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Hypervalent Iodonium Alkynyl Triflate Generated Phenylcyanocarbene and Its Reactivity with Aromatic Systems

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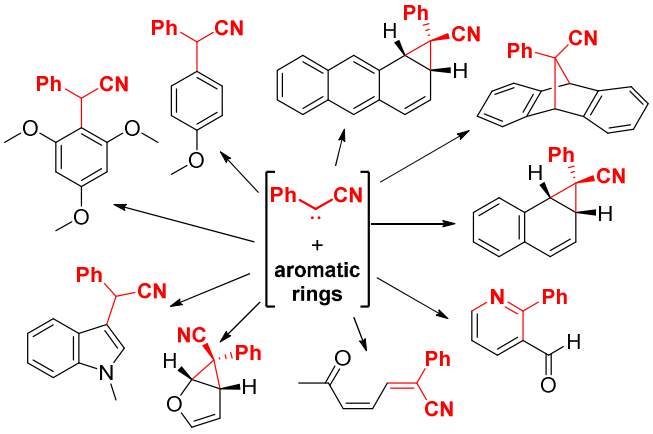
ABSTRACT: Phenylcyanocarbene was generated by the reaction of azide with a hypervalent iodonium alkynyl triflate and reacted *in situ* with 21 different carbocyclic and heterocyclic aromatic compounds. These reactions led to more complex products that frequently underwent subsequent rearrangements. The reactivity was further explored in a mechanistic study to ascertain the chemoselectivity and stereospecificity.



INTRODUCTION

The design and development of new reactions plays a crucial role in the continued advancement of organic synthesis. New reactions that generate a significant amount of molecular complexity and/or allow for previously unimagined retrosynthetic disconnections are particularly valuable.[1] Towards this end, our group[2] and others[3] have been interested in the formation of cyanocarbenes from alkynes and azides and the utilization of this reactive intermediate in a variety of reactions. These reactions are

valuable for both of the previously mentioned benefits since: 1) the molecular complexity increases significantly from these readily available starting materials; and 2) this reaction presents a novel disconnection by transforming the two carbons of the alkyne and one of the nitrogens of the azide into a carbene and a nitrile (Figure 1).

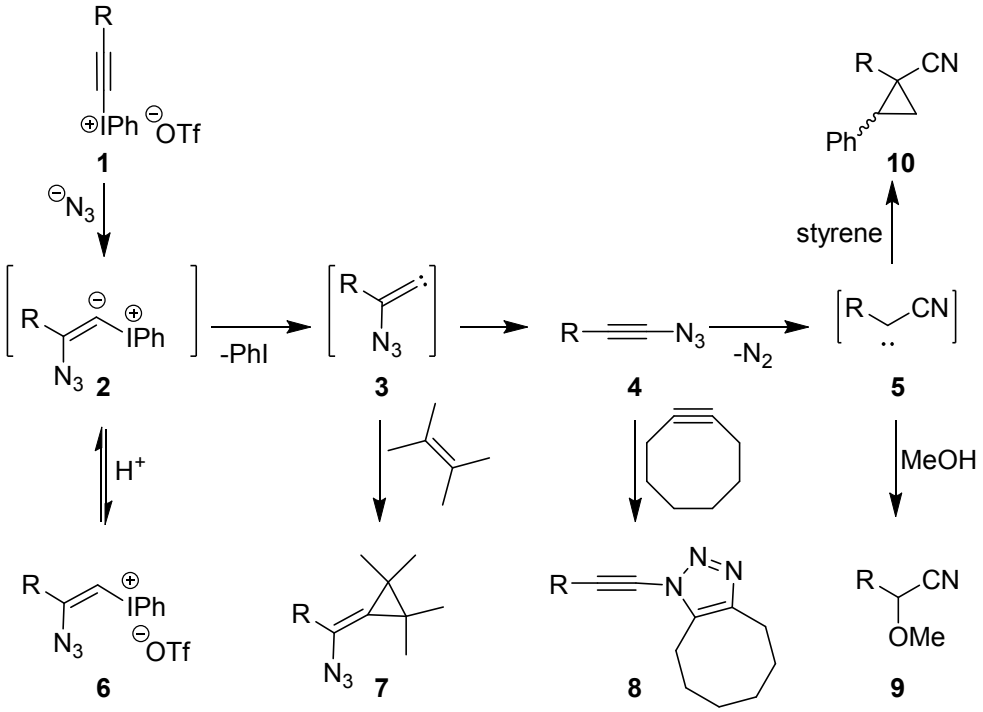


Figure 1. Generation of cyanocarbenes from alkynes and azides and the relevant products.

The logical first step in formation of a cyanocarbene (**5**) from alkynes and azides involves formation of a carbon-nitrogen bond. Earlier work from our group[2e] and others[3j, 4] attempted this process using a nucleophilic acetylide anion and electrophilic sulfonyl azide. The only products isolated were sulfonyl triazoles, however, Banert and coworkers later determined that highly sterically hindered trityl alkynes could yield the cyanocarbenes.[3f] In order to have an approach to cyanocarbenes from a wider variety of alkynes, the umpolung approach was explored using nucleophilic azide anions with electrophilic hypervalent iodonium alkynyl triflates (HIATs, Figure 1, **1**).[2a, 3a] Gratifyingly, this reaction led to cyanocarbenes, after traversing a series of reactive intermediates. This reaction proceeds by initial azide attack at the more electrophilic β-position of the HIAT to generate iodonium ylide **2**.[5] Evidence for iodonium ylides include protonation to generate alkenyl iodonium salt **6**[2a] and other reactivity reported by

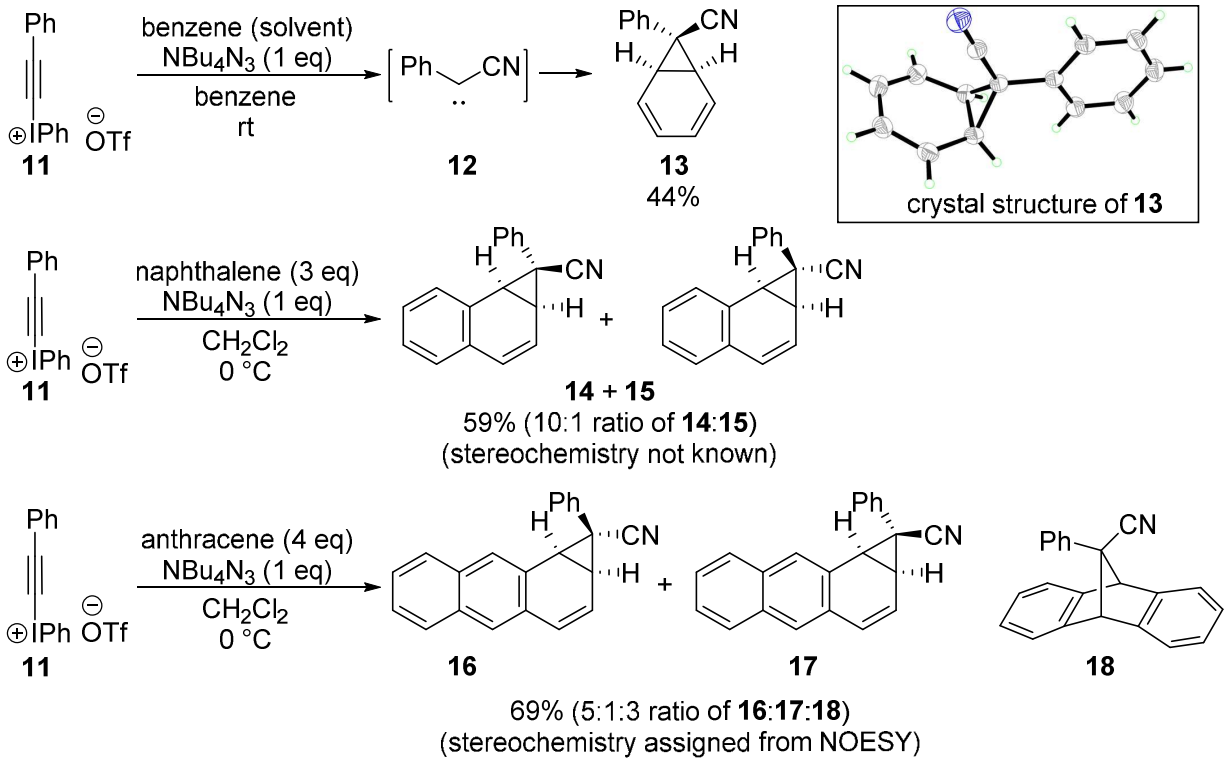
others.[5-6] The iodonium ylide is able to heterolytically cleave iodobenzene to generate vinylidene carbene **3**. Evidence for the vinylidene carbene is the capture with an alkene to generate methylenecyclopropane **7**.[3a] Alternatively, vinylidene carbene **3** can undergo a Fritsch–Buttenberg–Wiechell-like rearrangement to produce alkynyl azide **4**.

Despite the instability of the alkynyl azides, the Banert group has reported extensive characterization and derivatization of azidoacetylene (**4**, R = H) and (azidoethynyl)trimethylsilane (**4**, R = TMS).[3a, 3g] It has previously been proposed that the alkynyl azide undergoes loss of dinitrogen to generate an alkynyl nitrene,[3i] however, more recent studies indicate a direct conversion to the cyanocarbene.[3c, 3g] The typical means of accessing cyanocarbenes and other related carbenes involve decomposition of diazonitriles using metal catalysts. Although the use of metal catalysts can be highly beneficial in tuning the reactivity of the carbenes and induce a chirality by using chiral ligand, the generation of cyanocarbenes directly from HIATs and azide leads to a free carbene without any metal bound to modulate its reactivity. Thus far, the reactivity studies of cyanocarbenes generated from alkynes and azides have been limited to reactions with DMSO, alcohols, alkenes, alkynes and alkyl halides.[2a, 2c, 2d, 3a, 3b, 3d-h] Herein, we report reactions of phenylcyanocarbene with aromatic rings which frequently led to subsequent derivatization of the structure, along with a mechanistic analysis to assess the chemoselectivity and stereospecificity of phenylcyanocarbene.

RESULTS AND DISCUSSION

Reactions of Phenylcyanocarbene with Carbocyclic Aromatic Rings. A classic reaction of carbenes is to undergo a cyclopropanation reaction with an alkene.[5, 7] Much less common is the cyclopropanation of aromatic rings, typically referred to as the Buchner reaction.[8] To explore this reaction with phenylcyanocarbene (**12**), benzene was used as the reagent and solvent with HIAT **11** and one equivalent of azide at ambient temperature (Scheme 1). This reaction was complete within 5 minutes and produced norcaradiene **13** as a single diastereomer unlike the previously reported non-diastereoselective phenylcyanocarbene reactions with styrene and allyl benzene.[2a] The diastereoselectivity of this reaction,

determined by X-ray crystallography, is likely due to a thermodynamic equilibration via the cycloheptatriene instead of a kinetic effect.[9]



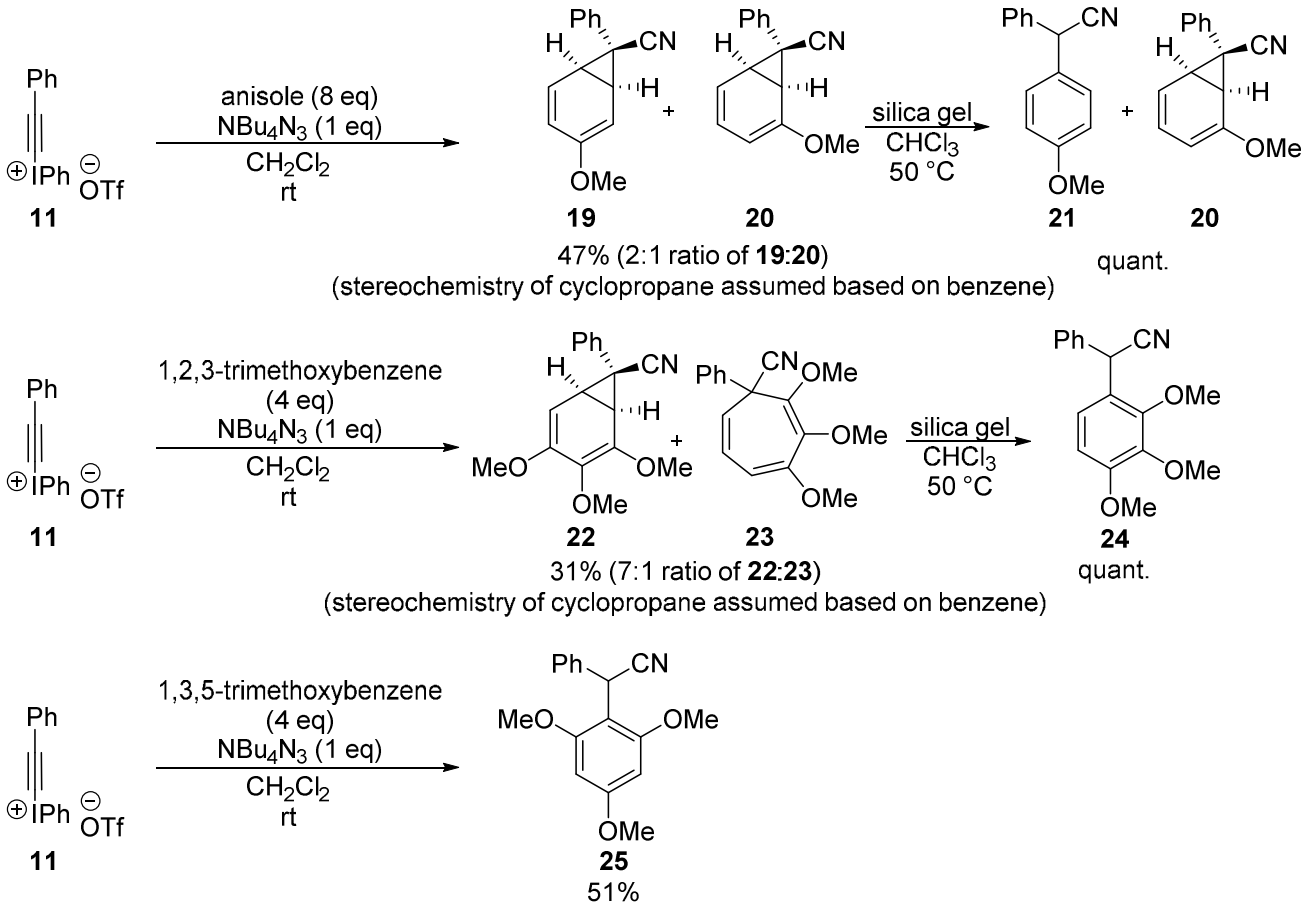
Scheme 1. Reactions of phenylcyanocarbene with benzene, naphthalene, and anthracene.

In addition to benzene, the more extended aromatic compounds, naphthalene and anthracene, were examined (Scheme 1). Since neither of these aromatic compounds is a liquid at room temperature, dichloromethane was used as the solvent. As expected, the 1,2-position was the most reactive for cyclopropanation in both systems since this type of reactivity maintains aromaticity in the system. Prior reactions of phenylcyanocarbene with styrene and allyl benzene led to an approximately 1:1 ratio of diastereomers, however, in the cases of naphthalene and anthracene there is a higher preference for one cyclopropane diastereomer over the other. This could again be a thermodynamic consequence via reversible six-electron DIS-rotatory electrocyclic ring opening of the product. Surprisingly, anthracene yielded bridged bicycle **18** where the cyanocarbene added across the diene of the central ring in a [4+1] fashion. Reactivity at the diene of the central ring of anthracene has been heavily reported in the past for Diels-Alder reactions,[10] but [4+1] reactivity with anthracene has been reported only in rare cases such as

with phenylcarbene[11] or NO.[12] This reaction also yielded trace amounts of dicyclopropanated product as suggested by HRMS data.

Beyond simple aromatic systems, the reactions of phenylcyanocarbene with electron-deficient and electron-rich carbocyclic aromatic rings was examined. The reactions of phenylcyanocarbene with electron-deficient aromatic rings, such as benzophenone, benzaldehyde, 3,5-dimethylbenzoic acid, and methyl benzoate were not successful and only moderate dimerization of the phenylcyanocarbene was observed in those reactions. These unsuccessful substrates illustrated the need for more nucleophilic aromatic systems to react with phenylcyanocarbene.

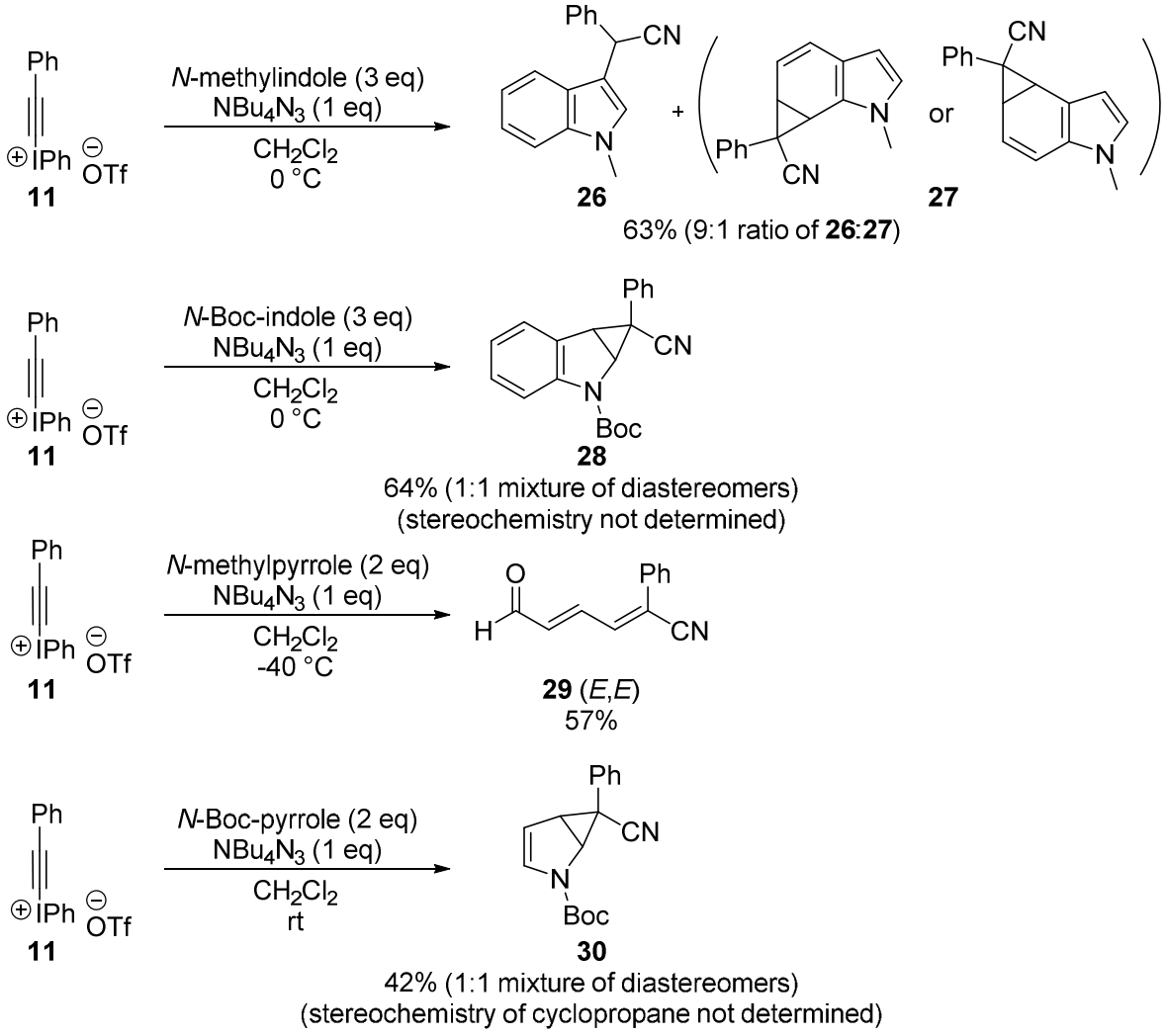
As anticipated, anisole, 1,2,3-trimethoxybenzene, and 1,3,5-trimethoxybenzene were all significantly more reactive than benzene, likely due to the π-donating effect of the methoxy groups (Scheme 2). Anisole reacted with phenylcyanocarbene, formed *in situ*, to give the expected cyclopropanated products at C3-C4 (**19**) and C2-C3 (**20**) with a ratio 2:1, respectively. Interestingly, when this mixture was treated with silica gel at 50 °C, compound **19** underwent an acid catalyzed ring opening to give compound **21**, whereas compound **20** was unchanged. This experiment indicates the difference in rates for bicycles **19** and **20** for their ring opening, due the electronic push-pull system of the methoxy-nitrile functional groups, and subsequent proton transfer. Trimethoxybenzene derivatives were also reacted with phenylcyanocarbene, and the outcomes were dependent on the substitution pattern. 1,2,3-Trimethoxy benzene reacted to give cyclopropanated product **22** in addition to the cycloheptatriene derivative **23**, with a 7:1 ratio, respectively. Acid catalyzed ring opening conditions resulted in the formation of compound **24** from both **22** and **23**. Presumably, cyclohepatriene **23** equilibrates with its analogous norcaradiene (not shown) under these conditions to genereate benzene **24**. 1,3,5-Trimethoxybenzene reacted with phenylcyanocarbene to directly give 2-phenyl-2-(2,4,6-trimethoxyphenyl)acetonitrile (**24**). The theoretical cyclopropane intermediate is less stable, and not isolated, since all three methoxy groups constructively add electron density to the same positions to open the strained ring.



Scheme 2. Reactions of phenylcyanocarbene with anisole, 1,2,3-trimethoxybenzene, and 1,3,5-trimethoxybenzene.

Reactions of Phenylcyanocarbene with Heteroaromatic Rings. Based on the interesting reactions observed with carbocyclic aromatic rings, heteroaromatic ring systems were also explored. The selection of heteroaromatic ring systems needed to be compatible with the *in situ* formation of phenylcyanocarbene. For example, indole, pyrrole, pyridine and pyridine-*N*-oxide were possibly too nucleophilic and reacted with the phenyl HIAT reagent (**11**). For the case of pyridine and its *N*-oxide analogue, the lack of reactivity migh be due to electronroic factors. Fortunately, *N*-methylindole, *N*-methylpyrrole, and their *N*-*tert*-butoxycarbonyl (Boc) analogues had sufficient steric hinderance or electronic modification to allow for compatibility with phenylcyanocarbene.

The reaction of phenylcyanocarbene with *N*-methylindole primarily led to a net C-H insertion reaction, presumably via the C2-C3 cyclopropane intermediate as described earlier (Scheme 3). Similar to the methoxy groups of 1,3,5-trimethoxybenzene, the strongly π-donating nitrogen atom readily opened the cyclopropane and proton transfer occurs over the course of the reaction. The *N*-*tert*-butoxycarbonyl indole (*N*-Boc-indole) derivative influenced the nitrogen atom to be less electron-rich and, therefore, cyclopropane **28** was isolated and purified as the major product. Unlike earlier aromatic systems, cyclopropane **28** was isolated as a ~1:1 mixture of cyclopropane diastereomers.



Scheme 3. Reactions of phenylcyanocarbene with indoles and pyrroles.

The reaction of methyl pyrrole did not yield the anticipated cyclopropane; instead, this reaction resulted in the formation of dienal **29** in a good yield (57%, Scheme 3). Presumably, a cyclopropanation reaction

occurred to generate bicycle **31**, which then underwent nitrogen assisted cyclopropane ring opening, via a push-pull mechanism, to generate zwitterion **A** (Figure 2). Unlike the prior reactions for the anisoles and indoles that underwent proton transfer, the zwitterionic intermediate (**A**) opened the heterocycle to generate imine **B**, which hydrolyzedto dienal **29** during work up or trace water in reaction mixture. The dienal would initially have a *cis*-geometry at the α,β-position due to its stereochemistry in the pyrrole, however, methylamine likely isomerized this system to the thermodynamically most stable mixture of double bond isomers. Notable, formation of a dienal via the reaction of *N*-methylpyrrole with a carbene has not been previously reported, although this reactivity is commonly observed with furan.[13] The usage of *N*-Boc-pyrrole resulted in a less electron-rich nitrogen atom such that the cyclopropane intermediate was isolable, as a mixture of diastereomers and rotamers, with no formation of dienal product (**29**, Scheme 3).

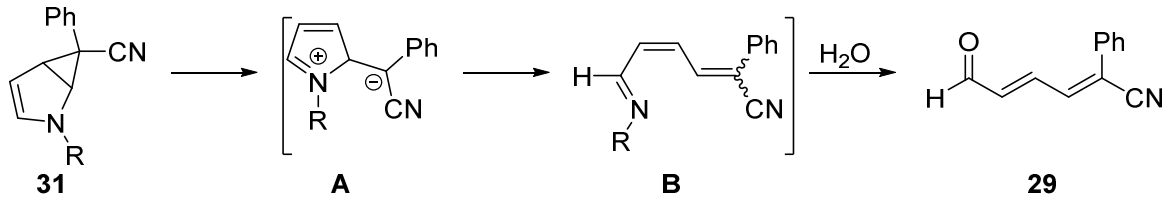
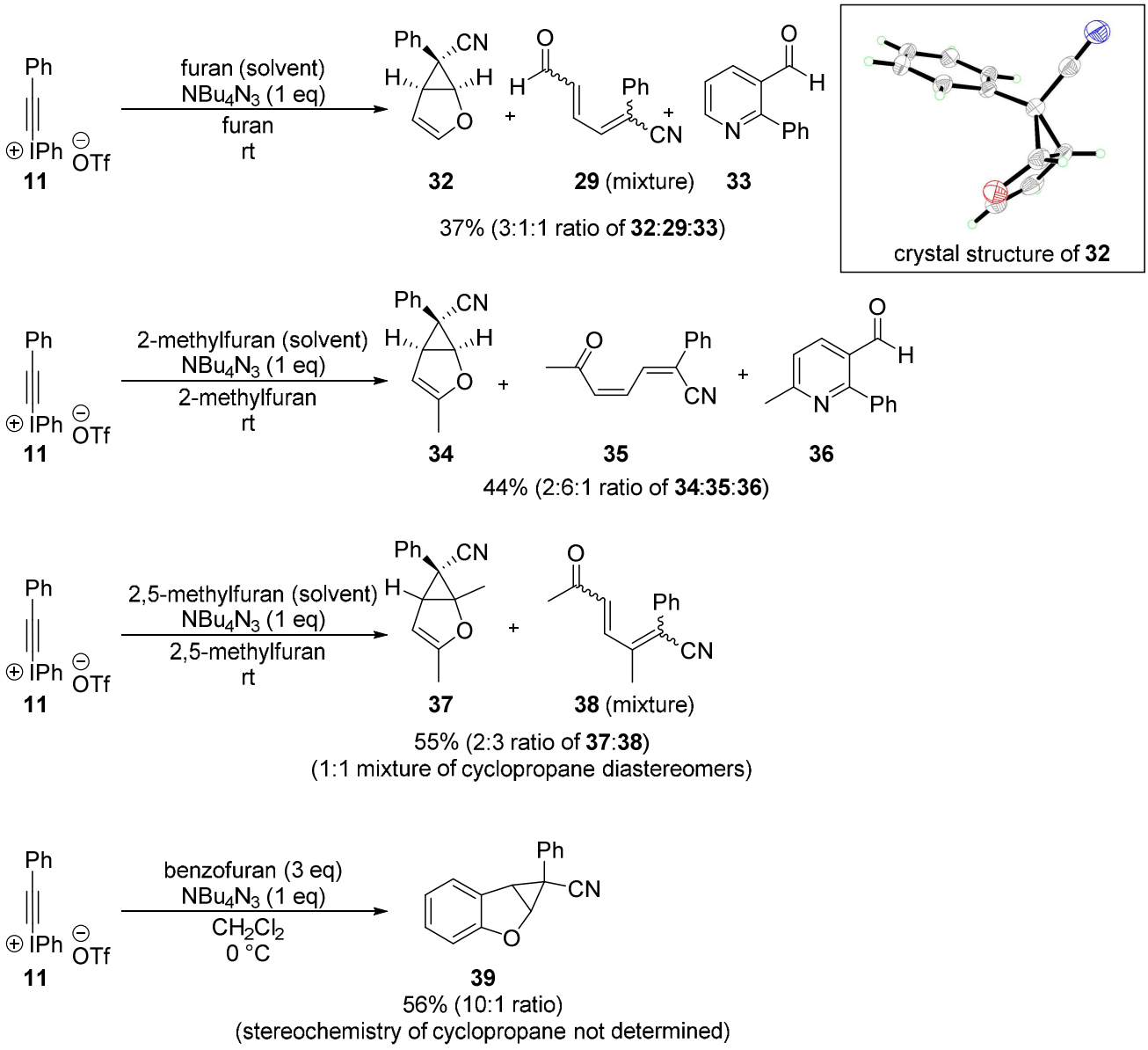


Figure 2. Mechanism for formation of dienals from pyrroles.

The reactivity of phenylcyanocarbene with furan derivatives was examined next, with the expectation of the formation of dienal products (Scheme 4). Interestingly, the reaction with furan gave cyclopropanated product **32** as a single diastereomer. The structure and the stereochemistry of this product was confirmed by X-ray crystallography. Unlike the stereochemistry of compound **13**, the nitrile is in the endo position. The selectivity observed in the furan reaction might be due to a secondary π-π interaction between the benzene ring and the vinyl ether. This furan reaction also resulted in the formation of a diastereomeric mixture of dienal products **29** (Scheme 4). Initially, the diastereomeric composition of dienal **29** is almost exclusively the *Z*-isomer at the 2,3-alkene, but treatment with protic solvents such as methanol isomerizes the structure to a mixture, primarily *E* at the 2,3-position. In addition to cyclopropane **32** and dienals **29**, known 2-phenylnicotinaldehyde (**33**)[14] was observed in this reaction in a low but reproducible yield.

Compound **33** is technically an isomer of the other products formed in this reaction, but unlike the other compounds, its formation was completely unexpected.

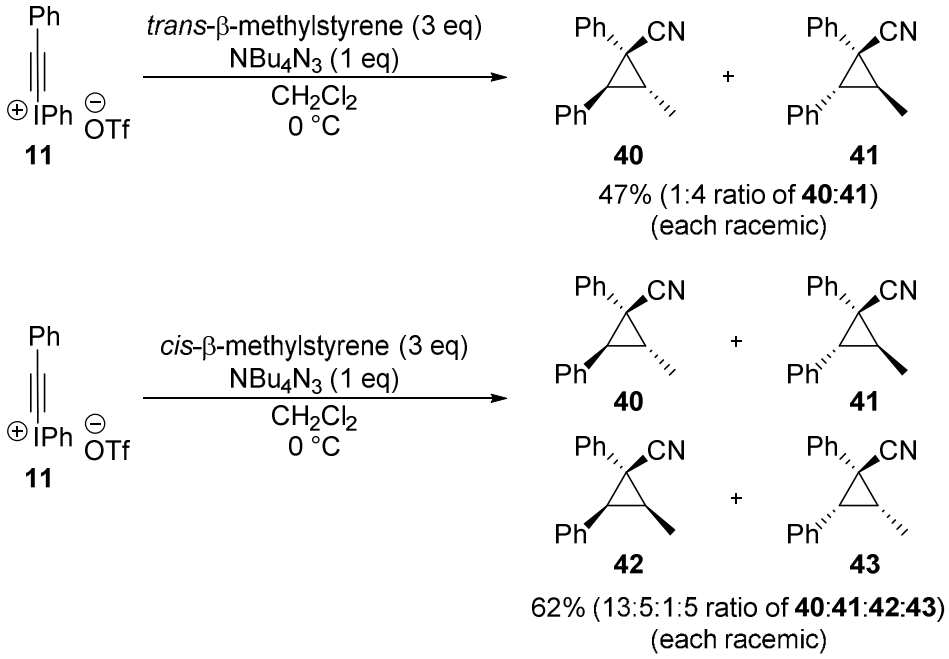


Scheme 4. Reactions of phenylcyanocarbene with furans.

To further explore the reactivity of phenylcyanocarbene, 2-methylfuran, 2,5-dimethylfuran, and benzofuran were utilized. With 2-methylfuran, cyclopropane **34** and dienone **35** were the major products

and 6-methyl nicotinaldehyde derivative **36** was also isolated. In comparison with dienal **29**, which was not stable and scrambling of the stereochemistry was observed, dienone **35** was stable and isolated as a single diastereomer. 2,5-Dimethylfuran reacted to yield cyclopropane **37** and dienone **38**, both as mixtures of diastereomers. Benzofuran produced the cyclopropanated product in a good yield and diastereoselectivity (59%, 10:1 *dr*), with no opening of any of the three rings of the product, similar to *N*-Boc-indole (Scheme 3). Pyridine products were observed in neither the reaction of 2,5-dimethylfuran nor that of benzofuran. Further experiments to explore the mechanism for the formation of pyridines from furans and phenylcyanocarbene are ongoing.

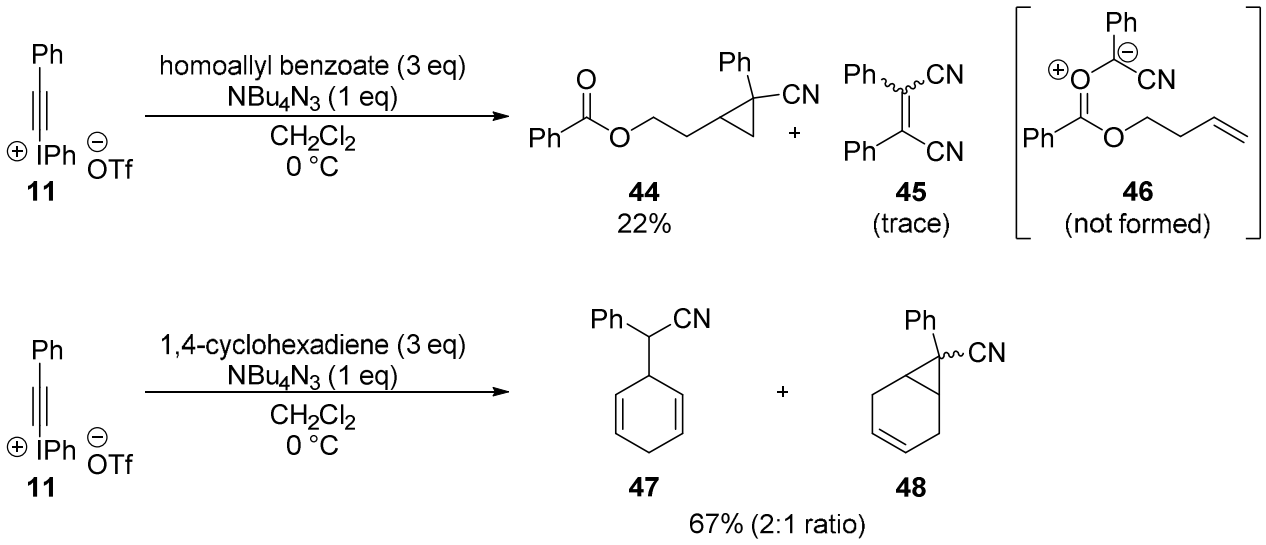
Mechanistic Analysis for Phenylcyanocarbene. The route to access phenylcyanocarbene is hypothesized to involve a series of reactive intermediates including iodonium ylide **2**, vinylidene carbene **3**, alkynyl azide **4**, and cyanocarbene **5** (Figure 1). As mentioned earlier, the Banert and Croatt groups have previously characterized compounds or derivatives to validate these different intermediates. The Banert group has done extensive analysis of a cyanocarbene (**5**, R = H) that results from the loss of nitrogen from azidoacetylene (**4**, R = H). In their analysis, they determined that it is likely a triplet carbene.[3h] To further analyze the properties of phenylcyanocarbene, it was decided to react it with the two different stereoisomers of β-methylstyrene. If phenylcyanocarbene is a singlet carbene it was anticipated that the reaction would be concerted and the reaction would be stereospecific. If phenylcyanocarbene is a triplet carbene, isomerization could occur to generate a mixture of compounds. Based on the lack of stereospecificity (Scheme 5), it appears that phenylcyanocarbene also reacts as a triplet carbene since the *cis*-β-methyl styrene starting material generated a mixture of all four diastereoisomers with the major products having the opposite stereochemistry of the original alkene.



Scheme 5. Reactions of phenylcyanocarbene with *cis*- and *trans*-β-methylstyrene.

As mentioned earlier, we have reported that phenylcyanocarbene reacts with methanol to undergo a net O-H insertion. Due to the strength of an O-H bond, it is unlikely that the carbene is doing a concerted insertion into that bond. Instead, it is hypothesized that the transformation is step-wise by the nucleophilic oxygen atom of methanol first adding into the electrophilic carbene followed by subsequent proton transfer. This type of reactivity is more typical of a singlet carbene. Therefore, it appears that the barrier for the conversion between singlet and triplet carbene may be small for phenylcyanocarbene. Interestingly, the singlet/triplet dichotomy was similarly reported for phenylcarbene, which was generated at 130 °C via a Bamford-Stevens reaction.[11] Based on the reactions in Scheme 5, the triplet carbene is preferred or kinetically formed for reactions with alkenes. To further explore this carbene selectivity, the reactions of phenylcyanocarbene with either homoallyl benzoate or 1,4-cyclohexadiene were examined (Scheme 6). If phenylcyanocarbene preferred to react as an electrophilic singlet carbene, it was hypothesized that the ester carbonyl would add to the carbene and form a carbonyl ylide (**46**).[15] Ylide **46** would then react intramolecularly with the pendant alkene. If phenylcyanocarbene preferentially reacted as a triplet carbene, the alkene would be more reactive in a cyclopropanation reaction. With homoallyl

benzoate, only cyclopropanation was observed. With 1,4-cyclohexadiene, the major product was C-H insertion (**47**), presumably via initial hydrogen atom abstraction and subsequent recombination, although cyclopropanation (**48**) occurred as well. Both experiments are further indicators of the preferred triplet reactivity.[16]



Scheme 6. Reactions of phenylcyanocarbene with homoallyl benzoate and 1,4-cyclohexadiene.

CONCLUSIONS

In this study, we explored the reactivity of phenylcyanocarbene with a series of carbocyclic aromatic rings and heteroaromatic rings. The reactions were complete within minutes at ambient temperature or colder temperatures and explored the reactivity of free phenylcyanocarbene since there is no use of a transition metal catalyst to affect its reactivity. The typical reaction observed was cyclopropanation of the most electron rich and sterically accessible bond in the aromatic ring. Depending on the nature of the system, subsequent reactions occurred to relieve the strain of cyclopropane. The net result of the reactions ranged from simple cyclopropanation, to C-H insertion or opening of the aromatic ring. A brief study into the reactivity profile of phenylcyanocarbene indicates a preferred triplet state based on its chemoselectivity and lack of stereospecificity. The diversity of structures available by the utilization of this readily available reactive intermediate underscores the value of phenylcyanocarbene and its precursor HIAT (**11**).

EXPERIMENTAL SECTION

General Information. All anhydrous reactions were performed in oven dried glassware under a nitrogen atmosphere. Unless otherwise noted, all solvents and reagents were obtained from commercial sources and used without further purification. HIAT **11** was generated following previously reported procedures.[2d] Chromatographic purification was performed using silica gel (60 Å, 32-63μm). NMR spectra were recorded in $CDCl_3$ using a JEOL ECA 400 spectrometer (400 MHz for ^1H and 100 MHz for ^{13}C), and JEOL ECA spectrometer (500 MHz for ^1H and 125 MHz for ^{13}C). Coupling constants, *J*, are reported in Hertz (Hz) and multiplicities are listed as singlet (s), doublet (d), triplet (t), quartet (q), quintet (quint), doublet of doublets (dd), triplet of triplets (tt), multiplet (m), etc. Melting points were determined using a MEL-TEMP 1101D melting point apparatus and are uncorrected. High Resolution Mass Spectra were acquired on a Thermo Fisher Scientific LTQ Orbitrap XL MS system using Atmospheric Pressure Photoionization (APPI). *Warning: Azides and hypervalent iodine species are commonly reported to be explosive when dried and made on larger scales. Use of a blast shield and small scale reactions are advised. The reactions described herein generate gas, N_2, so procedures must be used to allow for this gas to escape.*

General Procedure A: Formation of Phenylcyanocarbene Using Aromatic Ring as Solvent. A solution of phenyl hypervalent iodonium alkynyl triflate (**11**, 50 mg, 0.11 mmol, 1.0 equiv.) in a minimal amount (~4.0 – 8.0 mL) of aryl derivative was added to a dry flask under an argon atmosphere at ambient temperature. Tetrabutylammonium azide (31 mg, 0.11 mmol, 1.0 equiv.) was weighed in a glovebox to avoid water contamination and added into the reaction mixture. The reaction was stirred under a nitrogen atmosphere and when nitrogen gas stopped being generated, typically within five minutes, or TLC indicated completion of the reaction, the reaction mixture was evaporated to dryness under reduced pressures and the residual mixture was purified by column chromatography.

General Procedure B: Formation of Phenylcyanocarbene Using Aromatic Ring as Reagent and Dichloromethane as Solvent. A solution of phenyl hypervalent iodonium alkynyl triflate (50 mg, 0.11

mmol, 1.0 equiv.) in a minimal amount of dichloromethane (~4.0 – 8.0 mL) was added to a dry flask under an argon atmosphere and cooled to the indicated temperature. To this solution, the indicated equivalents of the aryl derivative were added followed by the addition of anhydrous tetrabutylammonium azide (31 mg, 0.11 mmol, 1.0 equiv.). The reaction was stirred under a nitrogen atmosphere and when nitrogen gas stopped being generated, typically within five minutes for ambient temperature and 15-20 minutes at lower temperature, or TLC indicated completion of the reaction, the reaction mixture was evaporated to dryness under reduced pressures and the residual mixture was purified by column chromatography.

General Procedure C: Silica Gel-Promoted Opening of Cyclopropanes. Cyclopropanated compound was dissolved in $CHCl_3$ (5.0 mL) and silica gel (100 mg) was added. This mixture was heated to 50 °C (water bath) for 3 hr. After that time, the reaction mixture was filtered to remove the silica gel, which was washed with $CHCl_3$ (2 x 3.0 mL). The solvent was removed under reduced pressure to obtain the desired product(s) in a pure form.

Benzene reaction. General procedure A was followed to generate *7-phenylbicyclo[4.1.0]hepta-2,4-diene-7-carbonitrile* (**13**) isolated after column chromatography (0 - 5% EtOAc: hexane) as an oil (9.4 mg, 44% yield). The ^{1}H NMR data matched the previously reported data.[9a] ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.44 – 7.28 (m, 5H), 6.43 (dd, J = 6.6, 3.0 Hz, 2H), 6.23 – 6.31 (m, 2H), 3.44 (dd, J = 4.5, 2.4 Hz, 2H). X-ray crystallography was used to determine the relative stereochemistry and the cif file is included in the Supporting Information.

Naphthalene reaction. General procedure B was followed using 3.0 equivalents of naphthalene at 0 °C to generate a 10:1 diastereomeric mixture of *1-phenyl-1a,7b-dihydro-1H-cyclopropa[a]naphthalene-1-carbonitrile* (**14** and **15**) isolated after column chromatography (0 - 10% EtOAc: hexane) as a pale yellow solid (15.8 mg, 59% yield). *Major isomer*: ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.56 (d, J = 7.7 Hz, 1H), 7.30 (t, J = 7.7 Hz, 1H), 7.14 (t, J = 7.7 Hz, 1H), 7.08 (d, J = 7.2 Hz, 1H), 7.03 (t, J = 7.2 Hz, 2H), 6.89 (d, J = 7.2 Hz, 2H), 6.79 (d, J = 7.7 Hz, 1H), 6.17 (d, J = 9.6 Hz, 1H), 6.09 (dd, J = 9.6, 5.1 Hz, 1H), 3.59 (d, J = 8.9 Hz, 1H), 3.16 (dd, J = 8.9, 5.1 Hz, 1H); *Minor isomer*: ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ

7.59 – 7.52 (m, 1H), 7.43 – 7.26 (m, 7H), 7.12 – 7.07 (m, 1H), 6.80 – 6.76 (m, 1H), 6.28 (dd, *J* = 9.6, 5.3 Hz, 1H), 3.37 (d, *J* = 8.3 Hz, 1H), 2.98 (dd, 8.3, 5.3 Hz, 1H). *Major isomer*: $^{13}C\{1H\}$NMR (100 MHz, $CDCl_3$, ppm) δ 132.4, 129.8, 129.6, 129.3, 129.2, 128.7, 128.4, 128.1, 128.0 (2C), 127.8 (2C), 125.3, 124.2, 121.0, 34.4, 31.8, 14.4. HRMS (APPI) calcd. for $[C_{18}H_{13}N+H]^+$: 244.1126, found: 244.1122.

Anthracene reaction. General procedure B was followed using 4.0 equivalents of anthracene at ambient temperature to generate a 5:1:3 isomeric mixture of *1-phenyl-1a,9b-dihydro-1H-cyclopropa[a]anthracene-1-carbonitrile* (**16** and **17** in a 5:1 ratio) and *11-phenyl-2,3,9,10-tetrahydro-9,10-methanoanthracene-11-carbonitrile* (with ~10% of a product of the addition of two phenylcyanocarbenes as determined by HMRS) *1-Phenyl-1a,9b-dihydro-1H-cyclopropa[a]anthracene-1-carbonitrile* (**16** and **17**) isolated after column chromatography (0 - 10% EtOAc: hexane) as a pale yellow solid (14.8 mg, 46% yield). *Major isomer* ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 8.04 (s, 1H), 7.86 (d, *J* = 8.1 Hz, 1H), 7.67 (d, *J* = 8.1 Hz, 1H), 7.51 – 7.37 (m, 3H), 7.08 – 7.02 (m, 1H), 7.01 – 6.94 (m, 2H), 6.94 – 6.87 (m, 2H), 6.34 (d, *J* = 9.7 Hz, 1H), 6.13 (dd, *J* = 9.7, 5.1 Hz, 1H), 3.74 (d, *J* = 8.7 Hz, 1H), 3.17 (dd, *J* = 8.7, 5.1 Hz, 1H); *Minor isomer* δ 8.04 (s, 1H), 7.86 (d, *J* = 8.1 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.51 – 7.37 (m, 3H), 7.08 – 7.02 (m, 1H), 7.01 – 6.94 (m, 2H), 6.94 – 6.87 (m, 2H), 6.34 (d, *J* = 9.7 Hz, 1H), 6.13 (dd, *J* = 9.7, 5.1 Hz, 1H), 3.51 (d, *J* = 8.2 Hz, 1H), 2.99 (dd, *J* = 8.2, 5.2 Hz, 1H). *Major + minor isomer*: $^{13}C\{1H\}$NMR (100 MHz, $CDCl_3$, ppm) δ 133.3, 132.9, 132.3 (2C), 130.9, 130.0, 129.9, 129.4, 129.0, 128.2 (2C), 128.1, 128.0, 127.4, 126.8, 126.7, 126.5, 126.4, 125.3, 123.9, 121.3, 33.7, 30.7, 16.9; HRMS (APPI) calcd. for $[C_{22}H_{15}N+H]^+$: 294.1283, found: 294.1273. Stereochemistry determined by NOESY cross peak between ortho protons on the benzene ring and a proton on the naphthalene ring. *11-Phenyl-2,3,9,10-tetrahydro-9,10-methanoanthracene-11-carbonitrile* (**18**) isolated as a red oil (7.4 mg, 23%). ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.46 – 7.43 (m, 2H), 7.33 – 7.28 (m, 2H), 7.22 – 7.16 (m, 5H), 7.11 (dd, *J* = 5.4, 3.1 Hz, 2H), 6.86 (dd, *J* = 5.3, 3.0 Hz, 2H), 4.92 (s, 2H); $^{13}C\{1H\}$NMR (125 MHz, $CDCl_3$, ppm, due to inseparable impurities where two phenylcyanocarbenes were added to anthracene, extra peaks were observed in the ^{13}C NMR spectra and are listed here) δ147.1 (2C), 144.9 (2C), 128.7 (2C), 128.2, 128.1 (2C), , 126.7 (2C), 126.4 (2C), 123.2 (2C), 59.1 (2C), 54.5,

48.2, 37.7; HRMS (APPI) calcd. for $[C_{22}H_{15}N+H]^+$: 294.1283, found: 294.1273; HRMS (APPI) calcd. for $[C_{30}H_{20}N_2+H]^+$: 409.1704, found: 409.1695.

Anisole reaction. General procedure B was followed using 8.0 equivalents of anisole at ambient temperature to generate a 2:1 isomeric mixture of *3-methoxy-7-phenylbicyclo[4.1.0]hepta-2,4-diene-7-carbonitrile* (**19**) and *2-methoxy-7-phenylbicyclo[4.1.0]hepta-2,4-diene-7-carbonitrile* (**20**) isolated after column chromatography (0 - 15% EtOAc: hexane) as a pale yellow solid (11.6 mg, 47% yield). *3-Methoxy-7-phenylbicyclo[4.1.0]hepta-2,4-diene-7-carbonitrile* (**19**): ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.40 – 7.20 (m, 5H), 6.34 – 6.20 (m, 1H), 6.14 (dd, *J* = 9.5, 2.1 Hz, 1H), 5.31 (dd, *J* = 6.5, 2.0 Hz, 1H), 3.65 (s, 3H), 3.30 (t, *J* = 7.0 Hz, 1H), 3.16 (t, *J* = 6.7 Hz, 1H). *2-Methoxy-7-phenylbicyclo[4.1.0]hepta-2,4-diene-7-carbonitrile* (**20**): ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.40 – 7.20 (m, 5H), 6.49 (dd, *J* = 9.7, 5.8 Hz, 1H), 6.34 – 6.20 (m, 1H), 5.82 (dd, *J* = 9.3, 4.8 Hz, 1H), 5.38 – 5.28 (m, 1H), 3.69 (s, 3H), 3.00 – 2.82 (m, 1H). Mixture of **19** and **20**: ^{13}C{1H}NMR (100 MHz, $CDCl_3$, ppm) δ 156.3, 155.1, 137.2, 129.0, 128.0, 127.5, 127.3, 126.8, 125.6, 125.3, 124.5, 122.8, 120.2, 116.7, 114.0, 98.2, 95.7, 95.1, 57.7, 55.7, 54.9; HRMS (APPI) calcd. for $[C_{15}H_{13}NO+H]^+$: 224.1075, found: 224.1066.

Following General Procedure C, *2-(4-methoxyphenyl)-2-phenylacetonitrile* (**21**) was formed in quantitative yield. The spectra for **21** matched previously reported data.[17] ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.30 – 7.39 (m, 5H), 7.23 – 7.26 (m, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 5.10 (s, 1H), 3.80 (s, 3H).

1,2,3-Trimethoxybenzene reaction. General procedure B was followed using 4.0 equivalents of 1,2,3-trimethoxybenzene at ambient temperature to generate 7:1 isomeric mixture of *2,3,4-trimethoxy-7-phenylbicyclo[4.1.0]hepta-2,4-diene-7-carbonitrile* (**22**) and *2,3,4-trimethoxy-1-phenylcyclohepta-2,4,6-triene-1-carbonitrile* (**23**) isolated after column chromatography (0 - 25% EtOAc: hexane) as a pale yellow solid (9.7 mg, 31% yield). *2,3,4-Trimethoxy-7-phenylbicyclo[4.1.0]hepta-2,4-diene-7-carbonitrile* (**22**): ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.37 (t, *J* = 7.5 Hz, 2H), 7.31 – 7.25 (m, 2H), 7.20 – 7.09 (m, 1H), 4.96 (dd, *J* = 4.6, 1.9 Hz, 1H), 3.85 (s, 3H), 3.69 (s, 6H), 2.93 (s, 2H). *2,3,4-Trimethoxy-1-phenylcyclohepta-2,4,6-triene-1-carbonitrile* (**23**): ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.37 (t, *J* = 7.5 Hz, 2H), 7.31 – 7.25 (m, 2H), 7.20 – 7.09 (m, 1H), 6.05 (dd, *J* = 11.5, 7.0 Hz, 1H), 5.88 (d, *J* = 11.5 Hz,

1H), 5.64 (d, *J* = 7.0 Hz, 1H), 3.90 (s, 3H), 3.88 (s, 3H), 3.73 (s, 3H). Mixture of **22** and **23**: ^{13}C{1H}NMR (100 MHz, Acetone-d_6) δ 157.3, 145.8, 143.1, 138.1, 134.81, 134.76, 134.73, 134.6, 133.6, 129.3, 129.2, 129.1, 129.0, 128.91, 128.85, 125.9, 125.7, 125.5, 125.2, 117.2, 116.7, 115.6, 110.4, 109.3, 107.7, 60.2, 57.2, 56.2; HRMS (APPI) calcd. for $[C_{17}H_{17}NO_3+H]^+$: 284.12867, found: 284.12867.

Following General Procedure C, *2-phenyl-2-(2,3,4-trimethoxyphenyl)acetonitrile* (**24**) was formed in quantitative yield. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.43 – 7.2 (m, 5H), 6.99 (d, *J* = 8.7 Hz, 1H), 6.64 (d, *J* = 8.7 Hz, 1H), 5.40 (s, 1H), 3.84 (s, 3H), 3.84 (s, 3H), 3.79 (s, 3H); ^{13}C{1H}NMR (100 MHz, $CDCl_3$, ppm) δ 154.2 (2C), 151.0, 136.1, 129.0 (2C), 128.0, 127.7 (2C), 123.3, 122.2, 120.2, 107.2, 61.0, 60.9, 56.1, 36.7 ; HRMS (APPI) calcd. for $[C_{17}H_{17}NO_3+H]^+$: 284.12867, found: 284.1279.

1,3,5-Trimethoxybenzene reaction. General procedure B was followed using 4.0 equivalents of 1,3,5-trimethoxybenzene at ambient temperature to generate *2-phenyl-2-(2,4,6-trimethoxyphenyl)acetonitrile* (**25**) isolated after column chromatography (0 - 20% EtOAc: hexane) as a solid (15.9 mg, 51% yield). Mp: 99 - 101 °C . ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.40 – 7.36 (m, 2H), 7.31 – 7.26 (m, 2H), 7.24 – 7.19 (m, 1H), 6.14 (s, 2H), 5.76 (s, 1H), 3.81 (s, 9H); ^{13}C{1H}NMR (100 MHz, $CDCl_3$, ppm) δ 161.5, 158.3 (2C), 136.3, 128.3 (2C), 127.0, 126.9 (2C), 119.9, 105.3, 91.0 (2C), 55.9 (2C), 55.4, 30.5; HRMS (APPI) calcd. for $[C_{17}H_{17}NO_3+H]^+$: 284.12867, found: 284.1280.

***N*-Methylindole reaction.** General procedure B was followed using 3.0 equivalents of *N*-methylindole at 0 °C to generate a 9:1 isomeric mixture of *2-(1-methyl-1H-indol-3-yl)-2-phenylacetonitrile* (**26**) and *3-methyl-6-phenyl-3,5a,6,6a-tetrahydrocyclopropa[e]indole-6-carbonitrile* or *1-methyl-6-phenyl-1,5a,6,6a-tetrahydrocyclopropa[g]indole-6-carbonitrile* (**27**, 1:1 mixture of diastereomers) isolated after column chromatography (0 - 25% EtOAc: hexane) as a red oil (17.1 mg, 63% yield). *2-(1-Methyl-1H-indol-3-yl)-2-phenylacetonitrile* (**26**): ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.49 – 7.40 (m, 2H), 7.40 – 7.29 (m, 5H), 7.28 – 7.21 (m, 1H), 7.10 (t, *J* = 7.4 Hz, 1H), 7.02 (s, 1H), 5.38 (s, 1H), 3.77 (s, 3H); ^{13}C{1H}NMR (100 MHz, $CDCl_3$, ppm) δ 137.4, 135.7, 129.1 (2C), 128.2, 127.9, 127.8 (2C), 125.8, 122.5, 120.0, 119.9, 118.9, 109.8, 109.4, 34.5, 33.0. *3-Methyl-6-phenyl-3,5a,6,6a-tetrahydrocyclopropa[e]indole-6-carbonitrile* or *1-methyl-6-phenyl-1,5a,6,6a-tetrahydrocyclopropa[g]indole-6-carbonitrile* (**27**, 1:1

mixture of diastereomers): ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.43 – 7.20 (m, 6H), 6.83 – 6.69 (m, 1H), 6.23 (d, *J* = 2.7 Hz, 0.5H), 6.14 (d, *J* = 2.9 Hz, 0.5H), 6.03 (dd, *J* = 9.8, 5.5 Hz, 0.5H), 5.88 (dd, *J* = 9.5, 5.3 Hz, 0.5H), 3.68 (s, 1.5H), 3.65 (s, 1.5H), 3.45 (d, *J* = 8.4 Hz, 0.5H), 3.38 (d, *J* = 9.0 Hz, 0.5H), 3.05 (dd, *J* = 8.9, 5.2 Hz, 0.5H), 2.95 (dd, *J* = 8.5, 5.5 Hz, 0.5H). Mixture of **26** and **27:** HRMS (APPI) calcd. for $[C_{17}H_{14}N_2+H]^+$: 247.1235, found: 247.1231.

***N*-Boc-indole reaction.** General procedure B was followed using 3.0 equivalents of *N*-Boc-indole at 0 °C to generate *tert-butyl 1-cyano-1-phenyl-1a,6b-dihydrocyclopropa[b]indole-2(1H)-carboxylate* (**28**) isolated after column chromatography (0 - 30% EtOAc: hexane) as a red oil (23.4 mg, 64% yield). The spectra of **28** is observed as a rotameric mixture of diastereomers. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.43 (d, *J* = 6.9 Hz, 1.8H), 7.36 – 7.30 (m, 1.2H), 7.06 (d, *J* = 13.6 Hz, 5.3H), 6.98 – 6.90 (m, 0.7H), 5.07 (d, *J* = 6.7 Hz, 0.4H), 4.93 (d, *J* = 6.7 Hz, 0.6H), 3.77 (d, *J* = 6.7 Hz, 0.8H), 3.51 (d, *J* = 6.7 Hz, 0.2H), 1.66 (s, 4.5H), 1.56 (s, 1.5), 1.56 (s, 3.0); ^{13}C{1H}NMR (100 MHz, $CDCl_3$, ppm) δ 151.3, 131.7, 131.3, 131.3, 129.5, 129.3, 129.1, 128.9, 128.8, 128.6, 127.5, 125.9, 125.5, 123.0, 115.6, 114.8, 84.5, 83.3, 82.7, 48.84, 48.78, 33.7, 33.2, 28.5, 28.4, 28.3, 28.1, 17.4; HRMS (APPI) calcd. for $[C_{21}H_{20}N_2O_2+H]^+$: 333.1603, found: 333.1599.

***N*-Methylpyrrole reaction.** General procedure B was followed using 2.0 equivalents of *N*-methylpyrrole at -40 °C to generate *6-oxo-2-phenylhexa-2,4-dienenitrile* (*E,E*-**29**) isolated after column chromatography (0 - 20% EtOAc: hexane) as a red solid with (11.5 mg, 57% yield). Mp: 84 °C (dec.) ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 9.78 (d, *J* = 7.8 Hz, 1H), 7.72 – 7.67 (m, 2H), 7.67 (d, *J* = 15.2 Hz, 1H), 7.50 – 7.47 (m, 3H), 7.45 (dd, *J* = 11.4, 0.8 Hz, 1H), 6.49 (ddd, *J* = 15.2, 7.8, 0.8 Hz, 1H); ^{13}C{1H}NMR (125 MHz, $CDCl_3$, ppm) δ 193.1, 145.2, 137.0 (2C), 131.9, 131.2, 129.5 (2C), 126.6 (2C), 122.5, 115.5. Stereochemistry determined by NOESY cross peak between the α-proton and the ortho-proton on the benzene ring. HRMS (APPI) calcd. for $[C_{12}H_9NO+H]^+$: 184.0762, found: 184.0759.

***N*-Boc-pyrrole reaction.** General procedure B was followed using 2.0 equivalents of *N*-Boc-pyrrole at ambient temperature to generate a ~1:1 diastereomeric mixture of *tert-butyl 6-cyano-6-phenyl-2-azabicyclo[3.1.0]hex-3-ene-2-carboxylate* (**30**) isolated after flash chromatography (0 - 100% EtOAc:

hexane, 400 ml) as a yellow solid with (13.0 mg, 42% yield). The spectra for **30** is observed as a rotomeric mixture of diastereomers. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.39 – 7.26 (m, 5H), 6.95 (d, *J* = 4.0 Hz, 0.2H), 6.80 (d, *J* = 4.0 Hz, 0.4H), 6.17 (d, *J* = 4.0 Hz, 0.2H), 6.01 (d, *J* = 4.0 Hz, 0.2H), 5.62 – 5.46 (m, 0.6H), 5.15 (t, *J* = 3.4 Hz, 0.2H), 5.07 (t, *J* = 3.4 Hz, 0.2H), 4.80 (d, *J* = 6.8 Hz, 0.2H), 4.66 (d, *J* = 6.8 Hz, 0.2H), 4.61 (d, *J* = 6.2 Hz, 0.4H), 4.40 (d, *J* = 6.0 Hz, 0.2H), 3.43 – 3.34 (m, 0.6H), 3.16 – 3.05 (m, 0.4H), 1.60 (s, 2H), 1.52 (s, 5H), 1.43 (s, 2H); ^{13}C{1H}NMR (100 MHz, $CDCl_3$, ppm) δ 151.01, 150.96, 150.8, 134.8, 133.2, 132.9, 132.1, 131.8, 131.7, 131.5, 131.3, 129.5, 129.3, 129.2, 129.1, 129.0, 128.9, 128.84, 128.76, 128.3, 128.1, 127.7, 127.6, 126.6, 125.6, 125.4, 122.0, 121.8, 115.9, 107.2, 107.0, 105.3, 105.2, 82.9, 82.8, 82.4, 50.6, 50.4, 47.5, 47.2, 40.9, 40.0, 37.6, 36.7, 28.5, 28.42, 28.38, 28.29, 28.25, 28.2, 18.4, 15.1; HRMS (APPI) calcd. for $[C_{17}H_{18}N_2O_2+H]^+$: 283.1446, found: 283.1440.

Furan reaction. General procedure A was followed using furan to generate a 3:1:1 isomeric mixture of *6-phenyl-2-oxabicyclo[3.1.0]hex-3-ene-6-carbonitrile* (**32**), *2-phenylnicotinaldehyde* (**33**), and *6-oxo-2-phenylhexa-2,4-dienenitrile* (**29**, mixture of diastereomers) isolated after column chromatography (0 - 35% EtOAc: hexane) . *6-Phenyl-2-oxabicyclo[3.1.0]hex-3-ene-6-carbonitrile* (**32**)) as a pale yellow solid (4.4 mg, 22% yield). Mp: 71-74 °C ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.30 – 7.28 (m, 5H), 5.96 (d, *J* = 2.7 Hz, 1H), 5.38 – 4.89 (m, 2H), 3.38 (dd, *J* = 5.7, 2.8 Hz, 1H); ^{13}C{1H}NMR (100 MHz, $CDCl_3$, ppm) δ 148.0, 131.9 (2C), 128.7 (3C), 127.9, 121.5, 102.4, 68.2, 37.7, 13.5; HRMS (APPI) calcd. for $[C_{12}H_9NO+H]^+$: 184.0762, found: 184.0760. X-ray crystallography was used to determine the relative stereochemistry and the cif file is included in the Supporting Information. Spectral data for *2-phenylnicotinaldehyde* (**33**) matched literature data:[14] yellow oil (1.5 mg, 7%) ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 10.06 (s, 1H), 8.88 (dd, *J* = 4.8, 1.9 Hz, 1H), 8.31 (dd, *J* = 8.0, 1.9 Hz, 1H), 7.59 (dd, *J* = 6.5, 3.1 Hz, 2H), 7.53 (dd, *J* = 4.7, 2.0 Hz, 3H), 7.45 (dd, *J* = 8.0, 4.8 Hz, 1H); ^{13}C{1H}NMR (100 MHz, $CDCl_3$, ppm) δ 191.7, 162.1, 153.4, 136.9, 136.2, 130.5 (2C), 129.8, 128.8 (2C), 128.58, 122.7; HRMS (APPI) calcd. for $[C_{12}H_9NO+H]^+$: 184.0762, found: 184.0762. *6-Oxo-2-phenylhexa-2,4-dienenitrile* (**29**) as a 4:4:1:1 diastereoisomeric mixture of compounds: (1.8 mg, 8%). ^{1}H NMR (400 MHz, Acetone-d_6, ppm) δ 10.38 (d, *J* = 7.4 Hz, 0.1H), 10.32 (d, *J* = 7.3 Hz, 0.4H), 9.77 (d, *J* = 7.8 Hz, 0.4H), 9.58 (d, *J* =

7.8 Hz, 0.1H), 8.55 (d, *J* = 12.4 Hz, 0.1H), 8.13 (d, *J* = 12.0 Hz, 0.4H), 7.86 (d, *J* = 11.3 Hz, 0.5H), 7.76 – 7.56 (m, 1.8H), 7.49 – 7.29 (m, 3.2H), 7.13 (t, *J* = 11.7 Hz, 0.4H), 6.83 – 6.44 (m, 0.4H), 6.39 (t, *J* = 11.7 Hz, 0.4H), 6.24 – 6.11 (m, 0.2H), 6.05 (dd, *J* = 11.2, 7.5 Hz, 0.4H), 5.74 (dd, *J* = 11.5, 5.8 Hz, 0.2H); HRMS: see compound 29 from reaction with Boc-Pyrrole.

2-Methylfuran reaction. General procedure A was followed using 2-methylfuran to generate a 2:6:1 isomeric mixture of *1-methyl-6-phenyl-2-oxabicyclo[3.1.0]hex-3-ene-6-carbonitrile* (**34**), *(2E,4Z)-6-oxo-2-phenylhepta-2,4-dienenitrile* (**35**), and *6-methyl-2-phenylnicotinaldehyde* (**36**) isolated after column chromatography (0 - 35% EtOAc: hexane). *6-Phenyl-2-oxabicyclo[3.1.0]hex-3-ene-6-carbonitrile* (**34**) isolated as a yellow solid with (2.1 mg, 10% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.28 (m, 3H), 7.24 – 7.20 (m, 2H), 5.90 (d, *J* = 2.6 Hz, 1H), 5.17 (t, *J* = 2.6 Hz, 1H), 3.09 (d, *J* = 2.6 Hz, 1H), 2.03 (s, 3H); ^{13}C{1H}NMR (125 MHz, $CDCl_3$, ppm) δ 147.6, 131.9 (2C), 128.9, 128.5, 128.5 (2C), 121.6, 102.9, 75.0, 41.7, 17.8, 17.1; HRMS (APPI) calcd. for $[C_{13}H_{11}NO+H]^+$: 198.0919, found: 198.0914. *(2Z,4Z)-6-Oxo-2-phenylhepta-2,4-dienenitrile* (**35**) isolated as an oil (6.7 mg, 30%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.63 (d, *J* = 11.8 Hz, 1H), 7.81 – 7.64 (m, 2H), 7.47 – 7.39 (m, 3H), 7.03 (t, *J* = 11.8 Hz, 1H), 6.40 (d, *J* = 11.8 Hz, 1H), 2.33 (s, 3H); ^{13}C{1H}NMR (100 MHz, $CDCl_3$, ppm) δ 199.0, 136.3, 136.1, 130.6, 130.2, 129.3 (2C), 128.6, 126.7 (2C), 115.9, 103.6, 32.1; HRMS (APPI) calcd. for $[C_{13}H_{11}NO+H]^+$: 198.0919, found: 198.0913. Stereochemistry determined by NOESY cross peaks between the α and β protons and between the γ and the ortho-phenyl protons. *6-Methyl-2-phenylnicotinaldehyde* (**36**) isolated as an oil (1.0 mg, 5%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 9.99 (s, 1H), 8.21 (d, *J* = 8.0 Hz, 1H), 7.60 – 7.54 (m, 2H), 7.52 – 7.49 (m, 3H), 7.30 (d, *J* = 8.0 Hz, 1H), 2.70 (s, 3H); ^{13}C{1H}NMR (100 MHz, $CDCl_3$, ppm) δ

191.6, 163.6, 130.5 (2C), 130.2, 130.1, 129.6, 129.0, 128.7 (2C), 127.4, 122.7, 25.2.; HRMS (APPI) calcd. for $[C_{13}H_{11}NO+H]^+$: 198.0919, found: 198.0914.

2,5-Dimethylfuran reaction. General procedure A was followed using 2,5-dimethylfuran to generate a 2:3 isomeric mixture of *1,3-dimethyl-6-phenyl-2-oxabicyclo[3.1.0]hex-3-ene-6-carbonitrile* (**37**) and *3-methyl-6-oxo-2-phenylhepta-2,4-dienenitrile* (**38**) isolated after column chromatography (0 - 35% EtOAc:

hexane). *1,3-Dimethyl-6-phenyl-2-oxabicyclo[3.1.0]hex-3-ene-6-carbonitrile* (**37**) as a white solid with (5.1 mg, 22% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.37 – 7.28 (m, 5H), 5.19 (d, J = 2.4 Hz, 1H), 3.10 (d, J = 2.4 Hz, 1H), 1.97 (s, 3H), 1.39 (s, 3H). *3-Methyl-6-oxo-2-phenylhepta-2,4-dienenitrile* (**38**) as a mixture of diastereomers (7.6 mg, 33%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.41 – 7.31 (m, 5H), 6.73 (d, J = 12.3 Hz, 0.6H), 6.38 (d, J = 12.1 Hz, 0.4H), 6.34 (d, J = 12.3 Hz, 0.6H), 6.22 (d, J = 12.1 Hz, 0.4H), 2.32 (s, 1.8H), 2.32 (s, 1.2H), 2.22 (s, 1.2H), 2.02 (s, 1.8H). Mixture of **37** and diastereoisomeric mixture of **38**: ^{13}C{1H}NMR (100 MHz, $CDCl_3$, ppm) 198.4, 159.2, 152.4, 139.6, 138.9, 133.2, 132.7, 131.4, 131.2, 129.5, 129.2 (2C), 129.1 (2C), 129.0, 128.8 (2C), 128.6, 128.5 (2C), 128.1, 117.8, 98.4, 76.3 38.7, 30.9, 29.8, 22.5, 22.3, 19.4, 14.8, 13.3; HRMS (APPI) calcd. for $[C_{14}H_{13}NO + H]^+$: 212.1075, found: 212.1071.

Benzofuran reaction. General procedure B was followed using 3.0 equivalents of benzofuran at 0 °C to generate *1-phenyl-1a,6b-dihydro-1H-cyclopropa[b]benzofuran-1-carbonitrile* (**39**, 10:1 diastereoisomeric ratio) isolated after flash chromatography (5 - 100% EtOAc: hexane, 400 mL as a yellow solid with (14.4 mg, 56% yield). *Major isomer*: ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.38 (dd, J = 7.4, 1.1 Hz, 1H), 7.19 – 7.15 (m, 2H), 7.13 – 7.08 (m, 3H), 6.95 (td, J_t = 7.9 Hz, J_d = 1.6 Hz, 1H), 6.84 (td, J_t = 7.4 Hz, J_d = 0.7 Hz, 1H), 6.50 (d, J = 8.3 Hz, 1H), 5.42 (d, J = 5.5 Hz, 1H), 3.84 (d, J = 5.5 Hz, 1H); ^{13}C{1H}NMR (100 MHz, $CDCl_3$, ppm) δ 159.2, 131.7 (2C), 129.1, 128.6, 128.5 (2C), 127.0, 125.4, 124.0, 122.0, 120.9, 110.1, 68.2, 35.9, 16.7; HRMS (APPI) calcd. for $[C_{16}H_{11}NO + H]^+$: 234.0919, found: 234.0914.

***Trans*-β-methylstyrene reaction.** General procedure B was followed using 3.0 equivalents of *trans*-β-methylstyrene at 0 °C to generate a 1:4 diastereoisomeric mixture of *2-methyl-1,3-diphenylcyclopropane-1-carbonitrile* (**40** and **41**) isolated after column chromatography (10% EtOAc: hexane)as an oil with (12.1 mg, 47% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.17 – 7.02 (m, 8H), 6.87 – 6.80 (m, 2H), 2.76 (d, J = 7.3 Hz, 1H), 2.30 (q, J = 7.6 Hz, 1H), 1.67 (d, J = 6.3 Hz, 3H), 1.04 (d, J = 6.4 Hz, 3H, minor isomer); ^{13}C{1H}NMR (100 MHz, $CDCl_3$, ppm) δ134.0, 132.3, 129.8, 129.6 (2C), 129.1, 128.8, 128.5 (3C), 128.24, 128.15 (2C), 128.0, 127.2, 121.6, 41.1, 36.4, 29.8, 28.0, 24.4, 16.0; HRMS (APPI) calcd. for $[C_{17}H_{15}N+H]^+$: 234.1283, found: 234.1276.

***Cis*-β-methylstyrene reaction.** General procedure B was followed using 3.0 equivalents of *trans*-β-methylstyrene at 0 °C to generate a 13:5:1:5 diastereoisomeric mixture of *2-methyl-1,3-diphenylcyclopropane-1-carbonitrile* (**40**, **41**, **42** and **43**) isolated after column chromatography (10% EtOAc: hexane) as an oil with (15.9 mg, 62% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.44 – 7.37 (m, 2.5H), 7.34 – 7.24 (m, 1.5H), 7.21 – 7.18 (m, 1.5H), 7.16 – 7.05 (m, 3H), 6.91 – 6.86 (m, 1H), 6.85 – 6.81 (m, 0.5H), 3.13 (d, *J* = 10.2 Hz, 0.5H), 2.94 (d, *J* = 9.3 Hz, 0.25H), 2.76 (d, *J* = 7.3 Hz, 0.25H), 2.37 (m, 0.5H), 2.29 (q, *J* = 6.5 Hz, 0.25H), 2.09 (m, 0.25H), 1.66 (d, *J* = 6.2 Hz, 0.75H), 1.38 (d, *J* = 6.4 Hz, 0.75H), 1.27 (d, *J* = 6.9 Hz, 1.5H); ^{13}C{1H}NMR (100 MHz, $CDCl_3$, ppm) δ 133.4, 131.4, 130.4, 130.3, 129.9, 129.6, 129.1, 128.8, 128.7, 128.5, 128.3, 128.2, 128.0, 127.8, 127.7, 127.2, 127.1, 126.0, 124.5, 41.1, 37.6, 35.4, 29.0, 28.0, 27.4, 26.8, 24.4, 22.1, 16.0, 12.5, 10.3; HRMS (APPI) calcd. for $[C_{17}H_{15}N+H]^+$: 234.1283, found: 234.1270.

Homoallylbenzoate reaction. General procedure B was followed using 3.0 equivalents of homoallylbenzoate at 0 °C to generate an approximately 1:1 diastereoisomeric ratio of *2-(2-cyano-2-phenylcyclopropyl)ethyl benzoate* isolated after column chromatography (15% EtOAc: hexane) as a yellow oil (7.0 mg, 22% yield). *Major isomer*: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 – 7.98 (m, 1H), 7.61 – 7.53 (m, 1H), 7.48 – 7.25 (m, 8H), 4.55 (t, *J* = 6.3 Hz, 2H), 2.33 – 2.23 (m, 1H), 2.21 – 2.12 (m, 1H), 1.71 – 1.65 (m, 2H), 1.54 – 1.50 (m, 1H). *Minor isomer*: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 – 7.98 (m, 1H), 7.47 – 7.25 (m, 9H), 4.35 – 4.23 (m, 2H), 2.01 (tdd, *J* = 8.8, 7.1, 5.8 Hz, 1H), 1.83 – 1.71 (m, 2H), 1.47 (dd, *J* = 7.1, 5.8 Hz, 1H), 1.17 (dddd, *J* = 14.6, 8.6, 6.8, 5.8 Hz, 1H). *Major* + *Minor isomer*: ^{13}C{1H}NMR (125 MHz, $CDCl_3$, ppm) δ 166.5, 166.4, 136.0, 133.12, 133.07, 131.9, 129.92, 129.88, 129.6, 129.5, 129.2, 129.0, 128.9, 128.5, 128.42, 128.39, 127.7, 125.8, 123.3, 120.7, 63.6, 63.3, 30.6, 28.0, 27.3, 25.6, 23.4, 20.0, 18.2, 18.1; HRMS (APPI) calcd. for $[C_{19}H_{17}NO_2+H]^+$: 292.1337, found: 292.1325.

Cyclohexa-1,4-diene reaction. General procedure B was followed using 3.0 equivalents of cyclohexa-1,4-diene at 0 °C to generate a 2:1 isomeric mixture of *2-(cyclohexa-2,5-dien-1-yl)-2-phenylacetonitrile* (**47**) and *7-phenylbicyclo[4.1.0]hept-3-ene-7-carbonitrile* (**48**) isolated after column chromatography

(10% EtOAc: hexane) as a yellow oil with (14.4 mg, 67% yield). *2-(Cyclohexa-2,5-dien-1-yl)-2-phenylacetonitrile* (**47**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.28 (m, 5H), 5.98 – 5.87 (m, 2H), 5.64 – 5.57 (m, 2H), 3.84 (d, *J* = 6.0 Hz, 1H), 3.33 – 3.18 (m, 1H), 2.67 – 2.45 (m, 2H); ^{13}C{1H}NMR (100 MHz, $CDCl_3$; due to instability of compound **47**, impurities were observed in the ^{13}C NMR spectra and listed) δ 137.4, 133.6, 129.9, 129.6, 129.0, 128.8 (2C), 128.6, 128.5, 128.4, 128.2, 128.1 (2C), 127.3, 125.2, 124.6, 123.4, 122.8, 119.6, 118.4, 44.2, 40.6, 27.4, 26.6, 20.8. *7-Phenylbicyclo[4.1.0]hept-3-ene-7-carbonitrile* (**48**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (s, 5H), 5.02 (dd, *J* = 1.7, 0.8 Hz, 2H), 2.61 – 2.39 (m, 4H), 2.14 (dd, *J* = 4.1, 1.9 Hz, 2H); ^{13}C{1H}NMR (100 MHz, $CDCl_3$) δ 131.3, 129.3 (2C), 128.9 (2C), 128.4, 124.2, 123.2 (2C), 23.9 (2C), 20.4 (2C), 18.1; HRMS (APPI) calcd. for $[C_{14}H_{13}N + H]^+$: 196.1126, found: 196.1128.

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ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jox.xxxxxxx.

1D and 2D NMR spectra for all new compounds and X-ray crystallographic data for compounds **13** and **32**.

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