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Aryl Vinyl Cyclopropane Cope Rearrangement of 1-cyano-1-phenyl-2-vinyl cyclopropanes.

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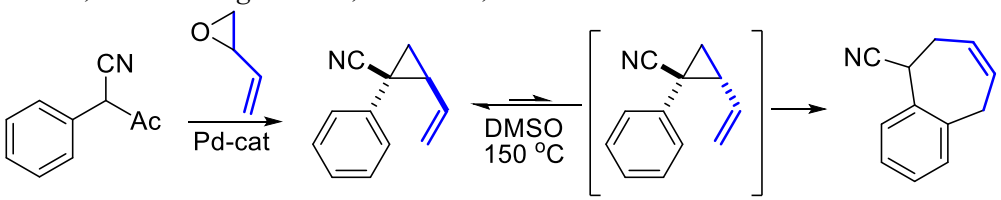

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Aryl vinyl cyclopropane Cope rearrangements

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ABSTRACT

While the divinyl cyclopropane Cope rearrangement is well-known, and has been broadly applied in synthesis, examples of the aryl vinyl cyclopropane Cope rearrangement are less common and generally limited in scope or reaction yield. The aryl vinyl cyclopropane Cope rearrangement gives access to the benzocycloheptene scaffold, which is present in a variety of naturally occurring and medicinally relevant products. Herein we report a method to obtain either of two regioisomeric benzocycloheptene products via an aryl vinyl cyclopropane Cope rearrangement, featuring additive-controlled regioselectivity. Mechanistic studies indicate a dynamic equilibration of cyclopropane stereoisomers, followed by rearrangement of the *cis* diastereomer.

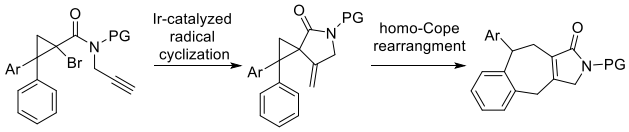
1. Introduction

Cope rearrangements are well-known and powerfully useful reactions in organic synthesis.[1] The Cope rearrangements of *cis* divinyl cyclopropanes are particularly interesting because they are facile at relatively low temperatures due to the rigidity of the system and the strain release which provides a thermodynamic driving force.[2] The related *aromatic* Cope rearrangements, however, are much less common due to the low reactivity of the aryl ring and the need to transiently destroy aromaticity.[3] Thus, aromatic Cope reactions tend to require forcing conditions and/or stereodefined starting materials, and suffer from low yield or limited scope.[3]

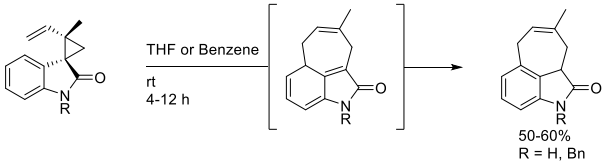
Recently, there have been several interesting examples of aromatic Cope rearrangements of aryl vinyl cyclopropanes that provide access to benzocycloheptenes (Scheme 1). In 2011, the Stephenson group reported a tandem photochemical cyclization and aryl vinyl cyclopropane Cope rearrangement.[4] The radical cyclization of diaryl substrates employed necessarily led to *cis* aryl vinyl cyclopropanes, which spontaneously rearranged under the conditions to form benzocycloheptenes. In 2012, Gaich and coworkers developed a bioinspired prenylation of the C4 position of indole via an aryl vinyl cyclopropane Cope rearrangement, mimicking the pathway believed to be active in the enzymatic prenylation of indole by DMAT synthase.[5] More recently, the Curran group disclosed a variety of rearrangements of 1,1-divinyl cyclopropanes, including five examples which underwent aromatic Cope rearrangements with yields ranging from 44% to 73%.[6] Those reactions cleverly utilized an ene reaction to drive rearomatization after the initial Cope rearrangement. Typically, a 1,3-proton transfer is exploited for the rearomatization. Finally, Ávilla-Zárraga and coworkers reported an aryl vinyl cyclobutane

Scheme 1. Previous work

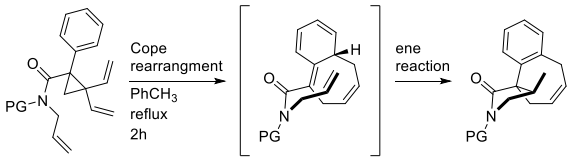
Stephenson's tandem radical cyclization/Cope rearrangement - 2011



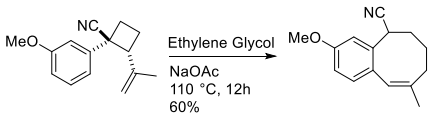
Gaich's bioinspired C4 prenylation of indole - 2012



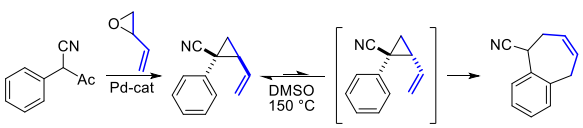
Curran's ene-driven aryl vinyl cyclopropane Cope rearrangment - 2015



Ávila-Zárraga's Cope rearrangment of aryl vinyl cyclobutanes - 2013, 2017



This work - Dynamic aromatic Cope rearrangments

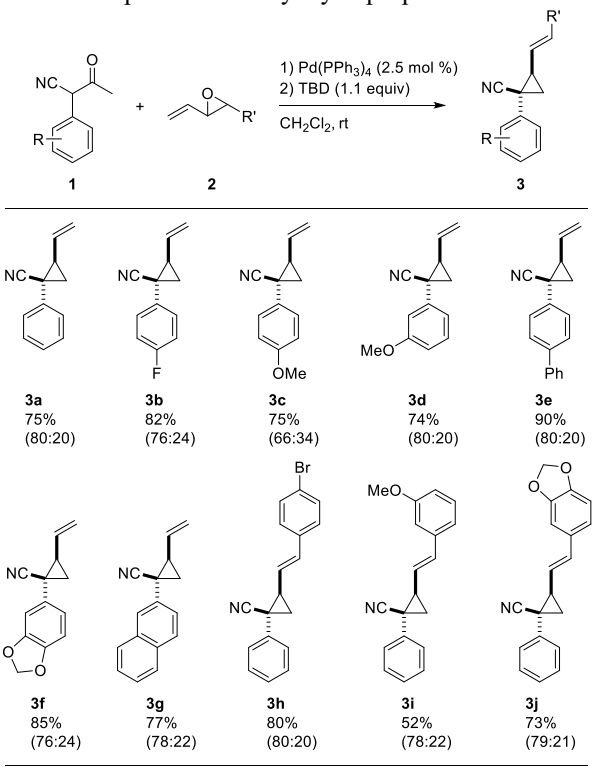


rearrangement to form a benzocyclooctene.[7] In the initial report, a single product was obtained in an optimized yield of just 45%. A subsequent publication in 2017 utilized an improved procedure to form a benzocyclooctene in 60% yield *en route* to the synthesis of (+/-)-parvifoline.[8] Given the target-oriented nature of the synthesis, only a single example was demonstrated. Moreover, to accomplish the reaction, the authors carefully controlled the relative stereochemistry to ensure that the aromatic ring and vinyl group were *cis* about the cyclobutane. Herein, we report a method for the synthesis of benzocycloheptenes from aryl vinyl cyclopropanes where dynamic equilibration of the diastereomers of the cyclopropane obviates the need to laboriously prepare cyclopropanes as a single diastereomer (Scheme 1).

2. Results and Discussion

Recently, as part of our interest in retro-Claisen activation of allylic alcohols for Tsuji-Trost chemistry,[9] we reported an anion relay cyclopropanation of vinyl epoxides.[10] The reaction proceeds via a Tsuji-Trost—retro-Claisen condensation—Tsuji-Trost reaction sequence and provides rapid access to useful vinylcyclopropanes,[11] primarily as the *cis* diastereomer (Scheme 2).

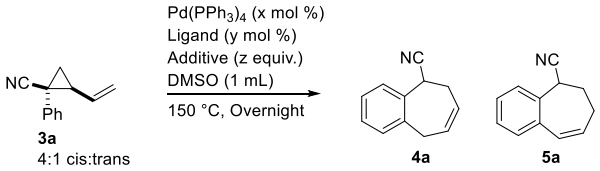
Scheme 2. Preparation of vinyl cyclopropanes



Isolated yield (d.r.)

During our investigations, it was noted that performing the anion relay cyclopropanation (ARC) at elevated temperatures led to the formation of an isomeric byproduct that was tentatively assigned as a benzocycloheptene. To further investigate byproduct formation at elevated temperatures, the vinylcyclopropane product was isolated and subjected to palladium catalysis at 150 °C. Indeed, it was found that the benzocycloheptene product (**4a)** was formed in 73% isolated yield (Table 1, entry 1). It was determined that this rearrangement warranted further investigation since reports of such aromatic Cope rearrangements are generally limited in scope and produce products in low yield. Next, the same rearrangement was performed in the presence of triazabicyclodecene (TBD) additive that is also present during cyclopropane formation. Under these conditions, the desired benzocycloheptene was not observed, but rather the regioisomeric benzocycloheptene **5a** was obtained in low yield (entry 2). The addition of dppe ligand increased the yield of **5a** significantly (entry 3). This result could be interpreted to mean that deactivation of Pd through chelation was beneficial to the reaction. Indeed, control reactions showed that palladium is not required for the isomerization (entries 4–5). In fact, conducting the reaction at 150 °C in the absence of palladium provided benzocycloheptene in better yield than when palladium was present.

Table 1. Optimization of Cope rearrangement

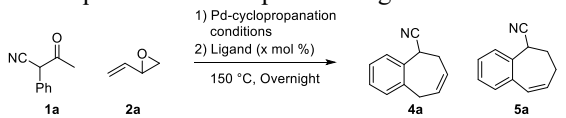


Entry	$Pd(PPh_3)_4$ mol %	Ligand (mol %)	Additive (equiv.)	yield **4a**	yield **5a**
1	2.5	n/a	n/a	73	0
2	2.5	n/a	TBD (1.1)	0	4
3	2.5	dppe (20)	TBD (1.1)	0	70
4	0	n/a	n/a	98%*	0
5	0	n/a	TBD (1)	0	83

*2 mL DMSO

While the optimal conditions for the rearrangement are metal-free, the above studies show that the rearrangement is compatible with palladium. This observation led us to attempt to develop a protocol which would incorporate the anion relay cyclopropanation and aryl vinyl cyclopropane Cope rearrangements in a single pot (Table 2). In CH_2Cl_2 containing $Pd(PPh_3)_4$, the benzocycloheptene **4a** was formed in 20% yield (entry 1). Increasing the amount of palladium favored the conjugated benzocycloheptene **5a**, but the yield was very low (entry 2). Addition of dppe favored the non-conjugated isomer **4a**, and the yield was slightly improved (entry 3). Interestingly, by simply allowing less time for the cyclopropane formation, the yield was improved to 40% (entry 4).

Table 2. Sequential ARC/Cope Rearrangement



Entry	solvent (mL)	Pd source (mol %)	time	Ligand (mol %)	yield **4a**	yield **5a**
1	DCM 0.8	$Pd(PPh_3)_4$ 2.5	3 hours	---	20	0
2	DCM 0.8	$Pd(PPh_3)_4$ 10	3 hours	---	0	4
3	DCM 0.8	$Pd(PPh_3)_4$ 10	3 hours	dppe (20)	24	0
4	DCM 0.8	$Pd(PPh_3)_4$ 2.5	5 min	---	40	0
5	DMSO 1	$Pd(PPh_3)_4$ 2.5	3 hours	---	0	20
6	DMSO 1	$Pd(PPh_3)_4$ 5	3 hours	---	0	25
7	DMSO 1	$Pd(dba)_2$ 2.5	---[b]	---	0	33
8	DMSO 1	$Pd(dba)_2$ 2.5	---[b]	dppe (10)	0	28
9	DMSO 1	$Pd(dba)_2$ 2.5	2 hours	dppe (20)	0	30
10	DMSO 1	$Pd(dba)_2$ 2.5	3 hours	dppe (20)	0	36

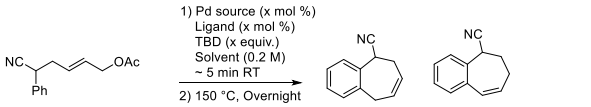
[a] Conditions: 1) **1a** and the Pd source were dissolved in the solvent and allowed to stir under Argon. **2a** was then added and the reaction was stirred at room temperature for the given time. TBD (1 equiv.) was added and the reaction was stirred at room temperature overnight. 2) The ligand was added and the reaction was stirred at 150 °C overnight. [b] Monitored for completion of the Tsuji-Trost allylation before adding TBD.

An improved yield of the conjugated isomer **5a** was obtained when the reaction was carried out in DMSO (entry 5). The yield was further improved by using $Pd(dba)_2$ instead of $Pd(PPh_3)_4$ to effect the cyclopropanation (entry 7). Addition of dppe decreased the yield, but when the first step was allowed to progress for 3 hours, the optimal yield was obtained (entries 8-10). Unfortunately, while the one-pot cyclopropanation – aromatic Cope rearrangement sequence was shown to be viable, the product yields were lower than desired.

Next, in order to determine whether the initial Tsuji-Trost reaction contributed to the low yields, that process was circumvented by isolating and purifying the allylic acetate intermediate necessary for cyclopropane formation. From this intermediate (**6a**), attempts were made to optimize a one-pot cyclopropane formation/aromatic Cope rearrangement. (Table 3).

Initial attempts with conditions known to affect cyclopropanation resulted in the formation of the benzocycloheptene **4a**, but the yield was low (entry 1). To investigate whether dppe could be used to inhibit palladium's interference with the aromatic Cope rearrangement, the cyclopropanation was performed followed by addition of dppe. Under these conditions, the non-conjugated benzocycloheptene was formed in 38% yield, but that procedure required a solvent swap prior to heating overnight. When the reaction was performed solely in DMSO with $Pd(PPh_3)_4$, benzocycloheptene did not form; instead, elimination to form a diene was favored (entry 4). However, when the catalyst was changed to $Pd(dba)_2$, benzocycloheptene formation was favored, resulting in 53% yield of the conjugate isomer **5a**. A brief ligand screen did not result in improved yields. Ultimately, while a moderate yield of the benzocycloheptene could be obtained in a one-pot transformation, the focus was shifted to maximizing the yield of benzocycloheptene synthesis through a two-pot procedure.

Table 3. Optimization of the Tsuji-Trost/Cope rearrangement sequence



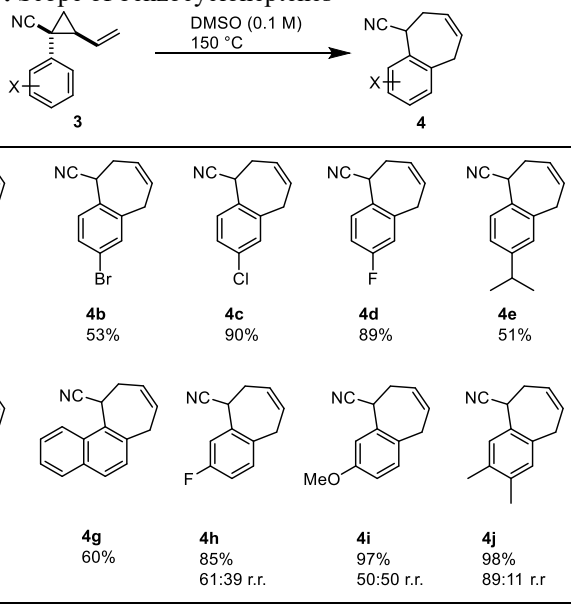
6a **4a** **5a**

Entry	Pd source (mol %)	Ligand (mol %)	TBD (equiv.)	solvent	yield **4a**	yield **5a**
1	$Pd(PPh_3)_4$ 1	n/a	1.1	DCM	7	0
2	$Pd(PPh_3)_4$ 1	n/a	0.5	DCM	24	0
3	$Pd(PPh_3)_4$ 2.5	dppe (20)[a]	1.1	DCM/DMSO	38	6
4	$Pd(PPh_3)_4$ 1	n/a	1.1	DMSO	0	0
5	$Pd(dba)_2$ 2.5	n/a	1.1	DMSO	0	53
6	$Pd(dba)_2$ 2.5	dppm (10)	1.1	DMSO	0	42
7	$Pd(dba)_2$ 2.5	dppe (10)	1.1	DMSO	0	52

Conditions: 1) The Pd source, the ligand and TBD were dissolved in the solvent in a dry flask under Argon. **6a** was added and the reaction was stirred at room temperature for 5 minutes. 2) The reaction was stirred at 150 °C overnight. [a] Ligand added in second step, first step allowed to continue overnight, solvent was changed between first and second steps.

The scope of the aromatic Cope rearrangement was then investigated using various substituted vinyl cyclopropanes (Scheme 3). These studies showed that *para*-substituted aryl vinyl cyclopropanes generally produced benzocycloheptenes in excellent yields (**4b**–**4e**). Substrates with extended aromatic systems performed equally well (**4f** and **4g**). *Meta*-substituted aryl rings were also well-tolerated, but led to regioisomeric products resulting from aromatic Cope rearrangement at both the proximal and distal positions to the substituent. While relatively small substituents (F and OMe, **4h** and **4i**) imparted little regioselectivity, the larger methyl substituent more effectively forced reaction at the distal position (**4j**, 89:11 regioselectivity).

Scheme 3. Scope of benzocycloheptenes



Interestingly, when styrenyl cyclopropanes were subjected to the conditions for aromatic Cope rearrangement, isomerization to cyclopentenes (**7**) was observed instead (Scheme 4).[3b-d,8,11c-e] Unfortunately, the products were formed with low diastereoselectivity, indicating that this rearrangement occurs via an indiscriminate cyclization

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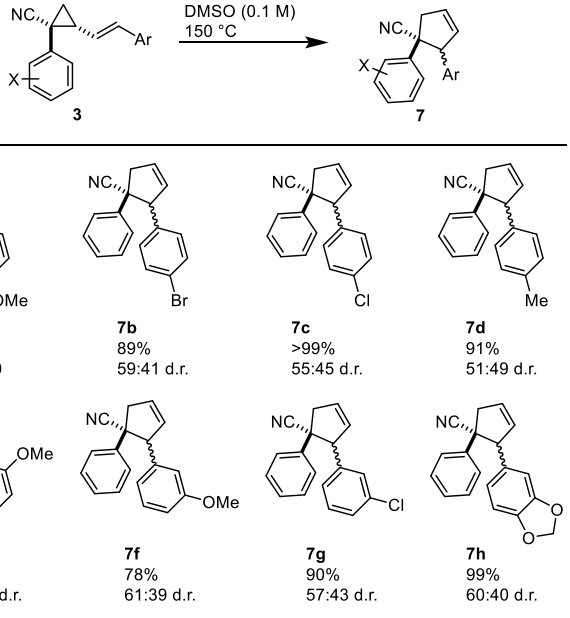
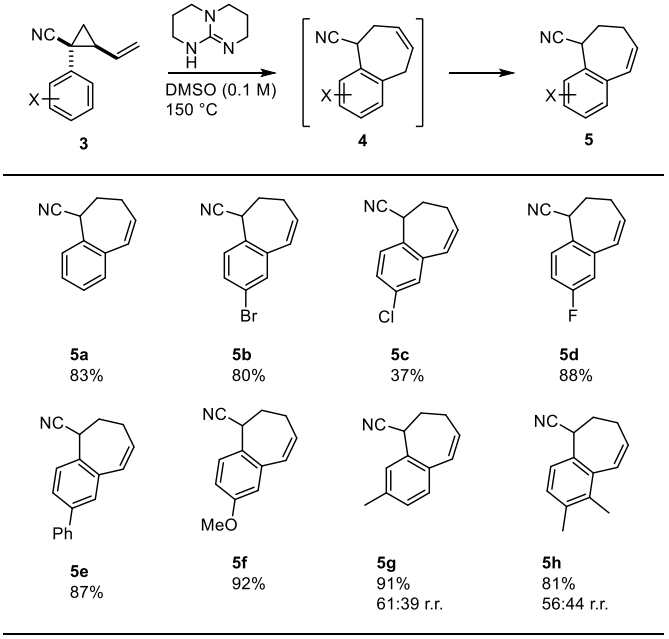
Scheme 4. Scope of cyclopentenes



Next, on the basis of our optimizations (*vide supra*), it was expected that use of triazabicyclodecene (TBD) base would equilibrate the benzocycloheptene isomers to form the conjugated isomer. Indeed, applying these basic reaction conditions to aromatic Cope rearrangements of terminal vinyl cyclopropanes had the same effect, leading to good yields of conjugated benzocycloheptenes (Scheme 5). Interestingly, the presence of TBD also had a small effect on the regiochemistry of the aromatic Cope rearrangement. For example, **4j** was obtained as an 89:11 mixture of regioisomers (Scheme 3), but the conjugated analog **5h** was formed with only 56:44 regioselectivity (Scheme 5).

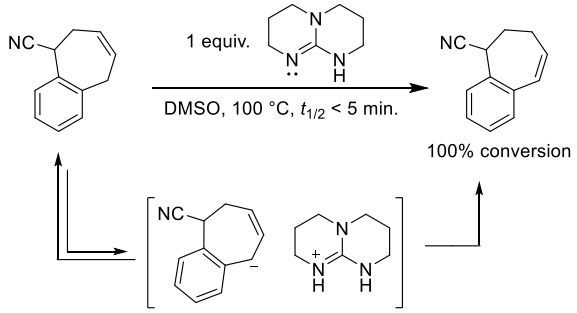
Interestingly, in the case of 5h the regioselectivity favored cyclization at the more sterically hindered carbon, indicating the presence of an electronic influence on regioselectivity.

Scheme 5. Scope of conjugated benzocycloheptenes



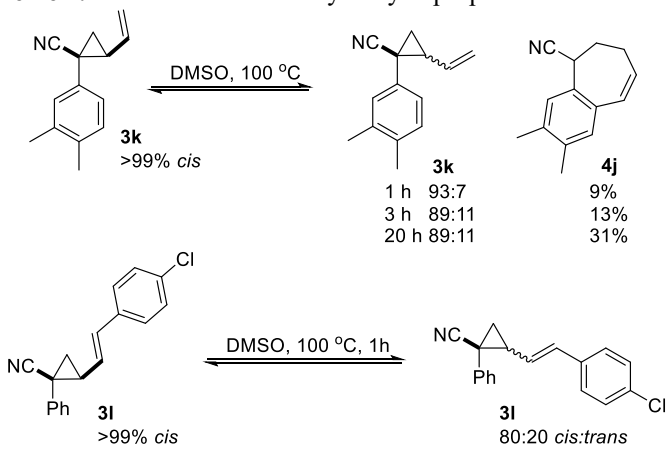
It was hypothesized that TBD ($pK_a \sim 26$)[12] plays a role in the isomerization to form the benzocycloheptene ($pK_a \sim 33$)[13]to its conjugated form by acting as a proton shuttle. This clearly would require reversible deprotonation of the far more acidic proton alpha to the nitrile ($pK_a \sim 22$).[12] In order to investigate this, the non-conjugated benzocycloheptene was isolated and exposed to TBD in DMSO at different temperatures (Scheme 6). It was found that the isomerization was slow at room temperature ($t_{1/2} \sim 12$ h) but occurred rapidly at 60 °C ($t_{1/2} < 1$ h) and 100 °C ($t_{1/2} < 5$ min). This indicates that, under the Cope rearrangement conditions, the non-conjugated benzocycloheptene is rapidly isomerized to the conjugated isomer in the presence of TBD.

Scheme 6. Role of TBD in the observed isomerization



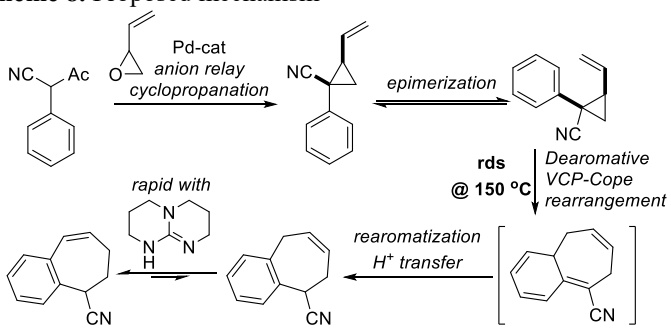
After studying the TBD-mediated isomerization, we turned our attention to another mechanistic question. It is interesting that high yields of benzocycloheptenes are observed starting from reactants where the vinyl and aryl groups primarily have a *trans* disposition; aromatic Cope rearrangements are known to require the *cis*-orientation of the aryl and vinyl groups.[3b] Thus, we hypothesized that the cyclopropane reactants were undergoing stereochemical equilibration on the timescale of the rearrangement.[3b] To investigate this potential isomerization, the stereochemical fidelity of a diastereomerically pure *cis* cyclopropane was investigated at various temperatures in DMSO (Scheme 7). While no isomerization occurred at room temperature, the cyclopropane epimerized at 100 °C, reaching the expected diastereomeric equilibrium within 3 hours. The aromatic Cope rearrangement was only slightly slower, having reached 13 % conversion at 3 hours and 31% conversion after 20 hours. As expected, a styrenyl cyclopropane underwent more rapid epimerization, reaching equilibrium after 1 hour at 100 °C. The fact that no cyclopentene was formed under these conditions indicates that cyclization to form the cyclopentene is the rate-limiting step in forming **7c**. The thermal epimerization of cyclopropanes could occur through diradical[3b-d,11d] or zwitterionic intermediates.[3c,11a] We favor the latter pathway since cyclopropanes **3l** are typical donor-acceptor cyclopropanes that would be expected to form zwitterionic intermediates in DMSO at elevated temperature. Indeed, addition of 2.5 mol % $Pd(PPh_3)_4$, which is known to stabilize zwitterionic intermediates of ring opening[14], catalyzed the *cis*/*trans* equilibration of cyclopropane **3l** in just 1 hour at room temperature.

Scheme 7. Stereochemical fidelity of cyclopropanes



Our observations lead us to propose the following mechanism (Scheme 8). At high temperatures, the isomerization of the vinyl cyclopropane becomes facile. In the case of styrenyl substrates, sterics slow the aromatic Cope rearrangement, leading to the alternate rearrangement to form cyclopentenes **7**. However, with sterically less demanding terminal alkenes, the pericyclic aryl vinyl cyclopropane Cope rearrangement of the *cis* cyclopropane predominates. The Cope rearrangement is believed to be the slowest step of the reaction. However, cyclopropane epimerization is not much slower and may influence the rates of reaction. The initially formed benzocycloheptene can be rapidly converted to the conjugated isomer via a TBD-catalyzed proton transfer.

Scheme 8. Proposed mechanism



3. Experimental section

All reactions were performed in flame dried glassware under an argon atmosphere unless otherwise noted. THF was dried over sodium in the presence of benzophenone. All other materials were obtained from Sigma-Aldrich, Acros Organics, Alfa Aesar or Fisher Scientific and were used without further purification unless otherwise noted. Reactions were monitored in 50 µL aliquots,

performing a simple aqueous workup, and observing the proton NMR spectrum in $CDCl_3$. Flash chromatography was performed using 230x400 mesh, 60 Å porosity silica, using mixtures of hexane (Hex) and ethyl acetate (EA) as eluent as noted. 1H NMR and 13C NMR spectra were obtained on a Bruker Avance 400 or a Bruker Avance 500 DRX spectrometer equipped with a QNP Cryoprobe and referenced to residual protio solvent signals.

Structural assignments are based on ^{1}H, ^{13}C, DEPT135, COSY and NOESY techniques. J values are reported in Hz. High resolution mass spectral analysis was done on a Waters LCT Premier mass spectrometer with a quadrupole and time of flight tandem mass analyzer and an electrospray ion source, or via LCMS using a Waters Q-Tof Premier in tandem with an Aquity UPLC using toluene assisted atmospheric pressure chemical ionization (TAPCI), as noted. Infrared analysis was performed on a Shimadzu FTIR-8400S infrared spectrometer. Melting points were obtained on a Digimelt MPA160 melting point apparatus.

General Experimental Procedures

General Procedure A: A 100 mg/mL solution of vinyl cyclopropane in DMSO was prepared, and 0.5 to 1 mL of this solution was added to a flame dried vial equipped with a stir bar and diluted to 0.2 M with DMSO. The vial was sealed and the atmosphere was replaced with argon by purging and refilling with argon 3×. The mixture was heated to 150 °C and monitored via NMR. Once the reaction was complete (generally 1–6 hours), the mixture was diluted with ethyl acetate (2 mL) and washed with water (5 mL). The first wash was back extracted with ethyl acetate (1mL), and the combined organic extracts were washed again with water (5 mL) and brine (1 mL). The organic layer was then dried with $MgSO_4$, filtered, and the solvents were evaporated to afford the non-conjugated benzocycloheptene. For most products, no further purification was needed. In some cases, additional purification via flash chromatography was required.

General Procedure B: A 100 mg/mL solution of vinyl cyclopropane in DMSO was prepared, and 0.5 to 1 mL of this solution was added to a flame dried vial equipped with a stir bar and diluted to 0.2 M with DMSO. TBD (1,5,7-Triazabicyclo[4.4.0]dec-5-ene) was added (0.5 mmol, 1 equiv.), the vial was sealed and the atmosphere was replaced with argon by purging and refilling with argon 3×. The mixture was heated to 150 °C and monitored via NMR. Once the reaction was complete (generally 1–6 hours), the mixture was diluted with ethyl acetate (2 mL) and washed with water (5 mL). The first wash was back extracted with ethyl acetate (1mL), and the combined organic extracts were washed again with water (5 mL) and brine (1 mL). The organic layer was then dried with $MgSO_4$, filtered, and the solvents were evaporated to afford the non-conjugated benzocycloheptene. For most products, no further purification was needed. In some cases, additional purification via flash chromatography was required.

Compound Characterization

Non-Conjugated Benzocycloheptenes generated using General Procedure A:

*6,9-dihydro-5H-benzo[7]annulene-5-carbonitrile (**4a**).*

Prepared from 0.057 g (0.34 mmol) 1-phenyl-2-vinylcyclopropane-1-carbonitrile according to General Procedure A to yield 0.056 g yellow of oil **4a** (0.0.33 mmol, 98%). IR ($\bar{\nu} - \bar{\nu}_{IR}$, neat) 3028.84, 2902.58, 2902.58, 2838.72, 2240.98, 2224.99, 1660.06, 1601.98, 1492.02, 1455.81. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.50 (dd, *J* = 7.5, 1.5 Hz, 1H Aromatic C<u>H</u>), 7.31 – 7.21 (m, 2H Aromatic C<u>H</u>, solvent overlap), 7.15 – 7.11 (m, 1H, Aromatic C<u>H</u>), 5.82 (dddt, *J* = 11.5, 7.1, 4.3, 2.2 Hz, 1H, Alkene C<u>H</u>), 5.49 (ddddd, *J* = 11.6, 4.6, 3.5, 2.4, 1.0 Hz, 1H Alkene C<u>H</u>), 4.47 (dd, *J* = 10.4, 3.2 Hz, 1H α-CN C<u>H</u>), 3.67 (dp, *J* = 17.5, 3.4 Hz, 1H, Alkane C<u>H$_a$H$_b$</u>), 3.47 – 3.36 (m, 1H Alkane CH$_a$<u>H$_b$</u>), 2.83 – 2.74 (m, 1H Alkane C<u>H$_a$H$_b$</u>), 2.66 – 2.54 (m, 1H Alkane CH$_a$<u>H$_b$</u>).^{13}C NMR (126 MHz, $CDCl_3$) δ 140.57, 134.49, 129.12, 128.25, 127.45, 126.85, 126.46, 125.95, 120.35, 34.14, 33.55, 33.14. HRMS (ESI, m/z) calcd. for $C_{12}H_{11}N$ [M+Na] 192.0784; found 192.0782.

*2-bromo-6,9-dihydro-5H-benzo[7]annulene-5-carbonitrile (**4b**).*

Prepared from 0.0747 g (0.301 mmol) 1-(4-bromophenyl)-2-vinylcyclopropane-1-carbonitrile according to General Procedure A. The crude product was purified by flash chromatography (silica gel, 2.5% EtOAc in Hexanes) to yield 0.0393 g of white solid **4b** (0.158 mmol, 53%). Melting point 85.1-89.2 °C. IR ($\bar{\nu} - \bar{\nu}_{IR}$, neat) 3026.00, 2921.00, 2850.45, 2237.96, 1695.13, 1583.71, 1484.02, 1396.72. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.23 (m, 3H Aromatic C<u>H</u>), 5.78 (dddt, *J* = 11.5, 6.6, 4.3, 2.2 Hz, 1H Alkene C<u>H</u>), 5.48 (ddddd, *J* = 11.6, 4.6, 3.5, 2.4, 0.9 Hz, 1H Alkene C<u>H</u>), 4.42 (dd, *J* = 10.4, 3.3 Hz, 1H α-CN C<u>H</u>), 3.63 (dp, *J* = 17.5, 3.4 Hz, 1H Alkane C<u>H$_a$H$_b$</u>), 3.40 – 3.28 (m, 1H Alkane CH$_a$<u>H$_b$</u>), 2.77 (dtdd, *J* = 18.0, 5.1, 3.5, 1.8 Hz, 1H Alkane C<u>H$_a$H$_b$</u>), 2.56 (ddtt, *J* = 17.9, 10.8, 3.7, 1.9 Hz, 1H Alkane CH$_a$<u>H$_b$</u>). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.55, 133.49, 131.96, 130.30, 128.47, 126.11, 125.71, 121.97, 119.84, 33.65, 33.27, 32.68. HRMS (ESI, m/z) calcd. for $C_{12}H_{10}BrN$ [M+Na] 269.9889; found 269.9898.

*2-chloro-6,9-dihydro-5H-benzo[7]annulene-5-carbonitrile (**4c**).*

Prepared from 0.0833 g (0.409 mmol) 1-(4-chlorophenyl)-2-vinylcyclopropane-1-carbonitrile according to General Procedure A to yield 0.0747 g of yellow oil **4c** (0.367 mmol, 90%). IR ($\bar{\nu} - \bar{\nu}_{IR}$, neat) 3025.26, 2917.35, 2846.35, 2243.29, 1661.44, 1596.73, 1573.77, 1487.33, 1406.93. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.42 (d, *J* = 8.2 Hz, 1H, Aromatic C<u>H</u>), 7.27 – 7.24 (m, 1H, Aromatic C<u>H</u>, solvent overlap), 7.14 (d, *J* = 2.2 Hz, 1H, Ar<u>H</u>), 5.79 (dddt, *J* = 11.4, 6.7, 4.2, 2.2 Hz, 1H, Alkene C<u>H</u>), 5.49 (dddd, *J* = 11.6, 4.7, 3.5, 2.4 Hz, 1H, Alkene C<u>H</u>), 4.43 (dd, *J* = 10.4, 3.3 Hz, 1H, α-CN C<u>H</u>), 3.67 – 3.59 (m, 1H, Alkane C<u>H$_a$H$_b$</u>), 3.36 (dd, *J* = 17.5, 7.2 Hz, 1H CH$_a$<u>H$_b$</u>), 2.77 (ddtd, *J* = 18.0, 6.8, 3.4, 1.7 Hz, 1H Alkane C<u>H$_a$H$_b$</u>), 2.57 (ddtd, *J* = 17.9, 10.7, 3.6, 1.9 Hz, 1H CH$_a$<u>H$_b$</u>). 13C NMR (126 MHz, CDCl3) δ 142.29, 133.90, 133.01, 129.16, 128.24, 127.34, 126.17, 125.78, 119.93, 33.65, 33.43, 32.83. HRMS (ESI, m/z) calcd. for $C_{12}H_{10}ClN$ [M+H] 204.0575; found 204.0569.

*2-fluoro-6,9-dihydro-5H-benzo[7]annulene-5-carbonitrile (**4d**).*

Prepared from 64.6 mg (0.355 mmol) 1-(4-fluorophenyl)-2-vinylcyclopropane-1-carbonitrile according to General Procedure A to yield 57.7 mg of yellow oil **4d** (0.317 mmol, 89%). IR ($\bar{\nu} - \bar{\nu}_{IR}$, neat) 3026.97, 2922.33, 2848.35, 2243.73, 1667.48, 1613.54, 1593.86, 1500.58. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.44 (dd, *J* = 8.5, 5.5 Hz, 1H Aromatic C<u>H</u>), 6.95 (td, *J* = 8.4, 2.7 Hz, 1H Aromatic C<u>H</u>), 6.85 (dd, *J* = 9.1, 2.7 Hz, 1H Aromatic C<u>H</u>), 5.79 (dddt, *J* = 11.5, 6.7, 4.4, 2.2 Hz, 1H Alkene C<u>H</u>), 5.49 (dq, *J* = 11.2, 3.6 Hz, 1H Alkene C<u>H</u>), 4.42 (dd, *J* = 10.3, 3.3 Hz, 1H α-CN C<u>H</u>), 3.62 (dp, *J* = 17.6, 3.4 Hz, 1H Alkane C<u>H$_a$H$_b$</u>), 3.38 (dd, *J* = 17.5, 7.1 Hz, 1H Alkane CH$_a$<u>H$_b$</u>), 2.82 – 2.71 (m, 1H Alkane C<u>H$_a$H$_b$</u>), 2.57 (dddt, *J* = 19.5, 11.9, 3.5, 1.6 Hz, 1H Alkane CH$_a$<u>H$_b$</u>). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 162.24 (d, *J* = 247.8 Hz),

142.90 (d, J = 7.9 Hz), 130.31 (d, J = 3.0 Hz), 128.59 (d, J = 8.9 Hz), 126.01 (d, J = 54.4 Hz), 125.79, 116.28 (d, J = 22.3 Hz), 113.88, 113.71, 33.57, 33.53, 33.02. HRMS (ESI, m/z) calcd. for $C_{12}H_{10}NF$ [M+Na] 210.0689; 210.0697.

*2-isopropyl-6,9-dihydro-5H-benzo[7]annulene-5-carbonitrile (**4e**).*

Prepared from 0.086 g (0.41 mmol) 1-(4-isopropylphenyl)-2-vinylcyclopropane-1-carbonitrile according to General Procedure A. The crude product was purified by flash chromatography (silica gel, 5% EtOAc in Hexanes) to yield 0.044 g of brown oil **4e** (0.21 mmol, 51%). IR ($\bar{\nu} - \bar{\nu}_{IR}$, neat) 3022.56, 2961.61, 2241.41, 1603.02, 1502.58, 2921.26, 2241.20, 1596.86, 1505.07. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.40 (d, J = 7.8 Hz, 1H Aromatic C<u>H</u>), 7.13 (dd, J = 7.9, 1.9 Hz, 1H Aromatic C<u>H</u>), 6.98 (d, J = 1.8 Hz, 1H Aromatic C<u>H</u>), 5.83 (dddt, J = 11.5, 6.8, 4.4, 2.2 Hz, 1H Alkene C<u>H</u>), 5.54 – 5.40 (m, 1H Alkene C<u>H</u>), 4.42 (dd, J = 10.2, 3.3 Hz, 1H α-CN C<u>H</u>), 3.64 (dt, J = 17.5, 3.5 Hz, 1H, Alkane C<u>H$_a$</u>H$_b$), 3.40 (dd, J = 17.5, 7.0 Hz, 1H Alkane CH$_a$<u>H$_b$</u>), 2.88 (p, J = 6.9 Hz, 1H, Alkane C<u>H</u>), 2.76 (dtdd, J = 17.9, 5.1, 3.4, 1.8 Hz, 1H, Alkane C<u>H$_a$</u>H$_b$), 2.59 (ddtd, J = 19.6, 12.2, 3.6, 2.0 Hz, 1H, Alkane CH$_a$<u>H$_b$</u>), 1.24 (d, J = 6.9 Hz, 6H methyl C<u>H$_3$</u>). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.03, 140.43, 131.85, 127.47, 126.94, 126.62, 125.98, 125.24, 120.52, 33.89, 33.86, 33.65, 33.37, 24.08, 24.04. HRMS (ESI, m/z) calcd. for $C_{15}H_{17}N$ [M+H] 212.1439; found 212.1436.

*2-phenyl-6,9-dihydro-5H-benzo[7]annulene-5-carbonitrile (**4f**).*

Prepared from 68.4 mg (0.279 mmol) 1-([1,1'-biphenyl]-4-yl)-2-vinylcyclopropane-1-carbonitrile according to General Procedure A to yield 62.3 mg of yellow solid **4f** (0.254 mmol, 91%). Melting point 78.0-83.3 °C. IR ($\bar{\nu} - \bar{\nu}_{IR}$, neat) 3028.11, 2904.43, 2838.60, 2242.22, 1661.81, 1600.36, 1567.91, 1486.01. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.62 – 7.31 (m, 8H Aromatic C<u>H</u>), 5.86 (dddt, J = 11.5, 6.7, 4.3, 2.2 Hz, 1H Alkene C<u>H</u>), 5.60 – 5.45 (m, 1H Alkene C<u>H</u>), 4.51 (dd, J = 10.4, 3.3 Hz, 1H α-CN C<u>H</u>), 3.73 (dp, J = 17.6, 3.5 Hz, 1H, Alkane C<u>H$_a$</u>H$_b$), 3.48 (dd, J = 17.5, 7.1 Hz, 1H Alkane CH$_a$<u>H$_b$</u>), 2.82 (dddt, J = 17.9, 5.0, 3.4, 1.7 Hz, 1H, Alkane C<u>H$_a$</u>H$_b$), 2.70 – 2.58 (m, 1H Alkane CH$_a$<u>H$_b$</u>).^{13}C NMR (126 MHz, $CDCl_3$) δ 141.31, 140.97, 140.45, 133.49, 128.97, 128.00, 127.70, 127.42, 127.26, 126.44, 126.07, 126.02, 120.33, 33.92, 33.64, 33.35. HRMS (ESI, m/z) calcd. for $C_{18}H_{15}N$ [M-CN] 219.1168; found 219.1163.

*10,11-dihydro-7H-cyclohepta[a]naphthalene-11-carbonitrile (**4g**).*

Prepared from 0.0978 g (0.446 mmol) 1-(naphthalen-1-yl)-2-vinylcyclopropane-1-carbonitrile according to General Procedure A. The crude product was purified by flash chromatography (silica gel, 2.5% EtOAc in Hexanes)to yield 0.0582 mg yellow oil **4g** (0.266 mmol, 60%). IR ($\bar{\nu} - \bar{\nu}_{IR}$, neat) 3053.79, 3021.69, 2924.55, 2850.81, 2237.65, 1666.73, 1623.77, 1599.11, 1511.69, 1430.27. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.98 (d, J = 8.7 Hz, 1H Aromatic C<u>H</u>), 7.88 (d, J = 8.2 Hz, 1H Aromatic C<u>H</u>), 7.76 (d, J = 8.4 Hz, 1H Aromatic C<u>H</u>), 7.58 (t, J = 7.8 Hz, 1H Aromatic C<u>H</u>), 7.49 (t, J = 7.6 Hz, 1H Aromatic C<u>H</u>), 7.29 (d, J = 8.4 Hz, 1H Aromatic C<u>H</u>), 5.96 (t, J = 10.0 Hz, 1H Alkene C<u>H</u>), 5.63 (ddd, J = 11.7, 5.8, 2.8 Hz, 1H Alkene C<u>H</u>), 5.08 (d, J = 4.3 Hz, 1H α-CN C<u>H</u>), 4.58 (dt, J = 18.9, 3.7 Hz, 1H Alkane Alkane C<u>H$_a$</u>H$_b$), 3.42 (dd, J = 18.7, 8.0 Hz, 1H Alkane CH$_a$<u>H$_b$</u>), 2.87 (dd, J = 18.1, 5.0 Hz, 1H Alkane C<u>H$_a$</u>H$_b$), 2.63 (d, J = 17.6 Hz, 1H Alkane Alkane CH$_a$<u>H$_b$</u>). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.00, 133.02, 130.48, 129.30, 129.03, 128.94, 128.80, 127.23, 126.76, 125.46, 125.24, 121.66, 120.22, 34.70, 30.90, 28.27. HRMS (ESI, m/z) calcd. for $C_{16}H_{13}N$ [M+H] 220.1121; found 220.1127.

*3-fluoro-6,9-dihydro-5H-benzo[7]annulene-5-carbonitrile (**4h**).*

Prepared from 0.0641 g (0.342 mmol) 1-(3-fluorophenyl)-2-vinylcyclopropane-1-carbonitrile according to General Procedure A to yield 0.0546 g of yellow oil **4h** as a mixture of regioisomers (0.292 mmol, 85%, r.r. 61:39). IR ($\bar{\nu} - \bar{\nu}_{IR}$, neat) 3026.69, 2917.26, 2846.37, 2244.21, 1668.50, 1616.10, 1500.69, 1466.48. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.29 (d, J = 7.7 Hz, 1H major Aromatic C<u>H</u>), 7.25 – 7.18 (m, overlapping 1H major 1H minor Aromatic C<u>H</u>), 7.09 (dd, J = 8.4, 5.6 Hz, 1H minor Aromatic C<u>H</u>), 7.02 (ddd, J = 9.3, 8.2, 1.2 Hz, 1H major Aromatic C<u>H</u>), 6.92 (td, J = 8.4, 2.7 Hz, 1H minor Aromatic C<u>H</u>), 5.80 (dddq, J = 11.5, 6.6, 4.3, 2.1 Hz, overlapping 1H major 1H minor Alkene C<u>H</u>), 5.56 – 5.41 (m, overlapping 1H major 1H minor Alkene C<u>H</u>). 4.48 (dd, J = 10.4, 3.3 Hz, 1H major α-CN C<u>H</u>), 4.44 (dd, J = 10.6, 3.3 Hz, 1H minor α-CN C<u>H</u>), 3.71 – 3.58 (m, 1H overlapping major and minor Alkane C<u>H$_a$</u>H$_b$), 3.48 (dp, J = 17.9, 3.5 Hz, 1H major Alkane CH$_a$<u>H$_b$</u>), 3.35 (dd, J = 17.7, 7.3 Hz, 1H minor Alkane CH$_a$<u>H$_b$</u>), 2.78 (ddtd, J = 16.4, 6.5, 3.3, 1.6 Hz, overlapping 1H major 1H minor Alkane C<u>H$_a$</u>H$_b$), 2.59 (ddtt, J = 18.0, 10.4, 3.8, 2.0 Hz, overlapping 1H major 1H minor Alkane CH$_a$<u>H$_b$</u>). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.79 (d, J = 246.0 Hz), 159.33 (d, J = 245.2 Hz), 136.99 (d, J = 3.4 Hz),, 136.28 (d, J = 7.4 Hz), 136.21 (d, J = 2.9 Hz), 130.52 (d, J = 8.1 Hz), 128.14, 128.07, 127.49 (d, J = 16.1 Hz), 126.40, 126.35, 125.80, 125.62, 122.32, 122.29, 119.89, 119.76, 115.30 (d, J = 23.7 Hz), 114.55 (d, J = 20.8 Hz), 114.13 (d, J = 23.6 Hz), 34.02 (d, J = 2.8 Hz), 33.90 (d, J = 1.2 Hz), 33.31, 33.25, 32.24, 22.39 (d, J = 6.2 Hz). HRMS (ESI, m/z) calcd. for $C_{12}H_{10}NF$ [M-CN] 161.0761; found 161.0773.

*3-methoxy-6,9-dihydro-5H-benzo[7]annulene-5-carbonitrile (**4i**).*

Prepared from 49.2 mg (0.247 mmol) 1-(3-methoxyphenyl)-2-vinylcyclopropane-1-carbonitrile according to General Procedure A to yield 48.6 mg of brown oil **4i** as a mixture of regioisomers (0.244 mmol, 97% r.r. 50:50). IR ($\bar{\nu} - \bar{\nu}_{IR}$, neat) 3006.95, 2939.04, 2838.96, 2243.63, 1661.29, 1608.34, 1502.88, 1264.69, 1038.89. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.23 (t, J = 8.0 Hz, 1H Aromatic C<u>H</u>), 7.13 (d, J = 7.7 Hz, 1H Aromatic C<u>H</u>), 7.06 (d, J = 2.6 Hz, 1H Aromatic C<u>H</u>), 7.04 (d, J = 8.3 Hz, 1H Aromatic C<u>H</u>), 6.86 (d, J = 8.4 Hz, 1H Aromatic C<u>H</u>), 6.76 (dd, J = 8.3, 2.7 Hz, 1H Aromatic C<u>H</u>), 5.82 (ddtt, J = 9.5, 5.7, 4.1, 2.1 Hz, overlapping 1H 1H Alkene C<u>H</u>), 5.47 (dp, J = 11.2, 3.7 Hz, overlapping 1H 1H Alkene C<u>H</u>), 4.50 (dd, J = 10.7, 3.2 Hz, 1H α-CN C<u>H</u>), 4.42 (dd, J = 10.4, 3.2 Hz, 1H α-CN C<u>H</u>), 3.82 (d, J = 1.4 Hz, overlapping 3H 3H OC<u>H$_3$</u>), 3.81 – 3.74 (m, 1H Alkane C<u>H$_a$</u>H$_b$), 3.59 (dp, J = 17.8, 3.5 Hz, 1H Alkane C<u>H$_a$</u>H$_b$), 3.43 (dq, J = 17.7, 3.5 Hz, 1H Alkane CH$_a$<u>H$_b$</u>), 3.33 (dd, J = 17.7, 7.1 Hz, 1H Alkane CH$_a$<u>H$_b$</u>), 2.77 (ddtd, J = 16.3, 4.9, 3.2, 1.6 Hz, overlapping 1H 1H Alkane C<u>H$_a$</u>H$_b$), 2.65 – 2.52 (m, overlapping 1H 1H Alkane CH$_a$<u>H$_b$</u>). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.89, 156.03, 136.20, 135.57, 132.59, 130.17, 129.14, 127.71, 127.03, 126.75, 126.29, 125.71, 120.53, 120.26, 118.95, 112.93, 110.70, 56.01, 55.57, 34.29, 34.11, 33.58, 32.32, 22.41. HRMS (ESI, m/z) calcd. for $C_{13}H_{13}NO$ [M+H] 200.1070; found 200.1080.

*2,3-dimethyl-6,9-dihydro-5H-benzo[7]annulene-5-carbonitrile (**4j**).*

Prepared from 0.0738 g (0.374 mmol) 1-(3,4-dimethylphenyl)-2-vinylcyclopropane-1-carbonitrile according to General Procedure A to yield 0.0729 g of yellow oil **4j** as a mixture of regioisomers (0.369 mmol, 98%, r.r. 89:11). IR ($\bar{\nu} - \bar{\nu}_{IR}$, neat) 3018.70, 2922.10, 2733.57, 2243.11, 1660.57, 1613.89, 1561.01, 1505.45.^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.24 (s, 1H Aromatic C<u>H</u>), 6.90 (s, 1H Aromatic C<u>H</u>), 5.81 (dddd, J = 11.7,

6.9, 4.4, 2.1 Hz, 1H Alkene CH), 5.46 (dq, *J* = 11.4, 3.6 Hz, 1H Alkene CH), 4.39 (dd, *J* = 10.3, 3.2 Hz, 1H α-CN CH), 3.65 – 3.49 (m, 1H Alkane CH_aH_b), 3.34 (dd, *J* = 17.6, 7.0 Hz, 1H Alkane CH_aH_b), 2.75 (dddd, *J* = 19.5, 6.1, 3.6, 1.8 Hz, Alkane CH_aH_b), 2.64 – 2.48 (m, 1H Alkane CH_aH_b), 2.26 (s, 3H Methyl CH_3), 2.23 (s, 3H Methyl CH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.76, 136.42, 135.55, 132.28, 132.20, 131.71, 130.57, 128.73, 128.63, 128.19, 126.85, 126.73, 125.86, 120.60, 33.77, 33.74, 32.65, 19.38, 19.35. HRMS (ESI, m/z) calcd. for $C_{14}H_{15}N$ [M+Na] 220.1102; found 220.1102.

Cyclopentenes generated using General Procedure A.

*2-(4-methoxyphenyl)-1-phenylcyclopent-3-ene-1-carbonitrile (**7a**).*

Prepared from 0.116 g (0.421 mmol) (E)-2-(4-methoxystyryl)-1-phenylcyclopropane-1-carbonitrile (1b) according to General Procedure A. The Prodcut was purified by flash chromatography (silica gel, 5% EtOAc in Hexanes) to yield 0.0716 g of yellow oil **7a** as separable diastereomers (0.260 mmol, 62%, 60:40 d.r.). IR ($\bar{\nu} - \bar{\nu}_{IR}$, neat) 3060.94, 3033.48, 3003.37, 2934.68, 2837.68, 2237.25, 1609.50, 1448.92, 1032.95. ^{1}H NMR (500 MHz, Chloroform-*d*) (major diastereomer) δ 7.52 – 7.48 (m, 2H Aromatic CH), 7.42 – 7.37 (m, 2H Aromatic CH), 7.37 – 7.31 (m, 1H Aromatic CH), 7.04 – 6.99 (m, 2H Aromatic CH), 6.88 – 6.82 (m, 2H Aromatic CH), 6.07 (dt, *J* = 6.6, 2.3 Hz, 1H Alkene CH), 5.89 (dq, *J* = 6.1, 2.1 Hz, 1H Alkene CH), 4.27 (p, *J* = 2.3 Hz, 1H Alkane CH, benzylic), 3.79 (s, 3H Methoxy CH_3), 3.37 (dq, *J* = 17.1, 2.3 Hz, 1H Alkane CH_aH_b), 3.16 (dq, *J* = 17.1, 2.2 Hz, 1H Alkane CH_aH_b).^{13}C NMR (126 MHz, $CDCl_3$) (major diastereomer) δ 159.44, 140.58, 132.59, 130.49, 129.55, 129.53, 129.06, 127.98, 125.91, 122.27, 114.04, 64.17, 55.34, 48.01, 29.86.^{1}H NMR (500 MHz, Chloroform-*d*) (minor diastereomer) δ 7.12 – 6.99 (m, 5H Aromatic CH), 6.75 – 6.65 (m, 2H Aromatic CH), 6.60 – 6.50 (m, 2H Aromatic CH), 6.19 (dq, *J* = 5.7, 2.4 Hz, 1H Alkene CH), 5.88 (dq, *J* = 6.1, 2.1 Hz, 1H Alkene CH), 4.65 (p, *J* = 2.3 Hz, 1H Alkane CH, benzylic), 3.69 (s, 2H Methoxy CH_3), 3.29 (q, *J* = 2.2 Hz, 2H Alkane CH_2).^{13}C NMR (126 MHz, $CDCl_3$) (minor diastereomer) δ 158.89, 136.21, 132.81, 130.43, 129.73, 128.95, 128.05, 127.60, 127.41, 125.47, 113.46, 62.74, 55.32, 51.44, 44.40. HRMS (ESI, m/z) calcd. for $C_{19}H_{17}NO$ [M+H] 276.1383; found 276.1374.

*2-(4-bromophenyl)-1-phenylcyclopent-3-ene-1-carbonitrile (**7b**).*

Prepared from 100 mg (0.308 mmol) 2-(4-bromostyryl)-1-phenylcyclopropane-1-carbonitrile according to General procedure A to yield 88.8 mg of yellow oil **7b** as a mixture of diastereomers (0.274 mmol, 89%, d.r. 59:41). IR ($\bar{\nu} - \bar{\nu}_{IR}$, neat) 3062.52, 2923.94, 2853.66, 2239.77, 1697.71, 1595.11, 1489.44, 1449.20. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.49 (dt, *J* = 8.1, 1.0 Hz, 2H, major Aromatic CH), 7.46 – 7.38 (m, overlapping 2H major 3H minor Aromatic CH), 7.38 – 7.33 (m, 1H, major Aromatic CH), 7.15 (d, *J* = 8.1 Hz, 2H, minor Aromatic CH), 7.10 (d, J = 7.3 Hz, 2H minor Aromatic CH), 7.06 – 7.01 (m, 2H, minor Aromatic CH), 6.95 (d, *J* = 8.2 Hz, 2H, major Aromatic CH), 6.67 (d, *J* = 8.2 Hz, 2H minor Aromatic CH), 6.28 – 6.20 (m, 1H minor Alkene CH), 6.16 – 6.08 (m, 1H major Alkene CH), 5.92 – 5.81 (m, overlapping 1H major 1H minor Alkene CH), 4.66 (q, *J* = 2.3 Hz, 1H minor Alkane CH, benzylic), 4.27 (q, *J* = 2.4 Hz, 1H major Alkane CH, benzylic), 3.37 (dq, *J* = 17.2, 2.2 Hz, 1H major Alkane CH_aH_b), 3.32 (p, *J* = 2.6 Hz, 2H minor Alkane CH_2), 3.19 (dq, *J* = 17.2, 2.3 Hz, 1H major Alkane CH_aH_b). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.84, 137.28, 135.92, 135.67, 131.78, 131.68, 131.60, 131.21, 131.03, 130.31, 130.15, 130.01, 129.04, 128.12, 128.07, 127.79, 127.14, 125.78, 124.89, 122.08, 121.76, 121.26, 64.06, 62.65, 55.01, 47.99, 44.54. HRMS (ESI, m/z) calcd. for $C_{18}H_{14}BrN$ [M+H] 324.0382; found 324.0386.

*2-(4-chlorophenyl)-1-phenylcyclopent-3-ene-1-carbonitrile (**7c**).*

Prepared from 100 mg (0.357 mmol) (E)-2-(4-chlorostyryl)-1-phenylcyclopropane-1-carbonitrile according to General Procedure A to yield 100 mg of brown oil **7c** as a mixture of diastereomers (0.357 mmol, 100% d.r. 55:45). IR ($\bar{\nu} - \bar{\nu}_{IR}$, neat) 3062.10, 2923.53, 2860.51, 2238.51, 1596.71, 1489.78, 1448.90. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.52 – 7.44 (m, 2H major Aromatic CH), 7.44 – 7.37 (m, 2H major Aromatic CH), 7.39 – 7.31 (m, 1H major Aromatic CH), 7.32 – 7.26 (m, 2H major Aromatic CH), 7.13 – 7.05 (m, 2H major Aromatic CH), 7.02 (ddd, *J* = 15.2, 7.9, 4.2 Hz, 7H minor Aromatic CH), 6.77 – 6.70 (m, 2H minor Aromatic CH), 6.24 (dq, *J* = 5.0, 2.3 Hz, 1H minor Alkene CH), 6.12 (dq, *J* = 4.9, 2.3 Hz, 1H major Alkene CH), 5.88 (tq, *J* = 6.3, 2.1 Hz, overlapping 1H major 1H minor Alkene CH), 4.68 (p, *J* = 2.3 Hz, 1H minor Alkane CH, benzylic), 4.29 (p, *J* = 2.3 Hz, 1H major Alkane CH, benzylic), 3.37 (dq, *J* = 17.2, 2.2 Hz, 1H major Alkane CH_aH_b), 3.32 (p, *J* = 2.5 Hz, 2H minor Alkane CH_2), 3.19 (dq, *J* = 17.1, 2.3 Hz, 1H major Alkane CH_aH_b). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.02, 136.91, 135.84, 135.53, 134.02, 133.25, 131.98, 131.81, 131.29, 130.39, 129.93, 129.79, 129.17, 128.86, 128.23, 128.20, 127.90, 127.27, 125.90, 125.04, 121.9, 64.14, 62.74, 55.17, 51.25, 48.12, 44.65. HRMS (ESI, m/z) calcd. for $C_{18}H_{14}ClN$ [M+H] 280.0888; found 280. 0902.

*1-phenyl-2-(p-tolyl)cyclopent-3-ene-1-carbonitrile (**7d**).*

Prepared from 100 mg (0.386 mmol) (E)-2-(4-methylstyryl)-1-phenylcyclopropane-1-carbonitrile according to General Procedure A to yield 91.1 mg of yellow oil **7d** as a mixture of diastereomers (0.351 mmol, 91.1% d.r. 51:39). IR ($\bar{\nu} - \bar{\nu}_{IR}$, neat) 3059.39, 3027.40, 2921.28, 2860.86, 2237.82, 1599.66, 1493.78, 1448.83. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.53 – 7.45 (m, 2H major Aromatic CH), 7.44 – 7.36 (m, 2H major Aromatic CH), 7.36 – 7.28 (m, 2H minor Aromatic CH), 7.25 (d, *J* = 5.5 Hz, 1H minor Aromatic CH), 7.12 (p, *J* = 6.8, 6.0 Hz, 2H major Aromatic CH), 7.04 (t, *J* = 5.5 Hz, overlapping 1H major 2H minor Aromatic CH), 7.02 – 6.92 (m, 2H major Aromatic CH), 6.83 (dd, *J* = 7.7, 4.8 Hz, 2H minor Aromatic CH), 6.67 (dt, *J* = 8.3, 5.3 Hz, 2H minor Aromatic CH), 6.18 (ddp, *J* = 7.1, 4.9, 2.4 Hz, 1H minor Alkene CH), 6.07 (tq, *J* = 8.4, 4.8, 3.5 Hz, 1H major Alkene CH), 5.89 (td, *J* = 5.6, 2.8 Hz, overlapping 1H major 1H minor Alkene CH), 4.66 (p, *J* = 4.0, 3.1 Hz, 1H minor Alkane CH, benzylic), 4.27 (h, *J* = 3.7, 3.0 Hz, 1H major Alkane CH, benzylic), 3.36 (ddt, *J* = 16.9, 5.0, 2.4 Hz, 1H major Alkane CH_aH_b), 3.29 (dp, *J* = 4.9, 2.4 Hz, 2H minor Alkane CH_2), 3.16 (ddq, *J* = 17.5, 5.5, 2.5 Hz, 1H major Alkane CH_aH_b), 2.32 (t, *J* = 5.3 Hz, 3H major CH_3), 2.22 – 2.11 (m, 3H minor CH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.65, 137.78, 136.98, 136.21, 135.42, 133.78, 132.77, 132.50, 132.29, 132.21, 132.08, 130.47, 129.62, 129.38, 129.05, 128.73, 128.57, 128.33, 127.98, 127.55, 127.42, 125.90, 125.45, 122.24, 64.49, 63.01, 55.03, 51.38, 48.12, 44.56, 21.32, 21.11. HRMS (ESI, m/z) calcd. for $C_{19}H_{17}N$ [M+Na] 282.1253; found 282.1265.

*2-(2-methoxyphenyl)-1-phenylcyclopent-3-ene-1-carbonitrile (**7e**).*

Prepared from 0.0739 g (0.268 mmol) E)-2-(2-methoxystyryl)-1-phenylcyclopropane-1-carbonitrile according to General Procedure A to yield 0.0625 g of yellow oil **7e** as a mixture of diastereomers (0.275 mmol, 85%, d.r. 68:32). IR ($\bar{\nu} - \bar{\nu}_{IR}$, neat) 3060.52, 2940.00, 2835.59, 2236.83, 1600.56, 1491.17, 1450.83,

1269.62, 1157.66, 1049.48.4. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.55 – 7.48 (m, 2H major Aromatic CH), 7.44 – 7.36 (m, 2H major Aromatic CH), 7.39 – 7.31 (m, 2H minor Aromatic CH), 7.24 (d, *J* = 7.9 Hz, 1H minor Aromatic CH), 7.12 – 7.04 (m, overlapping 2H major 2H minor Aromatic CH), 6.97 (t, *J* = 7.9 Hz, 1H minor Aromatic CH), 6.85 (dd, *J* = 8.3, 2.6 Hz, 1H major Aromatic CH), 6.70 (dt, *J* = 7.6, 1.2 Hz, 1H major Aromatic CH), 6.63 (t, *J* = 2.1 Hz, 1H major Aromatic CH), 6.60 (dd, *J* = 8.3, 2.6 Hz, 1H minor Aromatic CH), 6.47 (dd, *J* = 7.6, 1.4 Hz, 1H minor Aromatic CH), 6.26 (t, *J* = 2.0 Hz, 1H minor Aromatic CH), 6.22 (dq, *J* = 4.9, 2.3 Hz, 1H minor Alkene CH), 6.10 (dt, *J* = 6.5, 2.3 Hz, 1H major Alkene CH), 5.91 (tq, *J* = 5.8, 2.1 Hz, overlapping 1H major 1H minor Alkene CH), 4.67 (p, *J* = 2.2 Hz, 1H Alkane CH, benzylic), 4.28 (p, *J* = 2.3 Hz, 1H Alkane CH, benzylic), 3.75 (s, 3H major OCH_3), 3.58 (s, 3H major OCH_3), 3.38 (dq, *J* = 17.1, 2.3 Hz, 1H major Alkane CH_aH_b), 3.31 (q, *J* = 2.2 Hz, 2H minor Alkane CH_2), 3.17 (dq, *J* = 17.1, 2.2 Hz, 1H major Alkane CH_aH_b). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.76, 159.40, 140.66, 140.01, 138.45, 136.08, 132.34, 132.17, 130.89, 129.95, 129.65, 129.09, 129.01, 128.05, 128.03, 127.66, 127.38, 125.90, 125.28, 122.07, 121.26, 120.85, 114.23, 113.99, 113.43, 113.32, 64.79, 63.27, 55.30, 55.24, 54.86, 51.41, 48.17, 44.60. HRMS (ESI, m/z) calcd. for $C_{19}H_{17}NO$ [M+] 275.1305; found 275.1314.

*2-(3-methoxyphenyl)-1-phenylcyclopent-3-ene-1-carbonitrile (**7f**).*

Prepared from 50 mg (0.182 mmol) (E)-2-(3-methoxystyryl)-1-phenylcyclopropane-1-carbonitrile according to General Procedure A to yield 38.9 mg of pale yellow oil **7f** as a mixture of diastereomers (0.141 mmol, 77.6% d.r. 61:39). IR ($\bar{\nu} - \bar{\nu}_{IR}$, neat) 3060.70, 2939.38, 2835.62, 2237.97, 1600.29, 1583.82, 1490.97, 1449.88, 1269.17, 1157.36, 1035.66. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.54 – 7.49 (m, 2H major Aromatic CH), 7.40 (t, *J* = 7.7 Hz, 2H major Aromatic CH), 7.37 – 7.31 (m, 2H minor Aromatic CH), 7.24 (d, *J* = 7.9 Hz, 1H minor Aromatic CH), 7.12 – 7.03 (m, overlapping 2H major 2H minor Aromatic CH), 6.96 (t, *J* = 7.9 Hz, 1H minor Aromatic CH), 6.84 (dd, *J* = 8.3, 2.5 Hz, 1H major Aromatic CH), 6.70 (d, *J* = 7.6 Hz, 1H major Aromatic CH), 6.63 (d, *J* = 2.1 Hz, 1H major Aromatic CH), 6.60 (dd, *J* = 8.2, 2.6 Hz, 1H minor Aromatic CH), 6.47 (d, *J* = 7.5 Hz, 1H minor Aromatic CH), 6.26 (t, *J* = 2.0 Hz, 1H minor Aromatic CH), 6.22 (dq, *J* = 5.0, 2.4 Hz, 1H minor Alkene CH), 6.10 (dq, *J* = 6.2, 2.3 Hz, 1H major Alkene CH), 5.91 (tq, *J* = 5.6, 2.1 Hz, 1H overlapping 1H major 1H minor Alkene CH), 4.71 – 4.62 (m, 1H minor Alkane CH, benzylic), 4.28 (q, *J* = 2.3 Hz, 1H minor Alkane CH, benzylic), 3.75 (s, 3H major OCH_3), 3.58 (s, 3H minor OCH_3), 3.38 (dq, *J* = 17.1, 2.3 Hz, 1H major Alkane Alkane CH_aH_b), 3.31 (q, *J* = 2.2 Hz, 2H minor Alkane CH_2), 3.17 (dq, *J* = 17.1, 2.2 Hz, 1H major Alkane CH_aH_b).^{13}C NMR (126 MHz, $CDCl_3$) δ 159.77, 159.40, 140.66, 140.01, 138.46, 136.08, 132.35, 132.18, 130.89, 129.95, 129.65, 129.09, 129.01, 128.05, 128.03, 127.67, 127.38, 125.90, 125.29, 122.07, 121.26, 120.85, 114.23, 113.99, 113.43, 113.32, 64.79, 63.28, 55.30, 55.25, 54.86, 51.41, 48.18, 44.61. HRMS (ESI, m/z) calcd. for $C_{19}H_{17}NO$ [M+Na] 298.1202; found 298.1204.

*2-(3-chlorophenyl)-1-phenylcyclopent-3-ene-1-carbonitrile (**7g**).*

Prepared from 50 mg (0.179 mmol) (E)-2-(3-chlorostyryl)-1-phenylcyclopropane-1-carbonitrile according to General Procedure A to yield 45 mg of yellow oil **7g** as a mixture of diastereomers (0.161 mmol, 90% d.r. 59:41). IR ($\bar{\nu} - \bar{\nu}_{IR}$, neat) 3063.38, 2926.20, 2859.82, 2239.40, 1596.86, 1571.77, 1493.84, 1449.38. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 7.6 Hz, 2H major Aromatic CH), 7.41 (t, *J* = 7.5 Hz, 2H major Aromatic CH), 7.38 – 7.27 (m, overlapping 1H major 5H minor Aromatic CH), 7.13 – 6.94 (m, overlapping 4H major 2H minor Aromatic CH), 6.74 (s, 1H minor Aromatic CH), 6.72 (d, *J* = 7.7 Hz, 1H minor Aromatic CH), 6.25 (dt, *J* = 5.8, 2.4 Hz, 1H minor Alkene CH), 6.13 (dd, *J* = 5.8, 2.7 Hz, 1H minor Alkene CH), 5.88 (td, *J* = 5.8, 2.6 Hz, overlapping 1H major 1H minor Alkene CH), 4.67 (t, *J* = 2.3 Hz, 1H minor Alkane CH, benzylic), 4.27 (t, *J* = 2.3 Hz, 1H major Alkane CH, benzylic), 3.39 (dd, *J* = 17.2, 2.5 Hz, 1H major Alkane CH_aH_b), 3.33 (d, *J* = 2.4 Hz, 2H minor Alkane CH_2), 3.18 (dd, *J* = 17.2, 2.4 Hz, 1H major Alkane CH_aH_b). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.55, 140.31, 139.11, 135.74, 134.55, 134.04, 131.68, 131.56, 131.52, 130.60, 129.94, 129.26, 129.21, 129.03, 128.66, 128.51, 128.37, 128.24, 128.20, 127.95, 127.52, 127.48, 127.21, 126.95, 126.75, 125.79, 124.99, 121.79, 64.44, 62.97, 54.69, 51.27, 48.17, 44.66. HRMS (ESI, m/z) calcd. for $C_{18}H_{14}ClN$ [M+H] 280.0888; found 280. 0902

*2-(benzo[d][1,3]dioxol-5-yl)-1-phenylcyclopent-3-ene-1-carbonitrile (**7h**).*

Prepared from 0.0699 g (0.242 mmol) (E)-2-(2-(benzo[d][1,3]dioxol-5-yl)vinyl)-1-phenylcyclopropane-1-carbonitrile according to General Procedure A. Filtered through a silica gel plug in EtOAc. Yield 0.695 g brown oil (0.240 mmol, 99% d.r. 58:42). IR ($\bar{\nu} - \bar{\nu}_{IR}$, neat) 3061.21, 3028.68, 2896.65, 2778.98, 2236.90, 1600.85, 1502.85, 1443.89, 1250.81, 1099.31, 1039.31.^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.53 – 7.47 (m, 2H major Aromatic CH), 7.40 (t, *J* = 7.5 Hz, 2H major Aromatic CH), 7.34 (t, *J* = 7.3 Hz, 1H major Aromatic CH), 7.15 – 7.04 (m, overlapping 2H major 2H minor Aromatic CH), 6.76 (d, *J* = 7.8 Hz, 1H major Aromatic CH), 6.58 (s, 1H minor O-CH_2-O), 6.56 (d, *J* = 1.9 Hz, 1H minor Aromatic CH), 6.49 (d, *J* = 8.0 Hz, 1H minor Aromatic CH), 6.33 (dd, *J* = 8.0, 1.6 Hz, 1H minor Aromatic CH), 6.24 (d, *J* = 1.7 Hz, 1H minor Aromatic CH), 6.19 (dq, *J* = 5.0, 2.2 Hz, 1H minor Alkene CH), 6.08 (dq, *J* = 4.8, 2.2 Hz, 1H major Alkene CH), 5.95 (s, 2H major O-CH_2-O), 5.86 (dt, *J* = 6.1, 2.1 Hz, overlapping 1H major 1H minor Alkene CH), 5.83 – 5.79 (m, 1H minor Aromatic CH), 4.62 (t, *J* = 2.3 Hz, 1H minor Alkane CH, benzylic), 4.29 – 4.19 (m, 1H major Alkane CH, benzylic), 3.37 (dq, *J* = 17.1, 2.2 Hz, 1H major Alkane CH_aH_b), 3.29 (q, *J* = 2.2 Hz, 2H minor Alkane CH_2), 3.14 (dq, *J* = 17.1, 2.2 Hz, 1H major Alkane CH_aH_b). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.91, 147.46, 146.76, 140.73, 136.06, 132.55, 132.32, 130.74, 130.71, 129.83, 129.12, 128.70, 128.10, 128.04, 127.72, 127.35, 125.79, 125.35, 122.18, 122.11, 121.82, 108.92, 108.73, 108.42, 107.86, 101.23, 100.96, 64.71, 63.09, 54.83, 51.40, 48.09, 44.38. HRMS (ESI, m/z) calcd. for $C_{19}H_{15}NO_2$ [M+H] 290.1176; found 290.1192.

Conjugated Benzocycloheptenes generated using General Procedure B:

*6,7-dihydro-5H-benzo[7]annulene-5-carbonitrile (**5a**).*

Prepared from 0.0718 g (0.424 mmol) 1-phenyl-2-vinylcyclopropane-1-carbonitrile according to General Procedure B. The crude product was filtered through a silica gel plug in EtOAc to yield 0.0594 g of brown oil **5a** (0.351 mmol, 83%). IR ($\bar{\nu} - \bar{\nu}_{IR}$, neat) 3059.84, 3021.76, 2933.11, 2894.66, 2829.75, 2238.97, 1643.95, 1599.07, 1494.86, 1449.76, 1424.64. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.42 – 7.38 (m, 1H Aromatic CH), 7.30 (td, *J* = 7.5, 1.4 Hz, 1H Aromatic CH), 7.23 (ddd, *J* = 9.7, 7.8, 1.7 Hz, 2H Aromatic CH), 6.48 (dt, *J* = 12.1, 2.0 Hz, 1H Alkene CH), 6.00 (dt, *J* = 12.1, 4.8 Hz, 1H Alkene CH), 4.05 (dd, *J* = 6.4, 4.3 Hz, 1H α-CN CH), 2.55 (ddddd, *J* = 24.2, 18.7,

13.0, 5.0, 2.1 Hz, 2H Alkane C$\underline{H}_2$), 2.36 – 2.29 (m, 2H Alkane C$\underline{H}_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.57, 134.16, 131.70, 131.58, 129.57, 128.26, 127.88, 127.46, 119.93, 36.07, 31.88, 29.10. LRMS (EI, m/z) parent mass 169.2 found 169.0 %TIC 5.80. HRMS (ESI, m/z) calcd. for $C_{12}H_{11}N$ [M+Na] 192.0784; found 192.0786.

*2-bromo-6,7-dihydro-5H-benzo[7]annulene-5-carbonitrile (**5b**).*

Prepared from 77.8 mg mg (0.313 mmol) 1-(4-bromophenyl)-2-vinylcyclopropane-1-carbonitrile according to General Procedure B to yield 62.4 mg of brown oil **5b** (0.251 mmol, 80%). IR ($\bar{\nu} - \bar{\nu}_{IR}$, neat) 3023.84, 2933.78, 2828.17, 2239.48, 1644.52, 1561.82, 1486.13, 1447.83.^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.35 (d, *J* = 9.2 Hz, 2H Aromatic C$\underline{H}$), 7.27 (d, *J* = 8.0 Hz, 1H Aromatic C$\underline{H}$), 6.39 (dt, *J* = 12.1, 1.8 Hz, 1H Alkene C$\underline{H}$), 6.05 (dt, *J* = 11.9, 4.8 Hz, 1H Alkene C$\underline{H}$), 3.99 (dd, *J* = 6.4, 4.5 Hz, 1H α-CN C$\underline{H}$), 2.61 – 2.47 (m, 2H Alkane C$\underline{H}_2$), 2.35 – 2.24 (m, 2H Alkane C$\underline{H}_2$).^{13}C NMR (126 MHz, $CDCl_3$) δ 137.55, 134.05, 133.39, 133.07, 130.15, 129.42, 128.26, 122.10, 119.37, 35.53, 31.67, 29.00. HRMS (ESI, m/z) calcd. for $C_{12}H_{10}NBr$ [M+H] 248.0069; found 248.0077.

*2-chloro-6,7-dihydro-5H-benzo[7]annulene-5-carbonitrile (**5c**).*

Prepared from 0.0482 g (0.237 mmol) 1-(4-chlorophenyl)-2-vinylcyclopropane-1-carbonitrile according to General Procedure B. The crude product was purified by flash chromatography (silica gel, 2.5% EtOAc in Hexanes) to yield 0.0179 g of pale yellow oil **5c** (0.088 mmol, 37%). IR ($\bar{\nu} - \bar{\nu}_{IR}$, neat) 2924.12, 2850.33, 2241.31, 1592.36, 1563.79, 1488.91, 1448.10. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.37 – 7.30 (m, 1H Aromatic C$\underline{H}$), 7.20 (d, *J* = 7.6 Hz, 2H Aromatic C$\underline{H}$), 6.40 (dd, *J* = 12.2, 2.0 Hz, 1H Alkene C$\underline{H}$), 6.06 (ddd, *J* = 12.8, 7.3, 3.1 Hz, 1H Alkene C$\underline{H}$), 4.01 (dd, *J* = 6.7, 4.3 Hz, 1H α-CN C$\underline{H}$), 2.63 – 2.46 (m, 2H Alkane C$\underline{H}_2$), 2.30 (qd, *J* = 7.0, 1.8 Hz, 2H Alkane C$\underline{H}_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.32, 134.12, 133.36, 132.62, 131.20, 129.23, 128.45, 127.26, 119.51, 35.52, 31.83, 29.03. HRMS (ESI, m/z) calcd. for $C_{12}H_{10}NCl$ [M+H] 204.0575; found 204.0583.

*2-fluoro-6,7-dihydro-5H-benzo[7]annulene-5-carbonitrile (**5d**).*

Prepared from 54.9 mg (0.293 mmol) 1-(4-fluorophenyl)-2-vinylcyclopropane-1-carbonitrile according to General Procedure B to yield 48.3 mg of yellow oil **5d** (0.258 mmol, 88%). (KA7_115). IR ($\bar{\nu} - \bar{\nu}_{IR}$, neat) 3025.08, 2935.45, 2898.33, 2239.86, 1675.05, 1610.22, 1583.64, 1424.77, 1393.77. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.27 (dd, *J* = 9.4, 5.4 Hz, 1H Aromatic C$\underline{H}$), 6.84 (ddt, *J* = 8.0, 3.8, 2.0 Hz, 2H Aromatic C$\underline{H}$), 6.33 (dt, *J* = 12.1, 1.9 Hz, 1H Alkene C$\underline{H}$), 5.97 (dt, *J* = 12.0, 4.8 Hz, 1H Alkene C$\underline{H}$), 3.94 (dd, *J* = 6.3, 4.5 Hz, 1H α-CN C$\underline{H}$), 2.55 – 2.38 (m, 2H Alkane C$\underline{H}_2$), 2.26 – 2.18 (m, 2H Alkane C$\underline{H}_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.41 (d, *J* = 246.3 Hz), 137.80 (d, *J* = 8.1 Hz), 133.19, 130.07 (d, *J* = 3.5 Hz), 129.62 (d, *J* = 8.2 Hz), 128.62 (d, *J* = 1.8 Hz), 125.94 (d, *J* = 52.7 Hz), 119.68, 117.90 (d, *J* = 21.8 Hz), 113.98 (d, *J* = 21.7 Hz), 35.37, 31.77, 28.90. HRMS (ESI, m/z) calcd. for $C_{12}H_{10}NF$ [M-CN] 161.0761; found 161.0795.

*2-phenyl-6,7-dihydro-5H-benzo[7]annulene-5-carbonitrile. (**5e**).*

Prepared from 28.8 mg (0.117 mmol) 1-([1,1'-biphenyl]-4-yl)-2-vinylcyclopropane-1-carbonitrile according to General Procedure B to yield 25.0 mg of yellow oil **5e** (0.102 mmol, 87%). IR ($\bar{\nu} - \bar{\nu}_{IR}$, neat) 3028.73, 2931.92, 2239.76, 1666.70, 1599.82, 1484.80, 1449.23. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.63 – 7.56 (m, 2H Aromatic C$\underline{H}$), 7.51 – 7.42 (m, 5H Aromatic C$\underline{H}$), 7.42 – 7.33 (m, 1H Aromatic C$\underline{H}$), 6.56 (dt, *J* = 12.2, 1.9 Hz, 1H Alkene C$\underline{H}$), 6.05 (dt, *J* = 11.9, 4.8 Hz, 1H Alkene C$\underline{H}$), 4.14 – 4.05 (m, 1H α-CN C$\underline{H}$), 2.69 – 2.47 (m, 2H Alkane C$\underline{H}_2$), 2.40 – 2.29 (m, 2H Alkane C$\underline{H}_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.29, 140.25, 135.94, 133.11, 132.09, 130.37, 129.58, 128.97, 128.47, 127.75, 127.17, 126.03, 119.90, 35.80, 31.80, 29.12. HRMS (ESI, m/z) calcd. for $C_{18}H_{15}N$ [M-CN] 219.1168; found 219.1134.

*2-methoxy-6,7-dihydro-5H-benzo[7]annulene-5-carbonitrile (**5f**).*

Prepared from 96.8 mg (0.486 mmol) 1-(4-methoxyphenyl)-2-vinylcyclopropane-1-carbonitrile according to General Procedure B to yield 88.6 mg of brown oil **5f** (0.445 mmol, 92%). IR ($\bar{\nu} - \bar{\nu}_{IR}$, neat) 3008.66, 2934.97, 2836.50, 2236.68, 1604.15, 1574.29, 1505.17, 1463.63, 1248.49, 1036.74. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.32 – 7.22 (m, 1H Aromatic C$\underline{H}$), 6.74 (dd, *J* = 6.0, 2.8 Hz, 2H Aromatic C$\underline{H}$), 6.41 (dt, *J* = 12.1, 1.9 Hz, 1H Alkene C$\underline{H}$), 5.98 (dt, *J* = 12.0, 4.8 Hz, 1H Alkene C$\underline{H}$), 4.00 (dd, *J* = 7.7, 3.0 Hz, 1H α-CN C$\underline{H}$), 3.79 (d, *J* = 1.3 Hz, 3H OC$\underline{H}_3$), 2.62 – 2.40 (m, 2H Alkane C$\underline{H}_2$), 2.36 – 2.17 (m, 2H Alkane C$\underline{H}_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.27, 136.77, 132.03, 129.36, 129.14, 126.52, 120.02, 116.90, 112.33, 55.33, 35.24, 31.63, 28.76. HRMS (ESI, m/z) calcd. for $C_{13}H_{13}NO$ [M+H] 200.1070; found 200.1077.

*3-methyl-6,7-dihydro-5H-benzo[7]annulene-5-carbonitrile (**5g**).*

Prepared from 0.1047 g (0.572 mmol) 1-(3-methoxyphenyl)-2-vinylcyclopropane-1-carbonitrile according to General Procedure B to yield 0.0951 g of yellow oil **5g** as a mixture of regioisomers (0.519 mmol, 91%, r.r. 61:39). IR ($\bar{\nu} - \bar{\nu}_{IR}$, neat) 3026.12, 2945.09, 2864.11, 2239.83, 1672.16, 1610.06, 1501.30, 1461.44. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.41 (dd, *J* = 6.9, 2.1 Hz, 1H major Aromatic C$\underline{H}$), 7.20 (d, *J* = 18.4 Hz, overlapping 2H major 1H minor Aromatic C$\underline{H}$), 7.10 (d, *J* = 1.7 Hz, 2H minor aromatic C$\underline{H}$), 6.64 (dd, *J* = 11.1, 1.9 Hz, 1H major Alkene C$\underline{H}$), 6.45 (dd, *J* = 12.1, 2.0 Hz, 1H minor Alkene C$\underline{H}$), 6.22 (dt, *J* = 11.0, 6.2 Hz, 1H major Alkene C$\underline{H}$), 5.93 (dt, *J* = 12.1, 4.7 Hz, 1H minor Alkene C$\underline{H}$), 4.01 (dd, *J* = 6.5, 4.2 Hz, 1H minor α-CN C$\underline{H}$), 3.93 (dd, *J* = 10.3, 5.1 Hz, 1H major α-CN C$\underline{H}$), 2.62 – 2.44 (m, 1H Alkane C$\underline{H}_a$H$_b$), 2.44 – 2.33 (m, overlapping 3H methyl C$\underline{H}_3$, 1H Alkane C$\underline{H}_a$H$_b$), 2.33 – 2.18 (m, overlapping 3H methyl C$\underline{H}_3$, 1H Alkane CH$_a\underline{H}_b$), 2.17 – 2.06 (m, 1H Alkane CH$_a\underline{H}_b$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.29, 136.85, 135.01, 133.97, 133.89, 132.60, 132.14, 132.06, 131.55, 131.21, 130.52, 129.84, 129.25, 128.76, 128.54, 127.26, 124.70, 120.79, 119.94, 37.95, 35.96, 34.18, 31.57, 29.03, 25.51, 21.05, 20.01. HRMS (ESI, m/z) calcd. for $C_{13}H_{13}N$ [M+H] 184.1121; found 184.1124.

*2,3-dimethyl-6,7-dihydro-5H-benzo[7]annulene-5-carbonitrile (**5h**).*

Prepared from 37.4 mg (0.190 mmol) 1-(3,4-dimethylphenyl)-2-vinylcyclopropane-1-carbonitrile according to General Procedure B. Yield 30.2 mg yellow oil (0.153 mmol, 87% r.r. 56:44). IR ($\bar{\nu} - \bar{\nu}_{IR}$, neat) 3020.77, 2940.94, 2239.78, 1611.79, 1508.14, 1452.65. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.34 (d, *J* = 7.8 Hz, 1H major Aromatic C$\underline{H}$), 7.15 (s, 1H minor Aromatic

CH), 7.11 (d, J = 7.8 Hz, 1H major Aromatic CH), 6.99 (s, 1H minor Aromatic CH), 6.69 (dd, J = 10.7, 1.8 Hz, 1H major Alkene CH), 6.41 (dt, J = 12.1, 1.9 Hz, 1H minor Alkene CH), 6.24 (ddd, J = 10.8, 7.2, 6.3 Hz, 1H major Alkene CH), 5.91 (dt, J = 12.1, 4.7 Hz, 1H minor Alkene CH), 4.00 (t, J = 5.3 Hz, 1H minor α-CN CH), 3.88 (dd, J = 10.7, 5.8 Hz, 1H major α-CN CH), 2.64 – 2.44 (m, 1H Alkane CH_aH_b), 2.37 (dddd, J = 13.1, 11.0, 7.7, 3.5 Hz, 1H Alkane CH_aH_b), 2.31 (s, 3H methyl CH_3), 2.27 (s, 3H methyl CH_3), 2.24 (s, 3H methyl CH_3), 2.20 (s, 3H methyl CH_3), 2.14 (ddt, J = 14.2, 7.0, 3.5 Hz, 1H Alkane CH_aH_b), 2.04 – 1.95 (m, 1H Alkane CH_aH_b). ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.63, 136.43, 135.94, 135.25, 135.22, 133.01, 132.89, 131.50, 131.44, 130.79, 130.53, 129.86, 129.33, 129.30, 128.93, 124.07, 121.22, 120.15, 38.94, 35.72, 33.79, 31.57, 29.10, 24.55, 20.46, 19.39, 19.28, 15.82. HRMS (ESI, m/z) calcd. for $C_{14}H_{15}N$ [M+H] 198.1277; found 198.1282.

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Supplementary Material

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