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Modification of N-Heterocyclic Carbene Scaffolds: Insights into Reactivity and Electronic Properties

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Modification of N-Heterocyclic Carbene Scaffolds: Insights into Reactivity and Electronic Properties

by

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Abstract

Modification of N-Heterocyclic Carbene Scaffolds: Insights into Reactivity and Electronic Properties

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Starting from the initial efforts to prepare, study, and utilize carbenes, the choice of substituents has been recognized as a critical factor in determining their properties. Following the isolation of stable carbenes, a further aspect of design has become apparent; creation of a supporting scaffold to provide influence over the carbene's reactivity and electronic properties as well as providing a protective envelope to ensure stability. Modification of previous N-heterocyclic carbene scaffolds to provide a new range of diamidocarbenes, which demonstrated enhance electrophilic properties. Further elaboration of these scaffolds has allowed the synthesis of novel carbenes with tailored properties.

A series of six-membered carbenes featuring adjoining amino and/or amido groups were studied to determine the effect of substituent modification. A mono-amino/amido carbene (MAAC), a diamidocarbenes, and a diaminocarbene were systematically compared using crystallographic, spectroscopic, electrochemical, and density functional theory methods. Using single crystal X-ray diffraction analysis, the free MAAC was found

to exhibit inequivalent nitrogen-carbon bond lengths Iridium complexes of the carbenes were also evaluated and the collected data revealed that the introduction of carbonyl groups to the carbene-containing scaffold had a nearly linear, additive effect on the $E_{1/2}$ potential of the carbene-ligated iridium I/II redox couple (+165 mV per carbonyl added) as well as the TEP value of the corresponding carbene-Ir$(CO)_2$Cl complex. Beyond attenuated ligand donicity, the introduction of carbonyl groups expanded the carbene's reactivity: unlike prototypical NHCs, the MAAC was found to couple to isonitriles to form the respective ketenimines.

Additionally, remotely substituted diamidocarbenes (DACs) were prepared and characterized. These carbenes were compared to their parent carbene via spectroscopic and density functional theory methods, and subjected to reactivity trials to determine the effects of remote substitution. Spectroscopic examination of the carbene-Ir$(CO)_2$Cl complexes demonstrated a difference in TEP value, indicating a small effect of substitution on the carbene's electronic state. However, treatment of the differently substituted carbenes with substrates known to react with the parent DAC indicated no significant difference in reactivity scope; additionally, computational methodology demonstrated similarities in calculated geometries and orbital energy levels.

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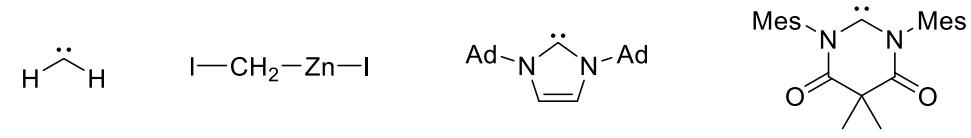
Chapter 1: Introduction

1.1 Introduction

Organic Chemistry concerns itself with the study of carbon-based molecules; so varied are these compounds that they range from gasoline to plastics to pharmaceutical products and complex biological systems. While tremendous variety exists among organic molecules, the overwhelming majority of stable compounds handled by chemists contain tetravalent carbon. In the pursuit of novel and useful molecules, chemists have experimented with and sought to understand carbon that is trivalent, such as carbocations, carbanions, and carbon radical species, moieties often postulated to be transition states that lie at the heart of organic transformations. The study throughout history of these trivalent species has provided insight into how to control reactivity, giving chemists the opportunity to design new reactions, control product yields, and gain a better understanding of the fundamental reactivity of carbon. While trivalent carbon has been extensively studied, structures containing divalent carbon have generally garnered less interest due to their extreme instability – until within the last 25 years, with the advent of stable carbene species. These compounds allowed an unprecedented ease of access to study unique forms of carbon as well as the promise of novel classes of reactive molecules.



Methylene Carbenoid **1** **2**

Figure 1.1: Methylene, a transient carbene, an organozinc carbenoid, the first isolable crystalline carbene (**1**), and a diamidocarbene (**2**) (Ad = adamantyl, Mes = 2,4,6-trimethylphenyl).

1.2 Development of Stable Carbenes

The earliest known attempt to prepare a carbene was Dumas' failed efforts to dehydrate methanol in 1835;[1] later, Regnault attempted the same feat. The first successful generation of a carbene was dichlorocarbene from chloroform in base, though this reaction was poorly controlled.[2] It was not until some seventy-five years later that a novel carbene was generated by Staudinger via the decomposition of diazo compounds under photolytic or thermal conditions, generating nitrogen gas and the corresponding carbene.[3,4] These reactions provided a strong impetus to explore the chemistry of divalent carbon, as the carbenes could be generated in a controllable manner and promised unique reactivies – they were among the first organic molecules to react with C-H bonds.[5] Nevertheless, while Staudinger had demonstrated a method to controllably generate carbenes on demand, they remained exclusively transient species, which complicated their study.

Attention turned towards methods by which the reactivity of carbenes could be married with an acceptable level of stability. Simmons and Smith published a novel reaction involving the *in-situ* generation of a stabilized methylene diradical formed from the oxidative addition of zinc into diiodomethane, which could subsequently add across the double bond to yield a cyclopropane (Figure 1.2).[6,7] While this sort of masked "carbenoid" system reacts in a manner similar to carbenes, allowing chemists a useful handle on carbene reactivity, it does not allow direct study of the carbene.

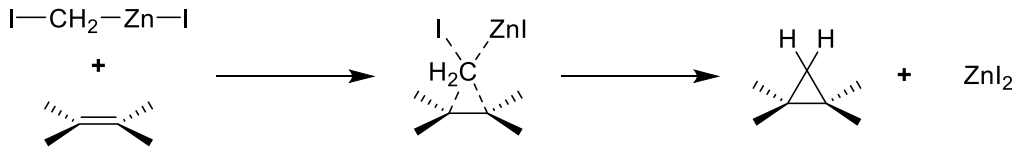


Figure 1.2: The Simmons-Smith reaction, wherein a carbenoid adds to an olefin to form a cyclopropane.

Novel insights would come from Ugai's work with thiazolium salts,[8] which were demonstrated to act as catalysts for the benzoin condensation under basic conditions, though the mechanism was not clear at the time. Breslow proposed[9] the now-accepted carbene-based mechanism within weeks of Simmon's and Smith's work, demonstrating the growing interest in divalent carbon species. The stability of the thiazolium-based carbenes, as demonstrated by their utility and prevalence in biological systems[10] indicates the potential utility of molecules of this type.

A short while afterward, Wanzlick reported the synthesis of a substituted tetraaminoethylene, derived from the vacuum pyrolysis of 1,3-diphenyl-2-(trichloromethyl)imidazoline (Figure 1.3).[11,12] The reaction was speculated to generate a carbene via loss of chloroform, which rapidly dimerized to the tetraminoethylene. It was proposed by Wanzlick[13] that the dimer and free carbene existed in an equilibrium that strongly favored the dimer. This view was challenged by work by Lemal[14] and Winberg,[15] who independently studied the tetraaminoethylenes and concluded there was no dynamic equilibrium based on cross-over experiments. While the Wanzlick equilibrium was later confirmed for certain subclasses of tetraaminoethylenes (namely those generated from benzimidazolylidenes),[16] it is generally believed the dimerization and disassociation is an acid-catalyzed reaction.[17,18]

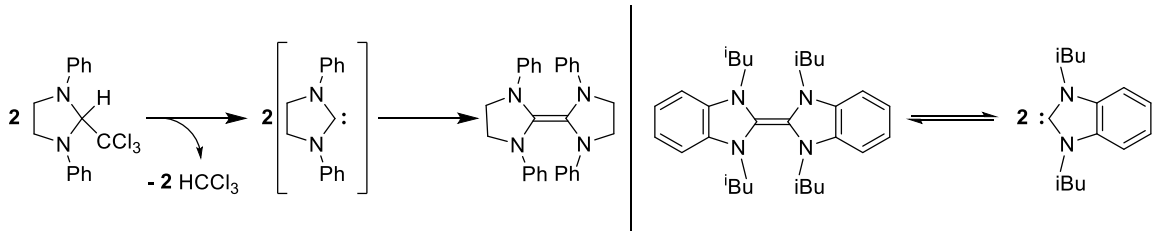


Figure 1.3: Left - Preparation of a a tetraaminoethylene via the thermally induced elimination of chloroform. Right – a benzimidazolylidene that undergoes Wanzlick equilibrium.

The debate over the Wanzlick equilibrium, and the lack of substantive evidence indicating the preparation of stable species cemented the reputation of carbenes as exclusively transient species. Despite finding some use as organocatalysts (generated *in situ*), divalent carbon moieties were largely viewed as novelties, unstable and too challenging to manipulate to be seriously considered as intermediates or reagents in organic reactions. There were few stable examples, and all incorporated transition metal elements; ranging from the organozinc carbenoid of the Simmons-Smith reaction to metal alkylidines, particularly those belonging to tungsten-based metathesis catalysts.[19–21]

However, the view that entirely organic, stable carbenes were impossible was disrupted when Bertrand disclosed a phosphinosilyl carbene in 1988.[22] The carbene was not only isolable, but was purified by distillation – indeed, the compound demonstrated such stability that it was initially assumed not to be a carbene. It was also unclear at the time whether to classify the structure as a true carbene or as either a phosphavinylylide or phosphaacetalyne, and the lack of an x-ray crystal structure further hampered analysis.[23] A short time later, Arduengo published the synthesis of a novel, crystalline imidazolylidene; this compound, the first N-Heterocyclic carbene (NHC) could be prepared quickly in reasonably quantities, and stored under inert atmosphere without fear of decomposition.[24] This report heralded the first of the N-heterocyclic carbenes (*vide infra*), and the combination of Bertrand's and Arduengo's work (Figure 1.4) provided ample evidence that certain divalent carbon species could be isolated, which led to a renaissance in the research efforts towards the design and utilization of carbenes.

N-Heterocylic Carbene Phosphinosilyl Carbene

Figure 1.4: The first isolable carbenes, an N-heterocyclic carbene and a phosphinosilyl carbene.

1.3 Stabilization of Isolable Carbenes

Carbenes can be broadly defined by their electronic configuration; triplet carbenes split their two nonbonding electrons into separate orbitals with the same spin, while singlet carbenes have a filled orbital of opposite spins and an empty orbital (Figure 1.5). Triplet states are favored due to the repulsion between electrons that inhabit the same orbital as well as electron exchange energy. Singlet carbenes arise when the difference in energy between the highest-occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) is sufficient to overcome the energy penalty of placing both electrons in the same orbital (Figure 1.6). Similarly, the bond angle of the carbene is influenced by the spin multiplicity; a pair of degenerate orbitals (a triplet) would necessitate a linear arrangement between the substituents and the carbene, while singlet states would be bent. In the case of carbenes, the gap between the HOMO and LUMO is termed the singlet-triplet gap (Δ_{ST}); in general, larger singlet triplet gaps are correlated with more stable species, lower reactivities, and a preference for more nucleophilic modes of reactivity.

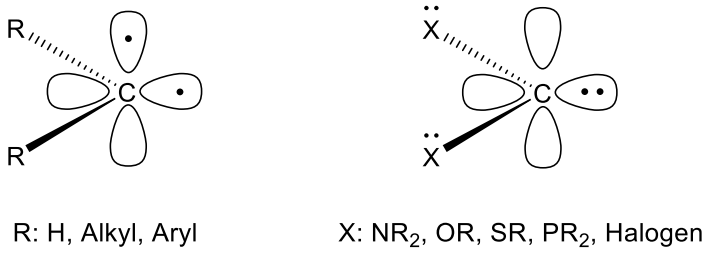


Figure 1.5: Representations of the electronic configuration of triplet carbenes (left) and singlet carbenes (right).

The assumption of singlet electronic character results from observation of a mixture of σ and π effects from neighboring substituents, with π effects playing a more decisive role. Hence, carbene scaffolds that lack strong π-donating properties and have weak σ interactions, such as those with α-alkyl, aryl, and hydrogen substituents tend to be triplet carbenes. Owing to their lack of electronic stabilization, these carbenes are generally transient; however, in recent years Tomioka and coworkers have demonstrated a triplet carbene with remarkable longevity.[25,26]

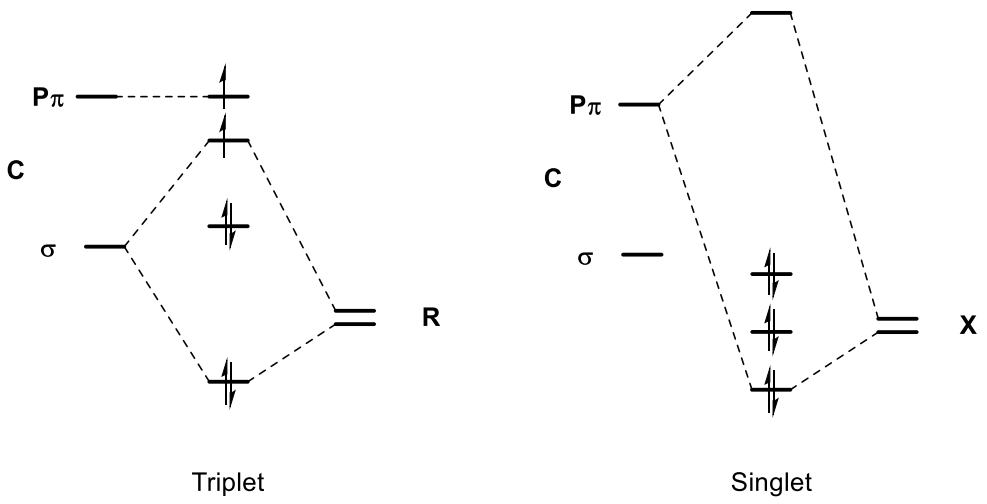


Figure 1.6: Orbital diagrams corresponding to triplet and singlet carbenes.

Those carbenes that bear π-donating α-substituents tend to be singlet in character. Resonance effects generally determine the electronic configuration by raising the energy of the LUMO via mixing with the p_π orbital, strongly biasing the carbene towards the singlet state. This is compounded by the fact that elements most often used to stabilize the carbene such as nitrogen, oxygen, and sulfur, are all more electronegative than carbon and act as σ-withdrawing moieties that act to lower the energy level of the HOMO, further increasing Δ_{ST}.

While electronic stabilization of the frontier orbitals is a significant aspect of generating stable carbenes, another important consideration is the steric environment the carbene nucleus is placed in. The majority of stable carbenes feature large substituents on the α-atom, often bulky aryl or alkyl groups such as diisopropylphenyl (DIPP), mesityl (Mes), or adamantly (Ad). These groups provide steric protection against molecules that would adversely affect the carbene, preventing the sort of Wanzlick dimerization mentioned earlier, and in the case where the carbene is acting as a ligand, they generate a steric environment around the metal center. In the absence of decisive electronic effects, steric factors can even determine the spin multiplicity of the carbene.[27] Cyclopentylidine has a singlet ground state as it is locked in a bent conformation,[28] whereas bulkier substituents such as those on di(*tert*-butyl)-[29] or diadamantylcarbene[30] force the carbene to adopt a more linear conformation, rendering them triplet in character.[31] The stabilization of the carbene nucleus can be roughly generalized into two factors; electronic stabilization provides the thermodynamic parameter, and steric protection provides the kinetic parameter. With the two effects working in concert, it is possible to synthesize a wide variety of stable carbenes with a range of properties.

1.4 N-Heterocyclic Carbene Reactivity

The isolation of the first stable carbenes lead to increased interest in the synthesis and application of divalent carbon species. The most extensively studied variants were NHCs; they combined excellent electronic stabilization from the dual nitrogen substituents and a secure steric environment for increased longevity. Fortuitously, many NHCs were based around imidazole and pyrimidine scaffolds, allowing a relatively large family to be assembled without undue synthetic challenge. Within a few years of the initial disclosure, a wide variety of carbenes had been developed, each offering different electronic and steric environments (Figure 1.7).[32–35]

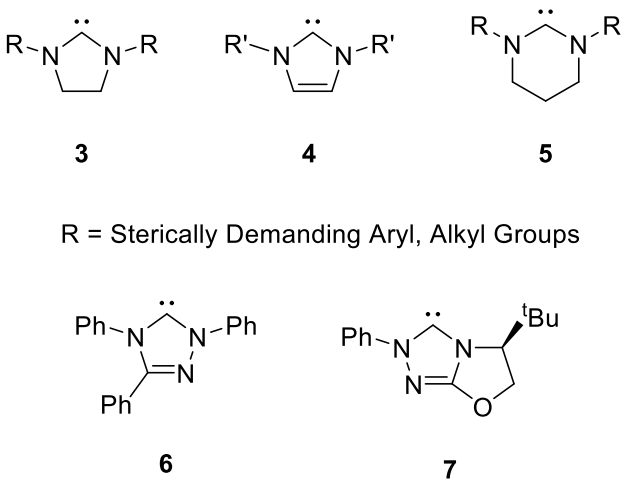
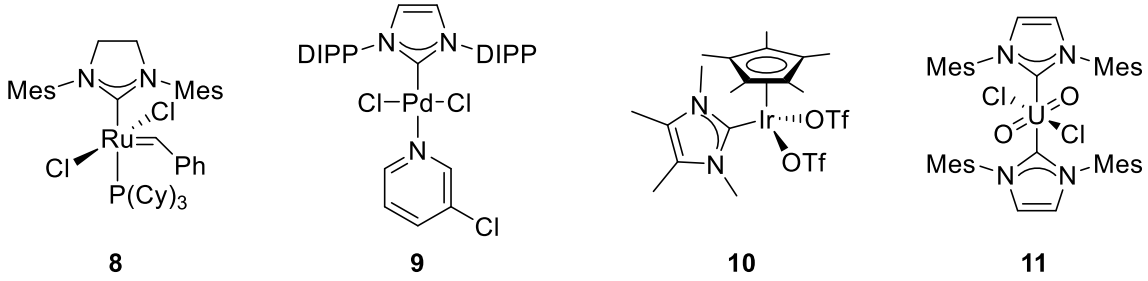


Figure 1.7: Representative NHCs, including both saturated (**3**), unsaturated (**4**), expanded ring (**5**), and 1,2,4-triazole based variants (**6**,**7**).

NHCs were rapidly adopted as ligands for transition metal catalysts; because the strongly singlet carbenes demonstrate a σ-donating ability that exceeded that of well-studied phosphine ligands, and the diversity of scaffolds allowed tuning of the in electronic and steric parameters.[36,37] Replacing phosphine ligands with NHCs often yielded substantially more active catalysts, perhaps most famously in the case of ruthenium-based

metathesis catalysts,[38] though they found additional applications in palladium coupling catalysts,[39–41] transition metal oxidation catalysts,[42] and as ligands to stabilize high-valent metal complexes[43] (Figure 1.8). In a similar vein, certain NHCs have been found to stabilize extraordinarily reactive phosphorous adducts.[44]



8 **9** **10** **11**

Figure 1.8: Examples of an olefin metathesis catalyst (**8**), palladium coupling catalyst (**9**), iridium-based oxidation catalyst (**10**), and a stabilized uranium (VI) compound bearing NHC ligands (DIPP = 2,6 diisopropylphenyl).

While stable carbenes served as excellent ligands for transition metal catalysts, NHCs serve as excellent nucleophilic catalysts for carbon-carbon bond forming reactions such as the benzoin condensation.[45,46] These organocatalytic reactions are generally performed under mild conditions, provide good levels of enantio- and diastereoselectivity, and give high yields.[47] As with transition metal systems, the ease of modification of the carbene scaffold allows tailoring of the particular catalyst to the specific needs of the reaction in question.

Curiously, one area where NHCs have found little applicability is in areas of traditional carbene reactivity; while transient carbenes are known to insert into C-H bonds and cyclopropanate olefins,[48] this behavior is all but unknown for stable carbenes; the C-H reactions observed in stable carbene species require activated C-H bonds and can more

readily be classified as a deprotonation event followed by nucleophilic attack of the generated carbanion.[49] To this end, recent research has focused on expanding the reactivity profile of stable carbenes to include more the characteristically electrophilic behavior of transient carbenes.

1.5 Stable Electrophilic Carbenes

The lack of reactivity characteristic of classical transient carbenes among NHCs has been attributed to their stabilization. The pair of nitrogen substituents widen the singlet-triplet gap to such a degree that a low-lying HOMO and a high-lying LUMO are unable to participate in more electrophilic reactions. To this end, recent research has shifted towards carbenes that are less extensively stabilized by changing the substituent elements. Several promising variants have been disclosed, including P-heterocylic carbenes,[50] amino-silyl carbenes,[51] and particularly so-called anti-Brendt carbenes,[52–55] which strongly resemble NHCs, though one nitrogen substituent's *p*-orbital is locked out of alignment with the carbene center. Perhaps the most significant advances of this type was the advent of alkyl-amino carbenes (AACs) by Bertrand.[56] The unsymmetrical design of this class of carbenes includes only one major stabilizing substituent, reducing Δ_{ST}, which drastically expands their reactivity scope. Cylic alkyl-amino carbenes have been shown to stabilize low coordinate transition metal centers,[57] react with nucleophiles and olefins,[58] stabilize reactive elemental allotropes,[59–62] and activate small molecules such as CO, H_2, and NH_3 (Figure 1.9).[63,64]

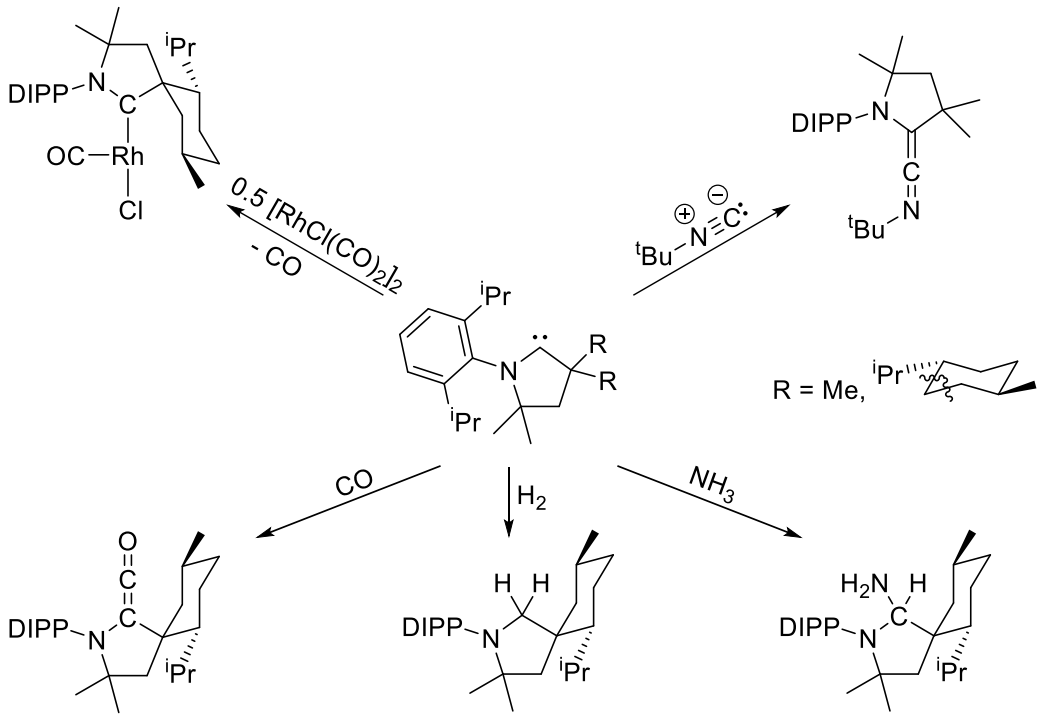


Figure 1.9: Reactions of cyclic alkyl-amino carbenes (CAACs), including ligation of metals, reaction with isocyanides, carbon monoxide, hydrogen, and ammonia.

Other efforts focused on modification of the scaffold to attenuate the donating capacity of the nitrogen substituents. Noting that all extant NHCs were based on two amine groups, Bielawski disclosed the first carbene with a diamide scaffold.[65] The amide groups were envisioned to split the electron donating capacity of the nitrogens between the carbene nucleus and the electron poor carbonyl carbon; this was predicted to directly lower the LUMO energy level, increase Δ_{ST}, and led to a more electrophilic carbene. Initial efforts were focused on the preparation of diamidocarbene (DAC) **6-DIPP** (Figure 1.10), though this analogue proved inisolable due to rapid C-H insertion into the isopropyl group at the benzylic position.[65] While the inability to isolate the free carbene was troublesome, it indicated progress toward novel modes of reactivity for NHCs. A second, more stable

variant, **6-Mes**, was prepared shortly thereafter,[66] and subsequently both seven[67] and later five[68] membered DACs were synthesized.

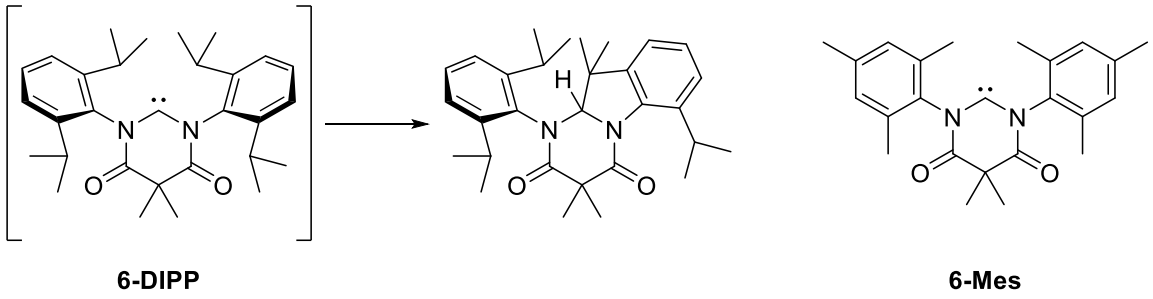


Figure 1.10: An inisolable diamidocarbene (DAC) bearing 2,6-diisopropylphenyl N-substituents that undergoes intramolecular C-H insertion (**6-DIPP**), and an archetypal 6-membered DAC bearing mesityl N-substituents (**6-Mes**).

This new class of stable carbenes demonstrated a drastically different reactivity profile from those observed for previous NHCs (Figure 1.11). In addition to the intramolecular C-H insertion that was observed with **6-DIPP**, **6-Mes** demonstrated intermolecular C-H insertion.[65] Diamidocarbenes have also demonstrated insertion into N-H bonds of organic amines as well as ammonia.[66,69] The attenuation of the electron donation from the nitrogen substituents led to electrophilic reactivity, including the ability to reversibly react with carbon monoxide to form ketenes and irreversibly with isonitriles to yield ketenimines. Also of note was the ability of DACs to insert into the P-H bonds of phosphines and phosphites[70] and the ability to react with boranes to form hydroboration reagents.[71] Perhaps most importantly, diamidocarbenes react readily with olefins in [2+1] cycloadditions, a type of reaction previously unobserved among NHCs.[72] This cycloaddition reactivity can be further generalized to alkynes, nitriles, ketones, and aldehydes, providing a wide variety of three membered rings – some of which can be

elaborated further to carboxylic acids or cyclopropenones.[72,73] Gratifyingly, diamidocarbenes are generally straightforward to synthesize, present no unordinary handling challenges, and function as superb ligands for metal catalysts,[74] indicating that the gain in reactivity comes at no significant disadvantage.

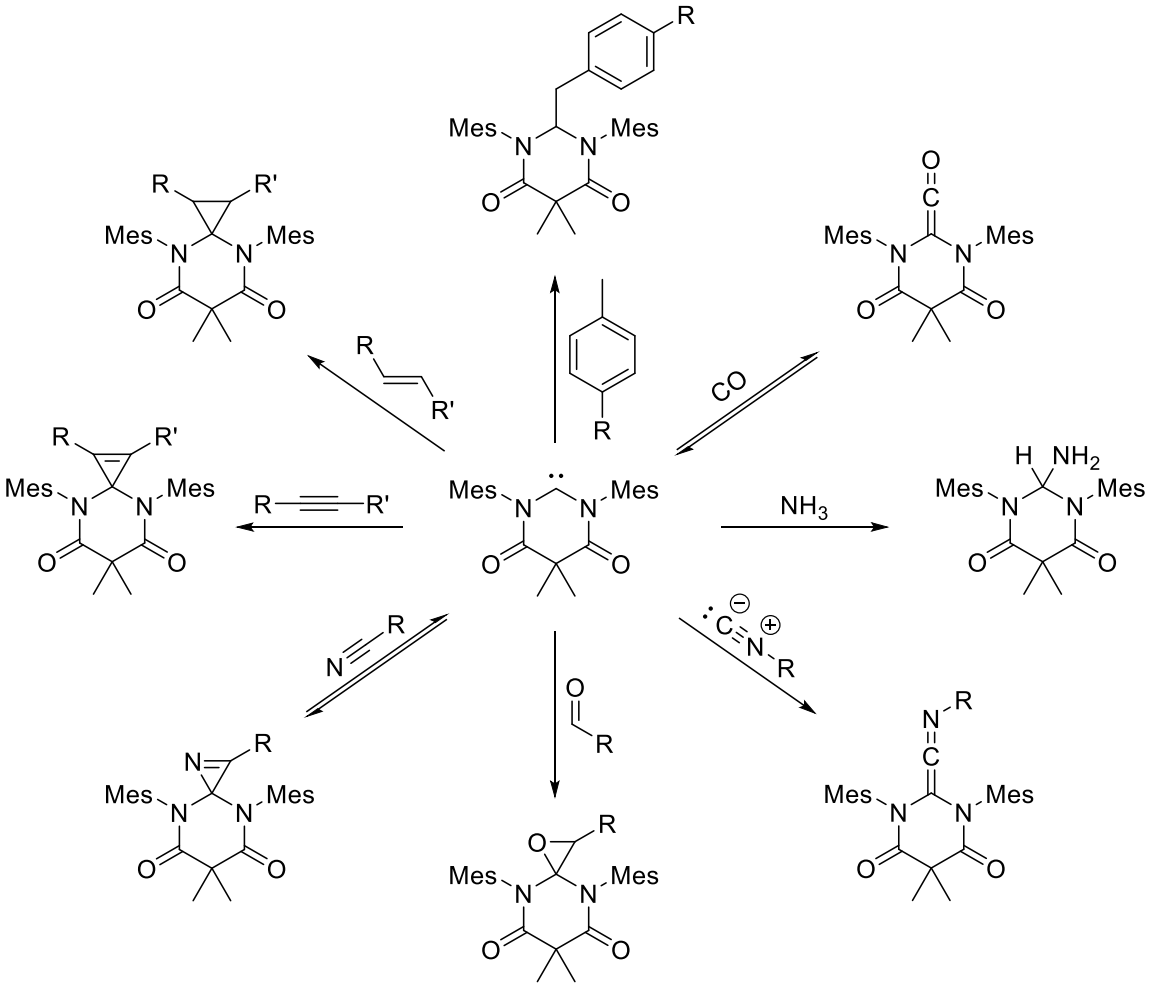


Figure 1.11: Novel reactivity exhibited by DACs, including intermolecular C-H insertion, reversible carbonylation, N-H bond activation, irreversible C=C bond formation, and [2+1] cycloaddition chemistry including the formation of epoxides, azirines, cyclopropenes, and cyclopropanes.

1.6 Perspectives and Future Outlook

Divalent carbon species have rapidly transitioned from laboratory curiosities to novel chemical reagents, industrially important ligands, and widely employed organocatalysts. The relatively short time period during which carbenes have transitioned from moieties deemed so unstable they were of no practical utility to commercial products gives ample evidence that with advances in chemical methodology and determined study, the challenges of analyzing and utilizing this class of compounds can be overcome. More recent advances promise a bright future for stable carbenes as a class; the advancement from strongly nucleophilic NHCs to more widely reactive and electrophilic CAACs and DACs indicate that by carefully tailoring the supporting scaffold of the carbene center can open up access to new areas of chemical space.

A critical point in the research into this subfield is a more generalizable understanding of how the scaffold affects the reactivity of the more electrophilic carbenes. This knowledge would allow the design of new families of carbenes with properties tailored toward intended function, expanding the value of this group of molecules. Further work on this topic may allow the design of carbene organocatalysts that function based on electrophilic mechanisms, more convenient exploitation of small molecules, and organic transition metal mimics. Future work in the field will no doubt expand the reactivity scope of these unique molecules and cement their place as valuable and interesting reagents

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Chapter 2: Tuning the Electronic Properties of Carbenes: A Systematic Comparison of Neighboring Amino versus Amido Groups[1]

2.1 Introduction

Although carbenes have been utilized as reactive intermediates for nearly 150 years,[1] the first isolable derivatives were not realized until the turn of the 1990's when Bertrand reported the isolation of the phosphinosilyl carbenes[2] and Arduengo disclosed a crystalline 1,3-diadamantyimidazol-2-ylidene.[3] Derivatives of the latter, which are often called N-heterocyclic carbenes (NHCs),[4-7] have found exceptional utility as ligands for transition metal catalysts[8] and as organocatalysts.[9] NHCs are stabilized primarily by the donation of the nitrogen lone pairs into the empty p-orbital of the carbene nucleus to which they are bound.[10] However, this stabilization phenomena renders the carbenes singlet in character and imposes limitations on the electronic properties as well as the reactivity displayed by these species, especially compared to more electrophilic triplet carbenes (e.g., methylene)[11] as well as transient singlet carbenes (e.g., dimethoxycarbene).[12-14]

Recently, the Bielawski group launched a program aimed at reducing the nucleophilicity of NHCs and thereby expanding their chemical reactivity. Through a variety of spectroscopic, crystallographic and other techniques, it has been demonstrated that N,N'-diamidocarbenes (DACs) exhibit significantly reduced nucleophilicity compared to NHCs and other diaminocarbenes, and engage in reactions frequently associated with more electrophilic carbenes.[15-17] For example, DACs have been found to facilitate N-H and intramolecular C-H bond activation processes, reversible couplings to carbon monoxide, irreversible couplings with isonitriles to form ketenimines, and [2+1]

[1] Portions of this chapter were reproduced from Blake, G. A.; Moerdyk, J. P.; Bielawski, C. W. *Organometallics* **2012**, *31,* 3373-3378. Copyright 2012 American Chemical Society. The author is grateful to Jonathan Moerdyk for his assistance with the design of the experiments and guidance, and to Christopher Bielawski and Jonathan Moerdyk for their roles in writing the original manuscript.

cycloadditions of electron-rich olefins, alkynes, aldehydes, and nitriles.[15,18-20] Given the broad reactivity displayed by DACs as well as the potential utility of such compounds in small molecule activation[21] and other applications, such as catalysis,[22] there is considerable interest in understanding how appropriately positioned carbonyl groups influence the chemical reactivity displayed by these reagents.[23-26] To address this fundamental question, a mono-amino/amido carbene (MAAC, **3**) was envisioned as a structural intermediate of DACs and NHCs, and anticipated to be an effective probe for quantifying how the number of carbonyl groups influences the reactivity and donicity of their parent diaminocarbene scaffold. We hypothesized that there would be a direct increase in the electrophilicity of the carbenes as additional carbonyls were incorporated. A comparison to Bertrand's 2-azaspiro[4.5]dec-1-ylidene,2-[2,6-bis(1-methylethyl)phenyl]-3,3,9-trimethyl-6-(1-methylethyl),[27,28] which is often called a cyclic alkyl amino carbene (CAAC), or more simply a mono-aminocarbene, was also pursued to provide additional insight into understanding how the adjoining nitrogen donors stabilize the carbene nucleus.

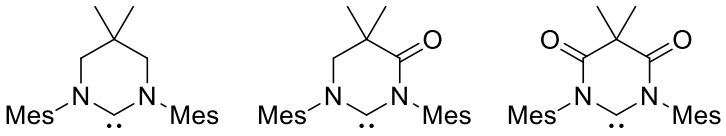


Figure 2.1: The structures of a six-membered diaminocarbene (SDAC) **5**, MAAC **3** and DAC **6** (Mes = 2,4,6-trimethylphenyl).

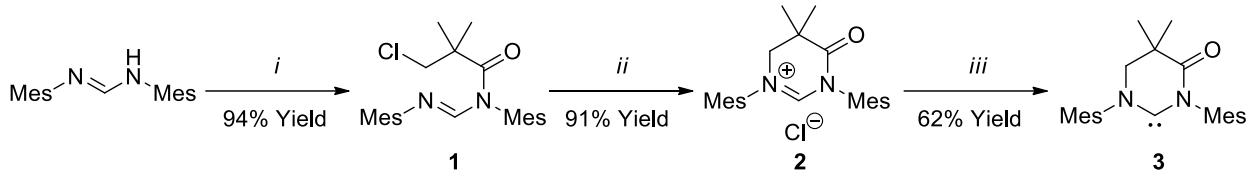
Herein we report the synthesis of the first isolable[29,30] mono-amino/amido carbene (MAAC), **3**. The chemical reactivity, electronic, and crystallographic properties of **3** were compared with analogous carbenes from within a systematic series that included a saturated diaminocarbene (SDAC; **5**) and a DAC (**6**) (Figure 2.1). These carbenes as well as their

Ir(COD)Cl and $Ir(CO)_2Cl$ complexes were collectively analyzed using a variety of crystallographic, spectroscopic, electrochemical and density functional theory techniques. The data obtained enabled a quantitative assessment of how the introduction of carbonyl groups influenced the fundamental chemical, physical, and electronic properties of carbenes that are stabilized by adjoining amino and/or amido functional groups.

2.2 Results and Discussion

As summarized in Scheme 2.1, the mono-amino/amido carbene **3** was synthesized in three steps from readily available starting materials in good overall yield. Condensation of N,N'-mesitylformamidine and 3-chloropivaloyl chloride in the presence of excess triethylamine at 0 °C afforded **1**, as indicated by the appearance of the ^{1}H NMR signals observed at δ = 1.20 ppm and 3.70 ppm (assigned to the backbone methyl and methylene protons) and the appearance of the amide carbon observed at 176.1 ppm in the ^{13}C NMR spectrum (C_6D_6) of the crude reaction mixture. Removal of the solvent followed by the addition of toluene, filtration, and concentration of the filtrate afforded pure **1** in excellent yield (94%). To induce intramolecular cyclization, a toluene solution of **1** was refluxed for 16 h, which resulted in the precipitation of a white solid that was later determined to exhibit a ^{1}H NMR signal at 10.24 ppm ($CDCl_3$). Diagnostic of a dihydropyrimidinium species,[31] the aforementioned NMR data supported the structure of the isolated compound as **2**, which was ultimately isolated in 91% yield via filtration. Subsequent treatment of **2** with sodium hexamethyldisilazane (NaHMDS) in benzene for 30 min at 25 °C followed by trituration with pentane afforded the free carbene **3**, as evidenced by the disappearance of the dihydropyrimidinium proton signal in the compound's ^{1}H NMR spectrum and the appearance of a new signal at 260.6 ppm in the ^{13}C NMR spectrum (C_6D_6), which was assigned to the carbene nucleus. On a practical note, the mono-amino/amido carbene **3** was

found to be a high melting solid (126-130 °C) and stable in anhydrous benzene for at least three days. Moreover, the compound was successfully stored under a dry nitrogen atmosphere in the solid state for months without decomposition, as determined by NMR spectroscopy.



Scheme 2.1: Synthesis of MAAC **3**. Conditions: (*i*) 3-chloropivaloyl chloride, Et_3N, CH_2Cl_2, 0 °C, 30 min; (*ii*) Toluene, 16 h, 110 °C; (iii) NaHMDS, C_6H_6, 25 °C, 30 min. Isolated yields are indicated.

To gain additional structural information, single crystals of **3** were grown by cooling a saturated hexane solution (Figure 2.2) to -40 °C. Single crystal X-ray diffraction analysis revealed that the $C_{carbene}$-N_{amide} distance in **3** (C1-N1 = 1.395(4) Å) was significantly elongated compared to the $C_{carbene}$-N_{amine} distance (C1-N2 = 1.323(4) Å). Additionally, the $C_{carbene}$-N_{amide} distance was longer than that measured in the solid state structure of **6** (1.371(3) Å), which has been previously reported,[15] signifying weaker donation from the amide nitrogen in **3** compared to those contained with **6**. The differential donation may explain the difference in bond angles observed: the N-C-N angle in **3** (114.0°) was slightly lower than the analogous angle measured in the solid state structure of **6** (114.8°). Regardless, the $C_{carbene}$-N_{amine} distance measured in **3** was comparable to that reported for the solid state structure of Bertrand's cyclic alkyl amino carbene (1.315(3) Å),[28] which suggested that donation by the amino group in the MAAC scaffold dominated the stabilization of the carbene nucleus.

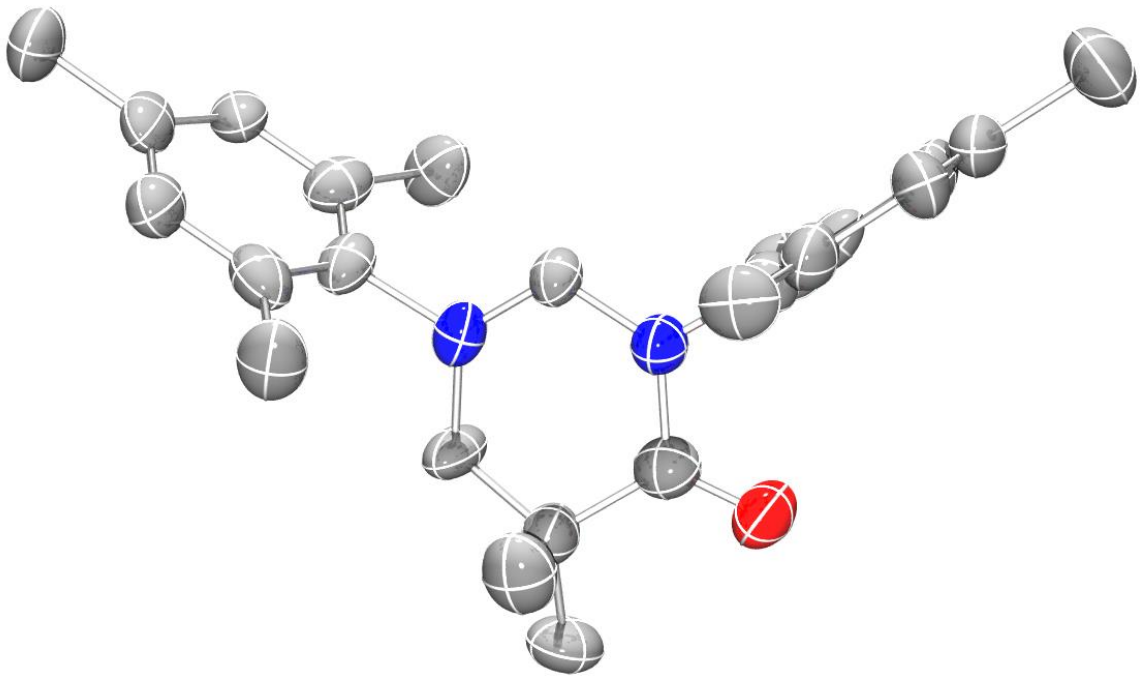
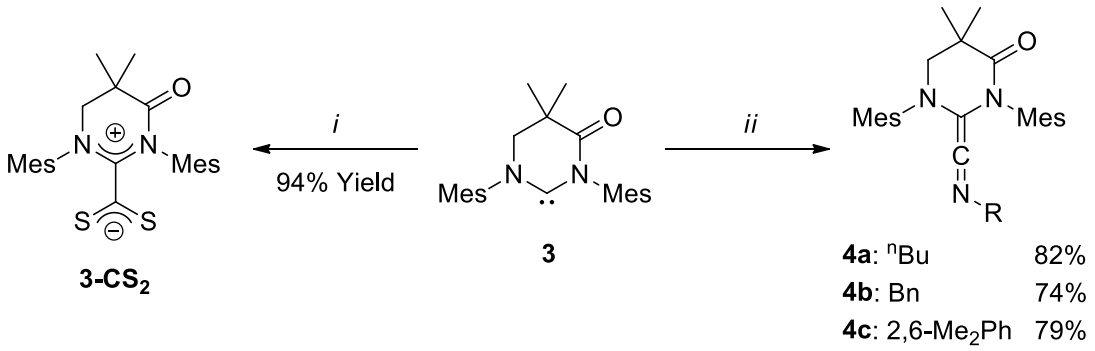


Figure 2.2: An ORTEP diagram of **3** with thermal ellipsoids drawn at 50% probability and H atoms omitted for clarity. Selected distances (Å) and angles (deg): C1-N1 1.395(4), C1-N2 1.323(4), N1-C2 1.411(5), N1-C1-N2 114.0(3).

Having isolated and characterized the free carbene **3**, our attention shifted to exploring its chemical reactivity. As diaminocarbenes are known to condense with electrophiles, we first turned our attention to determine if **3** would react with the electrophilic agent CS_2 (Scheme 2.2). The addition of CS_2 (1.05 equiv.) to a benzene solution of **3** ($[\mathbf{3}]_0$ = 14 mM) at ambient temperature resulted in the formation of deep red color. Concentration and subsequent addition of pentane induced precipitation, which enabled isolation of the expected product **3-CS$_2$** in excellent yield (94%), as evidenced by a new ^{13}C NMR resonance diagnostic of a dithioate species (δ = 158.7 ppm; C_6D_6) and an upfield carbenoid ^{13}C NMR resonance (i.e., 222.3 ppm in **3-CS$_2$** versus 260.6 ppm in **3**; C_6D_6). After demonstrating **3** may function as a nucleophile, we next turned our attention

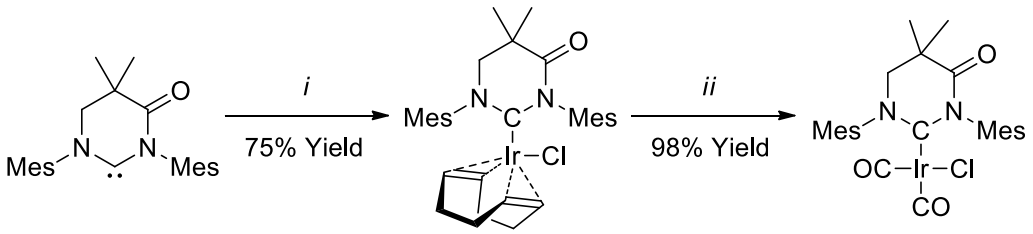
to exploring its ability to also act as an electrophile. Upon the addition of n-butyl isocyanide[18] (1.05 equiv.) to **3** ([**3**]$_0$ = 23 mM) in benzene at ambient temperature, a color change from light tan to bright yellow was observed. Subsequent stirring of the reaction mixture for 12 h ultimately yielded the corresponding ketenimine **4a** in 82% isolated yield, as indicated by new ^{13}C NMR resonances observed at 210.1 and 114.0 ppm (C_6D_6) which were diagnostic of the C***C***N and ***C***CN carbons, respectively.[18] Benzyl- and 2,6-diisopropylphenylisonitrile were found to react with **3** in a similar manner and afforded the corresponding ketenimines **4b** and **4c** in good yield (74-82%, Scheme 2.2).[32] Although structurally analogous to the diamidoketenimines derived from **6** and the corresponding isonitriles, **4a-c** were found to slowly decompose over time. However, unlike **6**, which was reported to readily react with carbon monoxide or ammonia, **3** showed no reactivity toward these reagents. The instability of these adducts may reflect a weaker interaction between the isonitriles and MAAC **3** as compared to DAC **6**.



Scheme 2.2: Synthesis of carbon disulfide adducts and ketenimines. Conditions: (*i*) CS_2, C_6H_6, 25 °C, 1 h. (*ii*) RNC, C_6H_6, 25 °C, 12 h. Isolated yields are indicated.

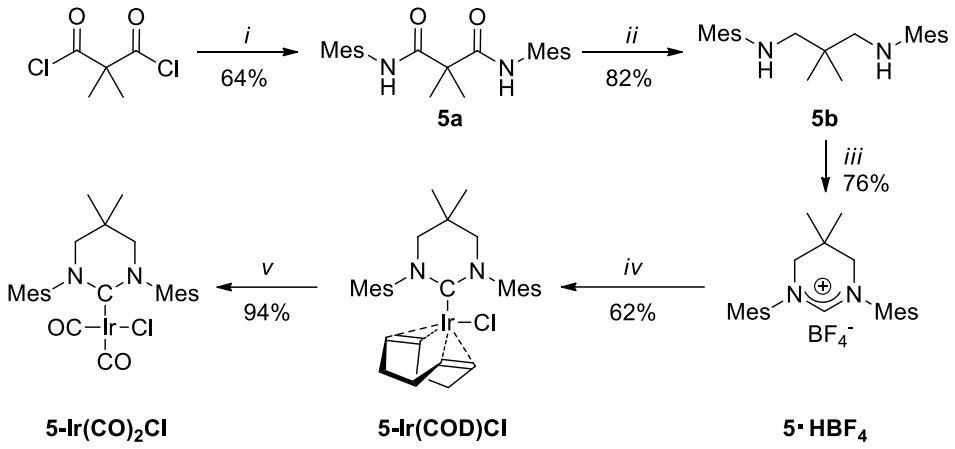
Having investigated the chemical reactivity, subsequent efforts were taken to characterize the electronic properties of **3**. Iridium carbonyl complexes are commonly used

to quantify the electron-donating ability of NHCs and other ligands through the calculation of the Tolman Electronic Parameter (TEP) based on the observed infrared ν_{CO} stretching frequencies.[33,34] As such, **3-Ir(CO)$_2$Cl** was first synthesized as shown in Scheme 2.3. Addition of **3** to a benzene solution of {Ir(COD)Cl}$_2$ at 25 °C for 16 h resulted in the formation of **3-Ir(COD)Cl** as indicated by the presence of the cyclooctadiene olefin signals observed at 3.06, 4.56 and 4.69 ppm in the ^{1}H NMR spectrum as well as the shift of the carbenoid resonance to 218.6 ppm in the ^{13}C NMR spectrum (C_6D_6) of the crude reaction mixture. Subsequent purification by column chromatography afforded the desired complex in 75% isolated yield. Exchange of the cyclooctadiene ligand for two carbonyls was achieved by bubbling CO through a CH_2Cl_2 solution of **3-Ir(COD)Cl** at ambient temperature followed by washing the dry solid with pentane to afford a bright yellow solid. The product was identified as **3-Ir(CO)$_2$Cl** by the absence of NMR signals associated with the starting material, the appearance of new ^{13}C NMR signals observed at 170.1 ppm and 179.5 ppm (C_6D_6), and the appearance of strong CO bands in the IR spectrum (1986 and 2066 cm^{-1}), which were attributed to the carbonyl ligands.



Scheme 2.3: Synthesis of iridium carbene complexes. Conditions: (*i*) {Ir(COD)Cl}$_2$, C_6H_6, 25 °C, 16 h; (*ii*) CO, CH_2Cl_2, 25 °C, 30 min. Isolated yields are indicated.

For comparative purposes, a saturated diamino-analogue **5-Ir(CO)$_2$Cl** was also prepared using a modified version of a literature procedure (Scheme 2.4).[35] Bisamide **5a** was obtained via the condensation of 2,2-dimethylmalonyl dichloride with mesityl amine in 64% yield and found to display a distinctive amide ^{13}C NMR resonance at 172.5 ppm (C_6D_6). Subsequent reduction of **5a** in a refluxing solution of $BH_3 \cdot SMe_2$ in THF afforded the diamine **5b** in 82% yield. A new signal was observed at 2.80 ppm in the ^{1}H NMR spectrum acquired for this material and the loss of the amide carbon resonances concomitant with the appearance of a new methylene resonance observed at 58.3 ppm in the ^{13}C NMR spectrum (C_6D_6) served to confirm the structure product as indicated. Formylative cyclization of **5b** to **5·HBF$_4$** was conducted with $CH(OEt)_3$ in n-heptane and facilitated with NH_4BF_4, as indicated by a characteristic dihydropyrimidinium resonance at 7.62 ppm in the respective ^{1}H NMR spectrum ($CDCl_3$).[36] Unfortunately, the free carbene **5** could not be isolated; efforts to concentrate benzene solutions of the carbene (generated in situ via treatment of **5·HBF$_4$** with NaHMDS) resulted in decomposition, as did attempts at selectively precipitation of the desired compound. However, in situ deprotonation of **5·HBF$_4$** in the presence of $\{Ir(COD)Cl\}_2$ in C_6H_6 afforded **5-Ir(COD)Cl** as an orange solid in 62% yield following purification via column chromatography. Bubbling CO through a CH_2Cl_2 solution of **5-Ir(COD)Cl** afforded **5-Ir(CO)$_2$Cl**; the formation of this complex was supported by the appearance of strong CO bands in the IR spectrum (1976 and 2061 cm^{-1}) and new ^{13}C NMR signals at 171.3 ppm and 180.7 ppm (C_6D_6) associated with carbonyl ligands.



Scheme 2.4: Synthesis of saturated carbene iridium complexes. Conditions: (*i*) 2,4,6-trimethylaniline, pyridine, CH_2Cl_2, -78 °C, 2 h; (*ii*) $BH_3{\cdot}SMe_2$, THF, 85°C, 12 h; (*iii*) NH_4BF_4, $CH(OEt)_3$, n-heptane, 90 °C, 12 h; (i*v*) 1) NaHMDS, C_6H_6, 25 °C, 1 h; 2) $(Ir(COD)Cl)_2$, C_6H_6, 25 °C, 12 h; (*v*) CO, CH_2Cl_2, 25 °C, 30 min. Isolated yields are indicated.

The ligand donating ability of the aforementioned carbenes was investigated by analyzing the corresponding Ir carbonyl complexes using IR spectroscopy. Using Nolan's method,[34] the TEP for **3** was calculated to be 2050 cm^{-1}; this value was significantly lower than that calculated for **6** from the analogous Ir complex (2056 cm^{-1})[22] but markedly higher than that of **5** (2042 cm^{-1}) (Figure 2.2). While TEPs are commonly used to analyze the donicity of NHCs, the measurement is indirect as it relies upon changes in the stretching frequency of the coordinated carbonyl groups.[22,23] To directly quantify the electronic properties of the carbene ligated metal centers, a series of cyclic voltammetry and differential pulse voltammetry measurements were performed (See Appendix A). As summarized in Table 2.1, **3-Ir(COD)Cl** displayed an oxidation potential 170 mV lower than the analogous **6** complex, indicating that **3** is a stronger donor than DAC. Likewise, the oxidation potential of **5-Ir(COD)Cl** was 160 mV lower than that of **3-Ir(COD)Cl**. In aggregate, the data suggested to us that the donating ability of **3** was intermediate of **5** and **6**, and that the

incorporation of additional carbonyl groups had an additive effect on attenuating the parent diaminocarbene donating ability.

To gain additional structural information, crystals of **3-Ir(COD)Cl** and **5-Ir(COD)Cl** were grown by the slow vapor diffusion of hexanes and pentane into concentrated benzene solutions of the respective compounds (Figure 2.3).[37] The solid state structure of **6-Ir(COD)Cl** has been previously reported.[15] The observed carbene-iridium bond lengths 1.985(6) Å, 2.040(6) Å, and 2.067(4) Å for **6-**, **3-** and **5-Ir(COD)Cl**, respectively, fall within the expected range for carbene-iridium complexes (1.95-2.10).[17,23,36] However, the inverse relationship between the observed M-$C_{carbene}$ bond distances and the ligand donicity derived from the aforementioned TEP and oxidation potentials was attributed to enhanced π-backbonding between the electron-rich metal centers and the less donating carbene ligands.[22,24,25,38-41]

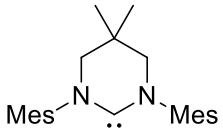
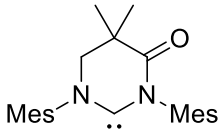
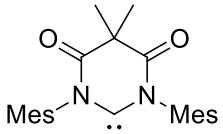
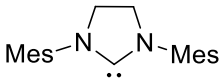
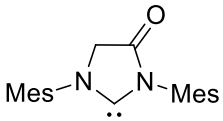
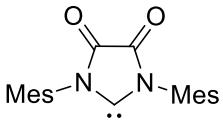
Carbene	TEP (cm^{-1})[a]	C-M Distance (Å)	$E_{1/2}$ (V)[b]	$\delta C_{Carbene}$ (ppm)	%Vbur (%)[g]
 **5**	2042	2.067(4)	0.61	242.7[c,d]	37.5
 **3**	2050	2.040(6)	0.77	260.6[c]	37.8
 **6**	2056	1.985(6)	0.94	277.7[c]	37.8
 **SIMes**	2053	2.121(1)	-	243.8[e]	34.5
 **7**	2058	2.020(3)[f]	-	-	33.4
 **8**	2068	1.931(9)	-	287.2[h]	34.7

Table 2.1: Summary of five- and six-membered saturated, diamido- and amino/amido carbenes, their TEP values, L-Ir(COD)Cl distances, $E_{1/2}$ potentials, and carbenoid ^{13}C NMR chemical shifts. [a] The TEP values were calculated from the corresponding $LIr(CO)_2Cl$ complexes using Nolan's method.[34] [b] The electrochemical data was obtained in CH_2Cl_2 with a 0.1 M $[Bu_4N][PF_6]$ electrolyte and referenced to a decamethylferrocene (Fc^*) internal standard. [c] In *d*$_6$-benzene. [d] The carbene was prepared *in-situ* from **5·HBF$_4$** and NaHMDS at 25 °C. [e] In *d*$_8$-toluene.[42] [f] Since **7**-Ir(COD)Cl is unknown, the metal-carbene distance reported was obtained from the corresponding Rh complex.[43,44] [g] Calculated using the Samb*V*ca application.[42] [h] The ^{13}C NMR shift for **8** refers to a variant with ^{t}Butyl substituents in lieu of mesityl.[26]

To determine if the effects outlined above were general, our attention shifted toward analyzing the five-membered analogues of the aforementioned carbenes (Figure 2.3): the prototypical NHC 1,3-dimesityl-dihydroimidazol-2-ylidine (**SIMes**), Lavigne's[29,43] mono-amino/amido carbene **7** and Ganter's diamidocarbene **8**.[24,26] Contrary to the six-membered series, the TEP value measured for **7** (2058 cm^{-1}) was found not to be the median of **SIMes** (2053 cm^{-1}) and **8** (2068 cm^{-1}), which may be explained by the partial formation of the more donating enol tautomer. Regardless, akin to their six-membered analogues, increasing the number of carbonyl groups incorporated into the five-membered diaminocarbene scaffold resulted in the reduction of carbene donicity, as evidenced by the increasing TEP values and decreasing carbene-metal bond distances.

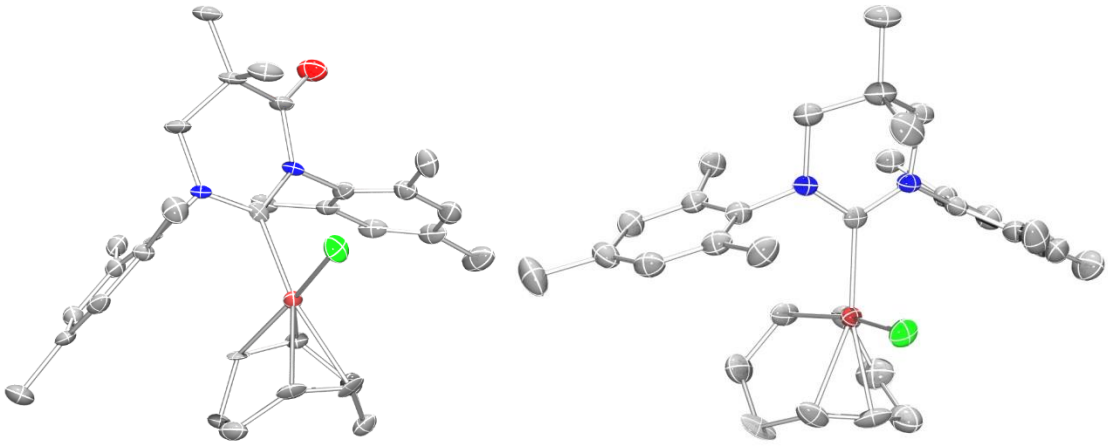


Figure 2.3: ORTEP diagram of **3-Ir(COD)Cl** and **5-Ir(COD)Cl** with thermal ellipsoids drawn at 50% probability and H atoms omitted for clarity. Selected distances (Å) and angles (deg): **3-Ir(COD)Cl**: Ir1-Cl1 2.378(5), Ir1-C1 2.040(6), Ir1-C25 2.131(6), Ir1-C28 2.170(5), Ir1-C29 2.207(5), Ir1-C32 2.108(6), N1-C1-N2 114.8(5), C1-Ir1-Cl1 87.67(2). **5-Ir(COD)Cl**: Ir1-Cl1 2.365(0), Ir1-C1 2.067(4), Ir1-C25 2.108(4), Ir1-C26 2.118(4), Ir1-C29 2.154(5), Ir1-C30 2.169(5), N1-C1-N2 116.3(4), C1-Ir1-Cl1 88.18(1).

In addition to the aforementioned spectroscopic and electrochemical evaluation, computational methods were employed to help elucidate the observed chemical reactivity and electronic properties displayed by diaminocarbenes compared to their carbonyl containing derivatives. As summarized in Figure A9, the HOMO-LUMO gap (ΔH_{S-T}),[44] calculated at the B3LYP 6-31+G(d) level of theory for the N-methyl analogues of **3**, **5**, and **6**, decreased relatively minimally between **5-Me** (116.06 kcal/mol) and **3-Me** (112.27 kcal/mol); however, a large difference was calculated between **6-Me** (98.19 kcal/mol) and **3-Me**. This observation, coupled with the asymmetry in the observed C-N bond lengths measured in the solid state structure of **3**, suggested to us that the amino group effectively compensated for the relatively weakly donating amido group. Likewise, the relatively small ΔH_{S-T} calculated for **6-Me** was consistent with the electrophilic character displayed by DAC **6**, particularly compared to prototypical NHCs.[15,16,18-25]

2.3 Conclusion

The first isolable mono-amino/amido carbene (**3**) and corresponding iridium complexes (**3-Ir(COD)Cl** and **3-Ir(CO)$_2$Cl**) were synthesized and characterized. MAAC **3** was found to exhibit an asymmetric electronic structure and exhibited reactivity intermediate of typical NHCs and DACs: **3** coupled with typical organic electrophiles (i.e., CS_2 and coordinatively unsaturated metal centers) but also nucleophilic isonitriles. In support of this observation, spectroscopic and electrochemical characterization of the various carbene-iridium compounds revealed the electronic properties of **3** were the intermediate of prototypical NHCs and DACs. Importantly, these findings provided a quantitative assessment of the effect of incorporating one versus two carbonyl moeties into an NHC scaffold, and that increasing the number of carbonyls had an additive effect on a carbene's electronic and chemical properties. Per carbonyl introduced, the $E_{1/2}$ potential of

the corresponding ligated iridium I/II redox couple increased by an average of 165 mV and the TEP value increased by 7 cm^{-1}. Considering that similar trends were observed between five- and six-membered carbene scaffolds,[46] we believe the results will help guide the general design of other electron-deficient NHC scaffolds.

2.4 EXPERIMENTAL

General Considerations. Unless otherwise noted, all procedures were carried out under a nitrogen atmosphere using standard Schlenk techniques or in a nitrogen-filled glove box. Solvents were dried and degassed by a Vacuum Atmospheres Company solvent purification system and stored over 3Å molecular sieves in a nitrogen-filled glove box. Mesityl formamidine was synthesized according to a literature procedure.[47] Infrared spectra were gathered on a Perkin Elmer Spectrum BX FTIR spectrophotometer. High resolution mass spectra were obtained with a VG Analytical ZAB2-E instrument (CI or ESI). NMR spectra were acquired on a Varian Mercury or DirectDrive 400 MHz instrument; chemical shifts (δ) are provided in ppm and are referenced to the residual solvent peak (^{1}H: $CDCl_3$, 7.26 ppm; C_6D_6, 7.14 ppm. ^{13}C: $CDCl_3$, 77.0 ppm; C_6D_6, 128.0 ppm). Melting points were obtained via either a Mel-Temp apparatus or an Optimelt MPA100 Automated Melting Point System and are uncorrected.

Synthesis of 3-Chloro-N-mesityl-N'-((mesitylimino)methyl)-2,2-dimethylpropanamide (1). A 250 mL Schlenk flask was charged with mesityl formamidine (3.00 g, 10.70 mmol, 1.0 equiv.) triethylamine (2.25 mL, 16.05 mmol, 1.5 equiv.), dichloromethane (125 mL) and a stir bar. The mixture was equilibrated at 0 °C in an ice bath while stirring for 15 min, after which 3-chloropivaloyl chloride (1.54 mL, 11.77 mmol, 1.1 equiv.) was added dropwise. The resulting mixture was stirred for 30 min at 0 °C before gradually warming to ambient temperature. Subsequent removal of the residual

volatiles under reduced pressure afforded a white powder, which was extracted with toluene and filtered through a medium frit. Removal of the residual solvent under reduced pressure afforded the desired product as a white solid (4.013 g, 10.058 mmol, 94% yield). m.p. 95-96 °C. ^{1}H NMR ($CDCl_3$, 300.14 MHz): δ 1.20 (s, 6H, C(C**H**$_3$)$_2$), 2.07 (s, 6H, Ar-C**H**$_3$), 2.24 (s, 3H, Ar-C**H**$_3$), 2.31 (s, 6H, Ar-C**H**$_3$), 2.34 (s, 3H, Ar-C**H**$_3$), 3.70 (s, 2H, CC**H**$_2$Cl), 6.81 (s, 2H, Ar-**H**), 7.01 (s, 2H, Ar-**H**), 8.75 (s, 1H, NC**H**N). ^{13}C NMR ($CDCl_3$, 75.47 MHz): δ 18.33, 18.71, 20.60, 21.09, 24.13, 47.40, 54.38, 127.71, 128.59, 129.47, 132.55, 133.35, 136.16, 138.65, 145.81, 150.35, 176.14. IR (KBr): ν_{CO} = 1657 cm^{-1}. HRMS (CI)): [M+H]$^+$ calcd. for $C_{24}H_{31}ClN_2O$ 398.2125, found 398.2119.

Synthesis of 1,3-Dimesityl-5,5-dimethyl-4-keto-tetrahydropyrimidin-1-ium chloride (2). Under ambient conditions, a 250 mL round bottom flask was charged with **1** (1 g, 2.5 mmol, 1 equiv.), toluene (125 mL) and a stir bar. The solution was refluxed at 110 °C for 16 h during which time a white precipitate formed. The solution was cooled, and the precipitate was collected via vacuum filtration, washed with cold toluene, and dried under reduced pressure to afford the desired product as a white solid (0.829 g, 10.058 mmol, 91% yield). m.p. 250-253 °C (decomp). ^{1}H NMR ($CDCl_3$, 300.27 MHz): δ 1.65 (s, 6H, C(C**H**$_3$)$_2$), 2.24 (s, 6H, Ar-C**H**$_3$), 2.27 (s, 6H, Ar-C**H**$_3$), 2.47 (s, 6H, Ar-C**H**$_3$), 4.12 (s, 2H, CC**H**$_2$N), 6.93 (s, 4H, Ar-**H**), 10.24 (s, 1H, N=C**H**-N). ^{13}C NMR ($CDCl_3$, 75.47 MHz): δ 18.37, 18.64, 20.83, 20.91, 23.68, 38.40, 59.01, 129.89, 130.43, 133.21, 134.79, 135.02, 140.45, 140.94, 160.42, 169.45. IR (KBr): ν_{CO} = 1752, 1650 cm^{-1}. HRMS (CI): [M]$^+$ calcd. for $C_{24}H_{31}N_2O$ 363.5145, found 363.2432.

Synthesis of N,N'-Dimesityl-5,5-dimethyl-4-keto-tetrahydropyrimidin-2-ylidene (3). A 100 mL Schlenk flask was charged with **2** (0.5 g, 1.375 mmol, 1 equiv.), sodium hexamethyldisilazide (13 mg, 1.444 mmol, 1.05 equiv.), benzene (45 mL) and a stir bar. The solution was stirred at ambient temperature for 30 min followed by filtration

through a 0.2 μm PTFE filter. Removal of the residual volatiles under reduced pressure afforded a tan solid, which was washed repeatedly with pentane until the supernatant was colorless. Removal of the residual solvent under reduced pressure afforded the desired product as an off-white solid (0.309 g, 0.854 mmol, 62% yield). m.p. 126-130 °C. ^{1}H NMR (C_6D_6, 300.27 MHz): δ 1.14 (s, 6H, C(C**H**$_3$)$_2$), 2.11 (s, 3H, Ar-C**H**$_3$), 2.14 (s, 3H, Ar-C**H**$_3$), 2.19 (s, 6H, Ar-C**H**$_3$), 2.28 (s, 6H, Ar-C**H**$_3$), 2.99 (s, 2H, CC**H**$_2$N), 6.74 (s, 2H, Ar-**H**), 6.84 (s, 2H, Ar-**H**). ^{13}C NMR (C_6D_6, 75.47 MHz): δ 18.35, 18.59, 20.90, 21.02, 24.18, 37.50, 57.8, 129.24, 129.71, 134.08, 134.88, 136.31, 136.77, 139.77, 143.27, 169.00, 260.56. IR (C_6H_6): ν_{CO} = 1657 cm^{-1}. HRMS (CI): [M+H]$^+$ calcd. for $C_{24}H_{30}N_2O$ 363.2437, found 363.2436.

Synthesis of 1,3-Dimesityl-5,5-dimethyl-4-keto-tetrahydropyrimidin-1-ium-2-carbodithioate (3-CS$_2$). A 40 mL vial was charged with **3** (75 mg, 0.21 mmol, 1 equiv.), benzene (15 mL), carbon disulfide (13 μL, 0.22 mmol, 1.05 equiv.) and a stir bar. The scarlet mixture was stirred for 1 h at 25 °C temperature before being concentrated under reduced pressure. After adding pentane (20 mL), the resultant mixture was filtered and then dried under reduced pressure to afford the desired product as a red solid. (86.7 mg, 0.197 mmol, 94% yield). m.p. 195-197 °C (decomp). ^{1}H NMR (C_6D_6, 300.27 MHz): δ 1.14 (s, 6H, C(C**H**$_3$)$_2$), 1.94 (s, 3H, Ar-C**H**$_3$), 1.959 (s, 3H, Ar-C**H**$_3$), 2.43 (s, 6H, Ar-C**H**$_3$), 2.458 (s, 6H, Ar-C**H**$_3$), 3.058 (s, 2H, CC**H**$_2$N), 6.56 (s, 2H, Ar-**H**), 6.62 (s, 2H, Ar-**H**). ^{13}C NMR (C_6D_6, 75.47 MHz): δ 19.81, 20.26, 20.83, 20.95, 37.72, 57.56, 129.93, 130.51, 131.54, 134.88, 136.22, 136.90, 139.65, 139.96, 158.70, 171.89, 222.26. IR (C_6H_6) ν_{CO} = 1657 cm^{-1}, ν_{CS} = 1091, 1062 cm^{-1}. HRMS (CI): [M]$^+$ calcd. for $C_{25}H_{31}N_2S_2O$ 439.1878, found 439.1876.

Synthesis of 2-((Butylimino)methylene)-1,3-dimesityl-5,5-dimethyltetrahydropyrimidin-4-one (4a). An 8 mL vial was charged with **3** (25 mg,

0.069 mmol, 1 equiv.), benzene (3 mL), n-butyl isocyanide (7.6 µL, 0.072 mmol, 1.05 equiv.) and a stir bar. The solution was stirred for 12 h at ambient temperature, after which removal of the residual solvent under reduced pressure afforded the desired product as a yellow liquid (25.2 mg, 0.057 mmol, 82% yield). ^{1}H NMR (C_6D_6, 300.14 MHz): δ 0.59 (m, 3H, CH_2CH_3), 0.67 (m , 2H, CH_2CH_3), 0.92 (m, 2H, -$CH_2CH_2CH_2$-), 1.37 (s, 3H, C(CH_3), 1.46 (s, 3H, C(CH_3), 2.06 (d, *J* = 7.5 Hz, 6H, Ar(CH_3), 2.28 (s, 3H, Ar(CH_3)), 2.32 (d, *J* = 4.8 Hz, 6H, Ar(CH_3)), 2.39 (s, 3H, Ar(CH_3)), 2.80 (t, *J* = 7 Hz, 2H, =NCH_2CH_2-), 2.98 (d, *J* = 11 Hz, 1H, NCH**H**C), 3.52 (d, *J* = 12 Hz, 1H, NC**H**HC), 6.69 (s, 4H, Ar-**H**). ^{13}C NMR (C_6D_6, 75.47 MHz): δ 13.64, 17.50, 17.57, 18.92, 18.98, 19.36, 19.42, 19.62, 20.41, 20.44, 20.64, 20.67, 23.89, 23.93, 25.00 25.04, 31.77, 40.80, 58.00, 59.10, 113.95, 128.77, 129.11, 129. 66, 133.67, 135.11, 135.38, 135.86, 136.53, 137.34, 137.39, 139.04, 169.90, 210.12. HRMS (CI): $[M+H]^+$ calcd. for $C_{29}H_{39}N_3O$ 446.3171, found 446.3155.

Synthesis of 2-((Benzylimino)methylene)-1,3-dimesityl-5,5-dimethyltetrahydropyrimidin-4-one (4b). A 8 mL vial was charged with **3** (25 mg, 0.069 mmol, 1 equiv.), benzene (3 mL), benzyl isocyanide (8.8 µL, 0.072 mmol, 1.05 equiv.) and a stir bar. After stirring the resulting solution for 12 h at ambient temperature, the residual solvent was removed under reduced pressure. Subsequent washing with pentane followed by drying under reduced pressure afforded the desired product as a yellow solid (24.5 mg, 0.051 mmol, 74% yield). m.p. 182-188 °C (decomp). ^{1}H NMR (C_6D_6, 300.14 MHz): δ 1.00 (s, 6H, C(CH_3), 1.86 (s, 3H, Ar(CH_3), 1.97 (s, 6H, Ar(CH_3)), 2.02 (s, 9H, Ar(CH_3)), 2.94 (s, 2H, NCH_2C), 5.42 (s, 2H, NCH_2Ph), 6.57 (d, *J* = 15 Hz, 4H, Ar-**H**), 6.75 (m, 5H, Ar-**H**). ^{13}C NMR (C_6D_6, 75.47 MHz): δ 17.69, 17.74, 19.09, 19.14, 20.55, 20.61, 20.74, 23.47, 23.52, 39.17, 59.03, 105.37, 128.51, 128.80, 129.48, 134.08, 134.11, 135.10, 135.63,

137.52, 138.50, 139.94, 143.38, 147.84, 171.25. IR (C_6H_6): HRMS (CI): $[M+H]^+$ calcd. for $C_{32}H_{37}N_3O$ 480.3015, found 480.3008.

Synthesis of 2-(((2,6-Dimethylphenyl)imino)methylene)-1,3-dimesityl-5,5-dimethyltetrahydropyrimidin-4-one (4c). An 8 mL vial was charged with **3** (25 mg, 0.069 mmol, 1 equiv.), 2,6-dimethylphenyl isocyanide (9.5 mg, 0.072 mmol, 1.05 equiv.), benzene (3 mL) and a stir bar. After stirring the solution for 12 h at ambient temperature, the residual solvent was removed under reduced pressure to afford the desired product as a red solid (26.9 mg, 0.055 mmol, 79% yield). m.p. 216-221 °C (decomp). ^{1}H NMR (C_6D_6, 300.14 MHz): δ 1.36 (s, 3H, C(C**H**$_3$), 1.48 (s, 6H, Ar-C**H**$_3$), 2.01 (s, 3H, Ar(C**H**$_3$), 2.06 (s, 3H, Ar(C**H**$_3$)), 2.28 (d, 6H, Ar(C**H**$_3$)), 2.31 (s, 6H, Ar(C**H**$_3$)), 3.30 (s, 2H, NC**H**$_2$C), 6.65 (br d, *J* = 7 Hz, 4H, Ar-**H**), 6.70 (m, 3H, Ar-**H**). ^{13}C NMR (C_6D_6, 75.47 MHz): δ 16.95, 17.76, 19.40, 20.30, 20.55, 20.20, 40.93, 59.71, 124.37, 128.25, 129.23, 129.80, 133.22, 135.72, 136.26, 137.89, 138.80, 143.78, 170.02, 219.91. HRMS (CI): $[M+H]^+$ calcd. for $C_{33}H_{39}N_3O$ 494.3171, found 494.3170.

Synthesis of (N,N'-Dimesityl-5,5-dimethyl-4-keto-tetrahydropyrimidin-2-ylidene)-iridium(I) (1,5-cyclooctadiene) chloride (3-Ir(COD)Cl). A 20 mL vial was charged with **3** (50 mg, 0.138 mmol, 2.5 equiv.), {Ir(COD)Cl}$_2$ (19 mg, 0.056 mmol, 1.0 equiv.), benzene (10 mL) and a stir bar. The solution was stirred for 16 h at ambient temperature in the dark after which the volatiles were removed under reduced pressure. The resultant orange solid was purified via column chromatography using silica gel as the stationary phase and 1:1 ethyl acetate/hexanes solution as the eluent. Removal of residual solvent and drying under reduced pressure afforded the desired product as an orange powder (55.7 mg, 0.084 mmol, 75% yield). m.p. 277-279 °C (decomp). ^{1}H NMR (C_6D_6, 300.27 MHz): δ 0.91 (s, 3H, C(C**H**$_3$)), 1.42 (m, 8H, CC**H**$_2$C**H**$_2$C), 1.69 (s, 3H, C(C**H**$_3$)), 1.99 (s, 3H, C(C**H**$_3$)), 2.08 (s, 3H, Ar(C**H**$_3$)), 2.17 (d, *J* = 4 Hz, 6H, Ar(C**H**$_3$)), 2.43 (d, *J* =

14 Hz, 1H, N-C**H**HC), 2.77 (d, *J* = 12 Hz, 6H, Ar(C**H**$_3$)), 3.06 (m, 1H, Ir-(C**H**=C**H**)), 3.28 (d, *J* = 14 Hz, 1H, N-CH**H**C), 4.56 (m, 1H, Ir-(C**H**=C**H**)), 4.69 (m, 1H, Ir-(C**H**=C**H**)), 6.70 (s, 1H, Ar**H**), 6.77 (s, 1H, Ar**H**), 6.79 (s, 1H, Ar**H**), 6.87 (s, 1H, Ar**H**). ^{13}C NMR (C_6D_6, 75.47 MHz): δ 8.84, 18.87, 19.28, 19.72, 20.59, 20.78, 20.92, 20.98, 22.26, 25.07, 27.19, 29.01, 32.38, 35.07, 37.27, 52.90, 54.29, 60.12, 83.24, 85.42, 129.16, 130.10, 130.53, 131.14, 133.64, 135.11, 135.49, 135.76, 136.58, 136.71, 137.80, 138.17, 138.18, 141.07, 165.50, 170.40, 173.44, 218.59. IR (KBr) ν_{CO} = 1714 cm^{-1}. HRMS (ESI): [M-Cl]$^+$ calcd. for $C_{32}H_{42}N_2OClIr$ 662.9040, found 663.2930.

Synthesis of (N,N'-Dimesityl-5,5-dimethyl-4-keto-6-tetrahydropyrimidin-2-ylidene)-iridium(I) (dicarbonyl) chloride (3-Ir(CO)$_2$Cl). An 8 mL vial was charged with **3-Ir(COD)Cl** (25 mg, 0.038 mmol, 1 equiv.) and dichloromethane (1 mL). A balloon filled with carbon monoxide was affixed to the aforementioned vial and the gas was introduced to the solution through a needle at ambient temperature. After the solvent had evaporated, 1 mL of dichloromethane was added and additional carbon monoxide was bubbled through the resulting solution; this procedure was repeated twice. The residual yellow solid was washed with cold pentane and dried under reduced pressure to afford the desired product as a yellow powder (24 mg, 0.036 mmol, 96% yield). m.p. 137-140 °C. ^{1}H NMR (C_6D_6, 300.27 MHz): δ 0.86 (s, 3H, C(C**H**$_3$)), 1.30 (s, 3H, C(C**H**$_3$)), 1.99 (s, 3H, C(C**H**$_3$)), 1.98 (s, 3H, Ar(C**H**$_3$)), 2.01 (s, 3H, Ar(C**H**$_3$)), 2.24 (s, 3H, Ar(C**H**$_3$)), 2.31 (s, 3H, Ar(C**H**$_3$)), 2.50 (s, 6H, Ar(C**H**$_3$)), 2.53 (d, *J* = 16 Hz, 1H, N-C**H**HC), 3.16 (d, *J* = 16 Hz, 1H, N-CH**H**C), 6.67 (s, 1H, Ar**H**), 6.68 (s, 1H, Ar**H**), 6.76 (s, 1H, Ar**H**), 6.83 (s, 1H, Ar**H**). ^{13}C NMR (C_6D_6, 75.47 MHz): δ 18.84, 18.87, 19.28, 19.72, 20.59, 20.78, 20.92, 20.98, 22.26, 25.07, 27.19, 29.01, 32.38, 35.07, 37.27, 52.90, 54.29, 60.12, 83.24, 85.42, 129.16, 130.10, 130.53, 131.14, 133.64, 135.11, 135.49, 135.76, 136.58, 136.71, 137.80, 138.17, 138.18,

141.07, 165.50, 170.40, 173.44, 210.68. IR (CH_2Cl_2): ν_{CO} = 2066, 1981 cm^{-1}. HRMS (ESI): $[M-Cl]^+$ calcd. for $C_{26}H_{30}N_2O_3ClIr$ 610.7438, found 611.1878.

Synthesis of N,N'-Dimesityl-2,2-dimethylmalonamide (5a). A 1 L round bottom flask was charged with freshly distilled 2,4,6-trimethylaniline (6.69 mL, 47.64 mmol, 2.1 equiv.), pyridine (3.84 mL, 47.69 mmol, 2.1 equiv.), dichloromethane (500 mL), and a stir bar. The flask was cooled to -78 °C in a dry ice/isopropyl alcohol bath and allowed to equilibrate for 15 min. To this mixture, 2,2-dimethyl malonyldichloride (3.0 mL, 22.69 mmol, 1.0 equiv.) was added dropwise, and the resultant mixture was stirred at -78 °C for 2 h. Afterward, the mixture was warmed to ambient temperature and the volatiles were removed under reduced pressure. The residue was charged with 250 mL of toluene and the resulting mixture was filtered to remove the insoluble salts. The filtrate was then concentrated under reduced pressure, triturated with hexanes and dried under reduced pressure to afford the desired product as a white solid. (5.32 g, 14.52 mmol, 64% yield). m.p. 164-166 °C. ^1H NMR (C_6D_6, 300.27 MHz): δ 1.67 (s, 6H, C(CH_3)$_2$), 2.13 (s, 12H, Ar-CH_3), 2.25 (s, 6H, Ar-CH_3), 6.87 (s, 4H, Ar-**H**), 8.19 (s, 2H, N**H**). ^{13}C NMR ($CDCl_3$, 75.47 MHz): δ 18.35, 21.10, 49.94, 129.09, 131.11, 135.00, 137.12, 172.54. IR (KBr): ν_{CO} = 1640 cm^{-1}, ν_{NH} = 3230 cm^{-1}. HRMS (CI): $[M+H]^+$ calcd. for $C_{23}H_{31}N_2O_2$ 367.2386, found 367.2382.

Synthesis of N,N'-Dimesityl-2,2-dimethylpropane-1,3-diamine (5b). A 250 mL round bottom flask was charged with **5a** (1.5 g, 4.09 mmol, 1.0 equiv.), THF (125 mL) and a stir bar. A solution of borane·dimethyl sulfide in THF (2 M, 10 mL, 20.5 mmol, 5.0 equiv.) was then added to the solution, which was then refluxed at 85 °C for 14 h. After cooling the mixture to ambient temperature, 1 M aqueous hydrochloric acid was added dropwise to quench the reaction. The mixture was brought to a basic pH with 1 M aqueous sodium hydroxide, and the organic volatiles were removed under reduced pressure. The

aqueous mixture was then extracted with 100 mL diethyl ether (3×) The combined ether layers were dried over sodium sulfate, filtered and then concentrated under reduced pressure. Purification of the residue via column chromatography using silica gel as the stationary phase and 1:3 ethyl acetate/hexanes solution as the eluent followed by removal of residual solvent under reduced pressure afforded the desired product as a white solid (1.36 g, 3.36 mmol, 82% yield). m.p. 65-67 °C. ^{1}H NMR (C_6D_6, 300.27 MHz): δ 1.20 (s, 6H, C(C**H**$_3$)$_2$), 2.24 (s, 6H, Ar-C**H**$_3$), 2.28 (s, 12H, Ar-C**H**$_3$), 2.80 (s, 4H, N-C**H**$_2$-C), 6.87 (s, 4H, Ar-**H)**. ^{13}C NMR (C_6D_6, 75.47 MHz): δ 18.50, 20.78, 24.52, 35.95, 58.30, 129.68, 130.56, 131.80, 143.94. IR (KBr): ν_{NH} = 3358 cm^{-1}. HRMS (CI): $[M]^+$ calcd. for $C_{23}H_{34}N_2$ 338.2722, found 338.2724.

Synthesis of 1,3-Dimesityl-5,5-dimethyl-tetrahydropyrimidin-1-ium tetrafluoroborate (5·HBF$_4$). A 25 mL round bottom flask equipped with a short-path distillation head was charged with **5b** (500 mg, 1.48 mmol, 1 equiv.), ammonium tetrafluoroborate (170 mg, 1.62 mmol, 1.1 equiv), triethylorthoformate (10 mL, 8.91 g, 60 mmol, 40 equiv.), n-heptane (0.5 mL), and a stir bar. Stirring the mixture for 12 h at 90 °C following by cooling to ambient temperature afforded an orange precipitate. The precipitate was isolated via vacuum filtration, recrystallized from methanol, and dried under reduced pressure to afford the desired product as an orange solid (393 mg, 0.228 mmol, 76% yield). m.p. 66-67 °C. ^{1}H NMR ($CDCl_3$, 399.68 MHz): δ 1.38 (s, 6H, C(C**H**$_3$)$_2$), 2.22 (s, 6H, Ar-C**H**$_3$), 2.30 (s, 12H, Ar-C**H**$_3$), 3.53 (s, 4H, NC**H**$_2$C), 6.91 (s, 4H, Ar-**H**), 7.62 (s, 1H, N=C**H**-N). ^{13}C NMR (C_6D_6, 75.47 MHz): δ 18.27, 21.18, 25.81, 29.06, 56.72, 130.69, 134.60, 135.88, 140.80, 154.04. HRMS (ESI): $[M\text{-}BF_4]^+$ calcd. for $C_{24}H_{33}N_2$ 349.2638, found 349.2636.

Synthesis of (N,N'-Dimesityl-5,5-dimethyl-4,6-tetrahydropyrimidin-2-ylidene)-iridium(I) (1,5 cyclooctadiene) chloride (5-IrCODCl). A 50 mL Schlenk flask

was charged with **5·HBF$_4$** (100 mg, 0.23 mmol, 1 equiv.), sodium hexamethyldisilazide (46 mg, 0.25 mmol, 1.1 equiv), benzene (20 mL) and a stir bar. After stirring the mixture for 1 h at ambient temperature, {Ir(COD)Cl}$_2$ (77 mg, 0.11 mmol, 0.5 equiv.) was added. Following stirring the resultant mixture for 12 h at ambient temperature in the dark, and removal of the volatiles under reduced pressure, the resultant orange solid was purified via column chromatography using silica gel as the stationary phase and 1:1 ethyl acetate/hexanes solution as the eluent. Removal of residual solvent under reduced pressure afforded the desired product as an orange powder (97 mg, 0.14 mmol, 62% yield). m.p. 192-194 °C. ^{1}H NMR ($CDCl_3$, 399.68 MHz): δ 0.44 (s, 3H, C(C**H$_3$**)), 1.46 (s, 3H, C(C**H$_3$**)), 2.16 (s, 6H, Ar-C**H$_3$**), 2.20 (s, 6H, Ar-C**H$_3$**), 2.36 (s, *J* = 11 Hz, 2H, NC**H$_2$**C), 2.72 (s, *J* = 11 Hz, 2H, NC**H$_2$**C), 2.79 (s, 6H, Ar-C**H$_3$**), 3.09 (s, 2H, C**H**=C**H**), 4.50 (m, 2H, C**H**=C**H**), 6.80 (s, 6H, Ar**H**), 6.86 (s, 2H, Ar**H**). ^{13}C NMR (C_6D_6, 75.47 MHz): δ 19.77, 21.21, 21.28, 24.96, 26.39, 28.90, 34.38, 51.62, 59.22, 80.24, 131.26, 135.38, 137.59, 137.70, 141.81, 205.77. HRMS (CI): $[M]^+$ calcd. for $C_{32}H_{44}N_2ClIr$ 684.2822, found 684.2821.

Synthesis of (N,N'-dimesityl-5,5-dimethyl-4,6-tetrahydropyrimidin-2-ylidene)-iridium(I) (dicarbonyl) chloride (5-IrCO$_2$Cl). An 8 mL vial was charged with **5-IrCODCl** (25 mg, 0.04 mmol, 1 equiv) and dichloromethane (2 mL). A balloon filled with carbon monoxide was affixed to the aforementioned vial and the gas was introduced to the solution through a needle at ambient temperature. After the solvent had evaporated, 1 mL of dichloromethane was added and additional carbon monoxide was bubbled through the resulting solution; this procedure was repeated twice. The residual yellow solid was washed with cold pentane and dried under reduced pressure to afford the desired product as a yellow solid (22 mg, 0.03 mmol, 94% yield). m.p. 188-189 °C. ^{1}H NMR ($CDCl_3$, 399.68 MHz): δ 0.46 (s, 3H, C(C**H**$_3$)$_2$), 1.10 (s, 3H, C(C**H**$_3$)), 2.05 (s, 6H, Ar-C**H**$_3$), 2.35 (s, *J* = 12 Hz, 2H, NC**H$_2$**C), 2.38 (s, 6H, Ar-C**H**$_3$), 2.57 (s, *J* = 12 Hz, 2H, NC**H$_2$**C), 2.56

(s, 6H, Ar-C**H**$_3$), 6.76 (s, 2H, Ar**H**), 6.81 (s, 2H, Ar**H**). ^{13}C NMR (C_6D_6, 75.47 MHz): δ 19.17, 20.72, 21.32, 25.44, 26.05, 28.45, 58.23, 129.89, 131.22, 135.00, 138.63, 141.21, 171.29, 180.67, 198.86. IR (C_6H_6): ν_{CO} = 1967, 2061 cm^{-1}. HRMS (ESI): $[M\text{-}Cl]^+$ calcd. for $C_{26}H_{34}N_2O_2Ir$ 597.2089, found 597.2084.

2.5 ACKNOWLEDGEMENTS

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Chapter 3: Substitution of Diamidocarbene Scaffolds and its Effects on Electronic Properties and Reactivity

3.1 Introduction

While divalent carbon species such as carbenes have been known of for well over a century,[1-4] their instability hampered their general application. Upon the first stable analogues development in 1988[5] and 1991,[6] ease of preparation and handling of these molecules sparked a renaissance in their study. Of particular note were the N-heterocyclic carbenes developed by Arduengo,[6-8] which have found wide utility as ligands for metal catalysts[9-11] as well as serving as organocatalysts in their own right.[12] The stability of these compounds is derived from the twin nitrogen atoms flanking the carbene center, which are able to donate their electron density to the empty p orbital of the carbene. This stabilization regime enhances the singlet character of the carbenes and serves to limit the reactivity toward highly nucleophilic mechanisms.[7]

More recent research has moved towards expanding the reactivity of stable carbenes; pioneering work by the Bertrand group introduced a cyclic alkyl amino carbene (CAAC), which displayed a reactivity profile more in line with transient carbenes.[13,14] A more direct modification of the NHC scaffold was envisioned by the Bielawski group; noting the limitations imposed by the strongly contributing amino substituents, a new scaffold was envisioned that attenuated the donating ability of the atoms directly adjacent to the carbene nucleus.[15] This scaffold incorporated amide functional groups in lieu of the amine functionality of NHCs, and are known as diamidocarbenes (DACs). This class of carbene featured a widened reactivity profile, demonstrating an ability to react with nucleophiles,[16] engage in [2+1] cycloadditions,[17,18] insertion into C-H, N-H, P-H, and B-H bonds,[19-21] as well as retaining the ability to ligate catalytically active metals.[22]

While previous efforts have catalogued the effect of modifying the functionality of the stabilizing substituents of the carbene nucleus,[23] work has been sporadic modification of the rest of the scaffold and its effect. Of particular interest is remote alteration of the scaffold such that the electronic properties can be altered without affecting the steric environment of the carbene. Noting that six-membered diamidocarbenes feature a gem-dimethyl functionality in the backbone to eliminate complications due to α-H deprotonation,[24] we envisioned a sp^2 linkage in its place that would allow introduction of a handle to remotely tune the electronic properties of the carbene, potentially allowing family of diamidocarbenes with a range of reactivity, ligand properties, and handling characteristics without undue effect on its steric envelope (Figure 3.1).

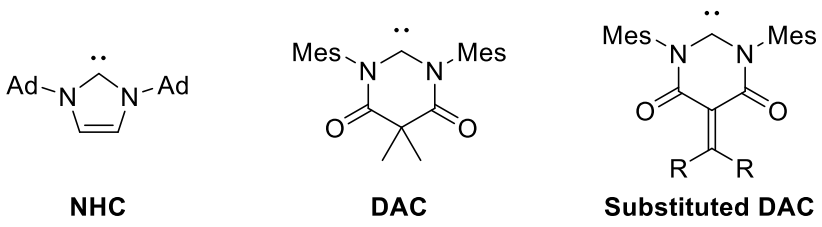
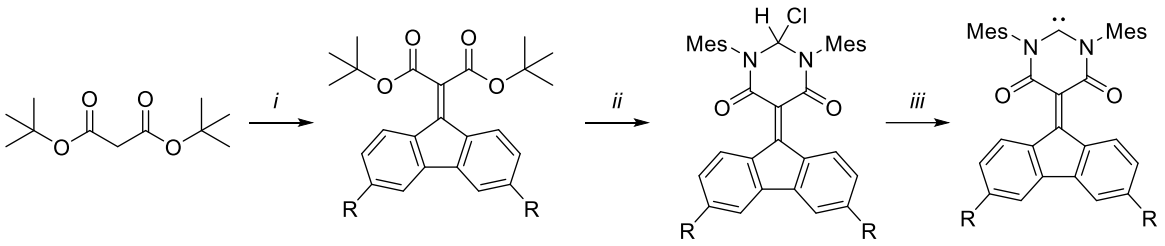


Figure 3.1: The structures of the first NHC, an archetypal DAC, and a substituted DAC.

We report the synthesis and characterization of a series of substituted diamidocarbenes, **3a-c**. The electronic properties of these carbenes were analyzed via their Ir(COD)Cl and $Ir(CO)_2Cl$ complexes, and their reactivity toward a variety of organic substrates was investigated. These results were compared to the parent diamidocarbenes scaffold in an effort to glean the effect of remote substitution on the chemical and electronic properties of diamidocarbenes and provide insight into the design of new classes of these unique molecules.

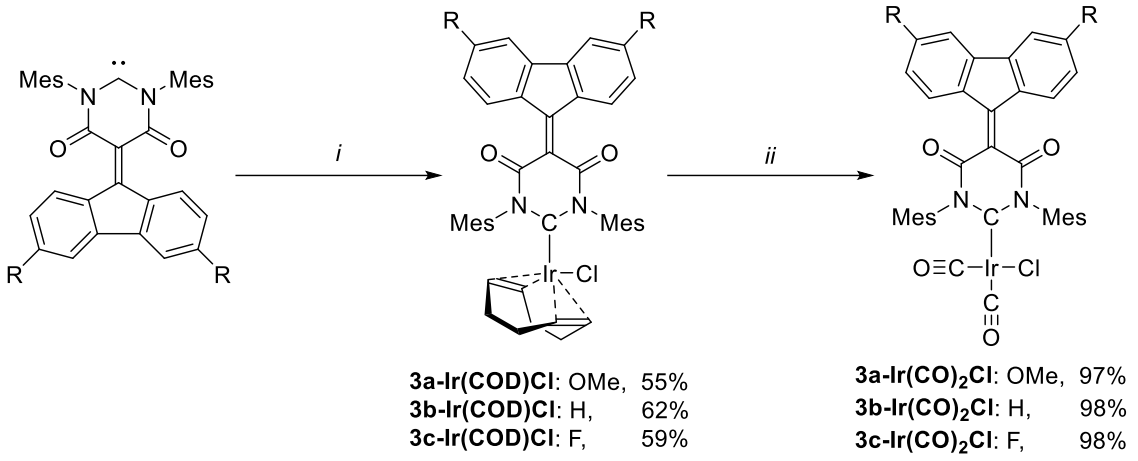
3.2 Results and Discussion

Efforts to synthesize the substituted DACs are summarized in Scheme 3.1. Preparation of the substituted malonate esters was conducted via Knoevenagel condensation of di-*tert*-butyl malonate and the corresponding fluoreneone with excess sodium hydride, furnishing **1a-c**. The successful conversion was indicated by the appearance of ^{1}H signals corresponding to aromatic hydrogens and the disappearance of the methylene signals observed at δ = 3.2 ppm. These esters were purified via column chromatography and sequentially reacted with trifluoroacetic acid for 1 h, excess thionyl chloride for 4 h, followed by removal of volatiles under reduced pressure, to which a solution of excess N,N'-dimesitylformamidine and pyridine in dichloromethane was added and the reaction was stirred at 25 °C for 16 h.[25] The resulting crude mixture was concentrated, treated with pentane and cooled to 0 °C, which induced the formation of a white precipitate, which was removed via filtration and the solvent removed from the filtrate *in vacuo*, affording crude compounds **2a-c** as indicated by the appearance of downfield ^{1}H resonances between δ = 6.91-6.94 ppm, characteristic of the methylene proton of a DAC precursor.[26] After purification, these precursors were treated with sodium hexamethyldisilazane (NaHMDS) in benzene at 25 °C for 30 minutes followed by addition of hexanes yielding crude **3a-c** as a precipitate; washing the solid with cold pentane gave the pure free carbene species as indicated by the appearance of the ^{13}C carbenoid resonances between δ = 275.68 and 278.52 ppm and disappearance of the ^{1}H resonance assigned to the methylene protons between δ = 6.91-6.94 ppm. The carbenes displayed handling characteristics similar to the parent DAC, possessing a several month shelf-life under anhydrous dinitrogen atmosphere in the solid state.



Scheme 3.1: Synthesis of substituted diamidocarbenes **3a-c**. Conditions: (i) substituted fluorenone, KO^{t}Bu, NaH, THF, -78 °C to 0 °C, 8 h. (ii) CF_3COOH, CH_2Cl_2, 0 °C, 1 h; followed by $SOCl_2$, 0 °C to 25 °C, 4 h; followed by N,N'dimesitylformamidine, pyridine, CH_2Cl_2, 0 °C to 25 °C, 16 h. (iii) NaHMDS, C_6H_6, 25 °C, 1 h. Isolated yields are indicated.

Following preparation of carbenes **3a-c**, efforts turned toward the investigation of their electronic properties. Iridium or rhodium complexes are commonly used proxies to measure the electronic character of carbenes and provide insight into their electron-donating capacity towards metal centers via calculation of the Tolman Electronic Parameter (TEP).[27,28] To this end, complexes **3a-c-Ir(COD)Cl** were synthesized as shown in Scheme 3.2. Treatment of a solution of $[Ir(COD)Cl]_2$ with the carbenes **3a-c** over 16 h at 25 °C followed by filtration through a silica gel plug yielded the corresponding iridium complexes, indicated by appearance of olefinic ^1H resonances at δ = 3.02-3.10 and 4.43-4.40 ppm and shift of the ^{13}C carbenoid signals to δ = 228-232 ppm. Carbon monoxide was bubbled through dichloromethane solutions of these complexes until the solvent was removed to affect exchange of the cyclooctadiene ligand for carbonyl ligands; washing the residual solid with cold pentane afforded **3a-c-Ir(CO)$_2$Cl** in excellent yields, as evidenced by disappearance of the signals observed for the cyclooctadiene ligand and concomitant appearance of characteristic CO stretches in the infrared spectra between 2030 and 2050 cm^{-1}.



Scheme 3.2: Synthesis of metal complexes **3a-c-Ir(COD)Cl** and **3a-c-Ir(CO)$_2$Cl**. Conditions: (*i*) [Ir(COD)Cl]$_2$, C_6H_6, 25 °C, 16 h. (*ii*) CO, CH_2Cl_2, 25 °C, 10 m. Isolated yields are indicated.

To analyze the electronic properties of the carbenes, the carbonyl complexes **3a-c-Ir(CO)$_2$Cl** were analyzed via IR spectroscopy and the CO stretches were analyzed via Nolan's method[28] to produce the TEPs. These results as well as the ^{13}C resonances of the carbene and Ir(COD)Cl complexes can be found in Table 3.1. While there is a difference in TEP between the differentially substituted carbenes, it is small – a difference of less than 1 cm^{-1} between each carbene totaling to 1.5 cm^{-1} across the set. This is considerably smaller than the difference between amino and amidocarbenes, as well as the difference between carbenes of different ring sizes, which are both on the order of tens of inverse centimeters.[29] Notably, a shift in the ^{13}C resonance of the carbene nucleus is observed that trends with the electron donating ability of the fluorenone substituent, indicating some electronic effect on the carbene nucleus.

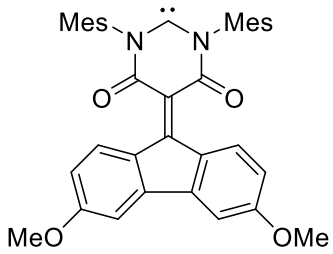
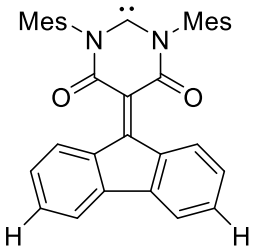
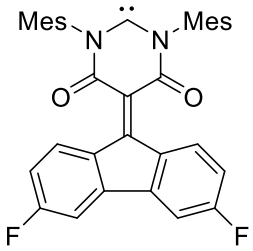
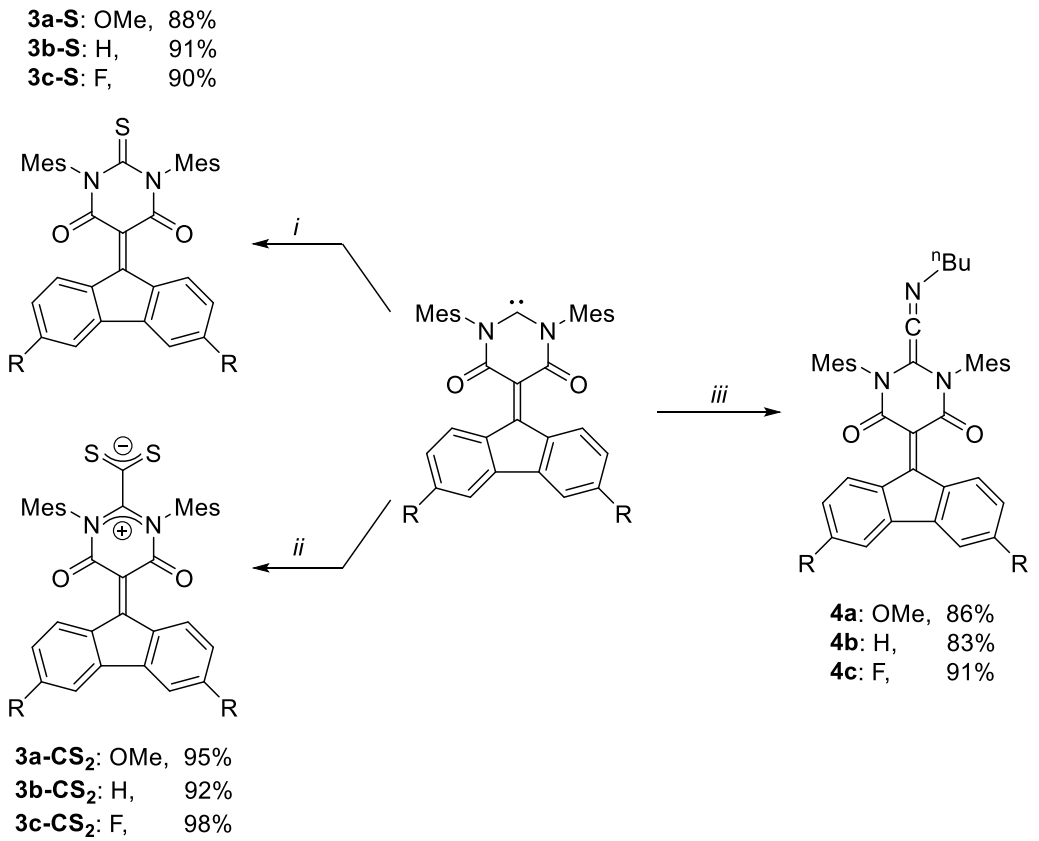
Carbene	TEP (cm^{-1})[a,b]	$\delta C_{Carbene}$ (ppm) [c]	$\delta C_{Carbene\text{-}Ir(COD)Cl}$ (ppm) [c]
 **3a**	2055.4	275.68	228.72
 **3b**	2056.1	277.31	231.09
 **3c**	2056.9	278.52	232.49

Table 3.1: Summary of the TEP values and ^{13}C carbenoid resonances for the free carbene and Ir(COD)Cl complexes. *a* The TEP values were calculated from the corresponding Carbene-Ir$(CO)_2$Cl complexes using Nolan's method.[28] *b* Owing to the small differences observed between **3a-c**, the spectra were confirmed via a separate spectrometers directly after calibration via polystyrene standards.[30] *c* In C_6D_6.

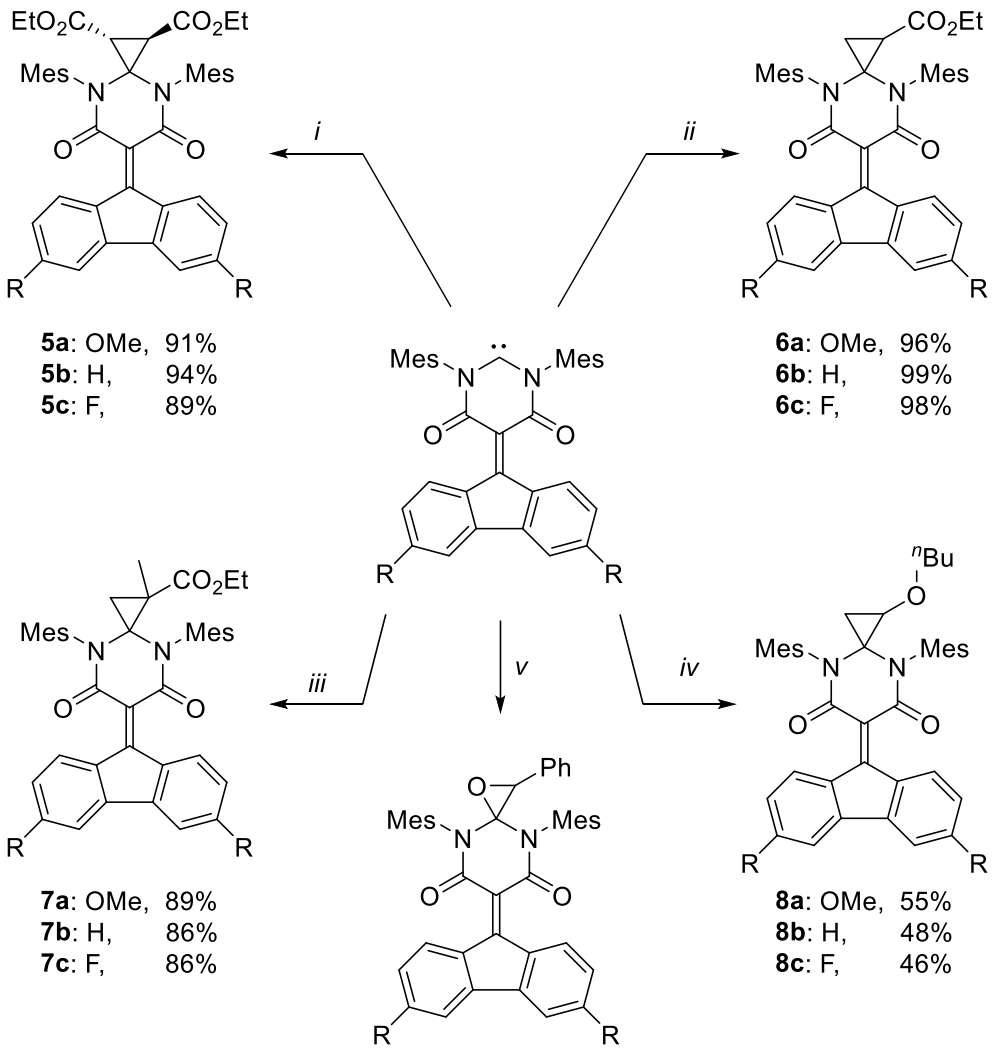
Next, our efforts turned to determining whether carbenes **3a-c** displayed differences in reactivity based on their substitution (Scheme 3.3). Initial tests focused on confirmation of the carbene's reactivity toward electrophiles in a manner consistent with diamidocarbenes; condensation with both S_8 and CS_2 (1.05 eq) at 25 °C afforded the expected thiobarbituates (**3a-c-S**) and dithioate (**3a-c-CS_2**) adducts in excellent yields (88-98%), respectively. Additionally, diamidocarbenes have been shown to display electrophilic behavior in the presence of nucleophiles such as isocyanides.[16] To probe this reactivity, solutions of **3a-c** in benzene ([**3a-c**]$_o$ = 0.01 m*M*) were treated with n-butyl isocyanide (1.05 equiv.), yielding the corresponding ketenimines (**4a-c**) in a manner consistent with previous reports. These results indicated substitution of the diamidocarbene scaffold insignificantly altered the reactivity of the carbene.



Scheme 3.3: Synthesis of carbene adducts **3a-c-S**, **3a-c-CS_2**, and **4a-c**. Conditions: (*i*) S_8, C_6D_6, 25 °C, 30 m. (*ii*) CS_2, C_6D_6, 25 °C, 30 m. (*iii*) CN^nBu, C_6D_6, 25 °C, 1 h. Isolated yields are indicated.

Having confirmed the carbene's amphiphilic reactivity toward both strongly nucleophilic and electrophilic reagents, their reactivity towards olefins and aldehydes was investigated, as summarized in Scheme 3.4. To study the cycloaddition chemistry of the carbenes, slight excesses of various olefins were added to solutions of carbene ([**3a-c**]$_0$ = 0.01 mM) and allowed to stir at 25 °C for 2 h. Gratifyingly, excellent yields of the expected cyclopropanes were observed for the additions of diethyl fumarate, methyl acrylate, and methyl methacrylate, as evidenced by the appearance of ^{1}H resonances diagnostic of new methylene (δ = 1.50 to 2.40 ppm) and methine (δ = 1.10 to 2.70 ppm) moieties concomitant

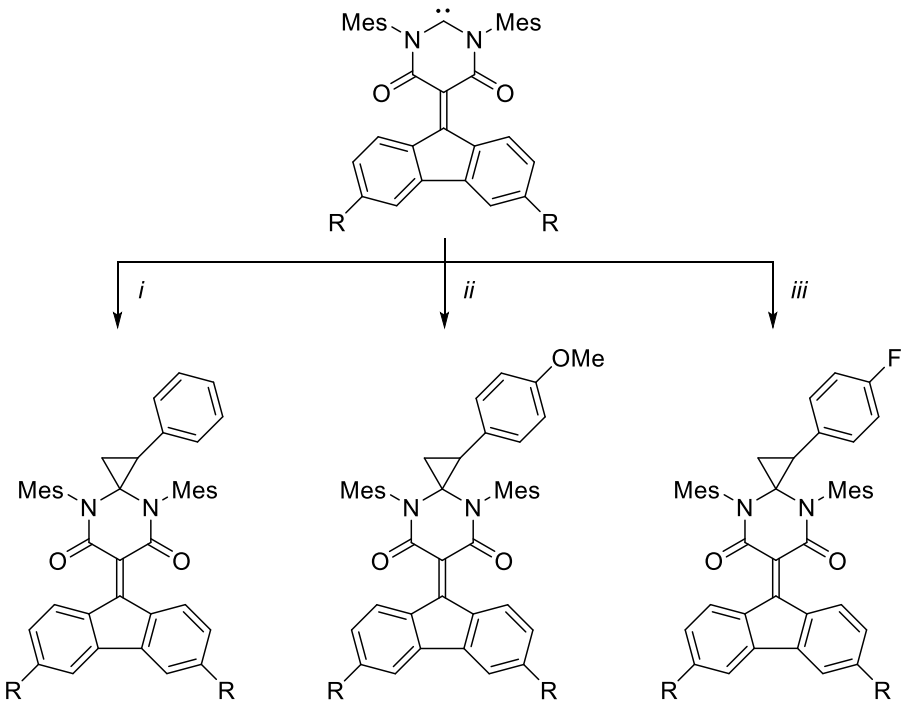
with disappearance of downfield resonances corresponding to olefinic protons. Though no reaction was observed with n-Butyl vinyl ether under conditions similar to the other olefins, conducting the reaction in the absence of solvent at elevated temperatures furnished the expected cyclopropane. No significant trend was observed in yield for any of the cyclopropane products based on the substituted fluorenone attached to the carbene scaffold. Addition of benzaldehyde to solutions of carbene ([**3a-c**]$_0$ = 0.01 m*M*) at 25 °C resulted in the generation of oxiranes **12a-c**. As was observed for the cyclopropanation reactions, these reactions displayed no trend in yield for differentially substituted carbenes. Despite the presence of the fluorene groups on the rear of the carbene scaffold, the yields of the cyclopropanes were largely unaffected compared to the parent diamidocarbene,[17] potentially indicating the effect of the substituents was superseded by the affinity of the diamidocarbene towards each substrate.



Scheme 3.4: Synthesis of cyclopropanes **5a-c**, **6a-c**, **7a-c**, **8a-c**, and oxiranes **12a-c**. Conditions: (*i*) diethyl fumarate, C_6D_6, 25 °C, 2 h. (*ii*) methyl acrylate, C_6D_6, 25 °C, 2 h. (*iii*) methyl methacrylate, C_6D_6, 25 °C, 2 h. (*iv*) butyl vinyl ether, 100 °C, 2 h. (*v*) benzaldehyde, C_6D_6, 25 °C, 2 h. Isolated yields are indicated.

To disambiguate the role of steric and electronic effects in cyclopropanation of olefins, the carbenes were exposed to styrenes bearing different *para* substituents (Scheme

3.5). While these reactions proceeded slowly under the previous cyclopropanation conditions (25 °C, 2 h), phenyl cyclopropanes were isolated in good yield after prolonged periods at elevated temperatures (60 °C, 16 h). Surprisingly, no trend was observed due to variance of the fluorene substituent on the carbene scaffold for a particular styrene, though the substituted styrenes resulted in lowered yields. This indicated to us that steric differences between cyclopropanation substrates obscure any trend in reactivity due to substitution.



9a: OMe, 85%
9b: H, 78%
9c: F, 84%

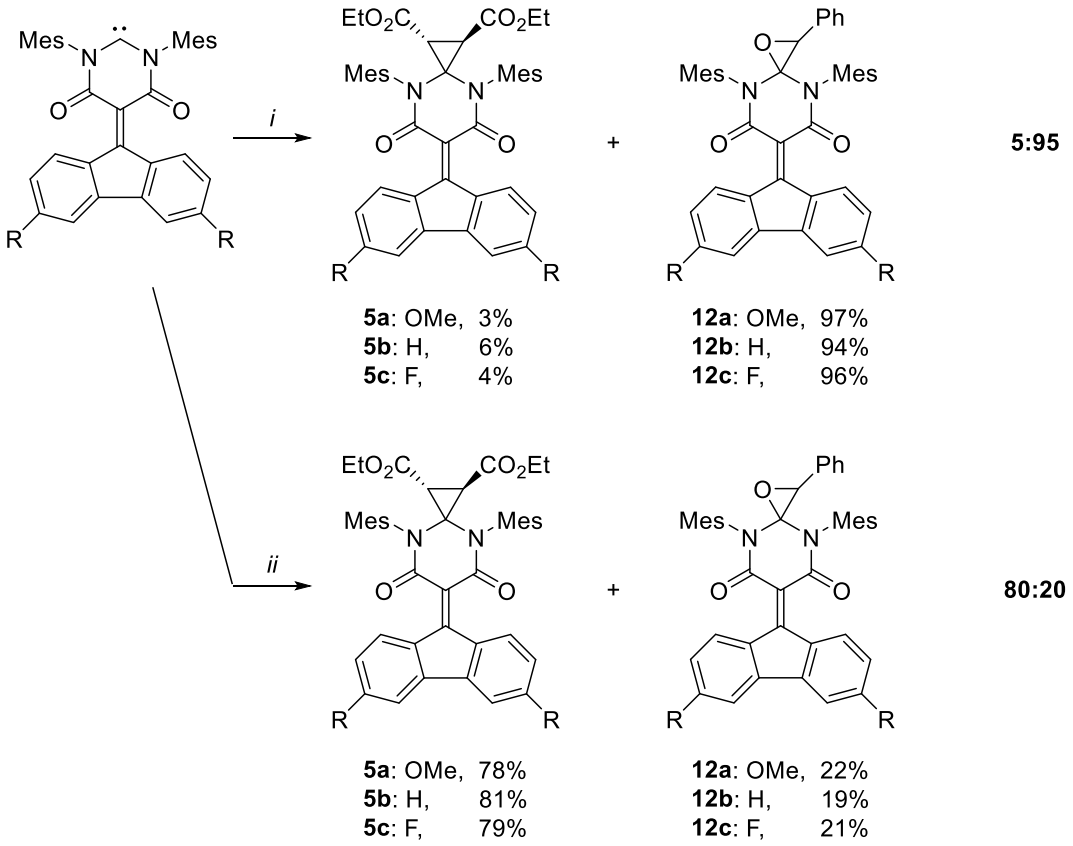
10a: OMe, 74%
10b: H, 76%
10c: F, 69%

11a: OMe, 65%
11b: H, 69%
11c: F, 63%

Scheme 3.5: Synthesis of styrenal cyclopropanes **9a-c**, **10a-c**, and **11a-c**. Conditions: (*i*) styrene, C_6H_6, 60 °C, 16 h. (*ii*) para-methoxystyrene, C_6H_6, 60 °C, 16 h. (*iii*) *para*-fluorostyrene, C_6H_6, 60 °C, 16 h. Isolated yields are indicated.

Based on the lack of significant differences in yield between differentially substituted carbenes and olefins, a competition experiment was performed (Scheme 3.6). To solutions of **3a-c** ($[3a\text{-}c]_o$ = 0.015 m*M*, C_6D_6) were added an equimolar mixture of benzaldehyde and diethyl fumarate (1.10 equiv.) and the reactions stirred at 25 °C for 30 m. Initially, the ratios of **5a-c** to **12a-c** were approximately 5:95 as measured by ^{1}H NMR spectroscopy. Upon heating the reaction mixtures at 80 °C for 16 h, the product ratios inverted to approximately 80:20 **5a-c** to **12a-c**, a result consistent with the parent diamidocarbene.[17] The slight differences in the ratios of differentially substituted carbenes did not trend with the electronic character of the substituted fluorenone, indicating a lack of significant influence of the remote substitution on carbene reactivity.

In addition to reactivity screening, computational methods were employed to shed further insight into the modulation of the electronic properties of the carbene; these results are summarized in Figure A10. The calculated HOMO-LUMO gaps ($\Delta H_{S\text{-}T}$) for N-phenyl analogues of **3a-c** were comparable across the differently substituted carbenes (67.80-65.35 kcal/mol). The similar $\Delta H_{S\text{-}T}$ values are indicative of carbenes with parallel reactivity in agreement with the experimental reactivity tests. The calculated geometries of the carbenes shed some light on these results; all of the carbene scaffolds adopt a bent geometry, placing the plane of the fluorene at angles ranging from 118.91° to 123.82° compared to the N-C-N plane (Figure A11). This cross-conjugated arrangement would necessarily limit the degree of electronic communication between the modifying substituents and the carbene.



Scheme 3.6: Competition experiment involving dimethyl fumarate and benzaldehyde. Conditions: (i) Diethyl fumarate, benzaldehyde, C_6D_6, 25 °C, 30 m; (ii) Diethyl fumarate, benzaldehyde, C_6D_6, 80 °C, 16 h. Ratios calculated via ^{1}H NMR.

3.3 CONCLUSION

Diamidocarbenes **3a-c** bearing electronically influencing substituents and their corresponding iridium complexes were synthesized and their electronic properties investigated. They were found to react in a manner similar to their parent DAC, including reactions with sulfur and carbon disulfide wherein the carbene reacted as a nucleophile. The carbenes also reacted as electrophiles, yielding ketenimines when exposed to isocyanides. Further reactivity matching the archetypal DAC towards electronically dissimilar olefins and benzaldehyde was observed, furnishing cyclopropanes and oxiranes.

However, the small difference observed in their direct electronic characterization did not carry over into a significant difference in their reactivity. The inability of the remote substitution to alter the mode or range of reactivity indicates a differentiation between primary and secondary tiers of electronic effect; the character substituents directly attached to the carbene nucleus are the primary method by which chemists can alter the character of the carbene, though these characteristics can be finely altered via changes in electron density in the rest of the carbene scaffold. These findings indicate that remote substitution of the carbene scaffold may have a role in ligand design to affect precise tuning of catalytic metals without changing the steric parameters of the carbene.

3.4 EXPERIMENTAL

General Considerations. Unless otherwise noted, all procedures were carried out under a nitrogen atmosphere using standard Schlenk techniques or in a nitrogen-filled glove box. Solvents were dried and degassed by a Vacuum Atmospheres Company solvent purification system and stored over 3Å molecular sieves in a nitrogen-filled glove box. Mesityl formamidine, 3,6-dimethoxyfluoren-9-one, and 3,6-dimethoxyfluoren-9-one were synthesized according to literature procedures.[31,32] Reagents exposed to the carbene were purified and dried immediately prior to use. Infrared spectra were gathered on a Perkin Elmer Spectrum BX FTIR spectrophotometer. High resolution mass spectra were obtained with a VG Analytical ZAB2-E instrument (CI or ESI). NMR spectra were acquired on a Varian Mercury or DirectDrive 400 MHz instrument; chemical shifts (δ) are provided in ppm and are referenced to the residual solvent peak or internal standard (^{1}H: $CDCl_3$, 7.26 ppm; C_6D_6, 7.14 ppm. ^{13}C: $CDCl_3$, 77.0 ppm; C_6D_6, 128.0 ppm. ^{19}F: CF_3COOH, -76.55 ppm). Melting points were obtained via on an Optimelt MPA100 Automated Melting Point System and are uncorrected.

Synthesis of di-tert-butyl 2-(3,6-dimethoxy-9H-fluoren-9-ylidene)malonate (1a). A 150 mL Schlenck flask was charged with 3,6-dimethoxyfluoren-9-one (5 g, 20.81 mmol, 1 equiv.), sodium hydride (1.05 g, 41.62 mmol, 2.1 equiv.), potassium *tert*-butoxide (5 mg), tetrahydrofuran (75 mL), and a stir bar. The flask was cooled to -78 °C in an acetone/dry ice bath and di-*tert*-butyl malonate (4.4 mL, 19.77 mmol, 0.95 equiv.) was added dropwise. The reaction was moved to a 0 C ice bath and stirred for 8 h. The reaction was then quenched with methanol, filtered through a pad of celite, and washed with 100 mL 0.1 *M* HCl. The volatiles were removed under reduced pressure and the resultant oil was purified via silica gel chromatography using 3:1 v/v hexanes/ethyl acetate as the eluent. Removal of the solvent under reduced pressure afforded the desired product as a semisolid (5.29g, 12.07 mmol, 58% yield). ^{1}H NMR (C_6D_6, 399.68 MHz): δ 3.76 (s, 3H), 1.42 (s, 9H), 7.07 (m, 2H), 7.25 (m, 2H), 7.44 (m, 2H). ^{13}C NMR (C_6D_6, 100.50 MHz): δ 54.07, 110.89, 115.8, 127.77, 130.06, 141.38, 160.18, 161.07, 166.42,. IR ν_{CO} = 1755.2, 1730.1 cm^{-1}. HRMS (CI): $[M+H]^+$ calcd. for $C_{26}H_{30}O_6$ 439.52074, found 439.52064.

Synthesis of di-tert-butyl 2-(9H-fluoren-9-ylidene)malonate (1b). A 150 mL Schlenck flask was charged with fluorenone (5 g, 27.74 mmol, 1 equiv.), sodium hydride (1.40 g, 55.49 mmol, 2.1 equiv.), potassium *tert*-butoxide (5 mg), tetrahydrofuran (75 mL), and a stir bar. The flask was cooled to -78 °C in an acetone/dry ice bath and di-*tert*-butyl malonate (5.9 mL, 26.36 mmol, 0.95 equiv.) was added dropwise. The reaction was moved to a 0 °C ice bath and stirred for 8 h. The reaction was then quenched with methanol, filtered through a pad of celite, and washed with 100 mL 0.1 *M* HCl. The volatiles were removed under reduced pressure and the resultant oil was purified via silica gel chromatography using 4:1 v/v hexanes/ethyl acetate as the eluent. Removal of the solvent under reduced pressure afforded the desired product as a semisolid (6.72 g, 17.75 mmol, 64% yield). ^{1}H NMR (C_6D_6, 399.68 MHz): δ 1.39 (s, 9H), 7.54 (m, 5H). ^{13}C NMR (C_6D_6,

100.50 MHz): δ 112.6, 120.49, 124.63, 127.6, 139.09, 139.82, 158.96, 167.25. IR ν_{CO} = 1749.9, 1732.7 cm^{-1}. HRMS (CI): $[M+H]^+$ calcd. for $C_{24}H_{26}O_4$ 379.46878, found 379.46868.

Synthesis of di-tert-butyl 2-(3,6-difluoro-9H-fluoren-9-ylidene)malonate (1c). A 150 mL Schlenck flask was charged with 3,6-difluorofluoren-9-one (5 g, 23.12 mmol, 1 equiv.), sodium hydride (1.16 g, 46.26 mmol, 2.1 equiv.), potassium *tert*-butoxide (5 mg,), tetrahydrofuran (75 mL), and a stir bar. The flask was cooled to -78 °C in an acetone/dry ice bath and di-*tert*-butyl malonate (4.8 mL, 21.97 mmol, 0.95 equiv.) was added dropwise. The reaction was moved to a 0 °C ice bath and stirred for 8 h. The reaction was then quenched with methanol, filtered through a pad of celite, and washed with 100 mL 0.1 *M* HCl. The volatiles were removed under reduced pressure and the resultant oil was purified via silica gel chromatography using 3:1 v/v hexanes/ethyl acetate as the eluent. Removal of the solvent under reduced pressure afforded the desired product as a semisolid (6.80 g, 16.41 mmol, 71% yield). ^{1}H NMR (C_6D_6, 399.68 MHz): δ 1.55 (s, 9H), 7.36 (d, 2H), 7.39 (d, 4H). ^{13}C NMR (C_6D_6, 100.50 MHz): δ 111.54, 116.12, 128.1, 129.37, 141.13, 159.83, 166.19, 167.06. ^{19}F NMR (C_6D_6, 282.41 MHz): δ -128.17. IR ν_{CO} = 1749.4, 1729.7 cm^{-1}. HRMS (CI): $[M+H]^+$ calcd. for $C_{24}H_{24}O_4F_2$ 415.4497, found 415.4496.

Synthesis of 2-chloro-5-(3,6-dimethoxy-9H-fluoren-9-ylidene)-1,3-dimesityldihydropyrimidine-4,6(1H,5H)-dione (2a). To a stirring solution of **1a** (2 g, 4.56 mmol, 1 equiv.) in dichloromethane (50 mL) in a 0 °C ice bath was added trifluoroacetic acid (0.7 mL, 9.12 mmol, 2.0 equiv.) and the reaction stirred for 1 h. The volatiles were removed *in vacuo* to afford a brown oil and excess thionyl chloride (30 mL) was added. This mixture was warmed to 25 °C and stirred for 4 h, after which the volatiles were removed under reduced pressure. The resultant mixture was dissolved in dichloromethane (30 mL), cooled to 0 °C in an ice bath and a solution of N,N'-

dimesitylformamidine (1.4 g, 5.01 mmol, 1.1 equiv.) and pyridine (0.71 mL, 9.57 mmol, 2.1 equiv.) in dichloromethane (20 mL) was added. The reaction was warmed to 25 °C stirred for 16 h. The solution was concentrated under reduced pressure, treated with 10 mL of pentane, and filtered through a pad of celite. The solvent was removed *in vacuo* and the solid recrystallized from toluene to afford the desired product as an off-white solid (1.33 g, 2.19 mmol, 48% yield). ^{1}H NMR (C_6D_6, 399.68 MHz): δ 2.16 (s, 12H), 2.10 (s, 6H), 3.83 (s, 3H), 6.80 (s, 4H), 6.11 (s, 1H), 7.09 (m, 2H), 7.18 (m, 2H), 7.52 (m, 2H). ^{13}C NMR (C_6D_6, 100.50 MHz): δ 18.47, 20.27, 54.3, 90.46, 112.82, 116.86, 127.22, 128.76, 128.91, 133.43, 135.23, 137.06, 140.61, 160.31, 160.92, 170.02. IR ν_{CO} = 1680.4, 1696.4 cm^{-1}. HRMS (CI): $[M+H]^+$ calcd. for $C_{37}H_{35}N_2O_4Cl$ 607.66159, found 607.66109. Anal. calcd. for $C_{37}H_{35}N_2O_4Cl$: C, 73.20; H, 5.81; N, 4.61; found C, 72.95; H, 6.10; N, 4.39.

Synthesis of 2-chloro-5-(9H-fluoren-9-ylidene)-1,3-dimesityldihydropyrimidine-4,6(1H,5H)-dione (2b). To a stirring solution of **1b** (2 g, 5.28 mmol, 1 equiv.) in dichloromethane (50 mL) in a 0 °C ice bath was added trifluoroacetic acid (0.81 mL, 10.56 mmol, 2.0 equiv.) and the reaction stirred for 1 h. The volatiles were removed *in vacuo* to afford a brown oil and excess thionyl chloride (30 mL) was added. This mixture was warmed to 25 °C and stirred for 4 h, after which the volatiles were removed under reduced pressure. The resultant mixture was dissolved in dichloromethane (30 mL), cooled to 0 °C in an ice bath and a solution of N,N'-dimesitylformamidine (1.63 g, 5.81 mmol, 1.1 equiv.) and pyridine (0.89 mL, 11.1 mmol, 2.1 equiv.) in dichloromethane (20 mL) was added. The reaction was warmed to 25 °C stirred for 16 h. The solution was concentrated under reduced pressure, treated with 10 mL of pentane, and filtered through a pad of celite. The solvent was removed *in vacuo* and the solid recrystallized from toluene to afford the desired product as an off-white solid (1.39 g, 2.534 mmol, 53% yield). ^{1}H NMR (C_6D_6, 399.68 MHz): δ 2.16 (s, 6H), 1.40 (s, 9H),

2.25 (s, 12H), 6.77 (s, 4H), 6.92 (s, 1H), 7.52 (m, 5H). ^{13}C NMR (C_6D_6, 100.50 MHz): δ 17.79, 21.79, 91.13, 111.8, 122.07, 124.69, 127.93, 128.82, 134.09, 134.58, 134.81, 136.75, 138.97, 160.34, 168.91. IR ν_{CO} = 1669, 1697.4 cm^{-1}. HRMS (CI): $[M+H]^+$ calcd. for $C_{35}H_{31}N_2O_2Cl$ 547.60963, found 547.60953. Anal. calcd. for $C_{35}H_{31}N_2O_2Cl$: C, 76.84; H, 5.71; N, 5.12; found C, 76.72; H, 5.97; N, 4.99.

Synthesis of 2-chloro-5-(3,6-difluoro-9H-fluoren-9-ylidene)-1,3-dimesityldihydropyrimidine-4,6(1H,5H)-dione (2c). To a stirring solution of **1c** (2 g, 4.83 mmol, 1 equiv.) in dichloromethane (50 mL) in a 0 °C ice bath was added trifluoroacetic acid (0.74 mL, 9.65 mmol, 2.0 equiv.) and the reaction stirred for 1 h. The volatiles were removed *in vacuo* to afford a brown oil and excess thionyl chloride (30 mL) was added. This mixture was warmed to 25 °C and stirred for 4 h, after which the volatiles were removed under reduced pressure. The resultant mixture was dissolved in dichloromethane (30 mL), cooled to 0 °C in an ice bath and a solution of N,N'-dimesitylformamidine (1.5 g, 5.31 mmol, 1.1 equiv.) and pyridine (0.82 mL, 10.1 mmol, 2.1 equiv.) in dichloromethane (20 mL) was added. The reaction was warmed to 25 °C stirred for 16 h. The solution was concentrated under reduced pressure, treated with 10 mL of pentane, and filtered through a pad of celite. The solvent was removed *in vacuo* and the solid recrystallized from toluene to afford the desired product as an off-white solid (1.35 g, 2.32 mmol, 44% yield). ^{1}H NMR (C_6D_6, 399.68 MHz): δ 2.00 (s, 6H), 1.41 (s, 9H), 2.24 (s, 12H), 6.78 (s, 4H), 6.94 (s, 1H), 7.26 (d, 2H), 7.48 (d, 4H). ^{13}C NMR (C_6D_6, 100.50 MHz): δ 19.05, 19.96, 90.39 111.1, 115.52, 128.92, 129.19, 129.31, 131.77, 135.04, 135.15, 141.22, 160.84, 164.44, 169.4. ^{19}F NMR (C_6D_6, 282.41 MHz): δ -128.21. IR ν_{CO} = 1675.4, 1698.9 cm^{-1}. HRMS (CI): $[M+H]^+$ calcd. for $C_{35}H_{29}N_2O_2F_2Cl$ 583.59055, found 583.59075. Anal. calcd. for $C_{35}H_{29}N_2O_2F_2Cl$: C, 72.10; H, 5.01; N, 4.80; found C, 72.01; H, 5.32; N, 4.71.

Synthesis of 5-(3,6-dimethoxy-9H-fluoren-9-ylidene)-1,3-dimesityl-4,6-dioxo-3,4,5,6-tetrahydropyrimidin-1-ium-2-ide (3a). A 40 mL vial was charged with **2a** (250 mg, 0.41 mmol, 1 equiv.), sodium hexamethyldisilazane (83 mg, 0.44 mmol, 1.1 equiv.) benzene (35 mL), and a stir bar. After stirring at 25 °C for 1 h, the cloudy solution was filtered through a plug of celite and the volatiles removed *in vacuo*. The resultant brown solid was triturated with cold pentane until the solvent no longer appeared brown, affording the desired product as a light yellow solid (162 mg, 0.284 mmol, 69% yield). ^{1}H NMR (C_6D_6, 399.68 MHz): δ 2.20 (s, 12H), 2.18 (s, 6H), 3.78 (s, 3H), 6.68 (s, 4H), 6.94 (m, 2H), 7.31 (m, 2H), 7.48 (m, 2H). ^{13}C NMR (C_6D_6, 100.50 MHz): δ 17.74, 21.22, 54.74, 112.09, 114.92, 126.95, 127.66, 130.44, 132.85, 134.78, 136.76, 140.31, 159.5, 160.64, 169.62, 275.68. IR ν_{CO} = 1680.1, 1691.6 cm^{-1}. HRMS (CI): $[M+H]^+$ calcd. for $C_{37}H_{34}N_2O_4$ 571.6848, found 571.6844. Anal. calcd. for $C_{37}H_{34}N_2O_4$: C, 77.87; H, 6.01; N, 4.91; found C, 77.76; H, 6.37; N, 4.76.

Synthesis of 5-(9H-fluoren-9-ylidene)-1,3-dimesityl-4,6-dioxo-3,4,5,6-tetrahydropyrimidin-1-ium-2-ide (3b). A 40 mL vial was charged with **2b** (250 mg, 0.46 mmol, 1 equiv.), sodium hexamethyldisilazane (92 mg, 0.52 mmol, 1.1 equiv.) benzene (35 mL), and a stir bar. After stirring at 25 °C for 1 h, the cloudy solution was filtered through a plug of celite and the volatiles removed *in vacuo*. The resultant brown solid was triturated with cold pentane until the solvent no longer appeared brown, affording the desired product as a light yellow solid (130 mg, 0.255 mmol, 62% yield). ^{1}H NMR (C_6D_6, 399.68 MHz): δ 2.16 (s, 12H), 2.17 (s, 6H), 6.87 (s, 4H), 7.38 (m, 5H). ^{13}C NMR (C_6D_6, 100.50 MHz): δ 18.54, 20.3, 112.59, 121.09, 124.1, 126.8, 128.41, 132.11, 134.85, 135.38, 137.69, 139, 160.53, 171.03, 277.31. IR ν_{CO} = 1674.8, 1694 cm^{-1}. HRMS (CI): $[M+H]^+$ calcd. for $C_{35}H_{30}N_2O_2$ 511.63284, found 511.63244. Anal. calcd. for $C_{35}H_{28}N_2O_2F_2$: C, 82.33; H, 5.92; N, 5.49; found C, 82.05; H, 6.23; N, 5.28.

Synthesis of 5-(3,6-difluoro-9H-fluoren-9-ylidene)-1,3-dimesityl-4,6-dioxo-3,4,5,6-tetrahydropyrimidin-1-ium-2-ide (3c). A 40 mL vial was charged with **2c** (250 mg, 0.43 mmol, 1 equiv.), sodium hexamethyldisilazane (86 mg, 0.48 mmol, 1.1 equiv.) benzene (35 mL), and a stir bar. After stirring at 25 °C for 1 h, the cloudy solution was filtered through a plug of celite and the volatiles removed *in vacuo*. The resultant brown solid was triturated with cold pentane until the solvent no longer appeared brown, affording the desired product as a light yellow solid (146 mg, 0.268 mmol, 65% yield). ^{1}H NMR (C_6D_6, 399.68 MHz): δ 2.02 (s, 6H), 2.14 (s, 12H), 6.74 (s, 4H), 7.28 (d, 2H), 7.43 (d, 4H). ^{13}C NMR (C_6D_6, 100.50 MHz): δ 21.13, 112.18, 115.7, 127.46, 128.47, 130.65, 131.94, 134.46, 136.48, 141.89, 16.9, 161.16, 164.3, 169.38, 278.52. ^{19}F NMR (C_6D_6, 282.41 MHz): δ -128.18. IR ν_{CO} = 1668.5, 1691.8 cm^{-1}. HRMS (CI): $[M+H]^+$ calcd. for $C_{35}H_{28}N_2O_2F_2$ 547.61376, found 547.61406. Anal. calcd. for $C_{35}H_{28}N_2O_2F_2$: C, 76.91; H, 5.16; N, 5.12; found C, C, 76.84; H, 5.21; N, 5.09.

Synthesis of 5-(3,6-dimethoxy-9H-fluoren-9-ylidene)-1,3-dimesityl-4,6-dioxo-3,4,5,6-tetrahydropyrimidin-1-ium-2-ide-iridium(I) (1,5-cyclooctadiene) chloride (3a-Ir(COD)Cl). To a 20 mL vial was added **3a** (50 mg, 0.088 mmol, 1 equiv.), $[Ir(COD)Cl]_2$ (27 mg, 0.097 mmol, 0.45 equiv.), benzene (15 mL), and a stir bar. The vial was wrapped in aluminum foil and allowed to stir 16 h at 25 °C, after which the solvent was removed under reduced pressure. The orange solid was dissolved in benzene, filtered through a silica plug, and freeze-dried to afford the desired product as an orange powder (44 mg, 0.048 mmol, 55% yield). ^{1}H NMR (C_6D_6, 399.68 MHz): δ 2.18 (m, 8H), 2.02 (s, 6H), 2.26 (s, 12H), 3.02 (s, 2H), 3.77 (s, 3H), 4.43 (s, 2H), 6.86 (s, 4H), 7.09 (m, 2H), 7.31 (m, 2H), 7.58 (m, 2H). ^{13}C NMR (C_6D_6, 100.50 MHz): δ 17.87, 20.22, 54.01, 54.05, 112.99, 228.72116.15, 126.83, 128.52, 129.03, 130.31, 133.12, 134.07, 135.85, 139.62, 141.61,

160.46, 160.98, 169.31. IR ν_{CO} = 1668.3, 1688.3 cm^{-1}. HRMS (CI): $[M+H]^+$ calcd. for $C_{45}H_{46}N_2O_4ClIr$ 905.79513, found 905.79563.

Synthesis of 5-(9H-fluoren-9-ylidene)-1,3-dimesityl-4,6-dioxo-3,4,5,6-tetrahydropyrimidin-1-ium-2-ide-iridium(I) (1,5-cyclooctadiene) chloride (3b-Ir(COD)Cl). To a 20 mL vial was added **3b** (50 mg, 0.098 mmol, 1 equiv.), $[Ir(COD)Cl]_2$ (30 mg, 0.11 mmol, 0.45 equiv.), benzene (15 mL), and a stir bar. The vial was wrapped in aluminum foil and allowed to stir 16 h at 25 °C, after which the solvent was removed under reduced pressure. The orange solid was dissolved in benzene, filtered through a silica plug, and freeze-dried to afford the desired product as an orange powder (46 mg, 0.054 mmol, 62% yield). ^{1}H NMR (C_6D_6, 399.68 MHz): δ 2.19 (s, 6H), 2.21 (m, 8H), 2.18 (s, 12H), 3.12 (s, 2H), 4.60 (s, 2H), 6.77 (s, 4H), 7.49 (m, 5H). ^{13}C NMR (C_6D_6, 100.50 MHz): δ 17.54, 21.6, 53.82, 111.37, 231.09122.14, 123.11, 126.79, 127.32, 129.94, 132.29, 135.3, 136, 139.23, 140.17, 140.64, 159.84, 168.94. IR ν_{CO} = 1676.7, 1694.8 cm^{-1}. HRMS (CI): $[M+H]^+$ calcd. for $C_{43}H_{42}N_2O_2ClIr$ 845.74317, found 845.74267.

Synthesis of 5-(3,6-difluoro-9H-fluoren-9-ylidene)-1,3-dimesityl-4,6-dioxo-3,4,5,6-tetrahydropyrimidin-1-ium-2-ide-iridium(I) (1,5-cyclooctadiene) chloride (3c-Ir(COD)Cl). To a 20 mL vial was added **3c** (50 mg, 0.092 mmol, 1 equiv.), $[Ir(COD)Cl]_2$ (28 mg, 0.10 mmol, 0.45 equiv.), benzene (15 mL), and a stir bar. The vial was wrapped in aluminum foil and allowed to stir 16 h at 25 °C, after which the solvent was removed under reduced pressure. The orange solid was dissolved in benzene, filtered through a silica plug, and freeze-dried to afford the desired product as an orange powder (46 mg, 0.052 mmol, 59% yield). ^{1}H NMR (C_6D_6, 399.68 MHz): δ 2.06 (s, 6H), 2.21 (s, 12H), 2.23 (m, 8H), 3.00 (s, 2H), 4.50 (s, 2H), 6.73 (s, 4H), 7.35 (d, 2H), 7.48 (d, 4H). ^{13}C NMR (C_6D_6, 100.50 MHz): δ 18.33, 21.1, 56.1, 112.51, 232.49114.84, 127.16, 127.35, 130.6, 130.73, 132.61, 134.58, 136.75, 140.3, 141.1, 159.35, 164.65, 169.58. ^{19}F NMR

(C_6D_6, 282.41 MHz): δ -128.18. IR ν_{CO} 1677.4, 1696.9 = cm^{-1}. HRMS (CI): $[M+H]^+$ calcd. for $C_{43}H_{40}N_2O_2F_2ClIr$ 881.72409, found 881.72389.

Synthesis of 5-(3,6-dimethoxy-9H-fluoren-9-ylidene)-1,3-dimesityl-4,6-dioxo-3,4,5,6-tetrahydropyrimidin-1-ium-2-ide-iridium(I) (dicarbonyl) chloride (3a-Ir(CO)$_2$Cl). An 8 mL vial was charged with **3a-Ir(COD)Cl** (25 mg, 0.028 mmol, 1 equiv.), and dichloromethane (5 mL). Carbon monoxide was bubbled through this solution at 25 °C via a needle until the solvent had evaporated (approximately 10 minutes). The resultant tacky solid was washed with cold pentane and dried under reduced pressure to afford the desired product as a dusky yellow solid (34 mg, 0.040 mmol, 97% yield). ^1H NMR (C_6D_6, 399.68 MHz): δ 2.22 (s, 12H), 2.09 (s, 6H), 3.80 (s, 3H), 6.71 (s, 4H), 6.92 (m, 2H), 7.23 (m, 2H), 7.41 (m, 2H). ^{13}C NMR (C_6D_6, 100.50 MHz): δ 18.51, 20.81, 54.07, 111.4, 216.84116.8, 127.98, 129.14, 130.02, 133.89, 135.58, 136.15, 140.79, 159.17, 160.69, 170.3180.76, 190.29,. IR ν_{CO} = 2029.9, 2055.4 cm^{-1}. HRMS (CI): $[M+H]^+$ calcd. for $C_{39}H_{34}N_2O_6ClIr$ 853.63445, found 853.63425.

Synthesis of 5-(9H-fluoren-9-ylidene)-1,3-dimesityl-4,6-dioxo-3,4,5,6-tetrahydropyrimidin-1-ium-2-ide-iridium(I) (dicarbonyl) chloride (3b-Ir(CO)$_2$Cl). An 8 mL vial was charged with **3b-Ir(COD)Cl** (25 mg, 0.030 mmol, 1 equiv.), and dichloromethane (5 mL). Carbon monoxide was bubbled through this solution at 25 °C via a needle until the solvent had evaporated (approximately 10 minutes). The resultant tacky solid was washed with cold pentane and dried under reduced pressure to afford the desired product as a dusky yellow solid (36 mg, 0.045 mmol, 98% yield). ^1H NMR (C_6D_6, 399.68 MHz): δ 2.10 (s, 6H), 2.23 (s, 12H), 6.73 (s, 4H), 7.45 (m, 5H). ^{13}C NMR (C_6D_6, 100.50 MHz): δ 17.58, 21.66, 110.83, 120.75, 124.31, 126.78, 127.95, 132.11, 133.79, 135.15, 137.03, 140.42, 159.5, 168.79, 179.26, 190.08, 222.15. IR ν_{CO} = 2056.1, 2030.8 cm^{-1}. HRMS (CI): $[M+H]^+$ calcd. for $C_{37}H_{30}N_2O_4ClIr$ 793.58249, found 793.58269.

Synthesis of 5-(3,6-difluoro-9H-fluoren-9-ylidene)-1,3-dimesityl-4,6-dioxo-3,4,5,6-tetrahydropyrimidin-1-ium-2-ide-iridium(I) (dicarbonyl) chloride (3c-Ir(CO)$_2$Cl). An 8 mL vial was charged with **3c-Ir(COD)Cl** (25 mg, 0.028 mmol, 1 equiv.), and dichloromethane (5 mL). Carbon monoxide was bubbled through this solution at 25 °C via a needle until the solvent had evaporated (approximately 10 minutes). The resultant tacky solid was washed with cold pentane and dried under reduced pressure to afford the desired product as a dusky yellow solid (35 mg, 0.042 mmol, 98% yield). ^{1}H NMR (C_6D_6, 399.68 MHz): δ 2.11 (s, 6H), 2.24 (s, 12H), 6.74 (s, 4H), 7.34 (d, 2H), 7.57 (d, 4H). ^{13}C NMR (C_6D_6, 100.50 MHz): δ 16.76, 20.72, 112.01, 115.27, 127.52, 129.02, 131.1, 132.77, 134.59, 135.58, 140.17, 160.69, 164.95, 170, 179.1, 190.75, 222.15. ^{19}F NMR (C_6D_6, 282.41 MHz): δ -128.21. IR ν_{CO} = 2031.8, 2056.9 cm^{-1}. HRMS (CI): $[M+H]^+$ calcd. for $C_{37}H_{28}N_2O_4F_2ClIr$ 829.56341, found 829.56301.

Synthesis of 5-(3,6-dimethoxy-9H-fluoren-9-ylidene)-1,3-dimesityl-2-thioxodihydropyrimidine-4,6(1H,5H)-dione (3a-S). An 8 mL vial was charged with **3a** (25 mg, 0.044 mmol, 1 equiv.), benzene (5 mL), elemental sulfur (2 mg, 0.048 mmol, 1.05 equiv.) and a stir bar. The mixture was stirred for 30 m at 25 °C, after which the solvent was removed *in vacuo*. The crude product was dissolved in 5 mL of toluene and precipitated by slow addition of approx.. 15 mL of cold hexanes to afford a yellow solid. (22 mg, 0.036 mmol, 88% yield). ^{1}H NMR (C_6D_6, 399.68 MHz): δ 2.13 (s, 6H), 2.19 (s, 12H), 3.81 (s, 3H), 6.68 (s, 4H), 7.10 (m, 2H), 7.15 (m, 2H), 7.46 (m, 2H). ^{13}C NMR (C_6D_6, 100.50 MHz): δ 18.51, 20.73, 55.68, 112.62, 115.63, 128.16, 128.2, 129.76, 133.79, 135.13, 135.53, 139.97, 160.4, 160.76, 170.17, 171.24. IR ν_{CO} = 1670.8, 1701.1 cm^{-1}. HRMS (CI): $[M+H]^+$ calcd. for $C_{37}H_{34}N_2O_4S$ 603.6555, found 603.6558.

Synthesis of 5-(9H-fluoren-9-ylidene)-1,3-dimesityl-2-thioxodihydropyrimidine-4,6(1H,5H)-dione (3b-S). An 8 mL vial was charged with **3b**

(25 mg, 0.049 mmol, 1 equiv.), benzene (5 mL), elemental sulfur (2 mg, 0.054 mmol, 1.05 equiv.) and a stir bar. The mixture was stirred for 30 m at 25 °C, after which the solvent was removed *in vacuo*. The crude product was dissolved in 5 mL of toluene and precipitated by slow addition of approx.. 15 mL of cold hexanes to afford a yellow solid. (23 mg, 0.042 mmol, 91% yield). ^{1}H NMR (C_6D_6, 399.68 MHz): δ 2.15 (s, 12H), 2.09 (s, 6H), 6.68 (s, 4H), 7.45 (m, 5H). ^{13}C NMR (C_6D_6, 100.50 MHz): δ 17.58, 20.97, 111.8, 121.48, 124.06, 128.5, 128.84, 133.55, 135.56, 136.68, 138.21, 138.76, 161.17, 169.27, 169.72,. IR ν_{CO} = 1671.6, 1701.9 cm^{-1}. HRMS (CI): $[M+H]^+$ calcd. for $C_{35}H_{30}N_2O_2S$ 543.60354, found 543.60384.

Synthesis of 5-(3,6-difluoro-9H-fluoren-9-ylidene)-1,3-dimesityl-2-thioxodihydropyrimidine-4,6(1H,5H)-dione (3c-S). An 8 mL vial was charged with **3c** (25 mg, 0.046 mmol, 1 equiv.), benzene (5 mL), elemental sulfur (2 mg, 0.051 mmol, 1.05 equiv.) and a stir bar. The mixture was stirred for 30 m at 25 °C, after which the solvent was removed *in vacuo*. The crude product was dissolved in 5 mL of toluene and precipitated by slow addition of approx.. 15 mL of cold hexanes to afford a yellow solid. (23 mg, 0.039 mmol, 90% yield). ^{1}H NMR (C_6D_6, 399.68 MHz): δ 2.17 (s, 6H), 2.3 (s, 12H), 6.71 (s, 4H), 7.34 (d, 2H), 7.54 (d, 4H). ^{13}C NMR (C_6D_6, 100.50 MHz): δ 17.87, 20.84, 111.7, 115.06, 127.95, 128.76, 130.78, 133.01, 136.17, 136.35, 142.01, 159.84, 164.25, 170.00, 170.26. ^{19}F NMR (C_6D_6, 282.41 MHz): δ -128.22. IR ν_{CO} = 1674.6, 1691.1 cm^{-1}. HRMS (CI): $[M+H]^+$ calcd. for $C_{35}H_{28}N_2O_2SF_2$ 579.58446, found 579.58496.

Synthesis of 5-(3,6-dimethoxy-9H-fluoren-9-ylidene)-1,3-dimesityl-4,6-dioxo-3,4,5,6-tetrahydropyrimidin-1-ium-2-carbodithioate (3a-CS_2). An 8 mL vial was charged with **3a** (25 mg, 0.044 mmol, 1 equiv.), benzene (5 mL), carbon disulfide (3 µL, 0.048 mmol, 1.05 equiv.) and a stir bar. The mixture was stirred for 30 m at 25 °C before adding pentane (10 mL), the resultant mixture was filtered and then dried under reduced

pressure to afford the desired product as an orange solid. (22.6 mg, 0.039 mmol, 95% yield). ^{1}H NMR (C_6D_6, 399.68 MHz): δ 2.20 (s, 6H), 2.12 (s, 12H), 3.78 (s, 3H), 6.69 (s, 4H), 7.05 (m, 2H), 7.18 (m, 2H), 7.44 (m, 2H). ^{13}C NMR (C_6D_6, 100.50 MHz): δ 21.82, 55.2, 112.37, 116.93, 128.35, 128.36, 130.6, 132.82, 134.66, 135.64, 139.88, 159.41, 16.8, 160.86, 170.21, 177.71, 218.88. IR ν_{CS} = 1053.2, 1097.7 cm^{-1}, ν_{CO} = 1674.6, 1689.9 cm^{-1}. HRMS (CI): $[M+H]^+$ calcd. for $C_{38}H_{34}N_2O_4S_2$ 647.6369, found 647.6369.

Synthesis of 5-(9H-fluoren-9-ylidene)-1,3-dimesityl-4,6-dioxo-3,4,5,6-tetrahydropyrimidin-1-ium-2-carbodithioate (3b-CS$_2$). An 8 mL vial was charged with **3b** (25 mg, 0.049 mmol, 1 equiv.), benzene (5 mL), carbon disulfide (3 µL, 0.54 mmol, 1.05 equiv.) and a stir bar. The mixture was stirred for 30 m at 25 °C before adding pentane (10 mL), the resultant mixture was filtered and then dried under reduced pressure to afford the desired product as an orange solid. (25 mg, 0.042 mmol, 92% yield). ^{1}H NMR (C_6D_6, 399.68 MHz): δ 2.05 (s, 6H), 2.20 (s, 12H), 6.77 (s, 4H), 7.51 (m, 5H). ^{13}C NMR (C_6D_6, 100.50 MHz): δ 19.15, 21.69, 111.57, 120.5, 124.8, 127.05, 129.16, 131.92, 134.8, 135.73, 139.16, 140.53, 160.21, 170.66, 176.67, 220.86. IR ν_{CS} = 1060.9 , 1093.4 cm^{-1}, ν_{CO} = 1674.4, 1691.9 cm^{-1}. HRMS (CI): $[M+H]^+$ calcd. for $C_{36}H_{30}N_2O_2S_2$ 587.58494, found 587.58504.

Synthesis of 5-(3,6-difluoro-9H-fluoren-9-ylidene)-1,3-dimesityl-4,6-dioxo-3,4,5,6-tetrahydropyrimidin-1-ium-2-carbodithioate (3c-CS$_2$). An 8 mL vial was charged with **3c** (25 mg, 0.046 mmol, 1 equiv.), benzene (5 mL), carbon disulfide (3 µL, 0.51 mmol, 1.05 equiv.) and a stir bar. The mixture was stirred for 30 m at 25 °C before adding pentane (10 mL), the resultant mixture was filtered and then dried under reduced pressure to afford the desired product as an orange solid. (26 mg, 0.042 mmol, 98% yield). ^{1}H NMR (C_6D_6, 399.68 MHz): δ 2.08 (s, 6H), 2.16 (s, 12H), 6.72 (s, 4H), 7.37 (d, 2H), 7.54 (d, 4H). ^{13}C NMR (C_6D_6, 100.50 MHz): δ 18.81, 21.41, 112.56, 114.87, 127.53,

128.97, 129.03, 133.91, 135.02, 136.88, 140.99, 161.14, 164.85, 170.69, 176.47, 220.76. ^{19}F NMR (C_6D_6, 282.41 MHz): δ -128.22. IR ν_{CS} = 1102, 1062.4 cm^{-1}, ν_{CO} = 1669.8, 1696.2 cm^{-1}. HRMS (CI): $[M+H]^+$ calcd. for $C_{36}H_{28}N_2O_2S_2F_2$ 623.56586, found 623.56626.

Synthesis of 2-((butylimino)methylene)-5-(3,6-dimethoxy-9H-fluoren-9-ylidene)-1,3-dimesityldihydropyrimidine-4,6(1H,5H)-dione (4a). An 8 mL vial was charged with **3a** (25 mg, 0.044 mmol, 1 equiv.), benzene (5 mL), n-Butyl isocyanide (5 µL, 0.048 mmol, 1.05 equiv.) and a stir bar. The reaction was stirred for 1 h at 25 °C before the volatiles were removed *in vacuo* to afford the desired product as a yellow solid. (24 mg, 0.035 mmol, 86% yield). ^{1}H NMR (C_6D_6, 399.68 MHz): δ 0.49-0.67 (m, 7H), 2.03 (s, 6H), 2.17 (s, 12H), 2.61 (m, 2H), 3.86 (s, 3H), 6.79 (s, 4H), 6.93 (m, 2H), 7.33 (m, 2H), 7.5 (m, 2H). ^{13}C NMR (C_6D_6, 100.50 MHz): δ 14.68, 18.47, 19.39, 21.17, 23.48, 56.23, 58.31, 111.03, 110.18, 115.71, 126.76, 128.89, 130.45, 132.03, 136.17, 137.08, 139.85, 159.68, 160.04, 169.44, 200.98. IR ν_{CN} = 1983.9 cm^{-1}, ν_{CO} = 1679.4, 1697.6 cm^{-1}. HRMS (CI): $[M+H]^+$ calcd. for $C_{42}H_{43}N_3O_4$ 654.81646, found 654.81696.

Synthesis of 2-((butylimino)methylene)-5-(9H-fluoren-9-ylidene)-1,3-dimesityldihydropyrimidine-4,6(1H,5H)-dione (4b). An 8 mL vial was charged with **3b** (25 mg, 0.049 mmol, 1 equiv.), benzene (5 mL), n-Butyl isocyanide (6 µL, 0.054 mmol, 1.05 equiv.) and a stir bar. The reaction was stirred for 1 h at 25 °C before the volatiles were removed *in vacuo* to afford the desired product as a yellow solid. (23 mg, 0.038 mmol, 83% yield). ^{1}H NMR (C_6D_6, 399.68 MHz): δ 0.49-0.67 (m, 7H), 2.04 (s, 6H), 2.12 (s, 12H), 2.64 (m, 2H), 6.72 (s, 4H), 7.46 (m, 5H). ^{13}C NMR (C_6D_6, 100.50 MHz): δ 14.82, 18.65, 19, 19.85, 23.27, 58.48, 112.96, 110.94, 121.85, 123.41, 126.77, 129.22, 133.65, 135.2, 135.93, 138.15, 140.3, 159.02, 170.69, 200.29. IR ν_{CN} = 1982.2 cm^{-1}, ν_{CO} = 1674.1, 1698.2 cm^{-1}. HRMS (CI): $[M+H]^+$ calcd. for $C_{40}H_{39}N_3O_2$ 594.7645, found 594.765.

Synthesis of 2-((butylimino)methylene)-5-(3,6-difluoro-9H-fluoren-9-ylidene)-1,3-dimesityldihydropyrimidine-4,6(1H,5H)-dione (4c). An 8 mL vial was charged with **3c** (25 mg, 0.046 mmol, 1 equiv.), benzene (5 mL), n-Butyl isocyanide (5 µL, 0.051 mmol, 1.05 equiv.) and a stir bar. The reaction was stirred for 1 h at 25 °C before the volatiles were removed *in vacuo* to afford the desired product as a yellow solid. (25 mg, 0.039 mmol, 91% yield). ^{1}H NMR (C_6D_6, 399.68 MHz): δ 0.49-0.67 (m, 7H), 2.24 (s, 12H), 2.14 (s, 6H), 2.51 (m, 2H), 6.78 (s, 4H), 7.45 (d, 2H), 7.38 (d, 4H). ^{13}C NMR (C_6D_6, 100.50 MHz): δ 14.83, 17.28, 170.7, 19.01, 21.19, 22.25, 58.85, 112.86, 109.63, 115.05, 127.79, 128.66, 130, 134.21, 135.15, 137.25, 140.69, 159.9, 164.67, 201.08. ^{19}F NMR (C_6D_6, 282.41 MHz): δ -128.21. IR ν_{CN} = 1977.4 cm^{-1}, ν_{CO} = 1678.2, 1691.5 cm^{-1}. HRMS (CI): $[M+H]^+$ calcd. for $C_{40}H_{37}N_3O_2F_2$ 630.74542, found 630.74542.

Synthesis of diethyl 6-(3,6-dimethoxy-9H-fluoren-9-ylidene)-4,8-dimesityl-5,7-dioxo-4,8-diazaspiro[2.5]octane-1,2-dicarboxylate (5a). An 8 mL vial was charged with **3a** (25 mg, 0.044 mmol, 1 equiv.), benzene (5 mL), diethyl fumarate (8 mg, 0.048 mmol, 1.05 equiv.) and a stir bar. The mixture was stirred for 2 h at 25 °C after which the volatiles were removed under reduced pressure. The resulting solid was washed with cold pentane to afford the desired product (28 mg, 0.037 mmol, 91% yield). ^{1}H NMR (C_6D_6, 399.68 MHz): δ 1.33 (d, 6H), 2.04 (s, 6H), 2.26 (s, 12H), 3.3 (m, 2H), 3.88 (s, 3H), 4.11 (t, 4H), 6.72 (s, 4H), 6.97 (m, 2H), 7.16 (m, 2H), 7.53 (m, 2H). ^{13}C NMR (C_6D_6, 100.50 MHz): δ 15.2, 18.45, 21.09, 27.62, 54.92, 62.4, 73.38, 110.97, 116.11, 126.95, 128.13, 129.43, 132.43, 134.97, 135.43, 141.08, 159.49, 160.38, 169.32, 176.15. IR ν_{CO} = 1671.5, 1693.3, 1716.9, 1743.5 cm^{-1}. HRMS (CI): $[M+H]^+$ calcd. for $C_{45}H_{46}N_2O_8$ 743.86328, found 743.86318.

Synthesis of diethyl 6-(9H-fluoren-9-ylidene)-4,8-dimesityl-5,7-dioxo-4,8-diazaspiro[2.5]octane-1,2-dicarboxylate (5b). An 8 mL vial was charged with **3b** (25

mg, 0.049 mmol, 1 equiv.), benzene (5 mL), diethyl fumarate (9 mg, 0.054 mmol, 1.05 equiv.) and a stir bar. The mixture was stirred for 2 h at 25 °C after which the volatiles were removed under reduced pressure. The resulting solid was washed with cold pentane to afford the desired product (29 mg, 0.043 mmol, 94% yield). ^{1}H NMR (C_6D_6, 399.68 MHz): δ 1.26 (d, 6H), 2.1 (s, 6H), 2.14 (s, 12H), 3.50 (m, 2H), 4.12 (t, 4H), 6.84 (s, 4H), 7.48 (m, 5H). ^{13}C NMR (C_6D_6, 100.50 MHz): δ 14.28, 18.92, 21.29, 28.76, 61.02, 73.75, 112.5, 120.58, 125.23, 127.68, 128, 133.87, 133.94, 135.4, 138.53, 139.78, 160.21, 169.64, 176.19. IR ν_{CO} = 1678, 1690.4, 1714.8, 1749.1 cm^{-1}. HRMS (CI): $[M+H]^+$ calcd. for $C_{43}H_{42}N_2O_6$ 683.81132, found 683.81132..

Synthesis of diethyl 6-(3,6-difluoro-9H-fluoren-9-ylidene)-4,8-dimesityl-5,7-dioxo-4,8-diazaspiro[2.5]octane-1,2-dicarboxylate (5c). An 8 mL vial was charged with **3c** (25 mg, 0.046 mmol, 1 equiv.), benzene (5 mL), diethyl fumarate (8 mg, 0.051 mmol, 1.05 equiv.) and a stir bar. The mixture was stirred for 2 h at 25 °C after which the volatiles were removed under reduced pressure. The resulting solid was washed with cold pentane to afford the desired product (27 mg, 0.038 mmol, 89% yield). ^{1}H NMR (C_6D_6, 399.68 MHz): δ 1.33 (d, 6H), 2.16 (s, 6H), 2.13 (s, 12H), 3.36 (m, 2H), 4.22 (t, 4H), 6.75 (s, 4H), 7.31 (d, 2H), 7.48 (d, 4H). ^{13}C NMR (C_6D_6, 100.50 MHz): δ 13.74, 17.9, 21.48, 28.11, 61.65, 73.38, 112.99, 115.81, 127.02, 127.23, 130.86, 131.83, 134.52, 136.87, 142.21, 160.75, 164.16, 169.07, 174.32,. ^{19}F NMR (C_6D_6, 282.41 MHz): δ -128.17. IR ν_{CO} = 1675.1, 1698, 1716.4, 1750.2 cm^{-1}. HRMS (CI): $[M+H]^+$ calcd. for $C_{43}H_{40}N_2O_6F_2$ 719.79224, found 719.79174.

Synthesis of ethyl 6-(3,6-dimethoxy-9H-fluoren-9-ylidene)-4,8-dimesityl-5,7-dioxo-4,8-diazaspiro[2.5]octane-1,2-carboxylate (6a). An 8 mL vial was charged with **3a** (25 mg, 0.044 mmol, 1 equiv.), benzene (5 mL), methyl acrylate (4 µL, 0.048 mmol, 1.05 equiv.) and a stir bar. The mixture was stirred for 2 h at 25 °C after which the volatiles

were removed under reduced pressure. The resulting solid was washed with cold pentane to afford the desired product (27 mg, 0.040 mmol, 96% yield). ^{1}H NMR (C_6D_6, 399.68 MHz): δ 1.38 (d, 6H), 1.63 (m, 1H), 1.91 (m, 2H), 2.10 (s, 6H), 2.14 (s, 12H), 3.82 (s, 3H), 4.27 (t, 4H), 6.87 (s, 4H), 6.93 (m, 2H), 7.18 (m, 2H), 7.47 (m, 2H). ^{13}C NMR (C_6D_6, 100.50 MHz): δ 13.12, 17.93, 18.03, 20.96, 21.68, 56.06, 62.51, 73.13, 112.87, 115.42, 128.37, 128.64, 129.53, 133.36, 135.38, 136.48, 141.99, 159.17, 159.92, 169.08, 175.15. IR ν_{CO} = 1675.5, 1691, 1752.9 cm^{-1}. HRMS (CI): $[M+H]^+$ calcd. for $C_{42}H_{42}N_2O_6$ 671.80062, found 671.80062.

Synthesis of ethyl 6-(9H-fluoren-9-ylidene)-4,8-dimesityl-5,7-dioxo-4,8-diazaspiro[2.5]octane-1,2-carboxylate (6b). An 8 mL vial was charged with **3b** (25 mg, 0.049 mmol, 1 equiv.), benzene (5 mL), methyl acrylate (5 µL, 0.054 mmol, 1.05 equiv.) and a stir bar. The mixture was stirred for 2 h at 25 °C after which the volatiles were removed under reduced pressure. The resulting solid was washed with cold pentane to afford the desired product (28 mg, 0.45 mmol, 99% yield). ^{1}H NMR (C_6D_6, 399.68 MHz): δ 1.38 (d, 6H), 1.64 (m, 1H), 2.03 (m, 2H), 2.17 (s, 6H), 2.14 (s, 12H), 4.23 (t, 4H), 6.67 (s, 4H), 7.49 (m, 5H). ^{13}C NMR (C_6D_6, 100.50 MHz): δ 13.2, 17.06, 18.33, 21.35, 22.86, 62.56, 70.92, 110.99, 121.57, 123.77, 127.42, 127.43, 134.07, 135.98, 136.83, 137.3, 141.14, 159.5, 170.67, 176.00. IR ν_{CO} = 1672.8, 1695.2, 1756.3 cm^{-1}. HRMS (CI): $[M+H]^+$ calcd. for $C_{40}H_{38}N_2O_4$ 611.74866, found 611.74876.

Synthesis of ethyl 6-(3,6-difluoro-9H-fluoren-9-ylidene)-4,8-dimesityl-5,7-dioxo-4,8-diazaspiro[2.5]octane-1,2-carboxylate (6c). An 8 mL vial was charged with **3c** (25 mg, 0.046 mmol, 1 equiv.), benzene (5 mL), methyl acrylate (4 µL, 0.051 mmol, 1.05 equiv.) and a stir bar. The mixture was stirred for 2 h at 25 °C after which the volatiles were removed under reduced pressure. The resulting solid was washed with cold pentane to afford the desired product (27 mg, 0.41 mmol, 96% yield). ^{1}H NMR (C_6D_6, 399.68

MHz): δ 1.42 (d, 6H), 1.69 (m, 1H), 2.09 (m, 2H), 2.05 (s, 6H), 2.16 (s, 12H), 4.11 (t, 4H), 6.84 (s, 4H), 7.37 (d, 2H), 7.42 (d, 4H). ^{13}C NMR (C_6D_6, 100.50 MHz): δ 14.79, 18.23, 19.47, 20.3, 20.77, 62.88, 72.42, 112.59, 116.99, 128.04, 128.38, 131.13, 133.32, 135.29, 135.5, 141.36, 159.76, 164.91, 169.27, 174.5. ^{19}F NMR (C_6D_6, 282.41 MHz): δ -128.19. IR ν_{CO} = 1678.2, 1695, 1754.6 cm^{-1}. HRMS (CI): $[M+H]^+$ calcd. for $C_{40}H_{36}N_2O_4F_2$ 647.72958, found 647.72968.

Synthesis of ethyl 6-(3,6-dimethoxy-9H-fluoren-9-ylidene)-1-methyl-4,8-dimesityl-5,7-dioxo-4,8-diazaspiro[2.5]octane-1,2-carboxylate (7a). An 8 mL vial was charged with **3a** (25 mg, 0.044 mmol, 1 equiv.), benzene (5 mL), methyl methacrylate (5 µL, 0.048 mmol, 1.05 equiv.) and a stir bar. The mixture was stirred for 2 h at 25 °C after which the solution was concentrated under reduced pressure. Slow addition of cold hexanes, filtration, and a wash with cold hexanes afforded the desired product as a tan solid (25 mg, 0.037mmol, 89% yield). ^{1}H NMR (C_6D_6, 399.68 MHz): δ 1.26 (d, 6H), 2.16 (s, 6H), 2.16 (s, 12H), 2.61 (s, 2H), 3.42 (s, 3H), 3.72 (s, 3H), 4.13 (t, 4H), 6.86 (s, 4H), 6.93 (m, 2H), 7.16 (m, 2H), 7.52 (m, 2H). ^{13}C NMR (C_6D_6, 100.50 MHz): δ 13.69, 18.32, 19.6, 19.77, 32.25, 54.64, 59.2, 67.97, 70.33, 111.57, 115.25, 127.53, 127.62, 130.12, 133.96, 135.18, 136.25, 14.38, 141.79, 159.19, 159.27, 169.89,. IR ν_{CO} = 1675, 1692.9, 1749.9 cm^{-1}. HRMS (CI): $[M+H]^+$ calcd. for $C_{43}H_{44}N_2O_6$ 685.8272, found 685.8275.

Synthesis of ethyl 6-(9H-fluoren-9-ylidene)-1-methyl-4,8-dimesityl-5,7-dioxo-4,8-diazaspiro[2.5]octane-1,2-carboxylate (7b). An 8 mL vial was charged with **3b** (25 mg, 0.049 mmol, 1 equiv.), benzene (5 mL), methyl methacrylate (6 µL, 0.054 mmol, 1.05 equiv.) and a stir bar. The mixture was stirred for 2 h at 25 °C after which the solution was concentrated under reduced pressure. Slow addition of cold hexanes, filtration, and a wash with cold hexanes afforded the desired product as a tan solid (25 mg, 0.039 mmol, 86% yield). ^{1}H NMR (C_6D_6, 399.68 MHz): δ 1.20 (d, 6H), 2.32 (s, 12H), 2.19 (s, 6H), 2.69 (s,

2H), 3.41 (s, 3H), 4.21 (t, 4H), 6.87 (s, 4H), 7.45 (m, 5H). ^{13}C NMR (C_6D_6, 100.50 MHz): δ 13.19, 13.58, 17.2, 19.49, 19.9, 33.53, 61.19, 69.89, 69.96, 110.75, 121.37, 124.59, 127.71, 128.14, , 132.83, 133.93, 135.37, 136.85, 140.21, 160.46, 169.95. IR ν_{CO} = 1673.9, 1692.5, 1751.4 cm^{-1}. HRMS (CI): $[M+H]^+$ calcd. for $C_{41}H_{40}N_2O_4$ 625.77524, found 625.77564.

Synthesis of ethyl 6-(3,6-difluoro-9H-fluoren-9-ylidene)-1-methyl-4,8-dimesityl-5,7-dioxo-4,8-diazaspiro[2.5]octane-1,2-carboxylate (7c). An 8 mL vial was charged with **3c** (25 mg, 0.046 mmol, 1 equiv.), benzene (5 mL), methyl methacrylate (5 μL, 0.051 mmol, 1.05 equiv.) and a stir bar. The mixture was stirred for 2 h at 25 °C after which the solution was concentrated under reduced pressure. Slow addition of cold hexanes, filtration, and a wash with cold hexanes afforded the desired product as a tan solid (24 mg, 0.037 mmol, 86% yield). ^{1}H NMR (C_6D_6, 399.68 MHz): δ 1.22 (d, 6H), 2.10 (s, 6H), 2.15 (s, 12H), 2.65 (s, 2H), 3.27 (s, 3H), 4.16 (t, 4H), 6.78 (s, 4H), 7.35 (d, 2H), 7.46 (d, 4H). ^{13}C NMR (C_6D_6, 100.50 MHz): δ 13.73, 14.16, 16.79, 19.93, 20.39, 33.74, 60.72, 69.16, 69.52, 111.05, 115.79, 127.1, 127.74, 130.68, 132.17, 134.91, 135.73, 142.00, 161.22, 164.05, 169.88,. ^{19}F NMR (C_6D_6, 282.41 MHz): δ -128.18. IR ν_{CO} = 1676.3, 1693.1, 1748.2 cm^{-1}. HRMS (CI): $[M+H]^+$ calcd. for $C_{41}H_{38}N_2O_4F_2$ 661.75616, found 661.75636.

Synthesis of 1-butoxy-6-(3,6-dimethoxy-9H-fluoren-9-ylidene)-4,8-dimesityl-4,8-diazaspiro[2.5]octane-5,7-dione (8a). A 25 mL Schlenck flask was charged with **3a** (25 mg, 0.044 mmol, 1 equiv.), n-butyl vinyl ether (10 mL) and a stir bar. The flask was capped with a septum, wired shut, and stirred for 2 h at 100 °C after which the volatiles were removed under reduced pressure. The resultant oil was purified via silica gel chromatography using a 3:1 v/v hexanes/ethyl acetate mobile phase. Removal of the solvent afforded the desired product as an off-white solid (15 mg, 0.023 mmol, 55% yield).

^{1}H NMR (C_6D_6, 399.68 MHz): δ 0.73-0.96 (m, 7H), 1.17 (m, 1H), 2.09 (s, 6H), 2.23 (s, 12H), 2.73 (t, 2H), 3.59 (m, 2H), 3.79 (s, 3H), 6.83 (s, 4H), 6.97 (m, 2H), 7.22 (m, 2H), 7.59 (m, 2H). ^{13}C NMR (C_6D_6, 100.50 MHz): δ 17.72, 19.91, 56.22, 111.83, 110.96, 116.82, 125.29, 126.3, 127.58, 128.43, 129.21, 129.22, 133.78, 135.2, 135.21, 135.63, 137.77, 140.05, 159.84, 160.56, 169.04. IR ν_{CO} = 1675.5, 1696.4 cm^{-1}. HRMS (CI): $[M+H]^+$ calcd. for $C_{43}H_{46}N_2O_5$ 671.84368, found 671.84388.

Synthesis of 1-butoxy-6-(9H-fluoren-9-ylidene)-4,8-dimesityl-4,8-diazaspiro[2.5]octane-5,7-dione (8b). A 25 mL Schlenck flask was charged with **3a** (25 mg, 0.049 mmol, 1 equiv.), n-butyl vinyl ether (10 mL) and a stir bar. The flask was capped with a septum, wired shut, and stirred for 2 h at 100 °C after which the volatiles were removed under reduced pressure. The resultant oil was purified via silica gel chromatography using a 2:1 v/v hexanes/ethyl acetate mobile phase. Removal of the solvent afforded the desired product as an off-white solid (13 mg, 0.022 mmol, 48% yield). ^{1}H NMR (C_6D_6, 399.68 MHz): δ 0.73-0.96 (m, 7H), 1.18 (m, 1H), 2.15 (s, 6H), 2.11 (s, 12H), 2.62 (t, 2H), 3.46 (m, 2H), 6.8 (s, 4H), 7.53 (m, 5H). ^{13}C NMR (C_6D_6, 100.50 MHz): δ 18.83, 20.25, 112.65, 110.54, 120.13, 123.38, 125.83, 127.25, 127.32, 127.33, 128.63, 132.4, 135.37, 135.61, 136.08, 138.86, 139.19, 139.24, 160.8, 171.18. IR ν_{CO} = 1678.1, 1690.2 cm^{-1}. HRMS (CI): $[M+H]^+$ calcd. for $C_{41}H_{42}N_2O_3$ 611.79172, found 611.79132.

Synthesis of 1-butoxy-6-(3,6-difluoro-9H-fluoren-9-ylidene)-4,8-dimesityl-4,8-diazaspiro[2.5]octane-5,7-dione (8c). A 25 mL Schlenck flask was charged with **3c** (25 mg, 0.046 mmol, 1 equiv.), n-butyl vinyl ether (10 mL) and a stir bar. The flask was capped with a septum, wired shut, and stirred for 2 h at 100 °C after which the volatiles were removed under reduced pressure. The resultant oil was purified via silica gel chromatography using a 2:1 v/v hexanes/ethyl acetate mobile phase. Removal of the solvent afforded the desired product as an off-white solid (13 mg, 0.20 mmol, 46% yield).

^{1}H NMR (C_6D_6, 399.68 MHz): δ 0.73-0.96 (m, 7H), 1.23 (m, 1H), 2.03 (s, 6H), 2.17 (s, 12H), 2.70 (t, 2H), 3.49 (m, 2H), 6.79 (s, 4H), 7.35 (d, 2H), 7.55 (d, 4H). ^{13}C NMR (C_6D_6, 100.50 MHz): δ 17.08, 20.37, 111.75, 109.56, 117.06, 124.11, 125.96, 127.6, 128.68, 128.8, 129.03, 133.64, 134.57, 135.25, 136.14, 137.4, 140.87, 160.00, 165.08, 169.96. ^{19}F NMR (C_6D_6, 282.41 MHz): δ -128.16. IR ν_{CO} = 1672.9, 1690.2 cm^{-1}. HRMS (CI): $[M+H]^+$ calcd. for $C_{41}H_{40}N_2O_3F_2$ 647.77264, found 647.77234.

Synthesis of 6-(3,6-dimethoxy-9H-fluoren-9-ylidene)-4,8-dimesityl-1-(phenyl)-4,8-diazaspiro[2.5]octane-5,7-dione (9a). A 25 mL Schlenck flask was charged with **3a** (25 mg, 0.044 mmol, 1 equiv.), benzene, styrene (6 µL, 0.048 mmol, 1.1 equiv.) and a stir bar. The mixture was heated for 16 h at 60 °C. Afterwards, the residual volatiles were removed under reduced pressure and the solid dissolved in a minimal amount of hot toluene. Addition of hexanes, cooling of the resultant solution, and filtration afforded the desired product (24 mg, 0.035 mmol, 85% yield). ^{1}H NMR (C_6D_6, 399.68 MHz): δ 1.34 (dd, 2H), 2.15 (s, 12H), 2.16 (s, 6H), 2.58 (dd, 1H), 3.87 (s, 3H), 6.58 (m, 2H), 6.77 (s, 4H), 7.03 (m, 2H), 7.34 (m, 5H), 7.35 (m, 2H), 7.46 (m, 2H). ^{13}C NMR (C_6D_6, 100.50 MHz): δ 16.16, 21.66, 24.46, 55.06, 72.04, 111.97, 115.47, 125.18, 125.51, 126.44, 127.43, 128.51, 129.04, 129.11, 132.63, 134.63, 135.92, 140.89, 160.77, 160.85, 17.27, 170.54. IR ν_{CO} = 1670.2, 1695 cm^{-1}. HRMS (CI): $[M+H]^+$ calcd. for $C_{45}H_{42}N_2O_4$ 675.83392, found 675.83392.

Synthesis of 6-(9H-fluoren-9-ylidene)-4,8-dimesityl-1-(phenyl)-4,8-diazaspiro[2.5]octane-5,7-dione (9b). A 25 mL Schlenck flask was charged with **3b** (25 mg, 0.049 mmol, 1 equiv.), benzene, styrene (6 µL, 0.054 mmol, 1.1 equiv.) and a stir bar. The mixture was heated for 16 h at 60 °C. Afterwards, the residual volatiles were removed under reduced pressure and the solid dissolved in a minimal amount of hot toluene. Addition of hexanes, cooling of the resultant solution, and filtration afforded the desired

product (22 mg, 0.036 mmol, 78% yield). ^{1}H NMR (C_6D_6, 399.68 MHz): δ 1.32 (dd, 2H), 2.00 (s, 6H), 2.27 (s, 12H), 2.4 (dd, 1H), 6.51 (m, 2H), 6.71 (s, 4H), 7.31 (m, 5H), 7.36 (m, 5H). ^{13}C NMR (C_6D_6, 100.50 MHz): δ 14.9, 18.88, 20.09, 23.23, 70.47, 112.69, 120.51, 122.86, 125.36, 125.37, 126.04, 126.81, 129.17, 129.17, 134.00, 135.38, 136.44, 138.49, 140.37, 159.17, 170.99. IR ν_{CO} = 1670.2, 1694.8 cm^{-1}. HRMS (CI): $[M+H]^+$ calcd. for $C_{43}H_{38}N_2O_2$ 615.78196, found 615.78226.

Synthesis of 6-(3,6-difluoro-9H-fluoren-9-ylidene)-4,8-dimesityl-1-(phenyl)-4,8-diazaspiro[2.5]octane-5,7-dione (9c). A 25 mL Schlenck flask was charged with **3c** (25 mg, 0.046 mmol, 1 equiv.), benzene, styrene (5 µL, 0.051 mmol, 1.1 equiv.) and a stir bar. Afterwards, the residual volatiles were removed under reduced pressure and the solid dissolved in a minimal amount of hot toluene. Addition of hexanes, cooling of the resultant solution, and filtration afforded the desired product (23 mg, 0.036 mmol, 84% yield). ^{1}H NMR (C_6D_6, 399.68 MHz): δ 1.41 (dd, 2H), 2.13 (s, 6H), 2.27 (s, 12H), 2.43 (dd, 1H), 6.63 (m, 2H), 6.76 (s, 4H), 7.41 (d, 2H), 7.19 (m, 5H), 7.49 (d, 4H). ^{13}C NMR (C_6D_6, 100.50 MHz): δ 14.29, 16.97, 20.39, 23.52, 71.36, 111.98, 115, 124.65, 126.00 126.66, 127.1, 128.64, 129.2, 130.16, 132.12, 135.31, 136.08, 140.1, 158.82, 164.64, 171.24. ^{19}F NMR (C_6D_6, 282.41 MHz): δ -128.24. IR ν_{CO} = 1677.2, 1697.9 cm^{-1}. HRMS (CI): $[M+H]^+$ calcd. for $C_{43}H_{36}N_2O_2F_2$ 651.76288, found 651.76258.

Synthesis of 6-(3,6-dimethoxy-9H-fluoren-9-ylidene)-4,8-dimesityl-1-(4-methoxyphenyl)-4,8-diazaspiro[2.5]octane-5,7-dione (10a). A 25 mL Schlenck flask was charged with **3a** (25 mg, 0.044 mmol, 1 equiv.), benzene, *para*-methoxystyrene (7 µL, 0.048 mmol, 1.1 equiv.) and a stir bar. The mixture was heated for 16 h at 60 °C. Afterwards, the residual volatiles were removed under reduced pressure and the solid triturated with benzene to afford the desired product (22 mg, 0.030 mmol, 74% yield). ^{1}H NMR (C_6D_6, 399.68 MHz): δ 1.61 (m, 2H), 2.19 (s, 6H), 2.23 (s, 12H), 2.49 (m, 1H), 3.87

(s, 3H), 3.75 (s, 3H), 6.59 (m, 2H), 6.69 (s, 4H), 6.86 (m, 2H), 6.94 (m, 2H), 7.29 (m, 2H), 7.44 (m, 2H). ^{13}C NMR (C_6D_6, 100.50 MHz): δ 14.65, 18.6, 21.25, 22.87, 54.7, 55.59, 71.5, 112.16, 116.57, 124.83, 124.95, 126.78, 127.68, 127.88, 128.59, 128.87, 131.85, 135.44, 137.03, 141.74, 160.93, 161.09, 169.06. IR ν_{CO} = 1676.2, 1692.3 cm^{-1}. HRMS (CI): $[M+H]^+$ calcd. for $C_{46}H_{44}N_2O_5$ 705.8599, found 705.8599.

Synthesis of 6-(9H-fluoren-9-ylidene)-4,8-dimesityl-1-(4-methoxyphenyl)-4,8-diazaspiro[2.5]octane-5,7-dione (10b). A 25 mL Schlenck flask was charged with **3b** (25 mg, 0.049 mmol, 1 equiv.), benzene, *para*-methoxystyrene (8 µL, 0.054 mmol, 1.1 equiv.) and a stir bar. The mixture was heated for 16 h at 60 °C. Afterwards, the residual volatiles were removed under reduced pressure and the solid triturated with benzene to afford the desired product (22 mg, 0.035 mmol, 76% yield). ^{1}H NMR (C_6D_6, 399.68 MHz): δ 1.54 (m, 2H), 2.11 (s, 6H), 2.3 (s, 12H), 2.44 (m, 1H), 3.86 (s, 3H), 6.49 (m, 2H), 6.74 (s, 4H), 6.77 (m, 2H), 7.37 (m, 5H). ^{13}C NMR (C_6D_6, 100.50 MHz): δ 14.26, 18.44, 20.07, 23.31, 55.53, 71.97, 113.15, 121.17, 124.49, 125.94, 126.76, 126.86, 127.32, 127.76, 128.82, 133.44, 135.21, 135.94, 137.56, 140.62, 160.64, 169.42. IR ν_{CO} = 1670.8, 1690.6 cm^{-1}. HRMS (CI): $[M+H]^+$ calcd. for $C_{44}H_{40}N_2O_3$ 645.80794, found 645.80764.

Synthesis of 6-(3,6-difluoro-9H-fluoren-9-ylidene)-4,8-dimesityl-1-(4-methoxyphenyl)-4,8-diazaspiro[2.5]octane-5,7-dione (10c). A 25 mL Schlenck flask was charged with **3c** (25 mg, 0.046 mmol, 1 equiv.), benzene, *para*-methoxystyrene (7 µL, 0.051 mmol, 1.1 equiv.) and a stir bar. The mixture was heated for 16 h at 60 °C. Afterwards, the residual volatiles were removed under reduced pressure and the solid triturated with benzene to afford the desired product (20 mg, 0.030 mmol, 69% yield). ^{1}H NMR (C_6D_6, 399.68 MHz): δ 1.49 (m, 2H), 2.29 (s, 12H), 2.01 (s, 6H), 2.38 (m, 1H), 3.88 (s, 3H), 6.49 (m, 2H), 6.80 (m, 2H), 6.68 (s, 4H), 7.31 (d, 2H), 7.54 (d, 4H). ^{13}C NMR (C_6D_6, 100.50 MHz): δ 14.29, 19.17, 22.01, 23.32, 54.88, 71.83, 111.22, 114.75, 124.56,

125.48, 126.19, 127.32, 127.33, 128.63, 129.58, 132.52, 134.89, 135.06, 140.21, 160.27, 163.81, 169.01. ^{19}F NMR (C_6D_6, 282.41 MHz): δ -128.22 IR ν_{CO} = 1679.6, 1693.2 cm^{-1}. HRMS (CI): $[M+H]^+$ calcd. for $C_{44}H_{38}N_2O_3F_2$ 681.78886, found 681.78906.

Synthesis of 6-(3,6-dimethoxy-9H-fluoren-9-ylidene)-4,8-dimesityl-1-(4-fluorophenyl)-4,8-diazaspiro[2.5]octane-5,7-dione (11a). A 25 mL Schlenck flask was charged with **3a** (25 mg, 0.044 mmol, 1 equiv.), benzene, *para*-fluorostyrene (6 µL, 0.048 mmol, 1.1 equiv.) and a stir bar. The mixture was heated for 16 h at 60 °C, after which the residual volatiles were removed under reduced pressure. The crude solid was recrystallized from a 1:1 v/v toluene:hexanes mixture, filtered, and dried under reduced pressure to afford the desired solid (19 mg, 0.027 mmol, 65% yield). ^{1}H NMR (C_6D_6, 399.68 MHz): δ 1.29 (m, 2H), 2.04 (s, 6H), 2.14 (s, 12H), 2.41 (m, 1H), 3.78 (s, 3H), 6.5 (m, 2H), 6.71 (s, 4H), 6.92 (m, 2H), 6.96 (m, 2H), 7.33 (m, 2H), 7.45 (m, 2H). ^{13}C NMR (C_6D_6, 100.50 MHz): δ 14.85, 17.89, 21.59, 23.51, 55.67, 70.41, 113.1, 115.51, 125.46, 126.53, 126.96, 127.04, 127.15, 127.41, 130.46, 132.72, 135.4, 136.03, 140.31, 158.88, 160.7, 169.41. ^{19}F NMR (C_6D_6, 282.41 MHz): δ -115.07. IR ν_{CO} = 1679.4, 1697.1 cm^{-1}. HRMS (CI): $[M+H]^+$ calcd. for $C_{45}H_{41}N_2O_4F$ 693.82438, found 693.82428.

Synthesis of 6-(9H-fluoren-9-ylidene)-4,8-dimesityl-1-(4-fluorophenyl)-4,8-diazaspiro[2.5]octane-5,7-dione (11b). A 25 mL Schlenck flask was charged with **3b** (25 mg, 0.049 mmol, 1 equiv.), benzene, *para*-fluorostyrene (7 µL, 0.054 mmol, 1.1 equiv.) and a stir bar. The mixture was heated for 16 h at 60 °C, after which the residual volatiles were removed under reduced pressure. The crude solid was recrystallized from a 1:1 v/v toluene:hexanes mixture, filtered, and dried under reduced pressure to afford the desired solid (20 mg, 0.030 mmol, 69% yield). ^{1}H NMR (C_6D_6, 399.68 MHz): δ 1.36 (m, 2H), 2.01 (s, 6H), 2.3 (s, 12H), 2.38 (m, 1H), 6.53 (m, 2H), 6.67 (s, 4H), 6.88 (m, 2H), 7.46 (m, 5H). ^{13}C NMR (C_6D_6, 100.50 MHz): δ 14.22, 17.97, 21.26, 23.52, 70.26, 111.49, 122.12,

124.62, 124.8, 125.26, 126.91, 127.02, 127.16, 128.7, 132.86, 134.71, 134.91, 138.78, 140.71, 158.81, 170.26. ^{19}F NMR (C_6D_6, 282.41 MHz): δ -115.49. IR ν_{CO} = 1678.7, 1692.2 cm^{-1}. HRMS (CI): $[M+H]^+$ calcd. for $C_{43}H_{37}N_2O_2F$ 633.77242, found 633.77202.

Synthesis of 6-(3,6-difluoro-9H-fluoren-9-ylidene)-4,8-dimesityl-1-(4-fluorophenyl)-4,8-diazaspiro[2.5]octane-5,7-dione (11c). A 25 mL Schlenck flask was charged with **3c** (25 mg, 0.046 mmol, 1 equiv.), benzene, *para*-fluorostyrene (6 µL, 0.051 mmol, 1.1 equiv.) and a stir bar. The mixture was heated for 16 h at 60 °C, after which the residual volatiles were removed under reduced pressure. The crude solid was recrystallized from a 1:1 v/v toluene:hexanes mixture, filtered, and dried under reduced pressure to afford the desired solid (18 mg, 0.027 mmol, 63% yield). ^{1}H NMR (C_6D_6, 399.68 MHz): δ 1.26 (m, 2H), 2.15 (s, 12H), 2.18 (s, 6H), 2.40 (m, 1H), 6.64 (m, 2H), 6.79 (s, 4H), 7.00 (m, 2H), 7.45 (d, 4H), 7.41 (d, 2H). ^{13}C NMR (C_6D_6, 100.50 MHz): δ 15.82, 17.34, 22.17, 22.8, 71.00, 112.25, 116.31, 124.18, 125.32, 127.43, 127.87, 128.27, 128.63, 129.65, 133.86, 136.08, 137.13, 139.8, 160.78, 165.82, 170.16. ^{19}F NMR (C_6D_6, 282.41 MHz): δ -115.43. IR ν_{CO} = 1676.5, 1691.3 cm^{-1}. HRMS (CI): $[M+H]^+$ calcd. for $C_{43}H_{35}N_2O_2F_3$ 669.75334, found 669.75344.

Synthesis of 6-(3,6-dimethoxy-9H-fluoren-9-ylidene)-4,8-dimesityl-2-phenyl-1-oxa-4,8-diazaspiro[2.5]octane-5,7-dione (12a). An 8 mL vial was charged with **3a** (25 mg, 0.044 mmol, 1 equiv.), benzene (5 mL), benzaldehyde (5 µL, 0.048 mmol, 1.05 equiv.) and a stir bar. The mixture was stirred for 2 h at 25 °C after which the volatiles were removed *in vacuo*. The residual solid was washed with cold pentane to afford the desired product (27 mg, 0.039 mmol, 95% yield). ^{1}H NMR (C_6D_6, 399.68 MHz): δ 2.08 (s, 6H), 2.16 (s, 12H), 3.8 (s, 3H), 5.85 (s, 1H), 6.77 (s, 4H), 7.03 (m, 2H), 7.25 (m, 2H), 7.21-7.28 (m, 5H), 7.55 (m, 2H). ^{13}C NMR (C_6D_6, 100.50 MHz): δ 19.09, 21.77, 55.67, 112.48, 109.46, 117.22, 125.73, 127.28, 127.95, 128.24, 128.52, 129.27, 133.00, 133.76, 135.38,

135.5, 138.46, 140.43, 160.86, 161.11, 170.29. IR ν_{CO} = 1672.2, 1693 cm^{-1}. HRMS (CI): $[M+H]^+$ calcd. for $C_{44}H_{40}N_2O_5$ 677.80674, found 677.80704.

Synthesis of 6-(9H-fluoren-9-ylidene)-4,8-dimesityl-2-phenyl-1-oxa-4,8-diazaspiro[2.5]octane-5,7-dione (12b). An 8 mL vial was charged with **3b** (25 mg, 0.049 mmol, 1 equiv.), benzene (5 mL), benzaldehyde (5 µL, 0.054 mmol, 1.05 equiv.) and a stir bar. The mixture was stirred for 2 h at 25 °C after which the volatiles were removed *in vacuo*. The residual solid was washed with cold pentane to afford the desired product (26 mg, 0.042 mmol, 92% yield). ^{1}H NMR (C_6D_6, 399.68 MHz): δ 2.08 (s, 6H), 2.29 (s, 12H), 5.97 (s, 1H), 6.76 (s, 4H), 7.21-7.28 (m, 5H), 7.36 (m, 5H). ^{13}C NMR (C_6D_6, 100.50 MHz): δ 18.43, 21.06, 113.1, 110.92, 120.28, 123.79, 125.99, 126.68, 126.96, 127.09, 127.7, 131.9, 135.44, 135.64, 136.53, 137.22, 138.62, 139.41, 161.21, 169.78. IR ν_{CO} = 1673.2, 1693.1 cm^{-1}. HRMS (CI): $[M+H]^+$ calcd. for $C_{42}H_{36}N_2O_3$ 617.75478, found 617.75488.

Synthesis of 6-(3,6-difluoro-9H-fluoren-9-ylidene)-4,8-dimesityl-2-phenyl-1-oxa-4,8-diazaspiro[2.5]octane-5,7-dione (12c). An 8 mL vial was charged with **3c** (25 mg, 0.046 mmol, 1 equiv.), benzene (5 mL), benzaldehyde (5 µL, 0.051 mmol, 1.05 equiv.) and a stir bar. The mixture was stirred for 2 h at 25 °C after which the volatiles were removed *in vacuo*. The residual solid was washed with cold pentane to afford the desired product (26 mg, 0.040 mmol, 94% yield). ^{1}H NMR (C_6D_6, 399.68 MHz): δ 2.19 (s, 6H), 2.11 (s, 12H), 5.9 (s, 1H), 6.69 (s, 4H), 7.21-7.28 (m, 5H), 7.35 (d, 2H), 7.48 (d, 4H). ^{13}C NMR (C_6D_6, 100.50 MHz): δ 17.34, 21.23, 112.23, 110.67, 117.03, 125.29, 125.96, 126.78, 127.00, 127.1, 130.04, 132.51, 134.47, 135.29, 136.93, 136.94, 140.95, 160.78, 164.6, 171.25. ^{19}F NMR (C_6D_6, 282.41 MHz): δ -128.19. IR ν_{CO} = 1671.9, 1691.9 cm^{-1}. HRMS (CI): $[M+H]^+$ calcd. for $C_{42}H_{34}N_2O_3F_2$ 653.7357, found 653.7357.

3.5 ACKNOWLEDGEMENTS

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Appendix A: Supporting Information

CHAPTER 2: TUNING THE ELECTRONIC PROPERTIES OF CARBENES: A SYSTEMATIC COMPARISON OF NEIGHBORING AMINO VERSUS AMIDO GROUPS

	3·1.5C_5H_{12}[b]	**3-Ir[COD]Cl**	**5-Ir[COD]Cl**
Formula	$C_{31.5}H_{48}N_2O$	$C_{32}H_{42}ClIrN_2O$	$C_{32}H_{44}ClIrN_2$
M_r	470.72	698.33	684.34
crystal size (mm^3)	0.14 x 0.04 x 0.03	0.20 x 0.20 x 0.20	0.26 x 0.17 x 0.08
crystal system	Trigonal	Monoclinic	Trigonal
space group	*R3c*	$P2_1/n$	$P6_1$
a (Å)	33.590(3)	11.756(3)	22.584(2)
b (Å)	33.590(3)	9.387(2)	22.584(2)
c (Å)	13.3249(12)	26.214(6)	10.3184(11)
α (°)	90	90	90
β (°)	90	97.739(5)	90
γ (°)	120	90	120
V ($Å^3$)	13020(2)	2866.6(12)	4557.6(8)
Z	18	4	6
ρ_{calc} (g cm^{-3})	1.081	1.618	1.496
μ (mm^{-1})	0.064	4.778	4.504
F(000)	4662	1400	2064
T (K)	150(2)	120(2)	150(2)
scan mode	ω	ω	ω
hkl range	-34 → 0 0 → 39 -15 → 13	-13 → 13 -11 → 11 -31 → 30	-26 → 26 -26 → 26 -12 → 12
measd reflns	4903	42544	66480
unique reflns [R_{int}]	4903 [0.000]	4882 [0.0902]	5336 [0.0552]
refinement reflns	4903	4882	5336
refined parameters	252	342	355
GOF on F^2	0.885	1.006	1.006
R1[a] (all data)	0.0663 (0.1299)	0.0374 (0.0399)	0.0185 (0.0200)
wR2 (all data)	0.1357 (0.1567)	0.0845 (0.0860)	0.0521 (0.0536)
ρ_{fin} (max/min) (e $Å^{-3}$)	0.129 -0.156	0.941 -1.116	0.723 -0.346

[a] $R1 = \sum||Fo| - |Fc||/\sum|Fo|$. [b] $wR2 = \{[\sum w(Fo^2 - Fc^2)^2]/[\sum w(Fo^2)^2]\}^{1/2}$. [b] SQUEEZE was used to remove 1.5 disordered solvent molecules.

Table A1: Summary of crystal data, data collection, and structure refinement details.

X-Ray Crystallography. Colorless, single crystals of **3** were obtained by the cooling of a saturated pentane solution to -20 °C; this compound co-crystallized in the trigonal space

group R3c with what appeared to be 1.5 equiv. of pentane were that were found to be poorly disordered. Attempts to model the disorder were unsatisfactory. The contributions to the scattering factors due to these solvent molecules were removed by use of SQUEEZE in PLATON98.[1] PLATON98 was used as incorporated in WinGX.[2] Yellow, single crystals of **3-Ir[COD]Cl** were grown by slow diffusion of hexane vapor into a saturated benzene solution; this compound crystallized in the monoclinic space group P21/n. Yellow, single crystals of **5-Ir[COD]Cl** were obtained by the slow diffusion of pentane into a saturated benzene solution; this compound crystallized in the P61 space group. Crystallographic measurements were carried out on a Rigaku Mini CCD or Rigaku AFC-12 with Saturn 724+ CCD area detector diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at 120 or 150 K using an Rigaku XStream low temperature device. A sample of suitable size and quality was selected and mounted onto a nylon loop. Data reductions were performed using CrystalClear. The structures were solved by direct methods which successfully located most of the non-hydrogen atoms. Subsequent refinements on F2 using the SHELXTL/PC package (version 5.1) allowed location of the remaining non-hydrogen atoms. Key details of the crystal and structure refinement data are summarized in Table S1. Further crystallographic details may be found in the respective CIFs which were deposited at the Cambridge Crystallographic Data Centre, Cambridge, UK. The CCDC reference numbers for **3**·1.5C_5H_{12}, **3-Ir[COD]Cl**, and **5-Ir[COD]Cl** were assigned as 866824, 866825, and 866826, respectively.

Electrochemical information for carbene-iridium complexes:

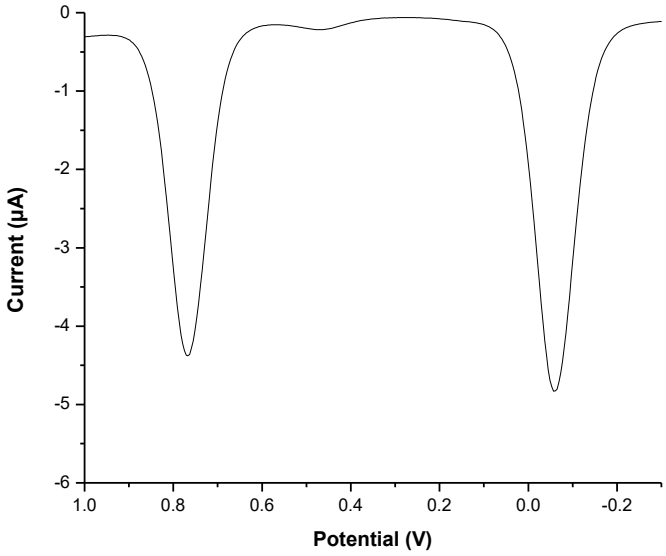


Figure A1: Differential pulse voltammogram (DPV) of **3-Ir[COD]Cl** in CH_2Cl_2 with 0.1 M $[Bu_4N][PF_6]$ and Fc^* internal standard.

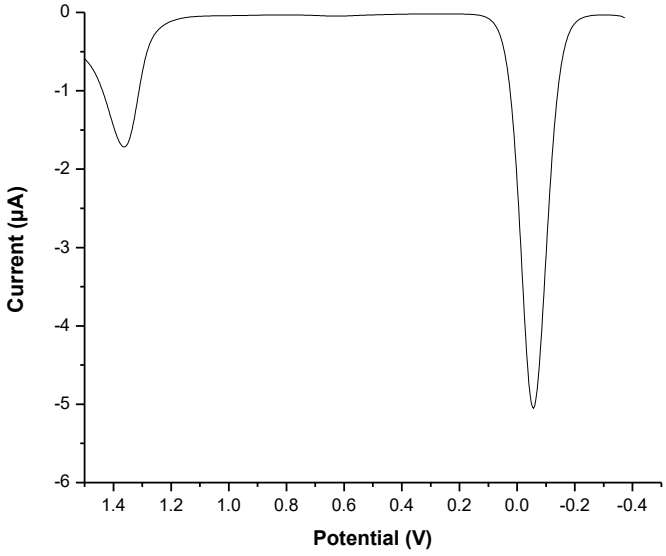


Figure A2: DPV of **3-Ir[CO]$_2$Cl** in CH_2Cl_2 with 0.1 M $[Bu_4N][PF_6]$ and Fc^* internal standard.

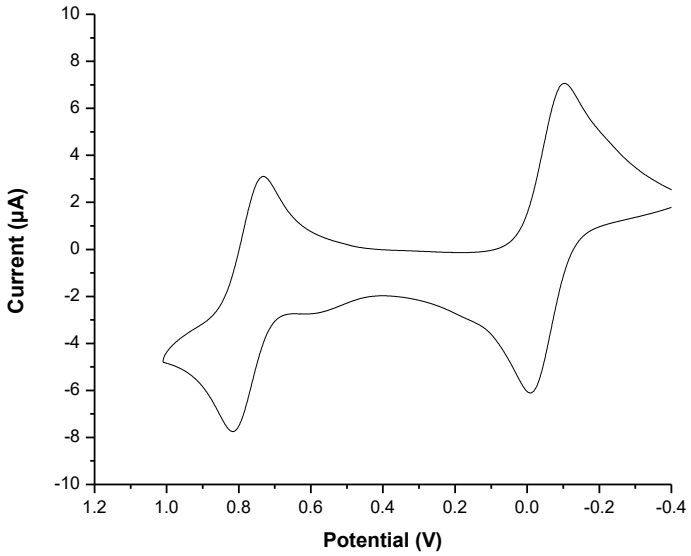


Figure A3: Cyclic voltammogram (CV) of **3-Ir[COD]Cl** in CH_2Cl_2 with 0.1 M $[Bu_4N][PF_6]$ and Fc^* internal standard.

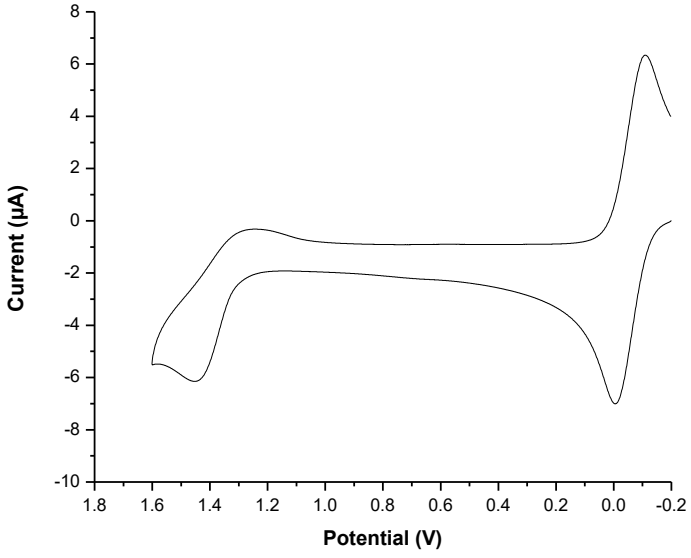


Figure A4: CV of **3-Ir[CO]$_2$Cl** in CH_2Cl_2 with 0.1 M $[Bu_4N][PF_6]$ and Fc^* internal standard.

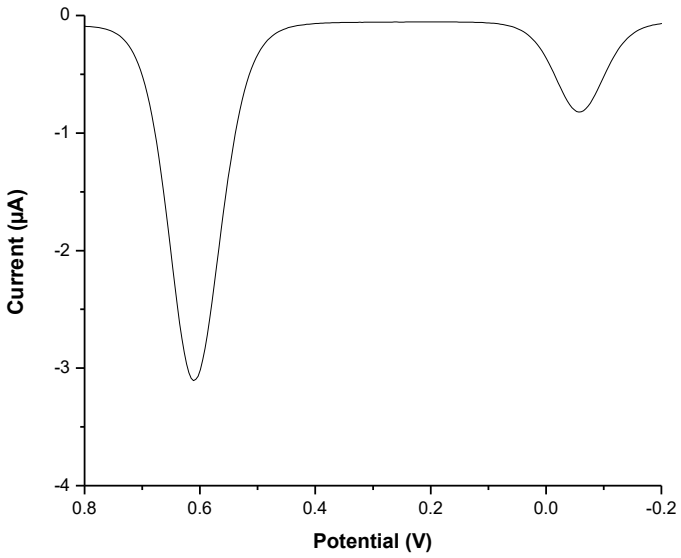


Figure A5: DPV of **5-Ir[COD]Cl** in CH_2Cl_2 with 0.1 M $[Bu_4N][PF_6]$ and Fc^* internal standard.

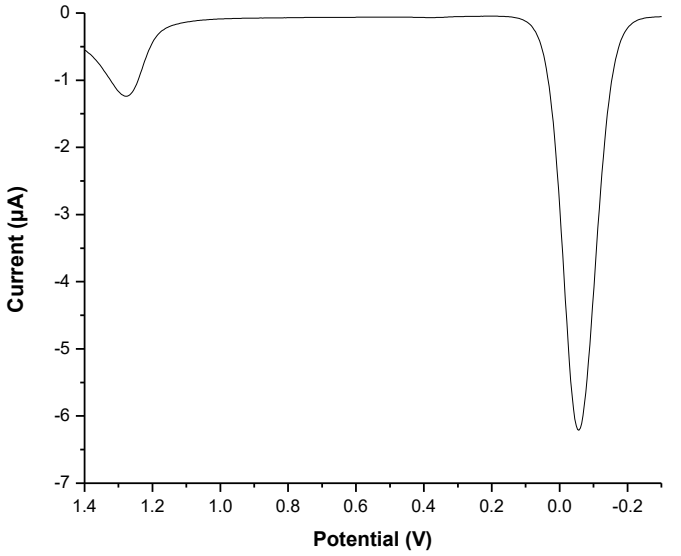


Figure A6: DPV of **5-Ir[CO]$_2$Cl** in CH_2Cl_2 with 0.1 M $[Bu_4N][PF_6]$ and Fc^* internal standard.

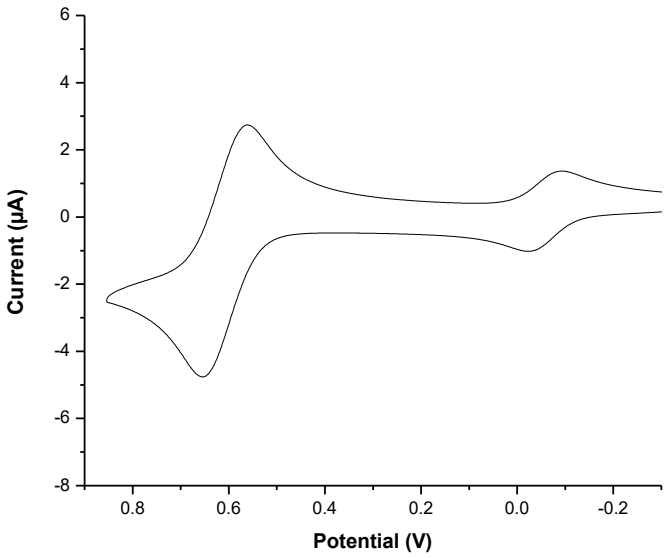


Figure A7: CV of **5-Ir[COD]Cl** in CH_2Cl_2 with 0.1 M $[Bu_4N][PF_6]$ and Fc^* internal standard.

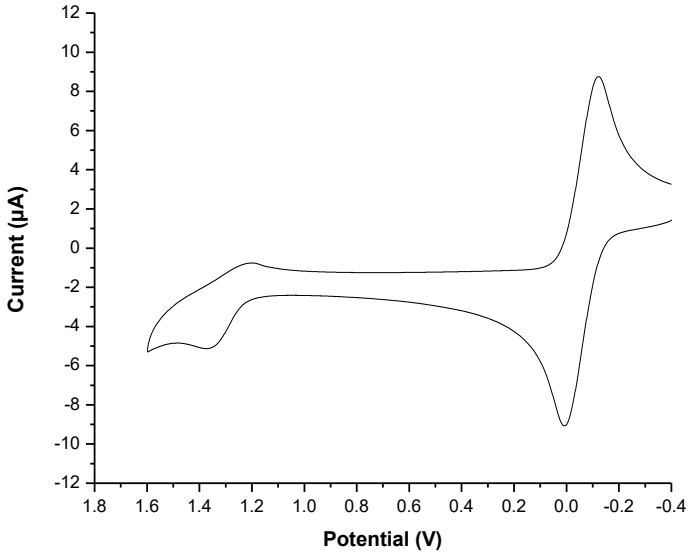
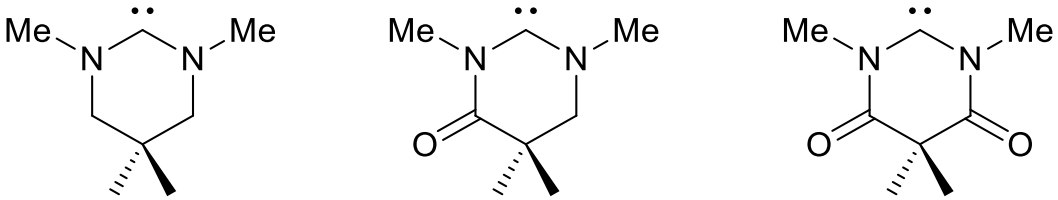
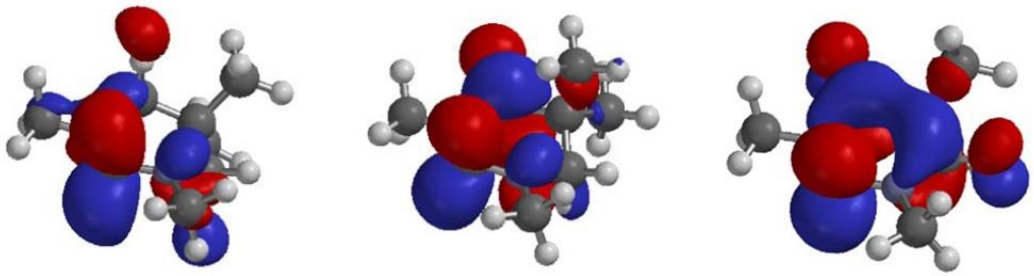


Figure A8: CV of 5-Ir[CO]2Cl in CH2Cl2 with 0.1 M [Bu4N][PF6] and Fc* internal standard.

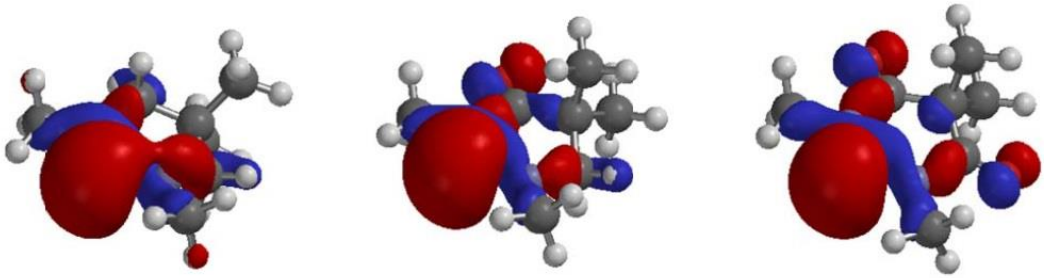
Computational Details. Calculations were performed using GAMESS (Version 11-64);[3] input files were generated with Avogadro (Version 1.0.3)[4] and the data was analyzed in MacMolPlt (Version 7.4.2). Geometries were optimized at the B3LYP 6-31+G(d) level and frequency calculations were undertaken to provide thermal correction factors to enthalpy calculations. Calculations were conducted in the gas phase with a singlet multiplicity.



5-Me **3-Me** **6-Me**



LUMO+1: +2.31 LUMO: -21.26 LUMO: -48.16



HOMO: -118.67 HOMO: -133.48 HOMO: -146.32

ΔH_{S-T}: 116.06 ΔH_{S-T}: 112.27 ΔH_{S-T}: 98.19

Figure A9: Selected molecular orbitals and energies (in kcal/mol) of **5-Me** (left), **3-Me** (middle), and the **6-Me** (right) calculated at the B3LYP 6-31+G(d) level.

5-Me

ATOM		X	Y	Z
1	C	-9.341749	13.209964	0.895747
2	N	-6.966637	14.567726	1.380714
3	C	-8.833130	10.498812	-0.016610
4	C	-6.921088	10.690416	-2.197094
5	N	-4.733029	12.247186	-1.480464
6	C	-11.297841	9.302315	-0.971771
7	C	-7.726670	8.902086	2.154582
8	C	-2.433110	11.778460	-2.909369
9	C	-7.149731	16.684055	3.123978
10	C	-4.727105	14.158998	0.216942
11	H	-7.777409	16.057807	5.003834
12	H	-8.502911	18.108330	2.440650
13	H	-5.280307	17.539344	3.269899
14	H	-10.477883	14.243542	-0.511398
15	H	-10.452952	13.164366	2.648357
16	H	-12.126402	10.399222	-2.523975
17	H	-12.704816	9.187170	0.547076
18	H	-10.966404	7.375875	-1.663249
19	H	-5.962281	9.714370	2.861163
20	H	-7.340413	6.967806	1.517293
21	H	-9.065369	8.791544	3.733416
22	H	-7.834572	11.486205	-3.891463
23	H	-6.248369	8.794924	-2.710179
24	H	-1.787252	9.817186	-2.672240
25	H	-0.987550	13.071162	-2.211616
26	H	-2.725696	12.111898	-4.951721

3-Me

ATOM		X	Y	Z
1	C	-7.880617	4.936278	-0.240334
2	C	-8.941824	2.278160	-0.685424
3	C	-10.289721	1.401799	1.724416
4	N	-9.298811	6.473682	1.375848
5	C	-11.517605	5.845246	2.644266
6	N	-12.002873	3.370782	2.678594
7	C	-6.790174	0.453966	-1.356431
8	C	-10.830808	2.473548	-2.911019
9	H	-12.411677	3.729933	-2.461326
10	H	-11.596661	0.599447	-3.357121
11	H	-9.877099	3.201714	-4.596509
12	H	-5.450131	0.257631	0.211180
13	H	-5.742052	1.153025	-2.992053
14	H	-7.549605	-1.422266	-1.800393
15	O	-6.024459	5.744962	-1.347602
16	C	-8.506916	9.132461	1.502711
17	C	-14.229061	2.494587	4.049133
18	H	-8.902239	0.945222	3.206656
19	H	-11.373710	-0.322597	1.344064
20	H	-8.487039	9.975797	-0.386081
21	H	-6.601482	9.282125	2.290721
22	H	-9.861562	10.102804	2.710738
23	H	-15.217424	4.154669	4.763877
24	H	-13.683932	1.274301	5.638073
25	H	-15.484315	1.414974	2.789214

Table A2: Continued on Next Page

6-Me

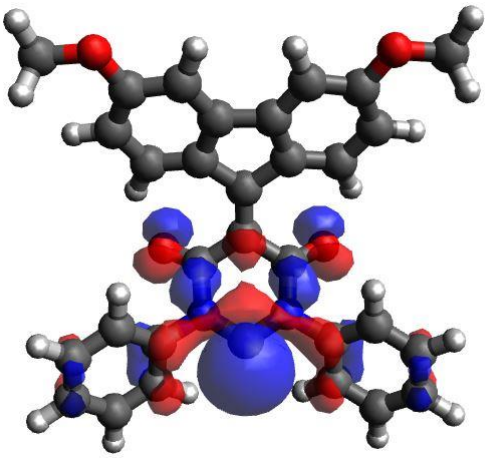
ATOM		X	Y	Z
1	C	4.270211	56.261586	23.276788
2	N	5.123203	58.503004	22.129358
3	O	4.820320	55.762715	25.453743
4	C	1.840434	55.590870	19.143967
5	O	0.315319	54.525506	17.791553
6	N	2.937163	57.899058	18.409053
7	C	4.523170	59.403166	19.784337
8	C	2.177707	58.836268	15.899929
9	H	3.211189	60.586260	15.581200
10	H	0.140050	59.176585	15.848825
11	H	2.636850	57.437693	14.450143
12	C	6.768388	60.102210	23.706785
13	C	2.728443	54.457755	21.640466
14	C	0.416666	53.509860	23.146826
15	C	4.485573	52.195168	20.978452
16	H	8.446502	59.043736	24.284064
17	H	5.763496	60.702255	25.409688
18	H	7.289250	61.729174	22.560877
19	H	-0.848090	55.074155	23.636049
20	H	1.048335	52.614827	24.896317
21	H	-0.639955	52.155603	22.002412
22	H	6.148151	52.805913	19.904097
23	H	3.434821	50.826588	19.840585
24	H	5.126260	51.297836	22.716456

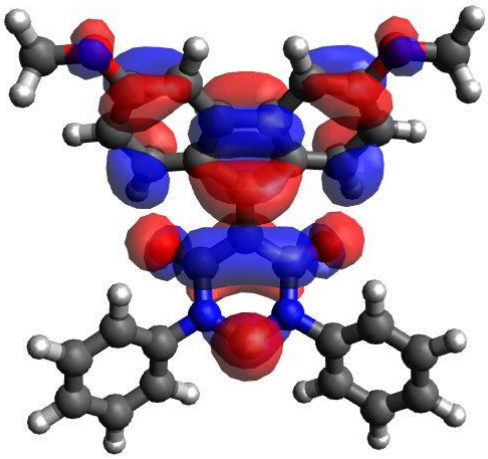
Table A2: B3LYP Cartesian coordinates for the compounds investigated in this study: **5-Me**, **3-Me**, and **6-Me**

Carbene	Point Group[a]	Enthalpy[b]
5-Me	C_s	- 423.6541
3-Me	C_1	- 497.6649
6-Me	C_s/C_{2v}	- 571.6700

Table A3: Calculated B3LYP point groups and enthalpies for the compounds investigated in this study: **5-Me**, **3-Me**, and **6-Me**

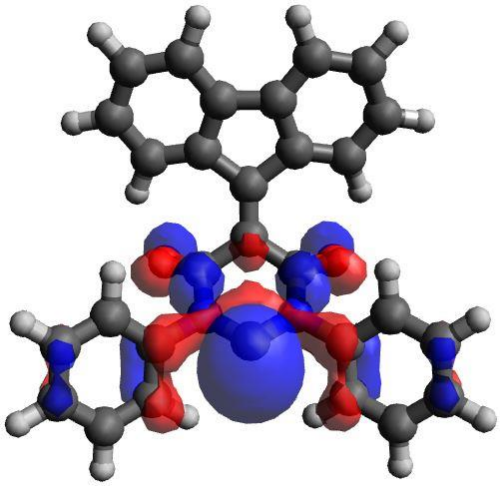
Computational Details. Calculations were performed and the data analyzed using Gaussian 09[5] and Avogadro 1.2.0.[6] Geometries were optimized at the B3LYP 6-31+G(d) level. Calculations were conducted in the gas phase with a singlet multiplicity.

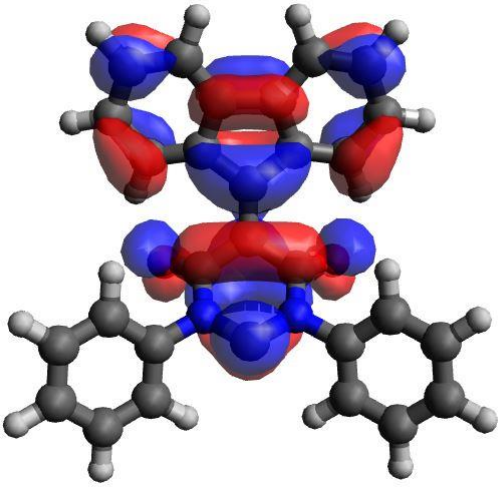




OMe HOMO: -5.613 eV **OMe** LUMO: -2.673 eV

OMe ΔH_{S-T}: 67.80

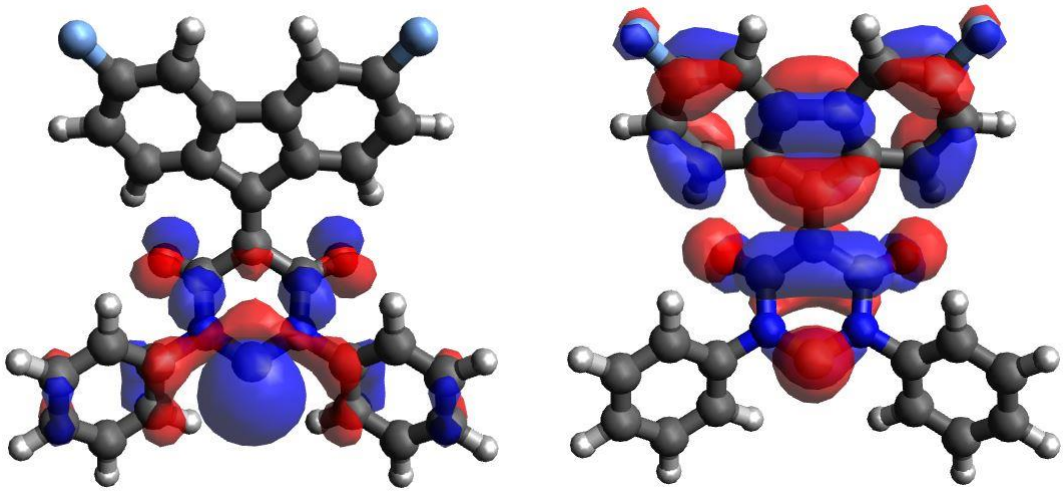




H HOMO: -5.815 eV **H** LUMO: -2.925 eV

H ΔH_{S-T}: 66.64

Figure A10: Continued on Next Page

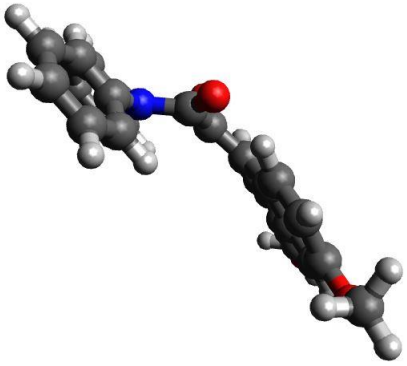


F HOMO: -5.908 eV **F** LUMO: -3.075 eV

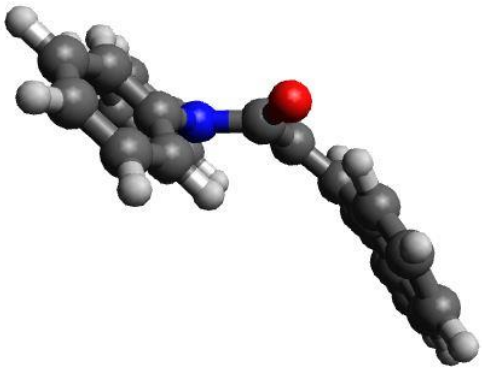
F $\Delta H_{S\text{-}T}$: 65.34 kcal/mol

Figure A10: Selected molecular orbitals and energies (in kcal/mol or eV) N-phenyl analogues of **3a-c**; **OMe** (top), **H** (middle), and the **F** (bottom) calculated at the B3LYP 6-31+G(d) level.

OMe:



H:



F:

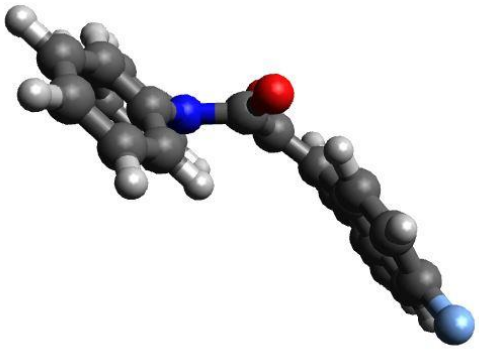


Figure A11: Side-on ball-and-stick representations of N-phenyl analogues of **3a-c**; **OMe** (top), **H** (middle), and the **F** (bottom).

OMe

	ATOM	X	Y	Z
1	C	-3.067204	0.000422	-0.229316
2	C	-1.214700	-1.233856	0.890674
3	C	-1.214329	1.234468	0.890370
4	C	-0.394026	0.000179	0.865555
5	N	-2.426562	1.146936	0.131787
6	N	-2.426902	-1.146193	0.132079
7	O	-0.952516	2.250651	1.507959
8	O	-0.953158	-2.249917	1.508584
9	C	0.988949	-0.000073	0.745443
10	C	1.870474	1.185158	0.508538
11	C	3.924692	2.976860	-0.238037
12	C	1.726550	2.561085	0.717505
13	C	3.104198	0.730817	-0.030233
14	C	4.112227	1.593771	-0.411896
15	C	2.740127	3.448457	0.338850
16	C	1.869987	-1.185639	0.508304
17	C	3.923406	-2.978036	-0.238841
18	C	3.103887	-0.731695	-0.030400
19	C	1.725468	-2.561565	0.716874
20	C	2.738647	-3.449274	0.337943
21	C	4.111530	-1.594984	-0.412331
22	H	0.847723	2.956416	1.201007
23	H	2.596157	4.506264	0.521327
24	H	5.048827	1.240525	-0.829928
25	H	5.048260	-1.242026	-0.830316
26	H	2.594219	-4.507068	0.520130
27	H	0.846498	-2.956672	1.200304
28	C	-3.123473	-2.385442	-0.149775
29	C	-2.442664	-3.450687	-0.742798
30	C	-4.484086	-2.491863	0.136244
31	C	-3.129087	-4.625644	-1.043655
32	H	-1.385671	-3.360780	-0.967478
33	C	-5.165586	-3.668762	-0.172003
34	H	-4.996378	-1.644987	0.577018
35	C	-4.491199	-4.739540	-0.759549
36	H	-2.597596	-5.451409	-1.507193
37	H	-6.225583	-3.746778	0.050509
38	H	-5.023120	-5.655890	-0.997215
39	C	-3.122772	2.386314	-0.150407
40	C	-2.441658	3.451193	-0.743737
41	C	-4.483350	2.493215	0.135599
42	C	-3.127741	4.626265	-1.044920
43	H	-1.384692	3.360920	-0.968393
44	C	-5.164510	3.670225	-0.172974
45	H	-4.995885	1.646614	0.576619
46	C	-4.489817	4.740639	-0.760832
47	H	-2.596014	5.451743	-1.508698
48	H	-6.224481	3.748614	0.049529
49	H	-5.021473	5.657077	-0.998753
50	O	4.956894	-3.762623	-0.640189
51	O	4.958530	3.761107	-0.639146
52	C	4.839172	-5.171861	-0.488343
53	H	3.988894	-5.567282	-1.056875
54	H	5.764651	-5.592930	-0.882472
55	H	4.732020	-5.454937	0.565722

Table A4: Continued on Next Page

56	C	4.841410	5.170356	-0.486931
57	H	5.767078	5.591131	-0.880928
58	H	3.991313	5.566291	-1.055376
59	H	4.734356	5.453198	0.567207

H

	ATOM	X	Y	Z
1	C	2.334342	-0.001134	0.197426
2	C	0.472212	-1.235962	-0.898445
3	C	0.473507	1.235339	-0.898642
4	C	-0.352193	0.000116	-0.836263
5	N	1.691123	1.148759	-0.152294
6	N	1.689891	-1.150412	-0.151878
7	O	0.203116	2.234728	-1.535491
8	O	0.201024	-2.235269	-1.535051
9	C	-1.715636	0.000894	-0.630868
10	C	-2.576821	1.191652	-0.323627
11	C	-4.539030	2.984070	0.596697
12	C	-2.439649	2.563921	-0.562921
13	C	-3.748116	0.733250	0.329665
14	C	-4.715238	1.612112	0.800564
15	C	-3.418425	3.447174	-0.090985
16	C	-2.578406	-1.188969	-0.324765
17	C	-4.543218	-2.979650	0.593311
18	C	-3.749124	-0.729642	0.328908
19	C	-2.443161	-2.561144	-0.565667
20	C	-3.423228	-3.443555	-0.094828
21	C	-4.717518	-1.607672	0.798727
22	H	-1.607832	2.946991	-1.132465
23	H	-3.303215	4.509563	-0.282911
24	H	-5.287348	3.685320	0.954030
25	H	-5.600763	1.240473	1.307411
26	H	-5.602589	-1.235372	1.305882
27	H	-5.292553	-3.680250	0.949787
28	H	-3.309512	-4.505885	-0.287969
29	H	-1.611807	-2.944684	-1.135564
30	C	2.391470	-2.390575	0.117116
31	C	1.714692	-3.459040	0.708609
32	C	3.749388	-2.494046	-0.181881
33	C	2.403510	-4.636227	0.995083
34	H	0.659645	-3.370897	0.943444
35	C	4.432984	-3.673151	0.112768
36	H	4.257958	-1.644622	-0.621994
37	C	3.763112	-4.747766	0.698581
38	H	1.875791	-5.465195	1.456944
39	H	5.490946	-3.749994	-0.119306
40	H	4.296853	-5.665782	0.925191
41	C	2.394157	2.388227	0.116107
42	C	1.718748	3.457599	0.707523
43	C	3.752082	2.490106	-0.183378
44	C	2.408951	4.634117	0.993404
45	H	0.663692	3.370655	0.942767
46	C	4.437073	3.668550	0.110686
47	H	4.259573	1.639996	-0.623414
48	C	3.768570	4.744079	0.696383
49	H	1.882308	5.463801	1.455206
50	H	5.495041	3.744165	-0.121764
51	H	4.303394	5.661580	0.922528

Table A4: Continued on Next Page

F

	ATOM	X	Y	Z
1	C	2.714955	0.000585	-0.224247
2	C	0.871742	1.236492	0.901511
3	C	0.872333	-1.235778	0.901889
4	C	0.046781	0.000152	0.863657
5	N	2.076403	-1.148589	0.136111
6	N	2.075828	1.149568	0.135673
7	O	0.611599	-2.239459	1.537268
8	O	0.610622	2.240335	1.536468
9	C	-1.325395	-0.000252	0.711666
10	C	-2.200894	-1.189370	0.448147
11	C	-4.199977	-2.961020	-0.350951
12	C	-2.052653	-2.565011	0.670399
13	C	-3.410600	-0.731480	-0.132323
14	C	-4.411039	-1.598644	-0.548194
15	C	-3.052527	-3.451159	0.259065
16	C	-2.201727	1.188363	0.448821
17	C	-4.202193	2.959067	-0.348839
18	C	-3.411137	0.729963	-0.131860
19	C	-2.054513	2.563947	0.672098
20	C	-3.055086	3.449637	0.261473
21	C	-4.412252	1.596669	-0.547042
22	H	-1.188111	-2.953067	1.184818
23	H	-2.954370	-4.517710	0.427069
24	H	-5.334671	-1.253025	-0.998948
25	H	-5.335674	1.250687	-0.997948
26	H	-2.957726	4.516141	0.430241
27	H	-1.190196	2.952234	1.186714
28	C	2.774425	2.389541	-0.143792
29	C	2.094174	3.451938	-0.741737
30	C	4.132520	2.497717	0.152034
31	C	2.779586	4.628721	-1.037853
32	H	1.039164	3.358986	-0.975199
33	C	4.812863	3.676361	-0.151947
34	H	4.643972	1.652660	0.597309
35	C	4.139387	4.745230	-0.744126
36	H	2.249467	5.453125	-1.505024
37	H	5.871032	3.757326	0.077576
38	H	4.670664	5.662768	-0.978166
39	C	2.775639	-2.388318	-0.142814
40	C	2.095974	-3.451277	-0.740425
41	C	4.133754	-2.495714	0.153201
42	C	2.781993	-4.627841	-1.036007
43	H	1.040949	-3.358921	-0.974058
44	C	4.814708	-3.674142	-0.150247
45	H	4.644743	-1.650235	0.598208
46	C	4.141818	-4.743572	-0.742082
47	H	2.252330	-5.452684	-1.502921
48	H	5.872891	-3.754501	0.079420
49	H	4.673569	-5.660941	-0.975706
50	F	-5.156854	3.822822	-0.739866
51	F	-5.153965	-3.825216	-0.742648

Table A4: B3LYP Cartesian coordinates for the compounds investigated in this study: **OMe**, **H**, **F.**

Carbene	Point Group[a]	Enthalpy[b]
OMe	C_1	- 1604.4276
H	C_1	- 1375.4416
F	C_1	- 1573.9207

Table A5: Calculated B3LYP point groups and enthalpies for the compounds investigated in this study: **OMe**, **H**, and **F**.

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