containing four aryl-methoxy groups for substitution (Scheme 2). When reacted with MD^{H}M under the Piers−Rubinsztajn conditions, the substrate reacted rapidly and cleanly to yield a molecular glass upon isolation, which ultimately crystallized over several weeks. The TDATA structure (**11**) was synthesized in two steps from tris(*p*-bromophenyl)amine (Scheme 3) and isolated as a crystalline solid. In this case, the reaction proceeded very slowly requiring approximately 16 h for completion. Both structures showed typical electrochemical behavior relative to their respective classes, and their synthesis demonstrates the ability of Piers−Rubinsztajn conditions to successfully install −OD(M)$_2$ units on large multinitrogen centered substrates.

Next, we chose to extend this chemistry to a related group of arylamine semiconductors: carbazoles. To this end, a number of *N*-phenylcarbazoles with methoxy-substituents in various positions were synthesized and subjected to the Piers−Rubinsztajn reaction conditions. Carbazoles, like triarylamines, are common materials in organic electronics and have been used as both *p*-type semiconductors and ambipolar host materials.[5,32] Four *N*-phenylcarbazole precursors were synthesized. For the structures with methoxy groups present on the carbazole ring itself (**14a−b**, Scheme 4), Suzuki coupling of 1-bromo-2-nitro-4-methoxybenzene and an arylhalide followed by a reductive ring-closing reaction promoted by triethylphosphite resulted in the desired carbazoles (**13a−b**).[33] These carbazoles were then *N*-arylated under Ullman coupling conditions[34] to yield the final methoxy-functionalized precursors (**14a−b**), of which **14b** has been previously described.[35] Those with methoxy groups on the phenyl ring (**14c−d**) were prepared in a one-step procedure under Ullman coupling conditions using carbazole and the appropriate halo-anisole. Carbazoles **14c**[35] and **14d**[36] have been previously described. Because of the planar molecular structure of compounds **14a−d**, they were further functionalized exclusively with −OD(M)$_2$ groups under Piers−Rubinsztajn conditions in order to inhibit any possible crystallization. In each case, the reaction proceeded extremely rapidly, and the resulting siloxane-functionalized carbazoles (**15a–d**) were isolated in good yields. For all but compound **15d**, the resulting materials were isolated as clear free-flowing liquids. Electrochemical analysis of the carbazoles **15a–d** showed that each underwent an irreversible one-electron oxidation typical for carbazoles.[32] Interestingly, the disubstituted **14b** appears to undergo two oxidations, which are poorly resolved under standard cyclic voltammetry conditions. It is unclear at this time whether these events represent two subsequent electrons being removed or that another chemical change is occurring. Full electrochemical and calorimetry data for these compounds is included in Table 1. The effect of substitution pattern on the physical properties of the carbazoles is in line with our previous observations in that the most symmetric substitution patterns (**15d**) result in a derivative that was crystalline, whereas the asymmetrically substituted structures are isolated as liquids.

Effect of Substrate on Catalyst Efficacy. In our approach to the synthesis of arylamine–siloxane hybrid materials, the use of Piers–Rubinsztajn conditions is critical to the installation of discrete siloxane groups while avoiding unwanted metathesis and redistribution reactions of the silicones. The previously studied simple triarylamines were found to react rapidly at room temperature (often reacting as quickly as silane could be added to the mixture). However, in this study, it was observed that the efficacy of this reaction (as indicated by its time to completion at room temperature) varied depending on the structure of the triarylamine substrate. The rate of the reaction for this series of compounds could be qualitatively observed by the evolution of methane gas. Compared to the triarylamines used in our previous study, the benzidine-based substrates reacted somewhat more slowly, with reactions typically finishing several minutes after complete silane addition. Substrates **1** and **10** stood out as the only substrates requiring heat to proceed rapidly; leaving the substrates to react at room temperature necessitated 7 and 16 h of reaction time for complete substitution, respectively. We also observed rapid reaction in the formation of triarylamines **9** and **11** and also for all carbazole derivatives (**14a–d**).

In our previous work, we found an interaction between the strongly Lewis acidic tris(pentafluorophenyl)borane (BCF) and the weakly Lewis basic tris(*p*-methoxyphenyl)amine did occur but that the level of interaction was quite weak.[9] This interaction between catalyst and substrate was shown to result in the formation of the triarylamine radical cation. However, we did not directly prove the existence of the corresponding radical anion of BCF. While such reactions are uncommon, several examples of BCF acting as an oxidant are noted in the literature.[37] A complete understanding of the strength of BCF as an oxidant has not been established owing to the instability of the borane anion.[38] Since the radical cation of an arylamine can be easily detected by its characteristic UV–vis–NIR absorption, we set out to see if the observed differences in reactivity between triarylamines could be explained by differing interactions between the precursor and the BCF catalyst.

Solutions of arylamines **1** and **4d** were prepared in toluene (our reaction solvent) along with varying molar equivalents of BCF. Compounds **1** and **4d** were chosen as representative compounds because their oxidized cations have been previously studied in the literature.[23] Furthermore, the observed reaction kinetics with these substrates varied greatly under the described conditions. To study this interaction under simulated reaction conditions, solutions of both BCF and substrate were prepared under ambient conditions and allowed to stand in open air for 15 min. These solutions were studied by UV–vis–NIR absorbance measurements, which found large changes in the visible and near-infrared region of the spectra upon addition of BCF (see Supporting Information, Figure S3). Compounds **1** and **4d** both exhibited broad absorption bands in the NIR as increasing amounts of BCF were added. These broad absorption bands can be assigned to intervalence charge transfer (IVCT) bands of the radical cations of the arylamines ($\mathbf{1}^{\bullet+}$ and $\mathbf{4d}^{\bullet+}$, respectively), which result from the partial delocalization of the charge between two conjugated redox centers. The UV–vis–NIR absorbance spectra of $\mathbf{1}^{\bullet+}$ and $\mathbf{4d}^{\bullet+}$ are well-studied as model charge transfer systems, and their molar extinction coefficients in dichloromethane are known.[22] A comparison between the published spectra of $\mathbf{1}^{\bullet+}$ and $\mathbf{4d}^{\bullet+}$ and the spectra generated by mixing the neutral triarylamines with BCF reveals that they are practically the same. Small differences in the $\lambda_{\max}$ found in the literature and in our study are likely due to differences in the solvents used for each measurement. Such charge transfer bands are inherently sensitive to solvent polarity.[39] The presence of atmospheric conditions can potentially complicate this experiment, as it is well-known that BCF readily forms adducts with water under the conditions of this study.[27] To rule out any possibility of water playing a role in the observed reaction, solutions were prepared under glovebox conditions. Under these anhydrous conditions, the exact same color changes were noted, and the samples were spectroscopically identical.

On the basis of these spectra and the known molar extinction coefficients of $\mathbf{1}^{\bullet+}$ and $\mathbf{4d}^{\bullet+}$ (albeit in different solvents) we can *estimate* the amount of arylamine that is oxidized (see the Supporting Information, Table S2). If an equimolar mixture of **1** and BCF is considered, the percentage of **1** oxidized is 5 mol % (corresponding to 5 mol % BCF reduced). If the same consideration is given to a mixture of **1** with catalytic amounts of BCF (0.01 equiv to **1**), the amount of **1** oxidized is 0.2 mol % (corresponding to 20 mol % of BCF reduced). In a similar manner for compound **4**, 2 mol % is oxidized at equal molar amounts (corresponding to 2 mol % BCF reduced), and 0.03 mol % is oxidized at catalytic amounts (corresponding to 3 mol % BCF reduced). We can therefore conclude that while the presence of $\mathbf{1}^{\bullet+}$ and $\mathbf{4d}^{\bullet+}$ is detectable, even by eye, the result is not the quantitative reduction of BCF to $\mathrm{BCF}^{\bullet-}$, rather it is only a partial reduction. Furthermore, given the partial reduction and the absence of the formation of a precipitate,[40] we hypothesize that the system is in a dynamic equilibrium between the charge transfer couple and the freely dissociated species. Taking into consideration our previous observation of the very slight oxidation of tris(*p*-methoxyphenyl)amine by BCF,[9] we propose that the extent of oxidation of the arylamine by BCF is directly related to the oxidation potential of the arylamine. That is, the equilibrium shifts toward formation of the radical cation/radical anion pair for arylamines with lower oxidation potentials. The oxidation potentials of the tris(*p*-methoxyphenyl)amine, **4d**, and **1** are 654,[41] 605, and 375 mV vs Ag/AgCl, respectively. Additionally, these values are proportional to the observed kinetic rates of the substrates under these conditions. This result suggests that the nature of interaction between triarylamines and BCF is a redox reaction where the BCF is acting as an oxidant. Furthermore, we can conclude that the redox reaction between certain triarylamines and BCF results in partial sequestration of the catalyst and retardation of the rate of the desired reaction.

To further support this hypothesis, mixtures of **1** and **4d** along with 1 mol % equiv of BCF were dissolved in toluene-d_8 and studied by ^{19}F and ^1H NMR. In each case, the ^1H spectra obtained were significantly broadened because of the presence of the paramagnetic arylamine radical cation (Supporting Information, Figures S14−S22). ^{19}F NMR spectra were difficult to obtain with a reasonable signal-to-noise ratio because of the highly dilute nature the BCF and the relatively low solubility of arylamines **1** and **4d**. The ^{19}F NMR of the mixture of compound **1** and 1 mol % BCF displayed a large number of resonances, with several corresponding to the free BCF (Supporting Information, Figure S15). Under the same conditions, the mixture of compound **4d** and 1 mol % BCF resulted in a cleaner spectrum comprising mostly of free BCF (but still with a poor signal-to-noise ratio; Supporting Information, Figure S17). Because of the poor signal-to-noise ratio obtained and the paramagnetic nature of the solution, concrete comparisons between the amount of free BCF in solution in the UV−vis−NIR experiment and the NMR experiment are difficult to make.

We therefore considered mixtures of arylamines **1** and **4d** and BCF in a 1:1 molar ratio (in C_6D_6; Supporting Information, Figure S19−20). Under these conditions, all three fluorine resonances of the free BCF are visible and make up the majority of the detected signal, although moderately broadened. This was particularly evident for compound **1**, and the difference in observed amount of free BCF between the two concentrations supports the idea of a dynamic chemical equilibrium between the free and bound state.

■ CONCLUSIONS

In summary, the scope and limitations of Piers−Rubinsztajn conditions for the synthesis of silicone−arylamine hybrids has been explored with an emphasis on obtaining liquid triarylamines having multiple nitrogen centers. The catalytic functionalization of a series of two nitrogen centered triarylamines was successful, and this substitution was found to have a significant effect on the physical properties of the arylamines, resulting in a number of new liquid triarylamines. We observed that by using the bulkier and branched $-OD(M)_2$ group, normally crystalline bis-arylamines could be made into free-flowing liquids by effectively lowering the glass transition temperature to below room temperature and inhibiting crystallization. The flexibility of this synthetic strategy was further explored by demonstrating that this chemistry can be used on larger multinitrogen centered arylamines as well as on carbazole-based precursors. The siloxane-functionalized triarylamines retained the electrochemical behavior of their parent compounds. Furthermore, the interaction between the Lewis acidic BCF (tris(pentafluorophenyl)borane) and the Lewis basic arylamine was further studied. It is proposed that the BCF catalyst can act as a one-electron oxidant, forming a radical cation/radical anion pair that is in equilibrium with the freely dissociated arylamine and BCF. This redox reaction sequesters the catalyst and retards the rate of the desired reaction in some cases. This mechanism is supported by UV−vis−NIR and ^{19}F NMR spectra. From studying these compounds, we hypothesize that the extent of the charge transfer interaction is dependent on the triarylamine oxidation potential. More easily oxidized triarylamines appear to achieve an equilibrium state further favoring the charge transfer pair than those triarylamines that are more electron-poor. This observation directly relates to the observed kinetics of the Piers−Rubinsztajn reaction on these substrates.

Through the work presented in both our preliminary study and this one, we have successfully increased the number of known liquid organic semiconductors from 2 to 15. These novel materials emulate the basic electrochemical properties of their widely used solid counterparts while spanning a wide range of oxidation potentials. Perhaps more importantly, we have shown that this synthetic strategy is quite general, which may also extend to other popular classes of organic semiconductors and possibly be used to produce other liquid organic semiconductor types in the future. This work will hopefully help further the study of organic electronic devices incorporating liquid layers and allow for the synthesis of device-specific liquid materials.

■ EXPERIMENTAL SECTION

***Safety note**: For reactions involving Piers−Rubinsztajn chemistry (coupling of silanes using tris(pentafluorophenyl)borane), the reaction can proceed extremely rapidly, evolving flammable gases with a noticeable exotherm. In our opinion, care should be exercised in scaling this chemistry. The careful dropwise addition of silane(s) at a moderate rate is recommended, and if no reaction is detected after several minutes, the addition of silane should be halted.*

General Piers−Rubinsztajn Procedure (General P−R procedure). The aryl-methoxy-functionalized substrate, tris(pentafluorophenyl)borane, and toluene were added to a generously sized round-bottom flask with a magnetic stirrer under atmospheric conditions. The flask should be at least four times the volume of the reagents to prevent any material from spilling out upon reaction. To maximize the reaction yield, the P−R reaction should be done at anhydrous conditions using predried reagents and solvent. Silane was added dropwise to this stirring solution, taking care to control the rate of methane evolving. Upon completion, standard activity basic alumina (~0.5 g) was added, and the solution was allowed to stir for 20 min. After this time, the solution was filtered to remove the added alumina and reduced under vacuum for purification.

Compound 1. 1,4-Phenylene diamine (1.000 g, 9.25 mmol), sodium *tert*-butoxide (5.33 g, 55.5 mmol), and bis(dibenzylideneacetone)palladium (106 mg, 0.184 mmol) were added to a round-bottom flask. This flask was sealed under an argon atmosphere. Anhydrous toluene (50.0 mL), 4-bromoanisole (7.61 g, 40.7 mmol), and tri-*tert*-butylphosphine (29.9 mg, 0.148 mmol, added as a stock solution in toluene) were added. This mixture was refluxed under an inert atmosphere for 2 h. Upon cooling, acidic clay (10.0 g, Montmorillonite K10) and acidic alumina (1.00 g, standard basic) were added to the mixture. This slurry was filtered, washing with toluene to yield a clear, pale yellow solution. This solution was concentrated under vacuum and precipitated into methanol. 4.24 g of a fine pale white powder was obtained (86% yield): ^1H NMR (400 MHz, C_6D_6) δ 7.14 (d, J = 9.08 Hz, integration obscured by solvent peak), 7.08 (s, 4H), 6.73 (d, J = 9.08 Hz, 8H), 3.30 (s, 12H); ^{13}C NMR (100 MHz, C_6D_6) δ 156.3, 143.8, 142.6, 126.4, 124.2, 115.5, 53.4; HRMS (ESI) [M$^+$] calcd for $C_{34}H_{32}N_2O_4$ 532.2356, found 532.2372.

Compound 2a. Using the general P−R procedure, **1** (500 mg, 0.939 mmol), anhydrous toluene (10.0 mL), tris(pentafluorophenyl)borane (5 mg, 0.01 mmol), and pentamethyldisiloxane (3.14 g, 21.3 mmol) were reacted. After 20 min, the solution was immersed in an oil bath at 50 °C. The solution vigorously evolved methane and was allowed to continue to stir for 20 min. The product was purified by column chromatography over silica gel eluting with 2:1 cyclohexane/toluene. 661 mg of a flakey crystalline solid was isolated (yield 66%): ^1H NMR (400 MHz, C_6D_6) δ 7.09 (d, J = 8.98 Hz, 8H), 7.01 (s, 4H), 6.91 (d, J = 8.98 Hz, 8H), 0.22 (s, 24H), 0.11 (s, 36H); ^{13}C NMR (100 MHz, C_6D_6) δ 151.0, 143.8, 143.3, 126.2, 124.6, 121.3, 2.1, 0.2; HRMS (ESI) [M + H] calcd for $C_{50}H_{81}N_2O_8Si_8$ 1061.4141, found 1061.4146.

Compound 2b. Using the general P−R procedure, compound **1** (0.500 g, 0.939 mmol), 1,1,1,3,5,5,5-heptamethyltrisiloxane (2.51 g, 11.3 mmol), tris(pentafluorophenyl)borane (5 mg, 0.01 mmol), and anhydrous toluene (5.00 mL) were reacted. The product was isolated by column chromatography over silica gel eluting with 2:1 cyclohexane/toluene. A viscous yellow oil was isolated (1.034 g, 81% yield): ^{1}H NMR (400 MHz, C_6D_6) δ 7.10 (d, J = 8.77 Hz, 8H), 7.07 (s, 4H), 6.97 (d, J = 8.77 Hz, 8H), 0.27 (s, 12H), 0.15 (s, 72H); ^{13}C NMR (100 MHz, C_6D_6) δ 150.2, 143.4, 143.1, 125.9, 124.1, 120.9, 1.7, −3.0; HRMS (ESI) [M^+] calcd for $C_{58}H_{104}N_2O_{12}Si_{12}$ 1356.4821, found 1356.4814.

Compound 3a.[23] Aniline (5.98 g, 64.2 mmol), 4-bromoanisole (10.0 g, 53.5 mmol), sodium *tert*-butoxide (7.71 g, 80.2 mmol), bis(dibenzylideneacetone)palladium (154 mg, 0.268 mmol), tri-*tert*-butylphosphine (43.0 mg, 0.212 mmol, as a 10 g/L solution in toluene), and anhydrous toluene (75.0 mL) were added to a round-bottom flask. The flask was refluxed for 2 h under argon gas. Once cool, acid-washed clay (montmorillonite K10 from Sigma Aldrich, 10.0 g) and standard basic alumina (1.00 g) were added to the slurry and stirred for 30 min. The slurry was filtered, and the clear light yellow mother liquor was collected. This organic phase was washed with 10% HCl solution three times and with brine once and then dried over magnesium sulfate. The organic phase was concentrated under vacuum and recrystallized from boiling heptanes to yield small silver needles. 7.43 g of product was isolated (67% yield): ^{1}H NMR (400 MHz, C_6D_6) δ 7.23 (t, J = 7.99 Hz, 2H), 7.09 (d, J = 8.57 Hz, 2H), 6.95−6.82 (m, 5H), 5.50 (s, broad, 1H), 3.81 (s, 3H).

Compound 3b.[24] Using the same general procedure as for compound **3a** above, *p*-toluidine (6.88 g, 64.2 mmol), 4-bromoanisole (10.0 g, 53.5 mmol), sodium *t*-butoxide (7.71 g, 80.2 mmol), bis(dibenzylideneacetone)palladium (154 mg, 0.268 mmol), tri-*tert*-butylphosphine (43 mg, 0.212 mmol), and anhydrous toluene (75.0 mL) were reacted at reflux for 2 h. Product recrystallized from heptanes to yield light brown flakes. 7.26 g of pure product was isolated (64% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06−7.00 (m, 4H), 6.88−6.82 (m, 4H), 5.39 (s, broad, 1H), 3.80 (s, 3H), 2.28 (s, 3H).

Compound 3c.[25] Using the same general procedure as for compound **3a** above, 3,4-dimethylaniline (3.56 g, 29.4 mmol), 4-bromoanisole (5.00 g, 26.7 mmol), sodium *t*-butoxide (3.84 g, 40.0 mmol), bis(dibenzylideneacetone)palladium (154 mg, 0.268 mmol), tri-*tert*-butylphosphine (43 mg, 0.212 mmol), and anhydrous toluene (35.0 mL) were refluxed for 2 h. Product recrystallized from heptanes to yield silver needles. 4.50 g of pure product was isolated (67% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05−6.95 (m, 3H), 6.83 Hz (d, J = 8.96 Hz, 2H), 6.76−6.64 (m, 2H), 5.33 (s, broad, 1H), 3.78 (s, 3H), 2.19 (s, 6H).

Compound 3d. Using the same general procedure as for compound **3a** above, 2-bromo-6-methoxynaphthalene (10.0 g, 42.2 mmol), *para*-anisidine (6.23 g, 50.6 mmol), sodium *t*-butoxide (5.95 g, 61.9 mmol), bis(dibenzylideneacetone)palladium (119 mg, 0.207 mmol), tri-*tert*-butylphosphine (33 mg, 0.163 mmol), and anhydrous toluene (50.0 mL) were refluxed for 1 h. Product recrystallized from heptanes to yield fine gray needles (5.54 g, 47% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 9.00 Hz, 1H), 7.39 (d, J = 0.99 Hz, 1H), 7.18 (dd, J_1 = 11.35 Hz, J_2 = 2.74 Hz, integration obscured by residual solvent peak), 7.02−6.91 (m, 4H), 6.79 (d, J = 8.61 Hz, 2H), 5.01 (s, broad, 1H), 3.44 (s, 3H), 3.37 (s, 3H). NMR (100 MHz, C_6D_6) δ 156.81, 156.09, 141.91, 137.09, 131.20, 130.49, 128.60, 128.50, 122.48, 120.45, 119.88, 115.42, 111.25, 106.85, 55.48, 55.19; HRMS (ESI) [M + H] calcd for $C_{18}H_{18}NO_2$ 280.1338, found 280.1346.

Compound 4a.[26] Compound **3a** (3.00 g, 15.1 mmol), 4,4′-dibromobiphenyl (2.24 g, 7.17 mmol), sodium *tert*-butoxide (2.07 g, 21.5 mmol), palladium(II) acetate (16 mg, 0.0713 mmol), tri-*tert*-butylphosphine (16 mg, 0.0791 mmol, added as a stock solution in toluene), and anhydrous toluene (25 mL) were added to a round-bottom flask. This solution was refluxed for 1 h under an argon atmosphere. Upon cooling, acid-washed clay (montmorillonite K10 from Sigma Aldrich, 2.00 g) and standard activity basic alumina (0.500 g) were added and allowed to stir into the mixture for 10 min. The solids were filtered out, washing with additional toluene. The mother liquor was collected and concentrated under vacuum until the solution began to become a viscous oil. This oil was precipitated into rapidly stirring methanol (50 mL) to yield a fine white powder. This powder was collected by filtration and washed with cold methanol. 2.635 g of product was isolated (67% yield): ^{1}H NMR (400 MHz, C_6D_6) δ 7.41 (d, J = 8.61 Hz, 4H), 7.19−7.13 (m, peak obscured by solvent peak), 7.10 (d, J = 7.41 Hz, 4H), 7.06 (d, J = 9.00 Hz, 4H), 6.85 (t, J = 7.04 Hz, 2H), 6.71 (d, J = 9.00 Hz, 4H), 3.29 (s, 6H).

Compound 4b. Using the same general procedure as for compound **4a**, compound **3b** (3 g, 14.1 mmol), 4,4′-dibromobiphenyl (2.09 g, 6.67 mmol), sodium *tert*-butoxide (1.93 g, 20.1 mmol), palladium(II) acetate (15 mg, 0.0668 mmol), tri-*tert*-butylphosphine (11 mg, 0.0544 mmol, added from stock solution in anhydrous toluene), and anhydrous toluene (25.0 mL) were reacted for 2 h at reflux. 7.06 g of isolated material was collected (87% yield): ^{1}H NMR (400 MHz, C_6D_6) δ 7.43, (d, J = 8.77 Hz, 4H), 7.11 (d, J = 8.77 Hz, integration obscured by solvent), 7.15−7.08 (m, integration obscured by solvent), 6.94 (d, J = 7.99 Hz, 4H) 6.72 (d, J = 8.96 Hz, 4H), 3.30 (s, 6H), 2.12 (s, 6H); ^{13}C NMR (100 MHz, C_6D_6) δ 156.7, 147.9, 146.3, 141.5, 134.4, 132.1, 130.3, 127.6, 127.4, 124.4, 123.0, 115.2, 55.0, 20.8; HRMS (EI) [M^+] calcd for $C_{40}H_{36}N_2O_2$ 576.2777, found 576.2769.

Compound 4c. Using the same general procedure as for compound **4a**, compound **3c** (6.41 g, 28.2 mmol), 4,4′-dibromobiphenyl (4.00 g, 12.8 mmol), sodium *tert*-butoxide (3.08 g, 32.0 mmol), palladium(II) acetate (115 mg, 0.512 mmol), tri-*tert*-butylphosphine (83 mg, 0.410 mmol, added from stock solution in anhydrous toluene), and anhydrous toluene (25.0 mL) were reacted for 3 h at reflux. The compound precipitated poorly in methanol and was purified by column chromatography over silica gel eluting with 1:1 cyclohexane/toluene. A fine white powder was collected (5.21 g, 67%): ^{1}H NMR (400 MHz, C_6D_6) δ 7.44 (d, J = 8.96 Hz, 4H), 7.22 (d, J = 8.77 Hz, 4H), 7.15 (d, integration and coupling obscured by residual solvent peak), 7.11 (d, J = 2.14 Hz, 2H), 7.03 (dd, J_1 = 8.18 Hz, J_2 = 2.14 Hz, 2H), 6.94 (d, J = 8.18 Hz, 2H), 6.73 (d, J = 8.96 Hz, 4H), 3.30 (s, 6H), 2.03 (s, 6H), 1.93 (s, 6H). ^{13}C NMR (100 MHz, C_6D_6) δ 156.6, 148.0, 146.6, 141.7, 137.7, 134.3, 131.0, 130.9, 127.6, 127.3, 126.0, 122.8, 122.4, 115.2, 55.0, 19.8, 19.1; HRMS (ESI) [M^+] calcd for $C_{42}H_{40}N_2O_2$ 604.3090, found 604.3100.

Compound 4d. Using the same general procedure as for compound **4a**, bis(4-methoxyphenyl)amine (3.82 g, 16.8 mmol), 4,4′-dibromobiphenyl (2.50 g, 8.01 mmol), sodium *t*-butoxide (1.92 g, 20.0 mmol), palladium(II) acetate (72 mg, 0.321 mmol), tri-*tert*-butylphosphine (52 mg, 0.257 mmol, added from stock solution in anhydrous toluene), and anhydrous toluene (20.0 mL) were reacted for 3 h at reflux. The compound was precipitated into methanol and recrystallized from EtOAc. Slightly yellow flakes were collected (3.33 g, 70%): ^{1}H NMR (400 MHz, C_6D_6) δ 7.46 (d, J = 8.61 Hz, 4H), 7.17 (m, obscured by residual solvent), 7.12 (d, J = 9.00 Hz, 8H), 6.74 (d, J = 9.00 H, 8H), 3.31 (s, 12H); ^{13}C NMR (100 MHz, C_6D_6) δ 156.4, 148.2, 141.7, 134.0, 127.6, 126.8, 122.0, 115.17, 55.0.

Compound 4e. Using the same general procedure as for compound **4a**, **3d** (2.43 g, 8.71 mmol), 4,4′-dibromobiphenyl (1.35 g, 4.34 mmol), sodium *t*-butoxide (1.29 g, 13.4 mmol), palladium(II) acetate (13 mg, 0.0579 mmol), tri-*tert*-butylphosphine (9 mg, 0.046 mmol), and anhydrous toluene (15.0 mL) were refluxed for 1 h. Compound was precipitated into methanol to yield a fine white powder. The product was further purified by recrystallization from toluene/EtOAc to yield small white crystals (2.66 g, 86% yield): ^{1}H NMR (400 MHz, C_6D_6) δ 7.56 (d, J = 1.96 Hz, 2H), 7.52 (d, J = 9.00 Hz, 2H), 7.47 (d, J = 8.61 Hz, 4H), 7.42 (dd, J_1 = 9.00 Hz, J_2 = 2.35 HZ, 2H), 7.27−7.22 (m, 6H), 7.17−7.09 (m, integration obscurd by residual solvent peak), 6.94 (d, J = 2.35 Hz, 2H), 6.75 (d, J = 9.00 Hz, 4H), 3.40 (s, 6H), 3.32 (s, 6H); ^{13}C NMR (100 MHz, C_6D_6) δ 157.8, 157.1, 148.2, 144.8, 144.8, 135.0, 131.9, 130.9, 129.3, 128.5, 128.1, 127.8, 125.6, 123.6, 121.1, 119.8, 115.7, 106.6, 55.4, 55.2; HRMS (ESI) [M + H] calcd for $C_{48}H_{41}N_2O_4$ 709.3066, found 709.3048.

Compound 5a. Using the general P−R procedure, **4a** (0.500 g 0.937 mmol), tris(pentafluorophenyl)borane (5 mg, 0.00977 mmol), and 5.00 mL of toluene were stirred, and pentamethyldisiloxane (1.35 g, 9.11 mmol) was added dropwise. The reaction proceeded vigorously and was allowed to stir for an additional 20 min after bubbling had ceased. The product was purified by column chromatography over silica gel eluting with 5:2 cyclohexane/toluene. The product was isolated as a viscous pale yellow oil (0.391 g, 51% yield): ^{1}H NMR (400 MHz, C_6D_6) δ 7.38 (d, J = 8.77 Hz, 4H), 7.16–7.12 (m, integration obscured by solvent), 7.12–7.02 (8H), 6.92 (d, J = 9.16 Hz, 4H), 6.84 (t, J = 7.21 Hz, 2H), 0.23 (s, 12H), 0.12 (s, 18H); ^{13}C NMR (100 MHz, C_6D_6) δ 151.5, 148.7, 147.6, 142.2, 135.0, 129.6, 127.7, 127.3, 123.9, 123.9, 122.5, 121.1, 1.8, −0.2; HRMS (ESI) [M$^+$] calcd for $C_{46}H_{56}N_2O_4Si_4$ 812.3317, found 812.3300.

Compound 5b. Using the general P−R procedure, **4b** (0.500 g, 0.867 mmol), pentamethyldisiloxane (1.29 g, 8.67 mmol), tris(pentafluorophenyl)borane (5 mg, 0.00977 mmol), and anhydrous toluene (5.00 mL) were reacted at room temperature; the reaction proceeded vigorously. The compound was purified by column chromatography eluting with 5:2 cyclohexane/toluene. The product was isolated as a viscous and pale yellow oil (0.350 g, 48% yield): ^{1}H NMR (400 MHz, C_6D_6) δ 7.40 (d, J = 8.77 Hz, 4H), 7.18 (m, obscured by solvent), 7.13–7.06 (m, 8H), 6.97–6.89 (m, 8H), 2.11 (s, 6H), 0.23 (s, 12H), 0.12 (s, 18H); ^{13}C NMR (100 MHz, C_6D_6) δ 151.2, 147.8, 146.2, 142.5, 134.6, 132.2, 130.3, 127.6, 126.9, 124.7, 123.3, 121.0, 20.8, 1.8, −0.1; HRMS (ESI) [M$^+$] calcd for $C_{48}H_{60}N_2O_4Si_4$ 840.3630, found 840.3639.

Compound 5c. Using the general P−R procedure, **4c** (0.500 g, 0.827 mmol), pentamethyldisiloxane (0.490 g, 3.30 mmol), tris(pentafluorophenyl)borane (4 mg, 0.00781 mmol), and anhydrous toluene (5.00 mL) were reacted. The product was purified by column chromatography eluting with 5:2 cyclohexane/toluene. The product was isolated as a viscous and pale yellow oil (0.467, 65% yield): ^{1}H NMR (400 MHz, C_6D_6) 7.41 (d, J = 8.96 Hz, 4H), 7.2 (d, J = 8.57 Hz, 4H), 7.13 (d, 8.96 Hz, 4H), 7.08 (d, J = 2.14 Hz, 2H), 7.01 (dd, J_1 = 5.65 Hz, J_2 = 2.14 Hz, 2H), 6.97–6.91 (m, 6H), 2.02 (s, 6H), 1.92 (s, 6H), 0.23 (s, 12H), 0.12 (s, 18H); ^{13}C NMR (100 MHz, C_6D_6) δ 151.1, 147.9, 146.5, 142.7, 137.7, 134.5, 131.2, 130.9, 127.6, 126.8, 126.3, 123.2, 122.7, 121.0, 19.8, 19.1, 1.9, −0.1; HRMS (ESI) [M$^+$] calcd for $C_{50}H_{64}N_2O_4Si_4$ 868.3943, found 868.3930.

Compound 5d. Using the general P−R procedure, **4d** (0.500 g, 0.821 mmol), pentamethyldisiloxane (0.975 g, 6.57 mmol), tris(pentafluorophenyl)borane (4 mg, 0.00781 mmol), and 10.0 mL of anhydrous toluene were reacted. The product was purified by passing the compound through a plug of silica gel eluting with 1:1 hexanes/toluene. A clear oil was obtained, which slowly crystallized to soft white crystals after several days (0.860 g, 92% yield): ^{1}H NMR (400 MHz, C_6D_6) δ 7.40 (d, J = 8.77 Hz, 4H), 7.14 (partially obscured by solvent peak), 7.08 (d, J = 8.96 Hz, 8H), 6.93 (d, J = 8.96 Hz, 8H), 0.23 (s, 24H), 0.12 (s, 36H); ^{13}C NMR (100 MHz, C_6D_6) δ 151.0, 148.0, 142.6, 134.3, 127.6, 126.5, 122.8, 121.0, 1.8, −0.2; HRMS (ESI) [M$^+$] calcd for $C_{56}H_{84}N_2O_8Si_8$ 1136.4382, found 1136.4368.

Compound 5e. Using the general P−R procedure, **4b** (0.500 g, 0.867 mmol), 1,1,1,3,5,5,5-heptamethyltrisiloxane (1.930 g, 8.67 mmol), tris(pentafluorophenyl)borane (4 mg, 0.00781 mmol), and anhydrous toluene (5 mL) were reacted at room temperature; the reaction proceeded rapidly. The compound was purified by column chromatography eluting with 5:2 cyclohexane/toluene. The final product was isolated as a viscous clear oil (0.592 g, 69% yield): ^{1}H NMR (400 MHz, C_6D_6) δ 7.41 (d, J = 8.77 Hz, 4H), 7.18 (d, J = 8.96 Hz, integration obscured by solvent), 7.13–7.07 (m, 8H), 7.00 (d, J = 8.96 Hz, 4H), 6.92 (d, J = 8.77 Hz, 4H), 2.11 (s, 6H), 0.28 (s, 6H), 0.17 (s, 36H); ^{13}C NMR (100 MHz, C_6D_6) δ 150.8, 147.8, 146.2, 142.6, 134.6, 132.2, 130.3, 127.7, 126.9, 124.6, 123.2, 121.0, 20.8, 1.7, −3.0; HRMS (ESI) [M$^+$] calcd for $C_{52}H_{72}N_2O_6Si_6$ 988.4006, found 988.3995.

Compound 5f. Using the general P−R procedure, **4d** (0.500 g, 0.821 mmol), 1,1,1,3,5,5,5-heptamethyltrisiloxane (1.46 g, 6.57 mmol), tris(pentafluorophenyl)borane (4 mg, 0.00781 mmol), and anhydrous toluene (10.0 mL) were reacted. Compound was purified by column chromatography eluting with 1:1 cyclohexane/toluene. The final product was isolated as a pale yellow oil (1.06 g, 90% yield): ^{1}H NMR (400 MHz, C_6D_6) δ 7.43 (d, J = 8.77 Hz, 8H), 7.16 (multiplicity and integration obscured by solvent peak), 7.09 (d, J = 8.77 Hz, 8H), 7.00 (d, J = 8.96 Hz, 4H), 0.28 (s, 12H), 0.16 (s, 72H); ^{13}C NMR (100 MHz, C_6D_6) δ 150.6, 148.0, 142.8, 134.3, 127.6, 128.5, 122.7, 121.0, 1.7, −3.0; HRMS (ESI) [M$^+$] calcd for $C_{64}H_{108}N_2O_{12}Si_{12}$ 1432.5134, found 1432.5153.

Compound 5g. Using the general P−R procedure, **4e** (0.500 g, 0.705 mmol), pentamethyldisiloxane (1.05 g, 7.06 mmol), tris(pentafluorophenyl)borane (4 mg, 0.00781 mmol), and toluene (10.0 mL) were reacted. Compound was purified by column chromatography eluting with 1:1 cyclohexane/toluene to yield a slightly green powder (0.426 g, 49% yield): ^{1}H NMR (400 MHz, C_6D_6) δ 7.54 (d, J = 2.14 Hz, 2H), 7.47 (d, J = 9.2 Hz, 2H), 7.44 (d, J = 8.77 Hz, 4H), 7.42 (d, J = 2.34 Hz, 2H), 7.34 (dd, J_1 = 8.96 Hz, J_2 = 2.34 Hz, 2H), 7.26 (d, J = 8.96 Hz, 2H), 7.20 (d, J = 8.77 Hz, 4H), 7.16 (obscured by solvent peak), 7.11 (d, J = 8.77 Hz, 4H), 6.97 Hz (d, J = 8.96 Hz, 4H), 0.27 (s, 12H), 0.24 (s, 12H), 0.14 (s, 12H), 0.13 (s, 12H); ^{13}C NMR (100 MHz, C_6D_6) δ 152.5, 151.7, 148.1, 145.0, 142.7, 135.2, 132.1, 131.4, 129.3, 127.4, 125.8, 124.0, 122.8, 121.4, 121.4, 115.6, 2.2, 2.2, 0.2, 0.1; HRMS (ESI) [M + H] calcd for $C_{64}H_{89}N_2O_8Si_8$ 1237.4773, found 1237.4715.

Compound 5h. Using the general P−R procedure, **4e** (400 mg, 0.564 mmol), 1,1,1,3,5,5,5-heptamethyltrisiloxane (748 mg, 3.36 mmol), tris(pentafluorophenyl)borane (3 mg, 0.00587 mmol), and toluene (10.0 mL) were reacted. Compound purified by column chromatography eluting with 1:1 cyclohexane/toluene to yield a viscous clear oil (803 mg, 93% yield): ^{1}H NMR (400 MHz, C_6D_6) δ 7.53–7.47 (m, 6H), 7.43 (d, J = 8.61 Hz, 4H), 7.34 (dd, J_1 = 9.00 Hz, J_2 = 1.96 Hz, 2H), 7.30 (d, J = 9.00 Hz, 2H), 7.22 (dd, J_1= 9.00 Hz, J_2 =2.35 Hz, 2H), 7.19 (d, J = 8.61 Hz, 4H), 7.07 (d, J = 9.00 Hz, 4H), 7.01 (d, J = 9.00 Hz, 4H), 0.32 (s, 6H), 0.29 (s, 6H), 0.17 (s, 72H); ^{13}C NMR (100 MHz, C_6D_6) δ 152.0, 151.3, 148.0, 145.0, 142.8, 135.2, 132.0, 131.4, 129.2, 127.5, 125.7, 124.0, 122.6, 121.5, 121.1, 115.5, 2.12, 2.10, −2.6, −2.7; HRMS (ESI) [M + H] calcd for $C_{72}H_{113}N_2O_{12}Si_{12}$ 1533.5519, found 1533.5583.

Compound 6.[31] 2-Bromobiphenyl (5.00 g, 21.4 mmol) in anhydrous THF (11.0 mL) was reacted with magnesium (0.567 g, 23.3 mmol) under inert gas at room temperature. Upon formation of the Grignard reagent, 9-fluorenone (3.90 g, 21.6 mmol in 5.00 mL of THF) was added, and the solution was refluxed for 4 h and allowed to cool. Upon cooling, a yellow precipitate was formed and collected, washing with cold methanol. This solid was stirred into a 5% HCl solution (22.0 mL) for 2 h at room temperature and washed with additional methanol. Finally, the solid was dissolved in acetic acid (22.0 mL) and refluxed for 40 min. Upon cooling, large white crystals of the pure product were obtained (3.73 g, 56% yield).

Compound 7.[31] Compound **6** (1.00 g, 3.16 mmol), $FeCl_3$ (2 mg, 0.0123 mmol), and 6 mL of chloroform were mixed under an inert atmosphere. Molecular bromine (2.02 g, 12.6 mmol) in 2.00 mL of chloroform was added, and the reaction was allowed to proceed at room temperature in the absence of light for 5 days. Upon completion, the reaction was quenched with aqueous ammonium hydroxide and recrystallized from chloroform/ethanol (50/50) to yield a pure white crystalline product (1.10 g, 55% yield).

Compound 8. Palladium(II) acetate (5 mg, 0.0223 mmol), **10** (200 mg, 0.316 mmol), **3b** (340 mg, 1.59 mmol), sodium *tert*-butoxide (145 mg, 1.51 mmol), and 2.30 mL of anhydrous toluene were added to a round-bottom flask under an atmosphere of argon. Once sealed, tri-*tert*-butylphosphine (3.75 mg, 0.0185 mmol) was added as a toluene stock solution. The mixture was refluxed for 5 h under argon and allowed to cool. The solution was filtered through a short plug of silica to yield a clear yellow liquid; this solution was concentrated and precipitated into stirring methanol to yield the product as a fine white powder (258 mg, 67% yield): ^{1}H NMR (400 MHz, C_6D_6) δ 7.12 (dd, J_1 = 7.82 Hz, J_2 = 2.93 Hz, 8H), 7.09–7.01 (m, 16H), 7.00 (dd, J_1 = 8.22 Hz, J_2 = 2.35 Hz, 4H), 6.95 (d, J = 8.22, 8H), 6.71 (d, J = 9.39 Hz, 8H), 3.25 (s, 12H), 2.05 (s, 12H); ^{13}C NMR (100 MHz, C_6D_6) δ 156.7, 151.1, 148.2, 146.9, 141.94, 135.6, 131.7, 130.3, 127.2, 124.0, 123.5, 121.1, 119.2, 115.4, 66.8, 55.3, 21.1. MS (ESI) [M$^+$] calcd for $C_{81}H_{68}N_4O_8$ 1160.5, found 1160.5

Compound 9. Using the general P–R procedure, **11** (200 mg, 0.172 mmol), 1,1,1,3,5,5,5-heptamethyltrisiloxane (445 mg, 2.00 mmol), 2.00 mL of toluene, and tris(pentafluorophenyl)borane (1 mg, 0.00195 mmol) were reacted at room temperature. Compound was purified by column chromatography on silica gel eluting with hexanes/toluene. Product was isolated as a glass (294 mg, 86% yield): ^{1}H NMR (400 MHz, C_6D_6) δ 7.18 (signal obscured by solvent), 7.09 (d, J = 2.35 Hz, 4H), 7.05–6.95 (m, 36H), 2.05 (s, 12H), 0.28 (s, 12H), 0.14 (s, 72H). ^{13}C NMR (100 MHz, C_6D_6) δ 151.0, 150.9, 148.1, 146.6, 143.0, 136.4, 132.2, 130.4, 126.8, 124.3, 123.5, 121.2, 120.8, 118.8, 66.8, 21.2, 2.1, −2.6; MS (ESI) [M + 3H] calcd for $C_{106}H_{145}N_4O_{11}Si_{12}$ 1984.8, found 1987.8.

Compound 10. Tris(4-bromophenyl)amine (0.500 g, 1.04 mmol), compound **3c** (0.786 g, 3.46 mmol), sodium *t*-butoxide (0.444 g, 4.63 mmol), palladium(II) acetate (5 mg, 0.00223 mmol), tri-*tert*-butylphosphine (3 mg, 0.00148 mmol), and anhydrous toluene (10.0 mL) were refluxed for 16 h. Upon cooling, the mixture was filtered, and the resulting liquor was concentrated and precipitated into methanol to yield a light yellow fine powder (742 mg, 78% yield): ^{1}H NMR (400 MHz, C_6D_6) δ 7.16–7.12 (m, integration obscured by residual solvent), 7.10–7.06 (m, 9H), 7.02 (dd, J_1 = 8.02 Hz, J_2 = 2.54 Hz, 3H), 6.92 (d, J = 8.22 Hz, 3H), 6.71 (d, J = 9.00 Hz, 6H); ^{13}C NMR (100 MHz, C_6D_6) δ 156.6, 147.2, 144.3, 143.1, 142.3, 137.9, 131.1, 130.8, 127.2, 125.7, 125.5, 124.5, 122.0, 115.5, 55.4, 20.2, 19.4; HRMS (ESI) [M + H] calcd for $C_{63}H_{61}N_4O_3$ 921.4744, found 921.4765.

Compound 11. Using the general P–R procedure, compound **10** (0.349 g, 0.379 mmol), 1,1,1,3,5,5,5-heptamethyltrisiloxane (0.871 g, 3.91 mmol), tris(pentafluorophenyl)borane (2 mg, 0.00391 mmol), and 5.00 mL of toluene were reacted for 16 h under ambient conditions. Product was purified by column chromatography eluting with hexanes/toluene and isolated as a white crystalline solid (269 mg, 46% yield): ^{1}H NMR (400 MHz, C_6D_6) δ 7.14–7.09 (m, 12H), 7.08–7.04 (m, 9H), 7.02–6.95 (m, 9H), 6.91 (d, J = 8.22 Hz, 3H), 2.01 (s, 9H), 1.92 (s, 9H), 2.07 (s, 9H), 0.15 (s, 54H); ^{13}C NMR (100 MHz, C_6D_6) δ 150.7, 147.1, 144.2, 143.3, 143.1, 137.9, 131.1, 130.9, 126.7, 126.0, 125.4, 124.7, 122.3, 121.3, 20.15, 19.4, 2.1, −2.7; HRMS (ESI) [M + H] calcd for $C_{81}H_{115}N_4O_9Si_9$ 1539.6587, found 1539.6546.

Compound 12a.[33] In an inert atmosphere glovebox, 4-bromo-3-nitroanisole (3.00 g, 12.9 mmol), phenylboronic acid (1.73 g, 14.2 mmol), cesium fluoride (3.93 g, 25.8 mmol), bis(dibenzylideneacetone)palladium (149 mg, 0.258 mmol), tri-*tert*-butylphosphine (52 mg, 0.258 mmol, added as a 10 g/L stock solution in anhydrous toluene), and anhydrous tetrahydrofuran (60.0 mL) were added to a stirred round-bottom flask. This flask was allowed to stir at ambient temperature for 24 h. The resulting solution was removed from the glovebox, and the solids were filtered, eluting with THF. This light brown solution was dried under vacuum. The remaining solids were taken up in toluene and washed with water and brine. The organic toluene phase was dried over magnesium sulfate and filtered through a short plug of silica gel, eluting with toluene. This light-yellow liquid was concentrated under vacuum until it resembled a viscous oil. Hexanes (5.00 mL) were added to this resulting oil to precipitate light yellow crystals. These crystals were collected and washed with cold hexanes and then dried under vacuum (2.44 g collected, 85% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.32 ppm (m, 5H), 7.30–7.25 (m, 2H), 7.15 (dd, J_1 = 8.6 Hz, J_2 = 2.7 Hz, 1H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 137.4, 132.9, 128.80, 128.76, 128.2, 128.0, 118.8, 109.2, 56.1; HRMS (EI) [M$^+$] calcd for $C_{13}H_{11}NO_3$ 229.0733, found 229.0739.

Compound 12b.[33] In an inert atmosphere glovebox, 4-bromo-3-nitroanisole (3.47 g, 15.0 mmol), 4-methoxyphenylboronic acid (2.50 g, 16.5 mmol), cesium fluoride (7.52 g, 49.5 mmol), bis(dibenzylideneacetone)palladium (259 mg, 0.45 mmol), tri-*tert*-butylphosphine (91 mg, 0.450 mmol, added as a 10 g/L stock solution in anhydrous toluene), and anhydrous tetrahydrofuran (30.0 mL) were added to a stirred round-bottom flask. This flask was allowed to stir at ambient temperature for 24 h. The resulting solution was removed from the glovebox, and the solids were filtered, eluting with THF. This light brown solution was dried under vacuum. The remaining solids were taken up in toluene and washed with water and brine. The organic toluene phase was dried over magnesium sulfate and filtered through a short plug of silica gel, eluting with toluene. This light yellow liquid was then concentrated under vacuum until it resembled a viscous oil. Hexanes (5.00 mL) were added to this resulting oil, and the solution was cooled in a refrigerator overnight. Light-yellow crystals were collected and washed with cold hexanes and then dried under vacuum (2.55 g collected, 65% yield). This product was used without further purification: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.30 (m, 2H), 7.21 (d, J = 8.96 Hz, 2H), 7.13 (dd, J_1 = 8.57 Hz, J_2 = 2.73 Hz, 1H), 6.96 (d, J = 8.96 Hz, 2H), 3.89 (s, 3H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 159.0, 132.9, 129.6, 129.3, 128.4, 118.8, 114.3, 109.0, 104.9, 56.1, 55.4; HRMS (ESI) [M$^+$] calcd for $C_{14}H_{13}NO_4$ 259.0845, found 259.0845.

Compound 13a.[33] Compound **12a** (2.20 g, 9.56 mmol) was added to a stirred round-bottom flask, and the flask was flushed with argon gas and sealed under a positive pressure of gas. Triethylphosphite (7.70 mL) was added via syringe, and the solution was heated at 160 °C for 16 h. The reaction was allowed to cool, and 10.0 mL of methanol was added to the solution. This was allowed to rest in a refrigerator overnight to yield white square crystals. These crystals were collected by filtration and washed sparingly with cold methanol. The collected crystals were then dried under vacuum (1.69 g was isolated, 56% yield): ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 11.10 (s, broad, 1H), 7.98 (m, 2H), 7.41 (d, J = 7.82 Hz, 1H), 7.28 (td, J_1 = 7.63 Hz, J_2 = 1.17 Hz, 1H), 7.10 (td, J_1 = 7.82 Hz, J_2 = 1.17 Hz, 1H), 6.96 (d, J = 2.35, 1H), 6.76 (dd, J_1 =8.61 Hz, J_2 = 2.35 Hz, 1H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $(CD_3)_2SO$) δ 158.4, 141.0, 139.7, 124.0, 122.6, 120.9, 119.2, 118.5, 116.1, 110.6, 107.6, 94.4, 55.2; HRMS (ESI) [M + H] calcd for $C_{13}H_{12}NO$ 198.0913, found 198.0906.

Compound 13b.[33] Compound **12b** (2.55 g, 9.81 mmol) and triethylphosphite (8.90 mL) were heated at 160 °C for 16 h under argon. The reaction was allowed to cool, and 10.0 mL of methanol was added to the solution. This was allowed to rest in a refrigerator overnight to yield small white needles. These crystals were collected by filtration and washed sparingly with cold methanol. The resulting white crystals were then dried under vacuum (1.83 g, 82% yield): ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 10.94 (s, broad, 1H), 7.83 (d, J = 8.38 Hz, 2H), 6.92 (d, J = 2.14 Hz, 2H), 6.72 (dd, J_1 = 8.38 Hz, J_2 = 2.14 Hz, 2H); ^{13}C NMR (100 MHz, $(CD_3)_2SO$) δ 157.5, 141.0, 119.9, 116.4, 107.3, 94.6, 55.2; HRMS (ESI) [M + H] calcd for $C_{14}H_{14}NO_2$ 228.1019, found 228.1011

Compound 14a. Iodobenzene (1.241 g, 6.08 mmol), copper(I) iodide (77 mg, 0.404 mmol), compound **13a** (0.800 g, 4.06 mmol), L-proline (94 mg, 0.816 mmol), and potassium carbonate (1.12 g, 8.10 mmol) were added to a stirred round-bottom flask. DMSO (7.00 mL) was added to the flask, and the solution was sparged with argon gas for 30 min. The solution was heated to 180 °C for 1 h. After the solution was cool, toluene was added (25.0 mL), and any solids were removed by filtration. The light brown liquor was concentrated under high vacuum to completely remove any solvent and excess iodobenzene. The resulting solids were taken up in toluene and passed through a short plug of silica, eluting with toluene. Solvent was removed under vacuum, resulting in large flakey white crystals. These crystals were recrystallized from boiling heptanes and dried under vacuum. 794 mg was isolated (72% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (dt, J_1 = 7.83 Hz, J_2 = 1.17 Hz, 1H), 8.00 (d, J = 8.22 Hz, 1H), 7.64–7.53 (m, 4H), 7.47 (m, 1H), 7.36–7.28 (m, 2H), 7.25 (m, 1H), 6.88 (td, J_1 = 10.96 Hz, J_2 = 2.35 Hz, 2H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 142.2, 141.1, 137.7, 129.90, 127.5, 127.1, 124.6, 123.5, 121.0, 112.0, 119.4, 117.2, 109.5, 108.5, 94.0, 55.6; HRMS (ESI) [M + H] calcd for $C_{19}H_{16}NO$ 274.1226, found 274.1227.

Compound 14b. Same general procedure as for compound **14a** was used. Iodobenzene (1.0 g, 4.90 mmol), compound **13b** (0.750 g, 3.27 mmol), copper(I) iodide (63 mg, 0.331 mmol), L-proline (76 mg, 0.660 mmol), potassium carbonate (912 mg, 6.60 mmol), and 7.00 mL of DMSO were reacted for 2 h. Product recrystallized from heptanes to yield white flakes. 821 mg of product was isolated (82% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 8.57 Hz, 2H), 7.61 (t, J = 7.41 Hz, 2H), 7.54 (d, J = 8.38 Hz, 2H), 7.47 (t, J = 7.41, 1H), 6.87 (dd, J_1

= 8.38 Hz, J_2 = 2.34 Hz, 2H), 6.82 (d, J = 2.34 Hz, 2H), 3.82 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 142.3, 137.6, 130.0, 127.5, 127.1, 120.1, 117.4, 108.2, 94.3, 55.7; HRMS (ESI) [M + H] calcd $C_{20}H_{18}NO_2$ 304.1332, found 304.1340.

Compound 14c. Same general procedure as for compound **14a** was used. 3-Iodoanisole (10.92 g, 46.6 mmol), carbazole, (6.00 g, 35.9 mmol), copper(I) iodide (684 mg, 3.59 mmol), L-proline (827 mg, 7.18 mmol), potassium carbonate (9.92 g, 71.8 mmol), and 60.0 mL of DMSO were reacted for 3 h. Product recrystallized from heptanes and isolated as white flakes (7.75 g, 79% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J = 7.75 Hz, 2H), 7.50 (t, J = 8.09 Hz, 1H), 7.45 (d, J = 7.99 Hz, 2H), 7.41 (t, d, J_1 = 6.63 Hz, J_2 = 1.36 Hz, 2H), 7.28 (ddd, J_1 = 7.75 Hz, J_2 = 6.63 Hz, J_3 = 1.36 Hz, 2H), 7.16 (dq, J_1 = 7.80 Hz, J_2 = 0.97 Hz, 1H), 7.11 (t, J = 2.24 Hz, 1H), 7.01 (ddd, J_1 = 8.38 Hz, J_2 = 2.53 Hz, J_3 = 0.97 Hz, 1H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 140.8, 138.8, 130.5, 125.9, 123.3, 120.3, 119.9, 119.3, 113.2, 112.6, 109.9, 55.5; HRMS (ESI) [M + H] calcd for $C_{19}H_{15}NO$ 274.1226, found 274.1220.

Compound 14d. Same general procedure as for compound **14a** was used. Carbazole (1.00 g, 5.98 mmol), 4-bromoanisole (1.34 g, 7.18 mmol), copper(I) iodide (114 mg, 0.599 mmol), L-proline (138 mg, 1.20 mmol), potassium carbonate (1.653 g, 12.0 mmol), and DMSO (10.0 mL) were added to a round-bottom flask. This solution was sparged with argon gas for 30 min and then heated to 180 °C for 16 h. The reaction was diluted with toluene, and the solids were filtered out. The mother liquor was passed through a plug of silica and then concentrated under high vacuum and heat to remove the solvents, residual 4-bromoanisole and residual carbazole. The resulting solids were recrystallized twice from boiling heptanes to yield long thin white needles. 685 mg were collected (42% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J_1 = 7.70 Hz 2H), 7.45 (d, 8.96 Hz, 2H), 7.40 (m, 2H), 7.32 (d, J = 8.38 Hz, 2H), 7.27 (t, J = 7.02 Hz, 2H), 7.11 (d, J = 8.96 Hz, 2H), 3.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.8, 141.4, 130.3, 128.6, 125.8, 123.1, 120.2, 119.6, 115.0, 109.7, 55.6; HRMS (ESI) [M^+] calcd for $C_{19}H_{16}NO$ 273.1148, found 273.1146.

Compound 15a. Using the general P−R procedure, tris(pentafluorophenyl)borane (10 mg, 0.0195 mmol), compound **14a** (0.500 g, 1.82 mmol), and anhydrous toluene (5.00 mL) were added to a open stirred vessel. 1,1,1,3,5,5,5-Heptamethyltrisiloxane (1.623 g, 7.32 mmol) was added dropwise to this solution and allowed to stir for 20 min. Upon evaporation, a colorless oil was obtained. This oil was diluted with hexanes and loaded onto a short plug of silica gel. This plug was washed with hexanes (100 mL) and then washed with toluene. The toluene fraction was collected and concentrated to yield a colorless oil (834 mg, 95% yield): ^{1}H NMR (400 MHz, C_6D_6) δ 8.00 (m, 1H), 7.93 (d, J = 8.61 Hz, 1H), 7.28−7.10 (m, integration obscured by solvent peak), 7.04 (t, J = 7.43 Hz, 1H), 0.30 (s, 3H), 0.12 (s, 18H); ^{13}C NMR (100 MHz, C_6D_6) δ 154.0, 142.8, 141.9, 138.2, 123.0, 127.5, 127.5, 125.2, 124.2, 121.4, 120.5, 120.1, 118.7, 113.8, 110.0, 101.0, 1.7, −3.1; HRMS (ESI) [M + H] calcd for $C_{25}H_{34}NO_3Si_3$ 480.1841, found 480.1863.

Compound 15b. Using the general P−R procedure, compound **14b** (0.500 g, 1.65 mmol), tris(pentafluorophenyl)borane (9 mg, 0.176 mmol), 1,1,1,3,5,5,5-heptamethyltrisiloxane (2.90 g, 13.2 mmol), and anhydrous toluene (5.00 mL) were reacted. Product was purified by loading onto a silica plug, washing first with hexanes and then washing with toluene. Product isolated as a clear oil (1.00 g, 85% yield): ^{1}H NMR (400 MHz, C_6D_6) δ 7.85 (d, J = 8.22 Hz, 2H), 7.21 (d, J = 8.22 Hz, 2H), 7.19−7.11 (m, integration obscured by solvent), 7.04 (t, J = 7.43 Hz), 0.30 (s, 6H), 0.12 (s, 36H); ^{13}C NMR (100 MHz, C_6D_6) δ 153.2, 143.1, 138.2, 130.1, 127.6, 127.6, 120.7, 118.9, 113.7, 101.1, 1.7, −3.1; HRMS (ESI) [M^+] calcd for $C_{32}H_{53}NO_6Si_6$ 715.2488, found 715.2486.

Compound 15c. Using the general P−R procedure, compound **14c** (4.00 g, 14.6 mmol), tris(pentafluorophenyl)borane (75 mg, 0.146 mmol), 1,1,1,3,5,5,5-heptamethyltrisiloxane (6.51 g, 29.2 mmol), and toluene (40.0 mL) were reacted. Product was purified by loading onto a silica plug, washing first with hexanes and then washing with toluene. Product was isolated as a clear oil (6.04 g, 86% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, J = 7.79 Hz, 2H), 7.50−7.40 (m, 5H), 7.00 (t, J = 7.00 Hz, 2H), 7.21 (dq, J_1 = 7.80 Hz, J_2 = 1.00 Hz, 1H), 7.17 (t, J = 1.95 Hz, 1H), 7.06 (ddd, J_1 = 7.60 Hz, J_2 = 2.34 Hz, J_3 = 0.80 Hz,1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.5, 140.8, 138.6, 130.3, 125.9, 123.3, 120.3, 120.2, 119.8, 119.0, 118.7, 109.9, 1.6, −3.3; HRMS (ESI) [M^+] calcd for $C_{25}H_{33}NO_3Si_3$ 479.1768, found 479.1755.

Compound 15d. Using the general P−R procedure, compound **14d** (0.500 g, 1.83 mmol), tris(pentafluorophenyl)borane (10 mg, 0.195 mmol), 1,1,1,3,5,5,5-heptamethyltrisiloxane (0.814 g, 3.66 mmol), and anhydrous toluene (5.00 mL) were reacted. Product was purified by loading onto a silica plug, washing first with hexanes and then washing with toluene. Product was isolated as a clear oil which crystallized into soft white needles after 2 months of storage (728 mg, 83% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, J = 7.43 Hz, 2H), 7.45−7.38 (m, 4H), 7.34 (d, J = 7.82, 2H), 7.27 (t, J = 7.43 Hz, integration obscured by solvent peak), 7.14 (d, J = 8.61 Hz, 2H), 0.28 (s, 3H), 0.15 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.6, 141.3, 131.1, 128.4, 125.81, 123.1, 121.1, 120.2, 119.6, 109.7, 1.6, −3.2; HRMS (ESI) [M^+] calcd for $C_{25}H_{33}NO_3Si_3$ 479.1768, found 479.1776.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

General experimental methods, cyclic voltammetry and NMR data for all compounds, and ^{1}H and ^{19}F data for catalyst interaction experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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