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Graphical Abstract

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Dehydrative Nazarov-type Electrocyclizations of Alkenyl (Hetero)aryl Carbinols via Calcium Catalysis: Access to Cyclopenta[*b*]thiophenes and Indenes

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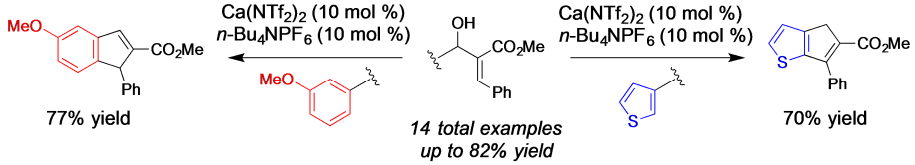
School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia 30332, USA



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Dehydrative Nazarov-type Electrocyclizations of Alkenyl (Hetero)aryl Carbinols via Calcium Catalysis: Access to Cyclopenta[*b*]thiophenes and Indene Derivatives

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ABSTRACT

A general approach to the understudied cyclopenta[*b*]thiophenes is reported. The products were directly generated from calcium-catalyzed, dehydrative, Nazarov-type electrocyclizations of alkenyl thienyl carbinols in up to 82% yield. The thienyl carbinols demonstrated good tolerance for aryl and heteroaryl substituents on the alkene. Aryl carbinols were also amenable to the calcium-catalyzed conditions and afforded indene derivatives in good yields. In most cases, the reaction was selective for the thermodynamic alkene isomer; however, substituent effects played a role in determining product outcomes. Mechanistically, the calcium catalyst initiated formation of alkenyl (hetero)aryl carbinyl cations which subsequently underwent a 4π electrocyclization and elimination that is reminiscent of the Nazarov reaction. This transformation is significant for two main reasons: 1) it represents one of the only examples of catalysis for dehydrative, Nazarov-type electrocyclizations in which thiophene was compatible; 2) it allowed for the direct formation of cyclopenta[*b*]thiophenes while circumventing the need for cyclopenta[*b*]thiophenones as precursors.

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1. Introduction

Cyclopenta[*b*]thiophenes represent a unique class of organic molecules that are interesting isosteres of indenes (Figure 1).[1] They exist in equilibrium as mixtures of the major 4*H*- and 6*H*-isomers and the transient 5*H*-isomer (isosteric with isoindene).[2] The parent compounds have been primarily used as precursors to thiophene-fused cyclopentadienyl metal complexes,[3] whereas, the 5,6-dihydro derivatives have been employed by materials scientists[4] (for use in conjugated polymers, liquid crystalline media, and organic field-effect transistors) and medicinal chemists[5] (as anti-cancer, anti-bacterial, anti-viral, and anti-fungal agents).

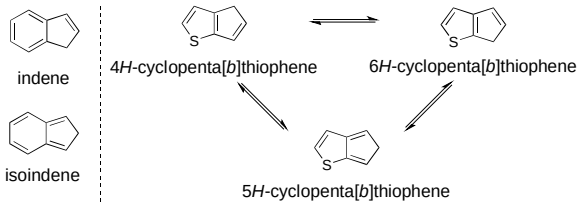
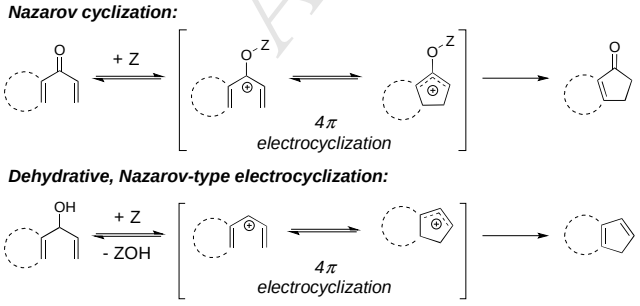


Figure 1. Isomeric Forms of Cyclopenta[*b*]thiophene

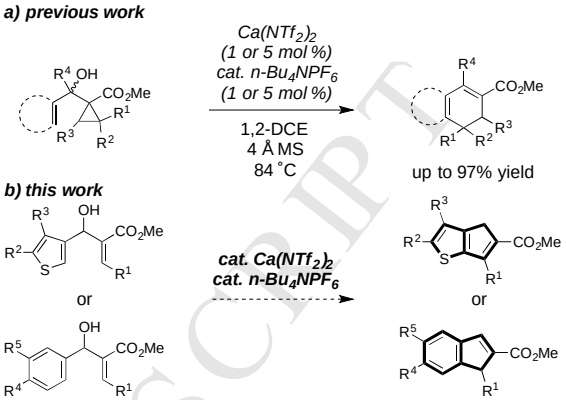
Despite these rich applications, there exists a lack of general and robust methods for the preparation of functionalized cyclopenta[*b*]thiophenes. Only a handful of syntheses have been reported to date, the majority of which start with derivatization of a thiophene-fused cyclopentanone. For example, the most robust method reported by Lee[3b,3c] involves the following three-step sequence: 1) a one-pot acid-promoted Friedel-Crafts acylation/Nazarov cyclization of thiophene with acrylic acid derivatives to form thiophene-fused cyclopentanones; 2) nucleophilic attack at the carbonyl to form the corresponding alcohols; and 3) acid-promoted dehydration to form the cyclopenta[*b*]thiophenes. Unfortunately, this approach affords limited scope (only methyl or phenyl substituents) and low functional group tolerance due to the use of strong acids. Therefore, the design of milder and more generalized approaches to cyclopenta[*b*]thiophenes represents a worthwhile synthetic endeavor, particularly one that circumvents the formation and derivatization of a thiophene-fused cyclopentanone.

Renewed interest in the Nazarov cyclization[6] has led to the breakthrough of many new methods for the initiation of the 4π-electrocyclization, central to the formation of functionalized cyclopentyl rings. One relevant example is the direct ionization of the C-O bond of divinyl alcohols and (hetero)aryl-substituted allyl alcohols (Scheme 1).[7,8] Explored by several groups, this dehydrative, Nazarov-type approach[9] provides straightforward routes to cyclopentadienes, indenes, and heteroaryl-fused cyclopentadienes.[10]



Scheme 1. Nazarov Cyclization vs. Dehydrative, Nazarov-type Electrocyclization

Over the past several years, we have developed a variety of Lewis acid-catalyzed protocols toward (hetero)aryl-fused five-, six-, and seven-membered rings using Nazarov-like reactions.[11,12] We have further sought to establish the catalytic, formal homo-Nazarov cyclization as a viable template for diversity-oriented synthesis.[13] Toward that end, we recently reported a calcium-catalyzed, dehydrative, ring-opening cyclization of (hetero)aryl cyclopropyl carbinols to form (hetero)aryl-fused cyclohexa-1,3-dienes in up to 97% yield (Scheme 2a).[14]



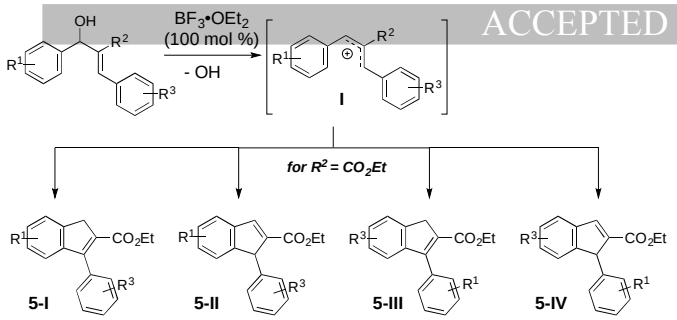
Scheme 2. Calcium-Catalyzed, Dehydrative Cyclizations of Cyclopropyl or Alkenyl (Hetero)aryl Carbinols

Inspired by this outcome, we sought to identify catalytic conditions that were amenable for the general cyclization of alkenyl (hetero)aryl carbinols that specifically allow for the formation of cyclopenta[*b*]thiophenes. It is important to note that thiophenes have been somewhat problematic in dehydrative, Nazarov-type cyclizations. For instance, in 2011, Singh[15] published a Nazarov-type electrocyclization initiated by a $Sc(OTf)_3$-catalyzed ionization of alkenyl (hetero)aryl carbinols to form [6,6,5,6] and [6,6,5,5] heterocyclic ring systems. While the reaction worked for arenes and indole, the thienyl- or benzothienyl-substituted substrates rapidly decomposed or afforded uncharacterized products. Yamamoto[16] was later able to accomplish cyclization with a benzothienyl substrate, although the corresponding thiophene provided no discernible product. With an eye towards overcoming these issues, we disclose an effective, calcium-catalyzed, dehydrative, Nazarov-type 4π-electrocyclization of alkenyl thienyl (or aryl) carbinols to form cyclopenta[*b*]thiophenes and/or indenes (Scheme 2b).

2. Results and Discussion

2.1. Mechanism

In 2010, Batey and co-workers extensively investigated substituent effects on the selectivity of the cyclizations of 1,3-diarylallylic cations **I**, derived from the diallyl alcohols using stoichiometric $BF_3{\bullet}OEt_2$ (Scheme 3).[17] The reactions worked when R^2 = Me or CO_2Et, but failed when R^2 = H. Depending on the choice of substituents, mixtures of indenes **5-II** (from cyclization onto the ring bearing R^1) and **5-IV** (from cyclization onto the ring bearing R^3) were most commonly obtained. Also observed in select cases was indene **5-I**, the product resulting from alkene isomerization. The authors argue that alkene isomerization is most likely due to base-catalyzed process given the increased acidity of the dibenzylic C-1 proton. A 1,5-hydrogen shift mechanism was ruled out since the reactions were performed at room temperature.

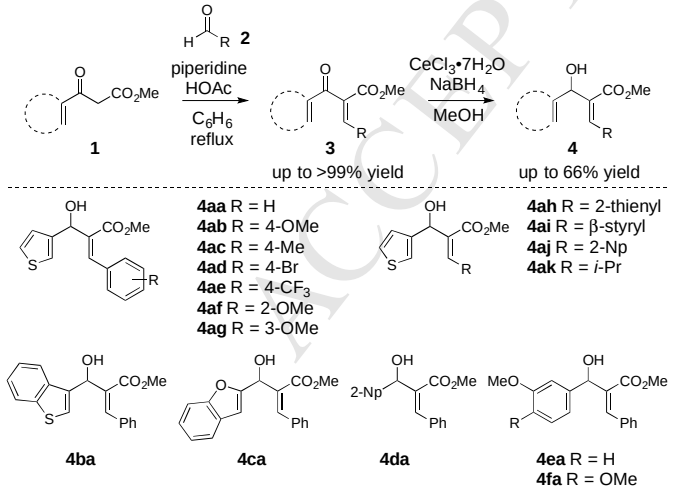


Scheme 3. Batey's Indene Synthesis Using 1,3-Diaryl Allylic Alcohols

Regarding substituent effects, electron-withdrawing aryl substituents disfavored cyclization and only the more electron-rich ring engaged in ring-formation. In the case of electron-donating groups, the selectivity was dependent upon the nature and position of the substituent. The authors then argue that, unlike in electrophilic aromatic substitution, no correlation of selectivity with calculated electron densities was observed, which is consistent with a cationic 4π conrotatory electrocyclization mechanism.

*2.2. Synthesis of Carbinols **4***

Guided by the work of Batey[17], we outlined a straightforward approach to allyl (hetero)aryl-substituted carbinols **4** using a two-step sequence starting from (hetero)aryl β-ketoesters **1** (Scheme 4). Knoevenagel condensation of **1** with aldehydes **2** afforded alkylidene β-ketoesters **3** in up to >99% yield. Subsequent Luche reduction[18] of **3** provided the desired carbinols **4** in up to 66% yield.[19] With the emphasis on accessing cyclopenta[*b*]thiophenes, most of the prepared substrates contained the 3-thienyl moiety, using **4aa** as the model compound selected for optimization. 3-Benzothienyl, 2-benzofuranyl-, 2-naphthyl-, and aryl-substituted allyl alcohols were also prepared in order to explore reaction scope once optimized conditions were identified. When **3ak** (bearing an *i*-Pr substituent) was subjected to Luche conditions, the desired product **4ak** proved inseparable from the fully reduced saturated alcohol.

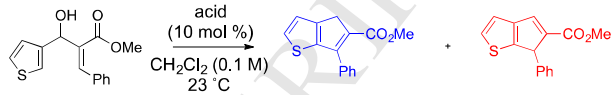


Scheme 4. Synthesis of Carbinols **4**

2.3. Reaction Optimization

3-Thienyl carbinol **4aa** was subjected to an initial screening of acid catalysts at 10 mol % loading in CH_2Cl_2 (Table 1). As expected, no reaction occurs in the absence of catalyst (entry 1). Given the work by Panda,[15] we were surprised to find that $Sc(OTf)_3$ afforded poor yield (11%) of **5aa-I** and **5aa-II** as a 1.2:1 mixture (entry 2). Similar isomeric ratios, but with higher yield (43%), were obtained with TfOH and BF_3•OEt_2 (entries 3 and 4). Employing stoichiometric BF_3•OEt_2 (Batey's conditions for indene synthesis) gave **5aa-I** as the only product with only a slight improvement in yield (entry 5). No desired product was formed with $Yb(OTf)_3$, $La(OTf)_3$, $Dy(OTf)_3$, or $Ni(OTf)_2$ after 24 h (entries 6-9), and trace amounts of product were detected with $Al(OTf)_3$ at 20 h (entry 10). In contrast, $Ga(OTf)_3$ and $In(OTf)_3$, each gave **5aa-I** as the only isomer in 47% and 51% yield, respectively (entries 11 and 12). $Bi(OTf)_3$ gave an increased yield of 57%, but with **5aa-I** and **5aa-II** as a 2:1 mixture (entry 13).

Table 1. Selection of Acid Catalyst[a]



entry	acid	time (h)	yield (%)[b]	**5aa-I** : **5aa-II**[c]
1	None	24.0	NR	--
2	$Sc(OTf)_3$	24.0	11	1.2:1
3	TfOH	0.5	43	1.4:1
4	BF_3•OEt_2	5.0	43	1.5:1
5[d]	BF_3•OEt_2	4.0	47	1.0:0
6	$Yb(OTf)$	>24.0	--[e]	--
7	$La(OTf)_3$	>24.0	--[e]	--
8	$Dy(OTf)_3$	>24.0	--[e]	--
9	$Ni(OTf)_2$	>24.0	--[e]	--
10	$Al(OTf)_3$	20.0	trace	--[f]
11	$Ga(OTf)_3$	4.0	47	1.0:0
12	$In(OTf)_3$	4.0	51	1.0:0
13	$Bi(OTf)_3$	4.0	57	2.0:1
14	$Ca(NTf_2)_2$ n-Bu_4NPF_6	4.0	55	1.0:0
15[g]	$Ca(NTf_2)_2$ n-Bu_4NPF_6	1.0	60	1:2.6

[a]Reaction was performed with carbinol **4aa** and acid catalyst (10 mol %) in CH_2Cl_2 (0.1 M) at 23 ˚C.

[b]Isolated yield after column chromatography.

[c]Ratio determined by ^{1}H NMR of the product mixture.

[d]Performed using 100 mol % BF_3•OEt_2.

[e]No desired product formed.

[f]Not determined.

[g]Reaction performed at reflux (~40 ˚C).

Inspired by our previous work on the ring-opening cyclizations of cyclopropyl carbinols,[14] the Niggemann combination[20] of $Ca(NTf_2)_2$ and additive n-Bu_4NPF_6 (10 mol % each) was employed. This combination has been shown to be effective in catalyzing the Nazarov cyclization and the reactions of carbinols.[21] Under these conditions, **5aa-I** was obtained as the only product in 55% yield (entry 14). In an attempt to improve the yields, the reaction was performed at reflux (~40 ˚C). Unexpectedly, although the yield improved to 60%, a 2.6:1 ratio was formed with **5aa-II** as the major isomer (entry 15).

Next, the effects of time at reflux on both the yield and product ratios were examined (Figure 2). Reactions were set up using the conditions above and then quenched at 30 min, 1 h, 1.75 h, and 2.5 h. Both 30 min and 1 h gave ~1:3 mixtures with **5aa-II** as the major component in 63% and 60% yield, respectively. Conversely, **5aa-I** was obtained in 65% yield as the only observable product at 1.75 h. At 2.5 h, some isomerization

is observed as the **5aa-I** to **5aa-II** ratio erodes to 5.5:1 along with a minor drop in yield (58%), possibly due to product degradation. Thus, to minimize product degradation while optimizing for yield and product ratios, 1.75 h was targeted as the ideal reaction time.

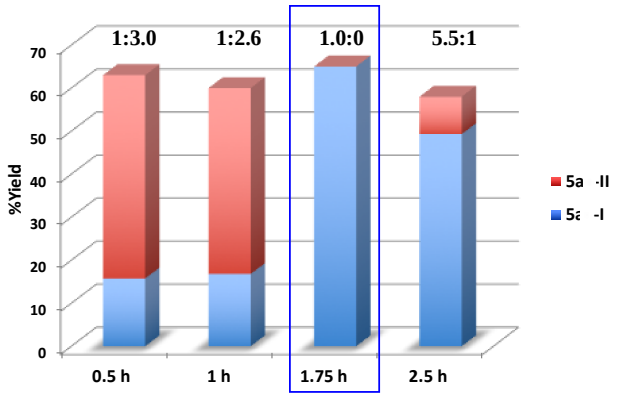
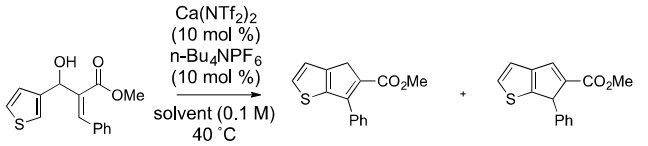


Figure 2. Effect of Reaction Time at Reflux on Product Ratios

Table 2. Final Reaction Optimization[a]



4aa **5aa-I** **5aa-II**

entry	solvent	time (h)	yield (%)[b]	**5aa-I** : **5aa-II**[c]
1	CH_2Cl_2	1.75	65	1.0:0
2[d]	CH_2Cl_2	1.5	63	4.5:1
3[e]	CH_2Cl_2	2.5	57	1.4:1
4	1,2-DCE	1.75	58	1.0:0
5	Toluene	1.75	53	1.0:0
6	CH_3CN	>24.0	--[f]	--
7	THF	3.0	57	6.0:1
8	Benzene	1.75	67 (60)[g]	1.0:0
9[h]	**Benzene**	**1.75**	**70**	**1.0:0**

[a]Reaction was performed with carbinol **4aa** and $Ca(NTf_2)_2$ (10 mol %), *n*-Bu_4NPF_6 (10 mol %) in indicated solvent (0.1 M) at 40 ˚C.

[b]Isolated yield after column chromatography.

[c]Ratio determined by ^{1}H NMR of the product mixture.

[d]5 mol % each of $Ca(NTf_2)_2$ and *n*-Bu_4NPF_6 were used.

[e]2.5 mol % each of $Ca(NTf_2)_2$ and *n*-Bu_4NPF_6 were used.

[f]No desired product formed.

[g]Yield in parentheses represents the product yield when performed at reflux (~80 ˚C).

[h]Reaction performed at a concentration of 0.05 M.

In the final phase of optimization, we examined the effects of (1) reducing the catalyst loading, (2) changing the solvent, and (3) changing the reaction concentration (Table 2). The reaction in CH_2Cl_2 at 40 ˚C with 10 mol % catalyst loading was used as the benchmark (65% yield of only **5aa-I**, entry 1). First, the catalyst loadings for $Ca(NTf_2)_2$ and *n*-Bu_4NPF_6 were each reduced to 5 and then 2.5 mol %. With each decrease in catalyst loading, a change in isomeric ratio is observed. At 5 mol % loading, a 4.5:1 isomeric mixture is formed, while a 1.4:1 mixture is seen with 2.5 mol %. It is likely that the reduced loading directly effects the rate of the base-promoted alkene isomerization due to the *in situ*-generated [*n*-Bu_4N]NTf_2. Moreover, a longer reaction time was necessary for the 2.5 mol % reaction to reach completion; product degradation was observed as a result.

In hopes of replacing CH_2Cl_2, a screening of solvents was then performed to determine the optimum solvent. The reaction temperature was maintained at 40 ˚C to minimize product degradation. Both 1,2-dichloroethane and toluene afforded **5aa-I** selectively, albeit with reduced yields (entries 4 and 5). In contrast, CH_3CN proved incompatible, as no desired products were detected (entry 6). This is most likely due to catalyst deactivation through solvent coordination. With THF, **5aa-I** was formed in 57% yield as a 6.0:1 isomeric mixture (entry 7). Benzene proved to be the best solvent for the reaction as **5aa-I** was selectively generated in 67% yield (entry 8). After further exploration of the reaction concentration, an improved yield (70%) was obtained using a more dilute reaction mixture (0.05 M, entry 9). Ultimately, these conditions (10 mol % $Ca(NTf_2)_2$, 10 mol % *n*-Bu_4NPF_6, benzene, 0.05 M, 40 ˚C, 1.75 h) were chosen as the optimized conditions for the remainder of the study.

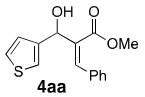
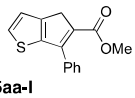
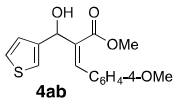
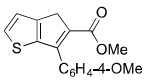
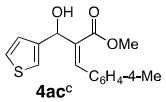
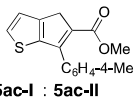
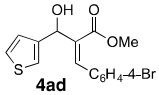
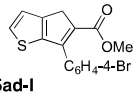
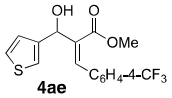
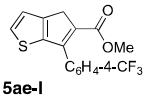
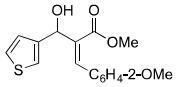
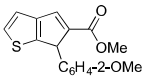
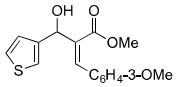
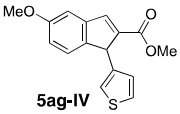
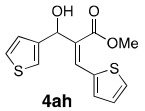
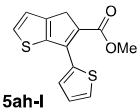
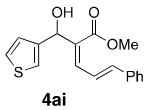
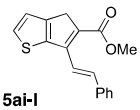
2.4. Examination of Substrate Scope

With working conditions, the effect of changing the alkenyl substituent of the carbinol was examined (Table 3). First, the existence of any stereoelectronic effects imparted by substituents on a phenyl ring was probed using carbinols **4ab-4ae**. When the more electron-rich 4-methoxy phenyl group was employed (as in **4ab**), **5ab-I** was obtained in 82% yield (entry 2). **4ac**, bearing a weakly-activating 4-tolyl substituent, cyclized to form **5ac-I** in 66% yield as a 6.5:1 isomeric mixture (entry 3). Products **5ad-I** and **5ae-I** were respectively obtained in 69% and 67% yield for substrates bearing a weakly electron-withdrawing 4-bromophenyl group (**4ad**) and a strongly withdrawing 4-trifluoromethyl phenyl substituent (**4ae**) (entries 4 and 5). These combined outcomes suggest that due to a slight inductive effect, higher yields are anticipated with strong donor groups on the phenyl rings.

To further probe substituent effects on the cyclization, the 2- and 3-methoxyphenyl substrates **4af** and **4ag** were subjected to the reaction conditions. In the case of **4af**, the cyclization occurred with higher yield (75%) to furnish **5af-II** as an 8:1 isomeric mixture with **5af-I** (entry 6). This result was unexpected given the previous substrates and thermodynamic preference of **5af-I** vs. **5af-II**. The most plausible explanation is that steric influences (imparted by the methoxy group) slow the rate of alkene isomerization. By comparison, **4ag** did not produce either **5af-I** or **5af-II**. Instead, **5af-IV**, where cyclization has occurred onto the aryl group, was isolated in 79% yield (entry 7). This result is consistent with Batey's work[16] in which the location of substituent has a direct influence on product outcome, with cyclization onto the more nucleophilic aromatic ring as the major product.[22] Ring closure is therefore expected to occur preferentially on the phenyl ring *para* to the methoxy group- a more nucleophilic position than C-2 on the thiophene ring.

In contrast, only **5ah-I** was generated (66% yield) with **4ah**, as no cyclization onto the 2-thienyl moiety was observed (entry 8). This outcome agrees with the greater nucleophilicity of the thiophene C-2 vs C-3. For **4ai** with a β-styryl substituent, only 22% yield of **5ai-I** was isolated along with significant degradation and uncharacterized compound mixtures (entry 9). Given the added delocalization, multiple cationic intermediates can be generated that may undergo competing reactions.

Table 3. Ca-Catalyzed Synthesis of Cyclopenta[*b*]thiophenes[a]

Entry	Carbinol **4**	Product **5**	Yield (%)[b]
1	 **4aa**	 **5aa-I**	70%
2	 **4ab**	 **5ab-I**	82%
3	 **4ac**[c]	 **5ac-I** : **5ac-II** (6.5 : 1)[d]	66%
4	 **4ad**	 **5ad-I**	69%
5	 **4ae**	 **5ae-I**	67%
6	 **4af**	 **5af-II** : **5af-I** (8.0 : 1)[d]	75%
7	 **4ag**	 **5ag-IV**	79%
8	 **4ah**	 **5ah-I**	66%
9	 **4ai**	 **5ai-I**	22%

[a]Reaction was performed with carbinol **4** and $Ca(NTf_2)_2$ (10 mol %), *n*-Bu_4NPF_6 (10 mol %) in benzene (0.05 M) at 40 ˚C over 1.45 h.

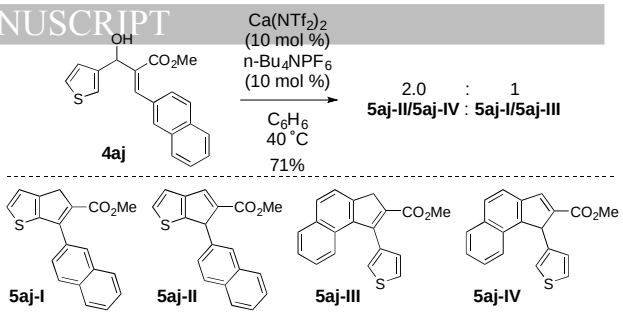
[b]Isolated yield after column chromatography.

[c] 7.0:1 ratio of **4ac** to unreduced alkylidene **3ac**.

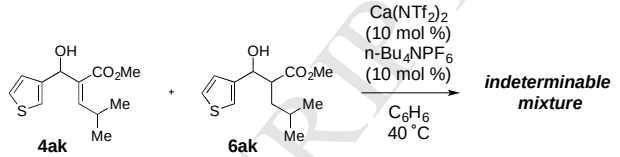
[d]Ratio determined by ^{1}H NMR of the product mixture.

When a 2-naphthyl group was employed as the alkenyl substituent (**4aj**), a 20:7.0:3.5:1.0 mixture of the four possible isomers was obtained in 71% yield (Scheme 5). Given the complexity of the NMR spectra, we were unable to unequivocally correlate each isomer with the observed ratios. Despite that limitation, we were able to determine that a 2.0:1 ratio of trisubstituted alkene isomers (**5aj-II** and **5aj-IV**) to tetra-substituted alkene isomers (**5aj-I** and **5aj-III**) exists.

Finally, encouraged by the outcome of **4ac** (employed as a mixture with left over starting material **3ac**), we subjected the isopropyl-substituted alkenyl substrate **4ak** to the cyclization conditions, despite it existing as a 2.0:1 mixture with the fully reduced alcohol **6ak** (Scheme 6). Disappointingly, the reaction only gave an indeterminable mixture and neither **4ak** nor **6ak** was recovered.



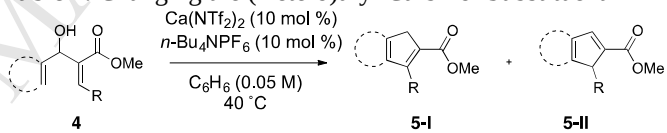
Scheme 5. Complex Products Outcomes from Cyclization of **4aj**

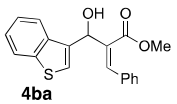
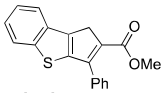
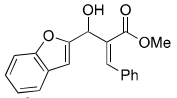
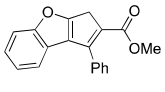
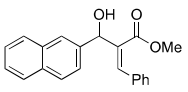
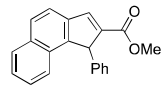
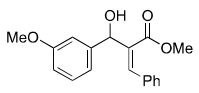
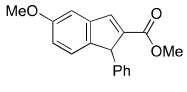
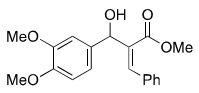
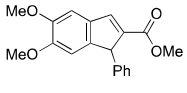


Scheme 6. Attempted Cyclization of **4ak** Mixture

Next, the effects of replacing the thienyl group with other (hetero)arenes were studied under the optimized conditions (Table 4). 2-Benzothienyl carbinol **4ba** cyclized to give benzo[*b*]cyclopenta[*d*]thiophene **5ba-I** in 53% yield (entry 1). With 2-benzofuranyl carbinol **4ca**, no product **5ca** was obtained, as significant decomposition was encountered (entry 2). This outcome is consistent with the low yield (10%) observed by Batey[17] for a similar 3-benzofuranyl derivative.

Table 4. Changing the (Hetero)aryl Carbinol Substituent[a]



Entry	Carbinol **4**	Product **5**	Yield (%)[b]
1	 **4ba**	 **5ba-I**	53%
2	 **4ca**	 **5ca-I**	--[c]
3	 **4da**	 **5da-II**	75%
4	 **4ea**	 **5ea-II**	77%
5	 **4fa**	 **5fa-II**	68%

[a]Reaction was performed with carbinol **4** and $Ca(NTf_2)_2$ (10 mol %), *n*-Bu_4NPF_6 (10 mol %) in benzene (0.05 M) at 40 ˚C over 1.45 h.

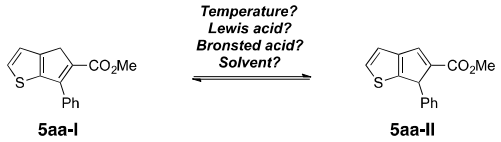
[b]Isolated yield after column chromatography.

[c]Decomposition.

2-Naphthyl carbinol **4da** proved a competent substrate (75% yield) with alkylation readily occurring at C-1 to form **5da-II** as the only observable product (entry 3). This result contrasts with what Batey[17] obtained for a 2-naphthyl derivative with a methyl group in place of the ester. In that case, a 3:1 mixture of product from C-1 alkylation and product from cyclization onto the phenyl group was formed. Lastly, in agreement with Batey's observations, 3-methoxy-substituted phenyl carbinols (**4ea**) expectedly gave the corresponding indene **5ea-II** in 77% yield (entry 4). A similar result was obtained with the 3,4-dimethoxy substrate **4fa** (entry 5).

2.5. Control Reactions and Mechanistic Studies

After establishing a good understanding of the effects of changes in substrate, questions about the nature of product ratios persisted. The reaction appeared to be more complicated than a simple kinetic vs thermodynamic product argument due to the fact that the ratios oscillated, changing in both directions. In an attempt to gain a deeper understanding of the interconversion between products **5aa-I** and **5aa-II**, a series of control reactions were performed.



Scheme 7. Probing the Interconversion of **5aa-I** and **5aa-II**

In the first experiment, performed before solvent optimization, a 1.7:1 mixture of **5aa-I**:**5aa-II** (obtained by combining previous products after column chromatography) was subjected to the initial reaction conditions [$Ca(NTf)_2$ (10 mol %), *n*-Bu_4NPF_6 (10 mol %), CH_2Cl_2, 40 ˚C] at both room temperature and at reflux (Table 5). No change in ratios was observed at room temperature; however, under reflux for 0.5 h, the **5aa-I**:**5aa-II** product ratio improved to 15.0:1. At 1.0 h, the product ratios deteriorated to 3.5:1. In both cases, product degradation was observed and about 65-69% of the mixture was recovered. This study suggests two things: (1) reflux time has a direct effect upon product ratios; and (2) product degradation is likely a competing pathway that must be considered.[23]

Table 5. Control Experiment to Probe Interconversion Between **5aa-I** and **5aa-II** Under Initial Reaction Conditions.[a]

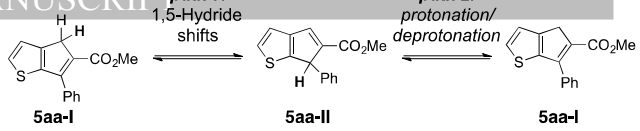
entry	time at reflux (h)	% recovery[b]	**5aa-I** : **5aa-II**[c]
1	0.0	>95	1.7:1
2	0.5	65	15.0:1
3	1.0	69	3.5:1

[a]Reaction was performed with indicated mixture of **5aa-I** and **5aa-II** and $Ca(NTf_2)_2$ and *n*-Bu_4NPF_6 (10 mol % each) in CH_2Cl_2 (0.1 M) at 40 ˚C. Each entry was a separate, isolated reaction.

[b]Percentage of **5aa-I**:**5aa-II** mixture recovered after column chromatography.

[c]Ratio determined by ^{1}H NMR of the product mixture.

Two plausible mechanisms for the interconversion exist (Scheme 8). In the first case, two 1,5-H shifts occur in tandem (converting from the 4*H*-, 5*H*-, and 6*H*-cyclopenta[*b*]thiophenes and vice versa). The second mechanism involves acid/base-mediated protonation/deprotonation. Another possibility, of course, would be some combination of the two if they occur concurrently.



Scheme 8. Plausible Mechanisms for Interconversion.

To further interrogate the effects of heat and the nature of the interconversion we sought to plot product ratios as a function of time using: (1) the optimized reaction conditions in benzene starting with **4aa**; (2) heating and stirring a known ratio of **5aa-I** to **5aa-II**; and (3) heating and stirring a ratio of **5aa-I** to **5aa-II** in the presence of a Brønsted acid ($HNTf_2$). The results of these studies, along with the data from Figure 2 (yellow line) and Table 5 (red line), are shown in Figure 3.

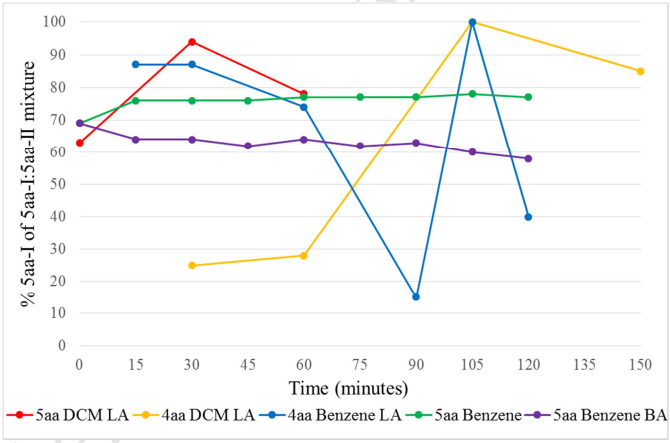
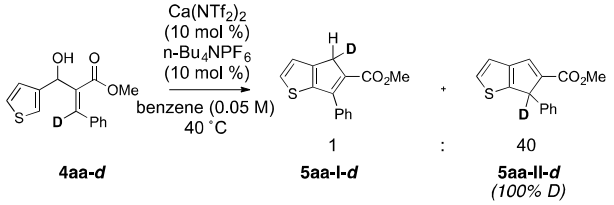


Figure 3. Control Reactions Probing Product Ratios as a Function of Time. Reactions were performed in indicated solvent (DCM or benzene) with indicated starting material (**4aa** or **5aa**) at 40 ˚C with either Lewis acid (LA = $Ca(NTf_2)_2$ and *n*-Bu_4NPF_6 (10 mol % each)), Brønsted acid (BA = $HNTf_2$ (10 mol %)), or no additive. 5aa DCM LA (red); 4aa DCM LA (yellow); 4aa Benzene LA (blue); 5aa Benzene (green); 5aa Benzene BA (purple)

Significant fluctuations in product ratios between 60 and 120 minutes were observed for the optimized reaction starting with **4aa** (Figure 3, blue line). Full conversion of **4aa** to **5aa** was observed within 15 min. Isolated product yields remained consistent for each time point (within 5%) of the optimized 67% yield (Table 3 entry 8). Oscillation of product ratios was observed under these conditions; however at 105 min, only **5aa-I** persists in solution. Finally, although product degradation is still a potential issue, it does not seem to worsen over the time span of 15 minutes and 120 minutes.

The next two experiments involved subjecting a 2.2:1 ratio of **5aa-I** to **5aa-II** to heating and stirring in benzene either with (purple line) or without (green line) 10 mol % $HNTf_2$. The reactions were set up using the same solution of **5aa** in benzene split into two flasks, both heated to 40 ˚C. If the interconversion were the result of purely thermodynamic H-shifts, product oscillation would be observed with simple heating and stirring over time. If it were protonation/deprotonation instead, oscillation should only occur with acid present. The results for both show a minor change (~5%) in ratio within the first 15 minutes, followed by little change at all (<5%). It seems as though interconversion is very slow or the system had reached equilibrium. This result is distinctly different from the other data sets involving the calcium catalyst, which seems to be responsible for the large oscillations. One can speculate that there may be some sort of complex involving the calcium catalyst and the products that facilitates interconversion.

In one final attempt at probing the hydride shift mechanism, the deuterated starting material, **4aa-*d***, was synthesized and subjected to the reaction conditions (Scheme 9). **5aa-II-*d*** was obtained as the major product in a 40:1 ratio of **5aa-II-*d***:**5aa-I-*d***. The product was fully deuterated. This result was repeated at 30 min and 60 min reaction times as well, with effectively identical results. Unfortunately, because of the small amounts of **5aa-I-*d*** formed, the extent of deuterium incorporation was not determined. Similarly, the control reaction of **4aa** in deuterated solvent showed no deuterium incorporation, although it did show a change in product ratio, indicating a solvent effect.



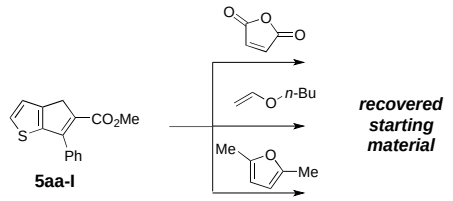
Scheme 9. Dehydrative Cyclization of **4aa-I-*d***

Some strong mechanistic conclusions can be drawn from these deuterium studies. The consistency over time and overwhelming prevalence of the **5aa-II-*d*** isomer indicates that it forms first in the reaction and the presence of the deuterium prevents isomerization, suggesting a very large kinetic isotope effect. Mechanistically, this means that the **II** isomer is the first to form in the reaction and it subsequently isomerizes in the instances that we see the **I** isomer. The same is true for the formation of the indenes where the **IV** isomer would before the **III** isomer.

Although we cannot make definitive conclusions on how and why the product seems to oscillate between the two isomers **5aa-I** and **5aa-II**, we have learned several important details about the reaction from our studies. (1) The reaction initially, and rapidly, generates isomers **II** (or **IV**) and any variations in isolated product ratios observed are the result of isomerization. (2) There is a large KIE for isomerization. (3) Although the isomerization does not require the calcium catalyst, it is likely the cause for the large oscillations in product ratios. (4) There are observable solvent effects on the isomerization rate. (5) Although some product degradation is detected, it can be ruled out as mostly irrelevant as a function of reaction time in our optimized conditions.

2.6. Attempted derivatizations

Inspired by Skramstad's report demonstrating that the transient 5*H*-cyclopenta[*b*]thiophene isomer can undergo Diels-Alder-type cyclizations,[2c] we reacted cyclopenta[*b*]thiophene product **5aa** with various dienophiles as well as a diene to explore reactivity (Scheme 10). Unfortunately, no reactivity was observed between **5aa** and maleic anhydride (to probe normal electron demand cycloaddition), *n*-butyl vinyl ether (to probe inverse electron demand cycloaddition), or 2,5-dimethylfuran (to probe if **5aa** can behave as a dienophile).



Scheme 10. Attempted Diels-Alder-type Cycloaddtions of **5aa-I**

3. Conclusion

In summary, we have disclosed a calcium-catalyzed protocol for the dehydrative, Nazarov-type electrocyclization of alkenyl (hetero)aryl carbinols that allows access to functionalized cyclopenta[*b*]thiophenes and indenes. Products are isolated in up to 82% yield. Good tolerance for aryl and heteroaryl substituents on the alkene was demonstrated, whereas a β-styryl substituent gave low yield. Substituent effects play a significant role in determining product outcomes and isomeric ratios. For systems with competing (hetero)aryl substituents, cyclization occurs preferentially on the most nucleophilic ring. When the relative nucleophilicities are close, mixtures are then observed. For the 3-thienyl series (without a competing aryl substituent), the reaction is selective for the thermodynamic alkene isomer in all but one case, whereas the arene series favors the kinetic alkene isomer for the resulting indenes. This transformation represents one of the only examples of catalytic, dehydrative, Nazarov-type electrocyclizations in which thiophenes are compatible. Thus, it allows for the direct formation of cyclopenta[*b*]thiopenes and it circumvents the need for cyclopenta[*b*]thiophenones as precursors. Future efforts will be focused in two primary directions. Firstly, improved methods for selective 1,2-reduction of the alkylidene β-ketoesters will be explored. Secondly, the method will be expanded to synthesize more functionalized cyclopenta[*b*]thiophenes, which can be used in organometallic chemistry and materials science.

4. Experimental section

4.1. General Information

Chromatographic purification was performed as flash chromatography with Silicycle SiliaFlash P60 silica gel (40-63μm) or preparative thin-layer chromatography (prep-TLC) using silica gel F254 (1000 μm) plates and solvents indicated as eluent with 0.1-0.5 bar pressure. For quantitative flash chromatography, technical grades solvents were utilized. Analytical thin-layer chromatography (TLC) was performed on Silicycle SiliaPlate TLC silica gel F254 (250 μm) TLC glass plates. Visualization was accomplished with UV light. Infrared (IR) spectra were obtained using an IRAffinity-1S FTIR from Shimadzu. The IR bands are characterized as broad (br), weak (w), medium (m), and strong (s). Proton and carbon nuclear magnetic resonance spectra (H^1 NMR and C^{13} NMR) were recorded on a Varian Mercury Vx 300 MHz spectrometer or a Bruker 500 MHz spectrometer with solvent resonances as the internal standard (H^1 NMR: $CDCl_3$ at 7.26 ppm; C^{13} NMR: $CDCl_3$ at 77.0 ppm). H^1 NMR data are reported as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, dd = doublet of doublets, dt = doublet of triplets, ddd = doublet of doublet of doublets, t = triplet, m = multiplet, br = broad), coupling constants (Hz), and integration. Mass spectra were obtained through EI on a Micromass AutoSpec machine or through ESI on a Thermo Orbitrap XL. The accurate mass analyses run in EI mode were at a mass resolution of 10,000 and were calibrated using PFK (perfluorokerosene) as an internal standard. The accurate mass analyses run in EI mode were at a mass resolution of 30,000 using the calibration mixture supplied by Thermo. Uncorrected melting points were measured with a digital melting point apparatus (DigiMelt MPA 160).

4.2. Synthesis of β-Keto Esters 1

General Procedure A: The starting aryl carboxylic acid (1.0 equiv) was added as a 0.5 M solution in dry CH_2Cl_2 to a dry round-bottom flask charged with a stir bar under nitrogen atmosphere. The solution was then cooled to 0 ˚C. Catalytic DMF

(few drops to 1 mL) was then added. Oxalyl chloride (1.2 equiv) was added over 1 minute with stirring at 0 ˚C using a needle to vent into a balloon. After 15 minutes, the reaction was allowed to warm to room temperature with continued stirring. Upon completion, the reaction was concentrated under reduced pressure; the generated acid chloride was re-dissolved in dry THF to make a 1M solution, and the solution was added slowly to the prepared enolate at -78 ˚C. The enolate was prepared by first adding MeOAc (1.05 equiv) to a dry flask charged with a stir bar under nitrogen. The flask was cooled down to -78 ˚C to which LHMDS (1M in THF, 2.10 equiv) was added dropwise and stirred for 45 min at -78 ˚C. The reaction was monitored by TLC until complete conversion of the acid chloride was observed. Upon completion, the reaction was quenched with NH_4Cl (aq) at -78 ˚C, extracted with EtOAc three times, dried over Na_2SO_4, and filtered through a celite plug. The combined organic layers were concentrated under reduced pressure and purified by flash chromatography on silica gel using EtOAc/Hexanes as the mobile phase.

General Procedure B: A dry round-bottom flask was charged with a stir bar, and sodium hydride (2.8 equiv) was added under nitrogen atmosphere. Dimethyl carbonate (2.0 equiv) was then added with toluene, and the reaction was stirred and heated to reflux. A solution of the aryl ketone (1.0 equiv.) in toluene was added drop-wise over 30 min using a syringe pump for an overall reaction concentration of 1.0 M. The reaction was monitored by TLC until complete conversion of the aryl ketone was observed. After the evolution of hydrogen gas, the reaction was allowed to cool to room temperature, and acetic acid (6 mL) was added drop-wise to the reaction mixture. Ice-cold water was added to dissolve any solid that formed, and then the solution was diluted with EtOAc. The organic layer was extracted with EtOAc three times, dried over Na_2SO_4, and filtered through a celite plug. The combined organic layers were concentrated under reduced pressure and purified by flash chromatography on silica gel using EtOAc/Hexanes as the mobile phase.

*Methyl 3-oxo-3-(thiophen-3-yl)propanoate (**1a**)*

Prepared following general procedure A using 3-thiophenecarboxylic acid (99 % pure, 3g, 23.4 mmol), oxalyl chloride (98% pure, 2.41 mL, 28.1 mmol) and DMF (1 mL) in CH_2Cl_2 (36 mL) over 3 h to form the acid chloride. The enolate was formed using LHMDS (1 M in THF, 49 mL) and MeOAc (99% pure, 1.95 mL, 24.6 mmol) in THF (30 mL) over 45 min. The previously generated acid chloride was added to the enolate and stirred for 30 min. After work up and purification, (35% EtOAc/Hexanes, R_f = 0.60), compound **1a** was afforded as a light orange oil (3.19 g, 74% yield). Characterizations were consistent with previously reported literature.[24]

*Methyl 3-(benzo[b]thiophen-3-yl)-3-oxopropanoate (**1b**)*

Prepared following general procedure A using 1-benzothiophene-3-carboxylic acid (2.5 g, 14.0 mmol), oxalyl chloride (1.45 mL, 16.8 mmol) and DMF (1 mL) in CH_2Cl_2 (25 mL) over 3h to form the acid chloride. The enolate was formed using LHMDS (1 M in THF, 30.9 mL) and MeOAc (1.16 mL, 14.7 mmol) in THF (28 mL) over 45 min. The previously generated acid chloride was added to the enolate and stirred for 30 min. After work up and purification, (25% EtOAc/Hexanes, R_f = 0.48), compound **1b** was afforded as an orange oil (1.75 g, 53% yield). *Keto:Enol Ratio* (30:1) **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.73 (td, *J* = 1.1, 8.2 Hz, 1 H), 8.31 (s, 1 H), 7.82 (td, *J* = 0.8, 8.1 Hz, 1 H), 7.47 (ddd, *J* = 1.1, 7.2, 8.2 Hz, 1 H), 7.42 - 7.37 (m, 1 H), 4.00 (s, 2 H), 3.74 (s, 3 H) **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 186.7, 167.7, 139.5, 138.7, 136.1, 134.0, 125.9, 125.6, 125.4, 122.1, 52.4, 47.2 **IR**: 3096 (w), 2949 (w), 1736 (s), 1662 (s) cm^{-1}. **HRMS (EI)** *m/z*: $[M]^+$ Calcd. for $C_{12}H_{10}O_3S$ 234.0351; Found 234.0352.

*Methyl 3-(benzofuran-2-yl)-3-oxopropanoate (**1c**)*

Prepared following general procedure A using benzofuran-2-carboxylic acid (5 g, 30.8 mmol), oxalyl chloride (3.18 mL, 37.0 mmol) and DMF (1 mL) in CH2CL2 (50 mL) over 3 h to form the acid chloride. The enolate was formed using LHMDS (1 M in THF, 64.8 mL) and MeOAc (2.57 mL, 32.8 mmol) in THF (60 mL) over 45 min. The previously generated acid chloride was added to the enolate and stirred for 30 min. After work up and purification, (20% EtOAc/Hexanes, R_f = 0.50), compound **1c** was afforded as a colorless oil (4.00 g, 60% yield). *Keto:Enol Ratio* (4:1) Characterizations were consistent with previously reported literature.[14]

*Methyl 3-(naphthalen-2-yl)-3-oxopropanoate (**1d**)*

Prepared following general procedure B using sodium hydride (60 % dispersion in mineral oil, 1.98 g, 49.4 mmol), dimethyl carbonate (99% pure, 2.97 mL, 35.2 mmol) and methyl β-naphthyl ketone (3g; 17.6 mmol) in toluene (17.6 mL) over 30 min. After work up and purification, (20% EtOAc/Hexanes, R_f = 0.52), compound **1d** was afforded as a light orange oil (2.98 g, 74% yield). *Keto:Enol Ratio* (4:1) **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 12.64 (s, 0.23 H), 8.38 (d, *J* = 0.6 Hz, 1.01 H), 8.30 (d, *J* = 0.9 Hz, 0.23 H), 7.96 (dd, *J* = 1.8, 8.5 Hz, 1.06 H), 7.90 (d, *J* = 8.2 Hz, 1.07 H), 7.86 - 7.76 (m, 2.84 H), 7.72 - 7.69 (m, 0.24 H), 7.57 (ddd, *J* = 1.2, 6.8, 8.2 Hz, 1.05 H), 7.53 - 7.45 (m, 1.51 H), 5.78 (s, 0.23 H), 4.14 - 4.08 (m, 2.12 H), 3.79 (s, 0.73 H), 3.74 (s, 3.00 H) **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 192.1, 173.3, 171.0, 167.9, 135.5, 134.4, 133.0, 132.5, 132.1, 130.4, 130.2, 129.5, 128.8, 128.7, 128.5, 128.0, 127.6, 127.4, 127.4, 126.7, 126.5, 126.5, 123.5, 122.3, 87.3, 52.2, 51.2, 45.5 **IR**: 3059 (w), 2951 (w), 1738 (s), 1678 (s) cm^{-1}. **HRMS (EI)** *m/z*: $[M]^+$ Calcd. for $C_{14}H_{12}O_3$ 228.0786; Found 228.0783.

*Methyl 3-(3-methoxyphenyl)-3-oxopropanoate (**1e**)*

Prepared following general procedure A using 3-methoxy benzoic acid (1.00 g, 6.57 mmol), oxalyl chloride (98% pure, 1.06 g, 7.88 mmol) and DMF (4 drops) in CH_2Cl_2 (13 mL) over 3h to form the acid chloride. The enolate was formed using LHMDS (1 M in THF, 14 mL) and MeOAc (0.55 mL, 6.9 mmol) over 45 min. The previously generated acid chloride was added to the enolate and stirred for 30 min. After work up and purification, (25% EtOAc/Hexanes, R_f = 0.42), compound **1e** was afforded as a light yellow oil (0.99 g, 72% yield). *Keto:Enol Ratio* (6:1) Characterizations were consistent with previously reported literature.[25]

*Methyl 3-(3,4-dimethoxyphenyl)-3-oxopropanoate (**1f**)*

Prepared following general procedure A using 3,4-dimethoxy benzoic acid (10.5 g, 57.0 mmol) in CH_2Cl_2 (114 mL), oxalyl chloride (8.84 g, 68.4 mmol), and 4 drops of DMF stirred at room temp for 3 hours to generate the acid chloride. The second step used LHMDS (1M in THF, 120 mL) and MeOAc (99% pure, 4.48 g, 59.9 mmol) to generate the enolate, and the generated acid chloride in THF (57 mL) was added at -78 ˚C and stirred for 30 minutes. After work-up and purification, compound **4a** was afforded as a thick peach oil (12.32 g, 91% yield). Characterizations were consistent with previously reported literature.[26]

4.3. Syntheses of Alkylidene β-Ketoesters: Knoevenagel Condensations

General Procedure C: A dry round-bottom flask was charged with a stir bar, and a solution of the β-keto ester **1x** (1.0 equiv.) in benzene (0.1 M to 0.5 M). The aldehyde (1.3 equiv.), acetic acid (0.5 equiv.) and piperidine (0.1 equiv.) were then added. A Dean-Stark trap was filled with benzene and attached to the flask. A Liebig condenser was then attached to the top of the Dean-Stark trap, and the reaction was heated to reflux with stirring. The reaction was monitored by TLC until complete conversion of the β-keto ester was observed. Upon completion, the reaction was quenched with water and extracted three times with EtOAc. The combined organic layers were washed with HCl and $NaHCO_3$, dried over Na_2SO_4, filtered through celite, concentrated under reduced pressure, and purified by flash chromatography on silica gel using EtOAc/Hexanes as the mobile phase.

*Methyl (Z)-3-phenyl-2-(thiophene-3-carbonyl)acrylate (**3aa**)*

Prepared following general procedure C using **1a** (1 g, 5.4 mmol), benzaldehyde (0.72 mL, 7.1 mmol), glacial acetic acid (0.16 mL, 2.7 mmol) and piperidine (0.054 mL, 0.54 mmol) in benzene (0.1 M, 54 mL) over 24 h. After work up and purification, (25% EtOAc/Hexanes, R_f = 0.42), compound **3aa** was afforded as a powdery light yellow solid (1.23 g, 83% yield). [m.p. = 60-66 ˚C] **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.93 (dd, *J* = 1.3, 2.9 Hz, 1 H), 7.91 (s, 1 H), 7.53 (dd, *J* = 1.3, 5.1 Hz, 1 H), 7.37 - 7.31 (m, 2 H), 7.28 - 7.17 (m, 4 H), 3.74 (s, 3 H) **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 188.9, 165.3, 142.3, 141.4, 134.9, 132.6, 131.3, 130.4, 130.1, 128.7, 126.9, 126.8, 52.5 **IR**: 3096 (w), 2949 (w), 1712 (s), 1651 (s) cm^{-1}. **HRMS (EI)** *m/z*: $[M]^+$ Calcd. for $C_{15}H_{12}O_3S$ 272.0507; Found 272.0499.

*Methyl (Z)-3-phenyl-2-(thiophene-3-carbonyl)acrylate-d (**3aa-d**)*

Prepared following general procedure C using **1a** (0.72 g, 3.89 mmol), α-d-benzaldehyde (0.50 g, 4.67 mmol), glacial acetic acid (0.12 g, 2 mmol) and piperidine (34 mg, 0.4 mmol) in benzene (0.1 M, 39 mL) over 18 h. After work up and purification, (20% EtOAc/Hexanes, R_f = 0.38), compound **3aa-d** was afforded as yellow oil in a 93% pure mixture, which was carried forward without further purification (1.04 g). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.96 (dd, *J* = 1.2, 3.1 Hz, 1 H), 7.57 (dd, *J* = 1.4, 5.0 Hz, 1 H), 7.39 - 7.36 (m, 2 H), 7.30 - 7.23 (m, 4 H), 3.78 (s, 3 H) **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 189.0, 165.4, 141.5, 135.0, 132.6, 131.3, 130.5, 130.2, 129.5, 128.8, 127.0, 127.0, 52.6 **IR**: 3098 (w), 2949 (w), 1705 (s), 1647 (s) cm^{-1}. **HRMS (EI)** *m/z*: $[M]^+$ Calcd. for $C_{15}H_{11}DO_3S$ 273.0570; Found 273.0562.

*Methyl (Z)-3-(4-methoxyphenyl)-2-(thiophene-3-carbonyl)acrylate (**3ab**)*

Prepared following general procedure C using **1a** (500 mg, 2.7 mmol), 4-methoxybenzaldehyde (0.43 mL, 3.5 mmol), glacial acetic acid (0.078 mL, 1.4 mmol) and piperidine (0.027 mL, 0.27 mmol) in benzene (0.1 M, 27 mL) over 24 h. After work up and purification, (25% EtOAc/Hexanes, R_f = 0.38), compound **3ab** was afforded as a yellow solid (0.66 g, 80% yield). [m.p. = 97-99 ˚C] **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.98 (dd, *J* = 1.2, 3.1 Hz, 1 H), 7.87 (s, 1 H), 7.58 (dd, *J* = 1.2, 5.2 Hz, 1 H), 7.35 - 7.31 (m, 2 H), 7.30 (dd, *J* = 2.9, 5.0 Hz, 1 H), 6.79 - 6.75 (m, 2 H), 3.77 (s, 6 H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 189.6, 165.7, 161.4, 142.2, 141.7, 134.9, 132.3, 128.7, 127.0, 126.9, 125.3, 114.3, 55.3, 52.5. **IR**: 3098 (w), 2951 (w), 2839 (w), 1703 (s), 1651 (s) cm^{-1}. **HRMS (EI)** *m/z*: $[M]^+$ Calcd. for $C_{16}H_{14}O_4S$ 302.0613; Found 302.0606.

*Methyl (Z)-2-(thiophene-3-carbonyl)-3-(p-tolyl)acrylate (**3ac**)*

Prepared following general procedure C using **1a** (1.01 g, 5.43 mmol), 4-methylbenzaldehyde (0.83 mL, 7.09 mmol), glacial acetic acid (99.7% pure, 0.16 mL, 2.72 mmol) and piperidine (99 % pure, 0.10 mL, 1.09 mmol) in benzene (0.16 M, 34 mL) over 18 h. After work up and purification, (20% EtOAc/Hexanes, R_f = 0.43), compound **3ac** was afforded as an orange solid (1.44 g, 92% yield). [m.p. = 118-121 ˚C] **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.96 (dd, *J* = 1.2, 2.7 Hz, 1 H), 7.90 (s, 1 H), 7.57 (dd, *J* = 1.2, 5.2 Hz, 1 H), 7.29 (dd, *J* = 2.9, 5.0 Hz, 1 H), 7.28 - 7.25 (m, 3 H), 7.06 (d, *J* = 7.9 Hz, 2 H), 3.78 (s, 3 H), 2.29 (s, 3 H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 189.3, 165.6, 142.5, 141.7, 141.1, 134.9, 130.3, 130.3, 129.9, 129.6, 127.0, 126.9, 100.0, 52.6, 21.4. **IR**: 3102 (w), 2951 (w), 1717 (s), 1653 (s) cm^{-1}. **HRMS (EI)** *m/z*: $[M]^+$ Calcd. for $C_{16}H_{14}O_3S$ 286.0664; Found 286.0664.

*Methyl (Z)-3-(4-bromophenyl)-2-(thiophene-3-carbonyl)acrylate (**3ad**):*

Prepared following general procedure C using **1a** (459 mg, 2.49 mmol), 4-bromobenzaldehyde (653 mg, 3.53 mmol), glacial acetic acid (0.08 mL, 1.36 mmol) and piperidine (0.05 mL, 0.54 mmol) in benzene (0.1 M, 27 mL) over 24 h. After work up and purification, (25% EtOAc/Hexanes, R_f = 0.48), compound **3ad** was afforded as a yellow solid (713 mg, 81% yield). [m.p. = 77-79 ˚C] **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.95 (dd, *J* = 1.2, 3.1 Hz, 1 H), 7.85 (s, 1 H), 7.55 (dd, *J* = 1.2, 5.2 Hz, 1 H), 7.41 - 7.37 (m, 2 H), 7.31 (dd, *J* = 2.9, 5.0 Hz, 1 H), 7.25 - 7.21 (m, 2 H), 3.79 (s, 3 H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 188.6, 165.2, 141.4, 140.9, 135.1, 132.1, 131.6, 131.5, 127.2, 126.9, 125.1, 52.8. **IR**: 3102 (w), 2951 (w), 1715 (s), 1651 (s) cm^{-1}. **HRMS (EI)** *m/z*: $[M]^+$ Calcd. for $C_{15}H_{11}O_3SBr$ 349.9612; Found 349.9613.

*Methyl (Z)-2-(thiophene-3-carbonyl)-3-(4-(trifluoromethyl)phenyl)acrylate (**3ae**)*

Prepared following general procedure C using **1a** (580 mg, 3.15 mmol), 4-(trifluoromethyl)benzaldehyde (0.56 mL, 4.09 mmol), glacial acetic acid (0.09 mL, 1.57 mmol) and piperidine (0.06 mL, 0.63 mmol) in benzene (0.16 M, 27 mL) over 24 h. After work up and purification, (20% EtOAc/Hexanes, R_f = 0.36), compound **3ae** was afforded as a yellow solid (0.783 g, 73% yield). [m.p. = 60-63 ˚C] **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.96 (dd, *J* = 1.2, 3.1 Hz, 1 H), 7.93 (s, 1 H), 7.55 (dd, *J* = 1.2, 5.2 Hz, 1 H), 7.54 - 7.50 (m, 2 H), 7.50 - 7.46 (m, 2 H), 7.33 - 7.31 (m, 1 H), 3.81 (s, 3 H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 188.2, 165.0, 141.3, 140.4, 136.1, 135.1, 133.9, 130.1, 127.3, 126.8, 125.8, 125.7, 125.7, 100.0, 52.9. **IR**: 3102 (w), 2955 (w), 1717 (s), 1655 (s) cm^{-1}. **HRMS (EI)** *m/z*: $[M]^+$ Calcd. for $C_{16}H_{11}O_3SF_3$ 340.0381; Found 340.0376.

*Methyl (Z)-3-(2-methoxyphenyl)-2-(thiophene-3-carbonyl)acrylate (**3af**)*

Prepared following general procedure C using **1a** (500 mg, 2.71 mmol), 2-methoxybenzaldehyde (0.43 mL, 3.53 mmol), glacial acetic acid (0.08 mL, 1.36 mmol) and piperidine (0.03 mL, 0.271 mmol) in benzene (0.1M, 27 mL) overnight. After work up and purification, (25% EtOAc/Hexanes, R_f = 0.267), compound **3af** was afforded as an off-white solid (579 mg, 71% yield). [m.p. = 73-79 ˚C] **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.27 (s, 1 H), 7.92 (dd, *J* = 1.2, 2.7 Hz, 1 H), 7.52 (dd, *J* = 1.4, 5.0 Hz, 1 H), 7.28 - 7.22 (m, 4 H), 6.82 (d, *J* = 7.9 Hz, 1 H), 6.77 - 6.73 (m, 1 H), 3.81 - 3.79 (m, 3 H), 3.78 (s, 3 H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 188.9, 165.7, 157.9, 141.9, 138.4, 134.5, 131.9, 131.1, 130.4, 127.1, 126.5, 122.2, 120.5, 110.7, 55.3, 52.5. **IR**: 3103 (w), 2949 (w), 2839 (w), 1709 (s), 1651 (s) cm^{-1}. **HRMS (EI)** *m/z*: $[M]^+$ Calcd. for $C_{16}H_{14}O_4S$ 302.0613; Found 302.0609.

*Methyl (Z)-3-(3-methoxyphenyl)-2-(thiophene-3-carbonyl)acrylate (**3ag**)*

Prepared following general procedure C using **1a** (693 mg, 3.76 mmol), 3-methoxybenzaldehyde (0.60 mL, 4.89 mmol), glacial acetic acid (0.11 mL, 1.88 mmol) and piperidine (0.04 mL, 0.376 mmol) in benzene (0.1M, 38 mL) over 18 h. After work up and purification, (25% EtOAc/Hexanes, R_f = 0.340), compound **3ag** was afforded as a yellow oil (981 mg, 86% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.97 (dd, *J* = 3.05, 1.22 Hz, 1 H) 7.89 (s, 1 H) 7.56 (dd, *J* = 5.19, 1.22 Hz, 1 H) 7.28 - 7.31 (m, 1 H) 7.16 (t, *J* = 7.93 Hz, 1 H) 6.95 - 6.99 (m, 1 H) 6.87 - 6.89 (m, 1 H) 6.83 (ddd, *J* = 8.24, 2.59, 0.76 Hz, 1 H) 3.78 (s, 3 H) 3.64 (s, 3 H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 188.9, 165.3, 159.4, 142.3, 141.6, 134.9, 133.8, 131.5, 129.7, 127.0, 126.8, 122.9, 116.9, 114.4, 55.0, 52.6 **IR**: 3094 (w), 2949 (w), 2835 (w), 1717 (s), 1651 (s) cm^{-1}. **HRMS (EI)** *m/z*: $[M]^+$ Calcd. for $C_{16}H_{14}O_4S$ 302.0613; Found 302.0616.

*Methyl (Z)-3-(thiophen-2-yl)-2-(thiophene-3-carbonyl)acrylate (**3ah**)*

Prepared following general procedure C using **1a** (580 mg, 3.15 mmol), 2-thiophenealdehyde (0.38 mL, 4.09 mmol), glacial acetic acid (0.09 mL, 1.57 mmol) and piperidine (0.06 mL, 0.63 mmol) in benzene (0.16 M, 20 mL) over 18 h. After work up and purification, (20% EtOAc/Hexanes, R_f = 0.36), compound **3ah** was afforded as a thick yellow oil (750 mg, 86% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.05 (dd, *J* = 1.2, 2.7 Hz, 1 H), 8.01 (t, *J* = 0.8 Hz, 1 H), 7.62 (dd, *J* = 1.2, 5.2 Hz, 1 H), 7.39 (td, *J* = 0.9, 5.3 Hz, 1 H), 7.34 (dd, *J* = 2.9, 5.0 Hz, 1 H), 7.28 - 7.26 (m, 1 H), 6.99 (dd, *J* = 3.7, 5.2 Hz, 1 H), 3.77 (s, 3 H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 188.5, 165.4, 141.6, 136.0, 135.0, 134.6, 134.1, 131.7, 128.2, 127.8, 127.1, 127.0, 52.5. **IR**: 3098 (w), 2949 (w), 1701 (s), 1647 (s), 1607 (s) cm^{-1}. **HRMS (EI)** *m/z*: $[M]^+$ Calcd. for $C_{13}H_{10}O_3S_2$ 278.0071; Found 278.0064.

*Methyl (2Z,4E)-5-phenyl-2-(thiophene-3-carbonyl)penta-2,4-dienoate (**3ai**)*

Prepared following general procedure C using **1a** (502 mg, 2.72 mmol), cinnamaldehyde (0.44 mL, 3.52 mmol), glacial acetic acid (99.7 % pure, 0.08 mL, 1.36 mmol) and piperidine (99 % pure, 0.05 mL, 0.52 mmol) in benzene (0.16 M, 17 mL) over 18 h. After work up and purification, (20% EtOAc/Hexanes, R_f = 0.36), compound **3ai** was afforded as an orange oil (319 mg, 39% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.00 (dd, *J* = 1.3, 3.0 Hz, 1 H), 7.66 (dd, *J* = 0.6, 11.7 Hz, 1 H), 7.59 (dd, *J* = 1.2, 5.0 Hz, 1 H), 7.39 - 7.34 (m, 3 H), 7.34 - 7.29 (m, 3 H), 7.03 (d, *J* = 15.4 Hz, 1 H), 6.79 (dd, *J* = 11.8, 15.3 Hz, 1 H), 3.76 (s, 3 H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 187.7, 165.5, 143.9, 143.5, 142.5, 135.4, 134.9, 131.4, 129.7, 128.9, 128.8, 127.9, 127.7, 127.1, 126.8, 122.8, 52.3. **IR**: 3107 (w), 3030 (w), 2949 (w), 1711 (s), 1655 (s) cm^{-1}. **HRMS (EI)** *m/z*: $[M]^+$ Calcd. for $C_{17}H_{14}O_3S$ 298.0664; Found 298.0652.

*Methyl (Z)-3-(naphthalen-2-yl)-2-(thiophene-3-carbonyl)acrylate (**3aj**)*

Prepared following general procedure C using **1a** (693 mg, 3.76 mmol), 2-naphthaldehyde (763 mg, 4.89 mmol), glacial acetic acid (0.11 mL, 1.88 mmol) and piperidine (0.04 mL, 0.376 mmol) in benzene (0.1M, 37 mL) overnight. After work up and purification, (25% EtOAc/Hexanes, R_f = 0.340), compound **3aj** was afforded as a yellow solid (438 mg, 36% yield). [m.p. = 150-157 ˚C] **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.10 (s, 1 H) 7.99 (dd, *J* = 2.90, 1.37 Hz, 1 H) 7.92 (d, *J* = 0.61 Hz, 1 H) 7.72 - 7.79 (m, 2 H) 7.67 (d, *J* = 8.55 Hz, 1 H) 7.61 (dd, *J* = 4.88, 1.22 Hz, 1 H) 7.45 - 7.51 (m, 2 H) 7.41 (dd, *J* = 8.85, 1.83 Hz, 1 H) 7.28 (dd, *J* = 5.04, 2.90 Hz, 1 H) 3.82 (s, 3 H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 189.1, 165.5, 142.5, 141.7, 135.0, 133.9, 132.9, 131.8, 131.3, 130.3, 128.7, 128.6, 127.7, 127.6, 127.0, 126.9, 126.7, 125.9, 52.7. **IR**: 3103 (w), 3055 (w), 2949 (w), 1719 (s), 1653 (s) cm^{-1}. **HRMS (EI)** *m/z*: $[M]^+$ Calcd. for $C_{19}H_{14}O_3S$ 322.0664; Found 322.0659.

*Methyl (Z)-4-methyl-2-(thiophene-3-carbonyl)pent-2-enoate (**3ak**)*

Prepared following general procedure C using **1a** (750 mg, 4.07 mmol), isobutyraldehyde (0.48 mL, 5.29 mmol), glacial acetic acid (0.12 mL, 2.04 mmol) and piperidine (0.04 mL, 0.407 mmol) in benzene (0.1 M, 41 mL) over 18 h. After work up and purification, (20% EtOAc/Hexanes, R_f = 0.36), compound **3ak** (*Diastereomeric ratio = 6:1*) was afforded as a colorless oil (860 mg, 89% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.93 - 7.97 (m, 0.92) 7.88 - 7.91 (m, 0.15) 7.51 - 7.55 (m, 0.97) 7.46 (d, *J* = 1.22 Hz, 0.16) 7.30 - 7.35 (m, 1.12) 6.87 - 6.93 (m, 0.97) 6.45 (d, *J* = 10.38 Hz, 0.16) 3.72 - 3.75 (s, 0.59) 3.67 - 3.71 (s, 3.00) 3.12 - 3.23 (m, 0.18) 2.35 - 2.47 (m, 1.01) 1.07 - 1.13 (m, 1.12) 0.96 - 1.04 (m, 6.29). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 187.8, 186.5, 165.1, 156.4, 153.7, 153.6, 142.4, 141.2, 134.5, 133.3, 132.8, 131.7, 127.7, 126.9, 126.8, 126.5, 52.2, 51.9, 29.1, 28.9, 22.0, 21.8. **IR**: 3102 (w), 2961 (w), 2870 (w), 1717 (s), 1656 (s) cm^{-1}. **HRMS (EI)** *m/z*: $[M]^+$ Calcd. for $C_{12}H_{14}O_3S$ 238.0664; Found 238.0660.

*Methyl (Z)-2-(benzo[b]thiophene-3-carbonyl)-3-phenylacrylate (**3ba**)*

Prepared following general procedure C using **1b** (1.00 g, 4.27 mmol), benzaldehyde (0.57 mL, 5.55 mmol), glacial acetic acid (0.12 mL, 2.13 mmol) and piperidine (0.08 mL, 0.85 mmol) in benzene (0.25 M, 17 mL) over 24 h. After work up and purification, (20% EtOAc/Hexanes, R_f = 0.39), compound **3ba** was afforded as an orange solid (1.38 g, >99% yield). [m.p. = 100-102 ˚C] **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.92 (d, *J* = 8.2 Hz, 1 H), 8.16 (s, 1 H), 7.97 (s, 1 H), 7.86 (td, *J* = 0.9, 8.1 Hz, 1 H), 7.57 (ddd, *J* = 1.1, 7.1, 8.2 Hz, 1 H), 7.47 (dt, *J* = 1.1, 7.6 Hz, 1 H), 7.44 - 7.39 (m, 2 H), 7.29 - 7.20 (m, 3 H), 3.78 (s, 3 H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 189.5, 165.6, 142.4, 140.9, 140.3, 136.2, 134.7, 132.7, 131.5, 130.5, 130.2, 128.9, 126.2, 125.8, 125.6, 122.3, 52.7. **IR**: 3088 (w), 3059 (w), 2949 (w), 1715 (s), 1645 (s) cm^{-1}. **HRMS (EI)** *m/z*: $[M]^+$ Calcd. for $C_{19}H_{14}O_3S$ 322.0664; Found 322.0652.

*Methyl (Z)-2-(benzofuran-2-carbonyl)-3-phenylacrylate (**3ca**)*

Prepared following general procedure C using **1c** (1.0 g, 4.6 mmol), benzaldehyde (0.61 mL, 6.0 mmol), glacial acetic acid (0.13 mL, 2.3 mmol) and piperidine (0.04 mL, 0.45 mmol) in benzene (0.5 M, 2 mL) over 24 h. After work up and purification, (25% EtOAc/Hexanes, R_f = 0.37), compound **3ca** was afforded as a yellow oil (0.94 g, 67 % yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.02 (s, 1 H), 7.63 - 7.60 (m, 1 H), 7.58 - 7.54 (m, 1 H), 7.46 (ddd, *J* = 1.2, 7.1, 8.5 Hz, 1 H), 7.43 - 7.40 (m, 2 H), 7.39 (d, *J* = 0.9 Hz, 1 H), 7.29 - 7.22 (m, 4 H), 3.78 (s, 3 H) **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 184.4, 165.1, 156.3, 152.0, 144.2, 132.5, 130.7, 130.2, 129.8, 129.8, 128.9, 128.9, 128.8, 126.8, 124.0, 123.6, 116.4, 112.6, 52.7 **IR**: 3059 (w), 2951 (w), 1719 (s), 1657 (s) cm^{-1}. **HRMS (EI)** *m/z*: $[M]^+$ Calcd. for $C_{19}H_{14}O_4$ 306.0892; Found 306.0881.

*Methyl (Z)-2-(2-naphthoyl)-3-phenylacrylate (**3da**)*

Prepared following general procedure C using **1d** (1.00 g, 4.38 mmol), benzaldehyde (0.58 mL, 5.70 mmol), glacial acetic acid (0.13 mL, 2.19 mmol) and piperidine (0.09 mL, 0.88 mmol) in

benzene (0.26 M, 17 mL) over 18 h. After work up and purification, (20% EtOAc/Hexanes, R_f = 0.39), compound **3da** was afforded as an off-white solid (1.24 g, 89% yield). [m.p. = 108-112 ˚C] **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.42 (d, *J* = 1.2 Hz, 1 H), 8.10 (dd, *J* = 1.7, 8.7 Hz, 1 H), 7.92 - 7.84 (m, 3 H), 7.60 (ddd, *J* = 1.4, 6.9, 8.2 Hz, 1 H), 7.55 - 7.50 (m, 1 H), 7.41 - 7.38 (m, 2 H), 7.27 - 7.19 (m, 4 H), 3.76 (s, 3 H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 195.5, 165.6, 143.0, 136.1, 133.4, 132.7, 132.5, 131.9, 130.8, 130.5, 130.2, 129.8, 128.9, 128.9, 128.8, 127.8, 126.8, 124.0, 52.7. **IR**: 3057 (w), 2951 (w), 1717 (s), 1663 (s), 1624 (s) cm^{-1}. **HRMS (EI)** *m/z*: $[M]^+$ Calcd. for $C_{21}H_{16}O_3$ 316.1099; Found 316.1088.

*Methyl (Z)-2-(3-methoxybenzoyl)-3-phenylacrylate (**3ea**)*

Prepared following the general procedure using **1e** (1 g, 4.8 mmol), benzaldehyde (0.63 mL, 6.2 mmol), glacial acetic acid (0.14 mL, 2.4 mmol) and piperidine (0.047 mL, 0.48 mmol) in benzene (0.1 M, 48 mL) over 24 h. After work up and purification, (25% EtOAc/Hexanes, R_f = 0.41), compound **3ea** was afforded as a white solid (1.0 g, 72 % yield). [m.p. = 50-56 ˚C] **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.97 (s, 1 H), 7.54 (dd, *J* = 1.5, 2.4 Hz, 1 H), 7.48 (td, *J* = 1.3, 7.8 Hz, 1 H), 7.36 - 7.33 (m, 2 H), 7.33 - 7.30 (m, 1 H), 7.29 (d, *J* = 3.4 Hz, 1 H), 7.27 - 7.22 (m, 3 H), 7.10 (ddd, *J* = 0.9, 2.7, 8.2 Hz, 1 H), 3.83 (s, 3 H), 3.77 - 3.75 (m, 3 H) **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 195.3, 165.4, 160.0, 142.8, 137.2, 132.7, 130.8, 130.4, 130.2, 129.9, 128.8, 122.3, 120.8, 112.6, 55.4, 52.6 **IR**: 3055 (w), 3005 (w), 2951 (w), 2837 (w), 1721 (s), 1668 (s) cm^{-1}. **HRMS (EI)** *m/z*: $[M]^+$ Calcd. for $C_{18}H_{16}O_4$ 296.1049; Found 296.1045.

*Methyl (Z)-2-(3,4-dimethoxybenzoyl)-3-phenylacrylate (**3fa**)*

Prepared following general procedure C using **1f** (1.00 g, 4.197 mmol), benzaldehyde (0.55 mL, 5.46 mmol), glacial acetic acid (0.12 mL, 2.10 mmol) and piperidine (0.04 mL, 0.420 mmol) in benzene (42 mL) overnight. After work up and purification, (25% EtOAc/Hexanes, R_f = 0.27), compound **3fa** was afforded as a yellow solid (1.18 g, 86% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.95 (s, 1 H) 7.60 (d, *J* = 2.05 Hz, 1 H) 7.46 (dd, *J* = 8.36, 2.05 Hz, 1 H) 7.33 - 7.39 (m, 2 H) 7.19 - 7.29 (m, 3 H) 6.78 (d, *J* = 8.36 Hz, 1 H) 3.93 (s, 3 H) 3.90 (s, 3 H) 3.76 (s, 3 H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 194.1, 165.6, 154.1, 149.3, 142.4, 132.8, 130.7, 130.3, 130.2, 129.1, 128.8, 125.0, 110.2, 110.1, 56.0, 55.9, 52.6. **IR**: 3059 (w), 3001 (w), 2951 (w), 2841 (w), 1717 (s), 1655 (s) cm^{-1}. **HRMS (EI)** *m/z*: $[M]^+$ Calcd. for $C_{19}H_{18}O_5$ 326.1154; Found 326.1144.

4.4. Syntheses of Carbinols 4: Luche Reductions

General Procedure D: To a dry round bottom flask under nitrogen atmosphere charged with $CeCl_3$•$7H_2O$ (2.0 equiv.) and a magnetic stir bar was added alkylidene *β*-ketoester **3** (1.0 equiv.) in MeOH (0.1 M), which was stirred at 0 ˚C for 5 min. Then, $NaBH_4$ (4.0 equiv.) was gradually added to the resulting mixture at 0 ˚C and allowed to stir for 2 h. The reaction was then quenched with 0.1 M HCl and CH_2Cl_2 was added and stirred vigorously for 5 min; the mixture was extracted with CH_2Cl_2 three times. The combined organic layers were dried over Na_2SO_4, filtered through celite, concentrated under reduced pressure, and purified by flash chromatography on silica gel using Et_2O/Hexanes as the mobile phase.

General Procedure E: To a dry round bottom flask under nitrogen atmosphere charged with $CeCl_3$•$7H_2O$ (2.0 equiv.) and a magnetic stir bar was added alkylidene *β*-ketoester **3** (1.0 equiv.) in a 9:1 ratio of THF:MeOH (0.05 M), which was stirred at 0 ˚C for 5 min. Then, $NaBH_4$ (4.0 equiv.) was gradually added to the resulting mixture at 0 ˚C and allowed to stir for 2 h. The reaction was then quenched with 0.1 M HCl and CH_2Cl_2 was added and stirred vigorously for 5 min; the mixture was extracted with CH_2Cl_2 three times. The combined organic layers were dried over Na_2SO_4, filtered through celite, concentrated under reduced pressure, and purified by flash chromatography on silica gel using Et_2O/Hexanes as the mobile phase.

*Methyl (Z)-2-(hydroxy(thiophen-3-yl)methyl)-3-phenylacrylate (**4aa**)*

Prepared following general procedure D using **3aa** (250 mg, 0.918 mmol), $NaBH_4$ (156 mg, 4.13 mmol) and $CeCl_3$•$7H_2O$ (684 mg, 1.84 mmol) in MeOH (0.1 M, 9.2 mL) After work up and purification, (20% EtOAc/Hexanes, R_f = 0.46), compound **4aa** was afforded as a white oil (78.1 mg, 31% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.91 (s, 1 H), 7.40 - 7.33 (m, 6 H), 7.31 (dd, *J* = 3.1, 4.9 Hz, 1 H), 7.18 (td, *J* = 1.5, 2.8 Hz, 1 H), 7.12 - 7.10 (m, 1 H), 5.84 (d, *J* = 11.0 Hz, 1 H), 4.24 (d, *J* = 11.6 Hz, 1 H), 3.80 (s, 3 H) **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 168.1, 144.6, 141.2, 134.1, 132.2, 129.3, 129.2, 128.7, 126.2, 126.1, 120.7, 67.5, 52.2 **IR**: 3497 (br), 3102 (w), 2949 (w), 2845 (w), 1692 (s) cm^{-1}. **HRMS (EI)** *m/z*: $[M]^+$ Calcd. for $C_{15}H_{14}O_3S$ 274.0664; Found 274.0667.

*Methyl 3-oxo-2-(phenylmethyl-d)-3-(thiophen-3-yl)propanoate (**4aa-d**)*

Prepared following general procedure D using mixture **3aa-d** (1.0 g), $NaBH_4$ (0.56 g, 14.93 mmol) and $CeCl_3$•$7H_2O$ (2.78 g, 7.46 mmol) in MeOH (0.1 M, 37 mL) After work up and purification, (20% EtOAc/Hexanes, R_f = 0.38), compound **4aa-d** was afforded as a white oil (397 mg, 37% yield over 2 steps from **1a**). **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.40 - 7.30 (m, 6 H), 7.20 - 7.16 (m, 1 H), 7.13 - 7.09 (m, 1 H), 5.85 (dd, *J* = 0.7, 11.6 Hz, 1 H), 4.26 (dd, *J* = 0.9, 11.6 Hz, 1 H), 3.80 (d, *J* = 0.9 Hz, 3 H) **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 168.1, 144.6, 133.9, 132.1, 129.3, 129.2, 128.7, 126.2, 126.1, 120.7, 67.5, 52.2 **IR**: 3497 (br), 3103 (w), 2949 (w), 2846 (w), 1686 (s) cm^{-1}. **HRMS (EI)** *m/z*: $[M]^+$ Calcd. for $C_{15}H_{13}DO_3S$ 275.0726; Found 275.0724

*Methyl (Z)-2-(hydroxy(thiophen-3-yl)methyl)-3-(4-methoxyphenyl)acrylate (**4ab**)*

Prepared following general procedure D using **3ab** (830 mg, 2.75 mmol), $NaBH_4$ (410 mg, 10.85 mmol) and $CeCl_3$•$7H_2O$ (1.31 g, 3.53 mmol) in MeOH (0.1 M, 27 mL). After work up and purification, (20% EtOAc/Hexanes, R_f = 0.28), a mixture of compounds **4ab** and **3ab** (352 mg) was isolated and re-exposed to the reduction conditions using $CeCl_3$•$7H_2O$ (560 mg, 1.50 mmol), $NaBH_4$ (175 mg, 4.63 mmol) in MeOH (12 mL). After workup and purification, compound **4ab** was isolated as a colorless oil (202 mg, 24% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.85 (s, 1 H), 7.33 - 7.28 (m, 3 H), 7.19 - 7.17 (m, 1 H), 7.13 (td, *J* = 1.1, 4.6 Hz, 1 H), 6.92 - 6.87 (m, 2 H), 5.90 - 5.85 (m, 1 H), 4.31 (d, *J* = 11.3 Hz, 1 H), 3.82 (s, 3 H), 3.79 (s, 3 H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 168.3, 160.6, 144.7, 141.1, 131.2, 130.2, 126.5, 126.4, 126.1, 120.8, 114.2, 67.6, 55.3, 52.0. **IR**: 3491 (br), 3102 (w), 2951 (w), 2837 (w), 1686 (s) cm^{-1}. **HRMS (EI)** *m/z*: $[M]^+$ Calcd. for $C_{16}H_{16}O_4S$ 304.0769; Found 304.0759.

*Methyl (Z)-2-(hydroxy(thiophen-3-yl)methyl)-3-(p-tolyl)acrylate (**4ac**)*

Prepared following general procedure D using **3ac** (201 mg, 0.702 mmol), $NaBH_4$ (106 mg, 2.79 mmol) and anhydrous $CeCl_3$ (231 mg, 0.937 mmol) in MeOH (0.1 M, 7 mL). After work up and purification by prep-TLC, (20% EtOAc/Hexane, R_f = 0.43), compound **4ac** was afforded as a white oil as a 4:1 mixture with **3ac** (51 mg, 21% yield of **4ac**). **^{1}H NMR** (300 MHz, $CDCl_3$) δ =

7.97 (M, 0.28 H), 7.91 (s, 0.21 H), 7.88 (s, 0.96 H), 7.59 - 7.50 (m, 0.39 H), 7.37 (d, *J* = 8.1 Hz, 0.31 H), 7.33 - 7.28 (m, 1.43 H), 7.28 - 7.21 (m, 2.78 H), 7.21 - 7.14 (m, 3.36 H), 7.14 - 7.09 (m, 1.13 H), 7.06 (d, *J* = 8.4 Hz, 0.68 H), 5.87 (d, *J* = 11.6 Hz, 1.00 H), 4.30 (dd, *J* = 0.4, 11.6 Hz, 0.97 H), 3.80 - 3.76 (m, 3.76 H), 2.36 (s, 3.21 H), 2.29 (s, 0.79 H), 2.18 - 2.16 (m, 0.32 H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 168.2, 144.7, 142.4, 141.3, 141.1, 139.6, 134.9, 131.3, 131.1, 130.3, 129.8, 129.6, 129.6, 129.5, 129.4, 129.3, 127.0, 126.9, 126.3, 126.0, 120.7, 67.5, 52.5, 52.1, 21.4, 21.3 **IR**: 3491 (br), 3100 (w), 2949 (w), 2849 (w), 1688 (s) cm^{-1}. **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{16}H_{16}O_3S$ 288.0820; Found 288.0822.

*Methyl (Z)-3-(4-bromophenyl)-2-(hydroxy(thiophen-3-yl)methyl)acrylate (**4ad**)*

Prepared following general procedure D using **3ad** (250 mg, 0.712 mmol), $NaBH_4$ (108 mg, 2.85 mmol) and $CeCl_3$•$7H_2O$ (530 mg, 1.42 mmol) in MeOH (0.04 M, 18 mL). After work up and purification, (20% EtOAc/Hexanes, R_f = 0.38), compound **4ad** was afforded as a colorless oil (111 mg, 44% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.80 (s, 1 H), 7.53 - 7.49 (m, 2 H), 7.32 (dd, *J* = 3.1, 4.9 Hz, 1 H), 7.22 - 7.18 (m, 2 H), 7.16 (td, *J* = 1.5, 2.8 Hz, 1 H), 7.09 - 7.07 (m, 1 H), 5.76 (dd, *J* = 0.6, 11.6 Hz, 1 H), 4.19 (d, *J* = 11.6 Hz, 1 H), 3.80 (s, 3 H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 167.8, 144.2, 139.8, 132.9, 132.9, 131.9, 130.7, 126.3, 126.1, 123.7, 120.9, 67.4, 52.3 **IR**: 3493 (br), 3102 (w), 2949 (w), 2845 (w), 1697 (s) cm^{-1}. **HRMS (EI)** *m/z*: $[M]^+$ Calcd. for $C_{15}H_{13}O_3SBr$ 351.9769; Found 351.9767.

*Methyl (Z)-2-(hydroxy(thiophen-3-yl)methyl)-3-(4-(trifluoromethyl)phenyl)acrylate (**4ae**)*

Prepared following general procedure D using **3ae** (250 mg, 0.735 mmol), $NaBH_4$ (111 mg, 2.94 mmol) and $CeCl_3$•$7H_2O$ (547 mg, 1.47 mmol) in MeOH (0.1 M, 7.4 mL). After work up and purification, (40% Et_2O/Hexanes, R_f = 0.36), compound **4ae** was afforded as a colorless oil (69.6 mg, 28% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.88 (s, 1 H), 7.64 (d, *J* = 8.2 Hz, 2 H), 7.45 (dd, *J* = 0.6, 7.9 Hz, 2 H), 7.32 (dd, *J* = 3.1, 4.9 Hz, 1 H), 7.19 - 7.14 (m, 1 H), 7.10 - 7.06 (m, 1 H), 5.76 - 5.69 (m, 1 H), 4.16 (d, *J* = 11.6 Hz, 1 H), 3.82 (s, 3 H) **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 167.6, 144.0, 139.3, 134.2, 129.3, 126.4, 126.0, 125.7, 125.7, 125.6, 125.6, 120.9, 67.4, 52.4 **IR**: 3497 (br), 3107 (w), 2953 (w), 2851 (w), 1701 (s) cm^{-1}. **HRMS (EI)** *m/z*: $[M]^+$ Calcd. for $C_{16}H_{13}O_3SF_3$ 342.0583; Found 342.0536.

*Methyl (Z)-2-(hydroxy(thiophen-3-yl)methyl)-3-(2-methoxyphenyl)acrylate (**4af**)*

Prepared following general procedure D using **3af** (500 mg, 1.65 mmol), $NaBH_4$ (250 mg, 6.62 mmol) and $CeCl_3$•$7H_2O$ (1.23 g, 3.31 mmol) in MeOH (0.1 M, 17 mL). After work up and purification, (40% Et_2O/Hexanes, R_f = 0.36), compound **4af** was afforded as a white solid (380 mg, 75% yield). [m.p. = 98-99 ˚C] **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.02 (s, 1 H), 7.37 - 7.32 (m, 1 H), 7.29 (dd, *J* = 2.9, 5.0 Hz, 1 H), 7.24 - 7.20 (m, 1 H), 7.18 - 7.16 (m, 1 H), 7.09 (td, *J* = 1.1, 4.6 Hz, 1 H), 6.93 - 6.89 (m, 2 H), 5.80 - 5.71 (m, 1 H), 4.34 - 4.17 (m, 1 H), 3.86 (s, 3 H), 3.81 - 3.78 (s, 3 H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 168.2, 157.6, 145.0, 137.8, 131.8, 130.9, 129.8, 126.3, 125.9, 123.1, 120.5, 120.4, 110.6, 67.9, 55.4, 52.0. **IR**: 3505 (br), 3103 (w), 2949 (w), 2837 (w), 1690 (s) cm^{-1}. **HRMS (EI)** *m/z*: $[M]^+$ Calcd. for $C_{16}H_{16}O_4S$ 304.0769; Found 304.0763.

*Methyl (Z)-2-(hydroxy(thiophen-3-yl)methyl)-3-(3-methoxyphenyl)acrylate (**4ag**)*

Prepared following general procedure D using **3ag** (255 mg, 0.843 mmol), $NaBH_4$ (128 mg, 3.374 mmol) and $CeCl_3$•$7H_2O$ (629 mg, 1.687 mmol) in MeOH (0.1 M, 8.4 mL). After work up and purification, (50% Et_2O/Hexanes, R_f = 0.39), compound **4ag** was afforded as a colorless oil (79 mg, 31% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.88 (s, 1 H) 7.25 - 7.32 (m, 2 H) 7.16 - 7.20 (m, 1 H) 7.12 (d, *J* = 4.58 Hz, 1 H) 6.88 - 6.95 (m, 2 H) 6.86 (s, 1 H) 5.86 (d, *J* = 11.60 Hz, 1 H) 4.26 (d, *J* = 11.60 Hz, 1 H) 3.79 (s, 3 H) 3.71 (s, 3 H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 167.9, 159.5, 144.5, 141.05, 135.3, 132.3, 129.6, 126.2, 126.1, 121.4, 120.8, 115.1, 114.2, 67.5,55.0, 52.1. **IR**: 3495 (br), 3098 (w), 2949 (w), 2835 (w), 1692 (s) cm^{-1}. **HRMS (EI)** *m/z*: $[M]^+$ Calcd. for $C_{16}H_{16}O_4S$ 304.0769; Found 304.0771.

*Methyl (Z)-2-(hydroxy(thiophen-3-yl)methyl)-3-(thiophen-2-yl)acrylate (**4ah**)*

Prepared following general procedure D using **3ah** (744 mg, 2.67 mmol), $NaBH_4$ (414 mg, 10.94 mmol) and $CeCl_3$•$7H_2O$ (1.29 g, 3.48 mmol) in MeOH (0.1 M, 26 mL). The reaction mixture was warmed to room temperature and stirred overnight. After workup and purification (20% EtOAc/Hexanes, R_f = 0.36), a mixture of compounds **4ah** and **3ah** (323 mg) was isolated and re-exposed to the reduction conditions using $CeCl_3$•$7H_2O$ (555 mg, 1.50 mmol), $NaBH_4$ (175 mg, 4.63 mmol) in MeOH (11 mL). After workup and purification, compound **4ah** was isolated as a yellow solid (143 mg, 19% yield). [m.p. = 95-99 ˚C] **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.94 (d, *J* = 0.6 Hz, 1 H), 7.51 - 7.49 (m, 1 H), 7.29 (dd, *J* = 3.1, 4.9 Hz, 1 H), 7.27 (td, *J* = 1.1, 3.6 Hz, 1 H), 7.23 - 7.21 (m, 1 H), 7.14 - 7.12 (m, 1 H), 7.09 (dd, *J* = 3.7, 5.2 Hz, 1 H), 6.20 (dd, *J* = 0.6, 11.3 Hz, 1 H), 4.53 (d, *J* = 11.3 Hz, 1 H), 3.80 (s, 3 H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 168.0, 143.6, 136.6, 133.2, 132.9, 130.6, 128.6, 127.8, 126.2, 126.1, 121.0, 68.0, 52.2. **IR**: 3470 (br), 3102 (w), 2949 (w), 1682 (s) cm^{-1}. **HRMS (EI)** *m/z*: $[M]^+$ Calcd. for $C_{13}H_{12}O_3S_2$ 280.0228; Found 280.0225.

*Methyl (2Z,4E)-2-(hydroxy(thiophen-3-yl)methyl)-5-phenylpenta-2,4-dienoate (**4ai**)*

Prepared following general procedure D using **3ai** (308 mg, 1.03 mmol), $NaBH_4$ (156 mg, 4.13 mmol) and $CeCl_3$•$7H_2O$ (769 mg, 2.07 mmol) in MeOH (0.1 M, 10 mL). After work up and purification, (40% Et_2O/Hexanes, R_f = 0.35), compound **4ai** was afforded as an orange oil (204 mg, 66% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.54 (d, *J* = 11.6 Hz, 1H), 7.51 - 7.47 (m, 2H), 7.41 - 7.25 (m, 6H), 7.24 - 7.21 (m, 1H), 7.09 (dd, *J* = 1.1, 5.0 Hz, 1H), 7.01 (d, *J* = 15.3 Hz, 1H), 6.01 (d, *J* = 10.1 Hz, 1H), 4.38 (d, *J* = 10.1 Hz, 1H), 3.79 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 167.8, 144.5, 142.3, 140.3, 135.8. 130.1, 129.3, 128.8, 127.4, 126.0, 125.9, 122.1, 120.5, 67.5, 51.9. **IR**: 3449 (br), 3024 (w), 2949 (w), 1682 (s) cm^{-1}. **HRMS (EI)** *m/z*: $[M]^+$ Calcd. for $C_{17}H_{16}O_3S$ 300.0820; Found 300.0824.

*Methyl (Z)-2-(hydroxy(thiophen-3-yl)methyl)-3-(naphthalen-2-yl)acrylate (**4aj**)*

Prepared following general procedure E using **3aj** (157 mg, 0.487 mmol), $NaBH_4$ (73.7 mg, 1.95 mmol) and $CeCl_3$•$7H_2O$ (363 mg, 0.974 mmol) in 9:1 ratio of THF:MeOH (0.05 M, 4.9 mL). After work up and purification, (40% Et_2O /Hexanes, R_f = 0.32), compound **4aj** was afforded as a yellow oil (27 mg, 17% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.06 (s, 1 H) 7.82 - 7.86 (m, 3 H) 7.79 (d, *J* = 7.32 Hz, 1 H) 7.48 - 7.54 (m, 2 H) 7.45 (dd, *J* = 8.54, 1.22 Hz, 1 H) 7.33 (dd, *J* = 5.04, 2.90 Hz, 1 H) 7.23 (dd, *J* = 2.59, 1.37 Hz, 1 H) 7.14 (d, *J* = 5.19 Hz, 1 H) 5.97 (d, *J* = 11.29 Hz, 1 H) 4.31 (d, *J* = 11.60 Hz, 1 H) 3.83 (s, 3 H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 168.1, 144.6, 141.3, 133.3, 132.9,

132.4, 131.5, 129.1, 128.4, 128.4, 127.7, 127.1, 126.6, 126.3, 126.2, 120.9, 67.6, 52.2. **IR**: 3482 (br), 3051 (w), 2949 (w), 2849 (w), 1694 (s) cm^{-1}. **HRMS (EI)** *m/z*: $[M]^+$ Calcd. for $C_{19}H_{16}O_3S$ 324.0820; Found 324.0828.

*Methyl (Z)-2-(hydroxy(thiophen-3-yl)methyl)-4-methylpent-2-enoate (**4ak**)*

Prepared following general procedure D using (Z)-methyl 4-methyl-2-(thiophene-3-carbonyl)pent-2-enoate (860 mg, 3.61 mmol), $NaBH_4$ (546 mg, 14.4 mmol) and $CeCl_3$•$7H_2O$ (2.69 g, 7.22 mmol) in MeOH (0.1 M, 36 mL). After work up and purification, (20% Et_2O/Hexanes, R_f = 0.45), compounds **4ak** and **6ak** (compound ratio: 2:1) were afforded as a colorless oil (383 mg, 44% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.27 - 7.31 (m, 3.04) 7.23 (dt, *J*=1.83, 0.92 Hz, 0.93) 7.11 - 7.14 (m, 1.78) 7.02 - 7.06 (m, 2.82) 6.75 (d, *J*=10.38 Hz, 1.89) 5.70 (br. s., 1.86) 5.02 (d, *J*=5.49 Hz, 0.95) 4.26 - 4.34 (m, 1.42) 3.73 (s, 5.72) 3.63 (s, 2.87) 2.80 - 2.89 (m, 2.99) 1.71 - 1.78 (m, 1.00) 1.40 - 1.53 (m, 2.01) 1.11 (d, *J*=6.71 Hz, 6.01) 1.07 (d, *J*=6.41 Hz, 6.00) 0.89 (d, *J*=6.41 Hz, 3.02) 0.85 (d, *J*=6.41 Hz, 2.97). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 175.5, 167.9, 151.1, 144.8, 143.0, 129.7, 126.0, 125.9, 125.8, 125.4, 121.3, 120.3, 71.3, 67.3, 51.8, 51.6, 50.6, 36.2, 27.5, 26.2, 23.4, 22.2, 22.1, 21.4. **IR**: 3451 (br), 3107 (w), 2957 (m), 2868 (w), 1694 (s) cm^{-1}. **HRMS (EI)** *m/z*: $[M]^+$ Calcd. for $C_{12}H_{16}O_3S$ 240.0820; Found 240.0820.

*Methyl (Z)-2-(benzo[b]thiophen-3-yl(hydroxy)methyl)-3-phenylacrylate (**4ba**)*

Prepared following general procedure D using **3ba** (500 mg, 1.55 mmol), $NaBH_4$ (235 mg, 6.20 mmol) and $CeCl_3$•$7H_2O$ (1.16 g, 3.10 mmol) in MeOH (0.1 M, 16 mL). After work up and purification, (20% EtOAc/Hexanes, R_f = 0.41), compound **4ba** was afforded as a colorless oil (109 mg, 22% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.96 - 7.92 (m, 1 H), 7.90 - 7.84 (m, 1 H), 7.40 - 7.30 (m, 6 H), 7.30 - 7.27 (m, 2 H), 6.15 - 6.09 (m, 1 H), 4.30 (d, *J* = 11.6 Hz, 1 H), 3.85 (s, 3 H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 168.3, 141.7, 140.8, 137.8, 137.3, 134.0, 131.3, 129.4, 129.3, 128.7, 124.5, 124.1, 123.3, 123.3, 122.7, 66.9, 52.3. **IR**: 3501 (br), 3061 (w), 2951 (w), 2847 (w), 1694 (s) cm^{-1}. **HRMS (EI)** *m/z*: $[M]^+$ Calcd. for $C_{19}H_{16}O_3S$ 324.0820; Found 324.0824.

*Methyl (Z)-2-(benzofuran-2-yl(hydroxy)methyl)-3-phenylacrylate (**4ca**)*

Prepared following general procedure D using **3ca** (500 mg, 1.63 mmol), $NaBH_4$ (247 mg, 6.53 mmol) and $CeCl_3$•$7H_2O$ (1.22 g, 3.26 mmol) in MeOH (0.1 M, 16 mL). After work up and purification, (20% EtOAc/Hexanes, R_f = 0.32), compound **4ca** was afforded as a pale yellow solid (307 mg, 61% yield). [m.p. = 99-100 ˚C] **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.01 (s, 1 H) 7.54 - 7.57 (m, 1 H) 7.47 - 7.51 (m, 1 H) 7.37 - 7.45 (m, 5 H) 7.20 - 7.30 (m, 3 H) 6.73 (s, 1 H) 5.95 (d, *J* = 11.29 Hz, 1 H) 4.48 (dd, *J*=11.44, 1.07 Hz, 1 H) 3.84 (s, 3 H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 167.9, 157.9, 154.9, 143.1, 133.7, 129.5, 129.5, 129.3, 128.6, 128.3, 124.0, 122.8, 121.0, 111.3, 103.4, 65.6, 52.3 **IR**: 3489 (br), 3063 (w), 2951 (w), 1694 (s) cm^{-1}. **HRMS (EI)** *m/z*: $[M]^+$ Calcd. for $C_{19}H_{16}O_4$ 308.1049; Found 308.1048.

*Methyl (Z)-2-(hydroxy(naphthalen-2-yl)methyl)-3-phenylacrylate (**4da**)*

Prepared following general procedure D using **3da** (259 mg, 0.819 mmol), $NaBH_4$ (546 mg, 14.4 mmol) and $CeCl_3$•$7H_2O$ (2.69 g, 7.22 mmol) in MeOH (0.1 M, 8.2 mL). After work up and purification, (40% Et_2O/Hexanes, R_f = 0.444), compound **4da** was afforded as a white oil (99.6 mg, 38% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.08 (s, 1 H), 7.92 - 7.83 (m, 4 H), 7.62 (dd, *J* = 1.7, 8.7 Hz, 1 H), 7.53 - 7.48 (m, 2 H), 7.47 - 7.43 (m, 2 H), 7.42 - 7.37 (m, 3 H), 6.09 (d, *J* = 11.3 Hz, 1 H), 4.30 (d, *J* = 11.6 Hz, 1 H), 3.77 (s, 3 H) **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 168.0, 142.0, 140.1, 134.1, 133.2, 132.7, 132.1, 129.3, 129.2, 128.7, 128.2, 128.1, 127.6, 126.1, 125.8, 124.0, 123.9, 69.9, 52.1. **IR**: 3501 (br), 3055 (w), 2949 (w), 1692 (s) cm^{-1}. **HRMS (EI)** *m/z*: $[M]^+$ Calcd. for $C_{21}H_{18}O_3$ 318.1256; Found 328.1258.

*Methyl (Z)-2-(hydroxy(3-methoxyphenyl)methyl)-3-phenylacrylate (**4ea**)*

Prepared following general procedure D using **3ea** (514 mg, 1.74 mmol), $NaBH_4$ (263 mg, 6.94 mmol) and $CeCl_3$•$7H_2O$ (1.29 g, 3.47 mmol) in MeOH (0.1 M, 17 mL). After work up and purification, (30% Et_2O/Hexanes, R_f = 0.208), compound **4ea** was afforded as an off-white oil (314 mg, 61% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.96 (s, 1 H) 7.34 - 7.39 (m, 5 H) 7.24 - 7.28 (m, 1 H) 7.03 (d, *J*=1.22 Hz, 1 H) 6.95 - 6.98 (m, 1 H) 6.82 (dd, *J*=8.24, 2.44 Hz, 1 H) 5.84 (d, *J*=9.16 Hz, 1 H) 4.07 (d, *J*=10.68 Hz, 1 H) 3.80 (s, 3 H) 3.76 (s, 3 H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 168.0, 159.8, 144.5, 141.9, 134.2, 132.2, 129.4, 129.3, 129.1, 128.7, 117.7, 112.7, 111.3, 69.6, 55.2, 52.1. **IR**: 3507 (br), 3024 (w), 2951 (w), 2835 (w), 1694 (s) cm^{-1}. **HRMS (EI)** *m/z*: $[M]^+$ Calcd. for $C_{18}H_{18}O_4$ 298.1205; Found 298.1205.

*Methyl (Z)-2-((3,4-dimethoxyphenyl)(hydroxy)methyl)-3-phenylacrylate (**4fa**)*

Prepared following general procedure D using **3fa** (262 mg, 0.803 mmol), $NaBH_4$ (121.5 mg, 3.21 mmol) and $CeCl_3$•$7H_2O$ (598 mg, 1.61 mmol) in MeOH (0.1 M, 8.0 mL). After work up and purification, (50% Et_2O/Hexanes, R_f = 0.174), compound **4fa** was afforded as a white oil (101 mg, 39% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.95 (s, 1 H), 7.40 - 7.33 (m, 5 H), 7.07 (d, *J* = 1.2 Hz, 1 H), 6.87 - 6.84 (m, 1 H), 6.84 - 6.81 (m, 1 H), 5.82 (dd, *J* = 0.6, 11.6 Hz, 1 H), 4.11 (d, *J* = 11.6 Hz, 1 H), 3.88 - 3.86 (m, 6 H), 3.78 (s, 3 H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 168.2, 149.1, 148.2, 141.7, 135.3, 134.2, 132.2, 129.3, 129.1, 128.8, 128.7, 117.3, 110.8, 109.1, 69.6, 55.8, 55.8, 52.1. **IR**: 3491 (br), 3057 (w), 2953 (w), 2835 (w), 1694 (s) cm^{-1}. **HRMS (EI)** *m/z*: $[M]^+$ Calcd. for $C_{19}H_{20}O_5$ 328.1311; Found 328.1317.

4.5. Reaction Optimizations

4.5.1. Procedure for Catalyst Screening

To a round bottom flask charged with the appropriate Lewis acid catalyst (10 mol %), and a magnetic stir bar in CH_2Cl_2 (1 mL) at the appropriate temperature under nitrogen atmosphere was added a solution of allylic alcohol **4aa** (1.0 equiv.) in CH_2Cl_2 (0.1 M). The reaction was monitored via TLC and allowed to cool to room temperature once the reaction reached completion, concentrated under reduced pressure and purified by flash chromatography on silica gel using EtOAc/Hexanes as the mobile phase.

4.5.2. Procedure for Optimization of Catalyst Loading

To a round bottom flask charged with x mol % $Ca(NTf_2)_2$, x mol % *n*-Bu_4NPF_6, and a magnetic stir bar in CH_2Cl_2 (1 mL) at 40 ˚C under nitrogen atmosphere was added a solution of allylic alcohol **4aa** (1.0 equiv.) in CH_2Cl_2 (0.1 M). The reaction was monitored via TLC and allowed to cool to room temperature once the reaction reached completion, concentrated under reduced pressure and purified by flash chromatography on silica gel using EtOAc/Hexanes as the mobile phase.

4.5.3. Procedure for Solvent Screening

To a round bottom flask charged with 10 mol % $Ca(NTf_2)_2$, 10 mol % *n*-Bu_4NPF_6, and a magnetic stir bar in the appropriate solvent (1 mL) at appropriate temperature under nitrogen atmosphere was added a solution of allylic alcohol **4aa** (1.0 equiv.) in appropriate solvent (0.1 M). After 1 h 45 min, the reaction mixture was allowed to cool to room temperature, concentrated under reduced pressure and purified by flash chromatography on silica gel using EtOAc/Hexanes as the mobile phase.

4.6. Dehydrative Nazarov-type Cyclizations

General Procedure F: To a round bottom flask charged with 10 mol % $Ca(NTf_2)_2$, 10 mol % *n*-Bu_4NPF_6, and a magnetic stir bar in benzene (1 mL) at 40 ˚C under nitrogen atmosphere was added a solution of allylic alcohol **4** (1.0 equiv.) in benzene (0.05 M). After 1.75 h, the reaction mixture was allowed to cool to room temperature, concentrated under reduced pressure and purified by flash chromatography on silica gel using EtOAc/Hexanes as the mobile phase.

*Methyl 6-phenyl-4H-cyclopenta[b]thiophene-5-carboxylate (**5aa-I**)*

The general procedure F was followed using allylic alcohol **4aa** (72 mg, 0.263 mmol) in benzene (5.3 mL), $Ca(NTf_2)_2$ (15.8 mg, 0.026 mmol), *n*-Bu_4NPF_6 (10.2 mg, 0.026 mmol). After work up and purification, (20% EtOAc/Hexanes, R_f = 0.44), compound **5aa-I** was afforded as a white solid (47.1 mg, 70% yield). [m.p. = 82-85 ˚C] **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.65 - 7.69 (m, 2 H), 7.41 - 7.49 (m, 5 H), 7.14 (d, *J* = 4.88 Hz, 1 H), 3.76 (s, 2 H), 3.72 (s, 3 H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 164.9, 150.2, 148.8, 147.2, 134.1, 130.3, 129.3, 128.9, 128.7, 128.0, 122.6, 51.1, 37.1. **IR**: 3028 (w), 2947 (w), 2841 (w), 1701 (s) cm^{-1}. **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{15}H_{12}O_2S$ 256.0558; Found 256.0561.

*Methyl 6-phenyl-6H-cyclopenta[b]thiophene-5-carboxylate-6-d (**5aa-II-d**)*

The general procedure F was followed using allylic alcohol **4aa-d** (60 mg, 0.233 mmol) in benzene (4.6 mL), $Ca(NTf_2)_2$ (13.5 mg, 0.023 mmol), *n*-Bu_4NPF_6 (9.0 mg, 0.023 mmol). After work up and purification, (20% EtOAc/Hexanes, R_f = 0.44), compound **5aa-II-d** was afforded as a white solid (41.9 mg, 70% yield). [m.p. = 94-96 ˚C] **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.74 (s, 1 H), 7.37 (d, *J* = 5.2 Hz, 1 H), 7.31 - 7.21 (m, 3 H), 7.13 - 7.08 (m, 3 H), 3.70 (s, 3 H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 163.9, 154.7, 145.9, 143.8, 137.9, 137.4, 129.7, 128.6, 127.7, 127.1, 119.9, 51.3. **IR**: 3080 (w), 3024 (w), 2947 (w), 2839 (w), 1703 (s) cm^{-1}. **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{15}H_{11}DO_2S$ 257.0621; Found 257.0630.

*Methyl 6-(4-methoxyphenyl)-4H-cyclopenta[b]thiophene-5-carboxylate (**5ab-I**)*

The general procedure F was followed using allylic alcohol **4ab** (59 mg, 0.194 mmol) in benzene (3.9 mL), $Ca(NTf_2)_2$ (11.6 mg, 0.019 mmol), *n*-Bu_4NPF_6 (7.5 mg, 0.019 mmol). After work up and purification, (20% EtOAc/Hexanes, R_f = 0.33), compound **5ab-I** was afforded as an off-white solid (45.4 mg, 82% yield). [m.p. = 117-120 ˚C] **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.65 - 7.69 (m, 2 H), 7.45 (d, *J* = 4.88 Hz, 1 H), 7.13 (d, *J* = 4.88 Hz, 1 H), 6.97 - 7.01 (m, 2 H), 3.87 (s, 3 H), 3.72 - 3.75 (m, 5 H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 165.1, 160.1, 150.0, 148.7, 147.3, 130.4, 130.2, 128.1, 126.3, 122.6, 113.4, 55.2, 51.1, 37.1. **IR**: 3105 (w), 3007 (w), 2947 (w), 2839 (w), 1701 (s) cm^{-1}. **HRMS (EI)** m/z: $[M]^+$ Calcd. for $C_{16}H_{14}O_3S$ 286.0664; Found 286.0677.

*Methyl 6-(p-tolyl)-6H-cyclopenta[b]thiophene-5-carboxylate (**5ac-I**)*

The general procedure was followed using a 4:1 mixture of allylic alcohol **4ac** and compound **3ac** (51 mg, 0.18 mmol) in benzene (3.6 mL), $Ca(NTf_2)_2$ (10.7 mg, 0.018 mmol), *n*-Bu_4NPF_6 (6.9 mg, 0.018 mmol). After work up and purification, (20% EtOAc/Hexanes, R_f = 0.56), compound **5ac-I** was afforded as a yellow oil (25.1 mg, 66% yield). (*Isomeric Ratio = 6.5:1)* Yield calculated based on starting material NMR. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.70 (d, *J* = 1.9 Hz, 0.14 H), 7.61 - 7.55 (m, 1.95 H), 7.47 - 7.43 (m, 0.96 H), 7.36 - 7.33 (m, 0.16 H), 7.30 - 7.24 (m, 2.21 H), 7.13 (d, *J* = 4.8 Hz, 1.01 H), 7.10 - 7.04 (m, 0.49 H), 7.00 (s, 0.33 H), 4.88 - 4.84 (m, 0.15 H), 3.76 - 3.73 (m, 2.00 H), 3.73 - 3.71 (m, 3.04 H), 3.70 - 3.69 (m, 0.41 H), 2.42 (s, 3.05 H), 2.30 (s, 0.46 H) **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 165.1, 150.3, 148.7, 147.3, 139.0, 131.1, 130.2, 129.3, 128.8, 128.7, 127.5, 122.6, 51.1, 37.1, 21.4 **IR**: 3076 (w), 3022 (w), 2947 (w), 1703 (s) cm^{-1}. **HRMS (EI)** m/z: $[M]^+$ Calcd. for $C_{16}H_{14}O_2S$ 270.0715; Found 270.0715.

*Methyl 6-(4-bromophenyl)-4H-cyclopenta[b]thiophene-5-carboxylate (**5ad-I**)*

The general procedure F was followed using allylic alcohol **4ad** (37 mg, 0.105 mmol) in benzene (2.1 mL), $Ca(NTf_2)_2$ (6.3 mg, 0.010 mmol), *n*-Bu_4NPF_6 (4.1 mg, 0.010 mmol). After work up and purification, (20% EtOAc/Hexanes, R_f = 0.57), compound **5ad-I** was afforded as a white solid (24.2 mg, 69% yield). [m.p. = 127-128 ˚C] **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.57 - 7.61 (m, 2 H), 7.51 - 7.55 (m, 2 H), 7.46 (d, *J* = 4.88 Hz, 1 H), 7.14 (d, *J* = 4.88 Hz, 1 H), 3.74 (s, 2 H), 3.72 (s, 3 H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 164.8, 149.1, 148.9, 146.7, 133.0, 131.3, 130.5, 130.4, 129.8, 123.2, 122.7. **IR**: 3103 (w), 2947 (w), 2841 (w), 1697 (s) cm^{-1}. **HRMS (EI)** m/z: $[M]^+$ Calcd. for $C_{15}H_{11}BrO_2S$ 333.9663; Found 333.9657.

*Methyl 6-(4-(trifluoromethyl)phenyl)-4H-cyclopenta[b]thiophene-5-carboxylate (**5ae-I**)*

The general procedure F was followed using allylic alcohol **4ae** (34 mg, 0.099 mmol) in benzene (2.0 mL), $Ca(NTf_2)_2$ (6.0 mg, 0.010 mmol), *n*-Bu_4NPF_6 (3.8 mg, 0.010 mmol). After work up and purification, (20% EtOAc/Hexanes, R_f = 0.55), compound **5ae-I** was afforded as a white solid (21.6 mg, 67% yield). [m.p. = 133-134 ˚C] **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.70 - 7.78 (m, 4 H), 7.48 (d, *J* = 4.58 Hz, 1 H), 7.16 (d, *J* = 4.58 Hz, 1 H), 3.78 (s, 2 H), 3.72 (s, 3 H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 164.7, 149.1, 148.8, 146.6, 137.9, 130.9, 130.6, 129.1, 125.1, 125.0, 125.0, 122.8, 51.3, 37.2. **IR**: 3107 (w), 2951 (w), 1701 (s) cm^{-1}. **HRMS (EI)** m/z: $[M]^+$ Calcd. for $C_{16}H_{11}F_3O_2S$ 324.0432; Found 324.0417.

*Methyl 6-(2-methoxyphenyl)-6H-cyclopenta[b]thiophene-5-carboxylate (**5af-II**)*

The general procedure F was followed using allylic alcohol **4af** (54 mg, 0.18 mmol) in benzene (3.6 mL), $Ca(NTf_2)_2$ (10.7 mg, 0.018 mmol), *n*-Bu_4NPF_6 (6.9 mg, 0.018 mmol). After work up and purification, (20% EtOAc/Hexanes, R_f = 0.46), compound **5af-II** was afforded as a white oil (38.0 mg, 75% yield). (Isomeric Ratio = 8:1) **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.83 (dd, J = 0.7, 2.0 Hz, 1.00 H), 7.45 - 7.35 (m, 0.37 H), 7.27 - 7.17 (m, 2.33 H), 7.12 - 7.08 (m, 0.14 H), 7.02 (dd, J = 0.6, 5.0 Hz, 1.25 H), 6.95 (d, J = 8.2 Hz, 1.09 H), 6.80 - 6.74 (m, 2.05 H), 5.34 (d, J = 2.1 Hz, 0.97 H), 3.99 (s, 3.22 H), 3.80 (s, 0.40 H), 3.74 (d, J = 0.6 Hz, 3.49 H), 3.67 (d, J = 0.7 Hz, 0.44 H) **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 164.3, 157.1, 154.3, 144.8, 141.6, 138.9, 128.8, 128.1, 126.8, 126.5, 120.6, 119.7, 110.6, 55.4, 51.4, 47.7. **IR**:

3080 (w), 2947 (w), 2835 (w), 1703 (s) cm^{-1}. **HRMS (EI)** m/z: $[M]^+$ Calcd. for $C_{16}H_{14}O_3S$ 286.0664; Found 286.0663.

*Methyl 5-methoxy-1-(thiophen-3-yl)-1H-indene-2-carboxylate (**5ag-IV**)*

The general procedure F was followed using allylic alcohol **4ag** (78 mg, 0.256 mmol) in benzene (5.1 mL), $Ca(NTf_2)_2$ (15.4 mg, 0.026 mmol), *n*-Bu_4NPF_6 (9.9 mg, 0.026 mmol). After work up and purification, (20% EtOAc/Hexanes, R_f = 0.545), compound **5ag-IV** was afforded as an off-white solid (58.2 mg, 79% yield). [m.p. = 101-119 ˚C] **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.69 (d, *J* = 1.8 Hz, 1 H), 7.19 (d, *J* = 8.2 Hz, 1 H), 7.17 (dd, *J* = 2.9, 5.0 Hz, 1 H), 7.13 (dd, *J* = 1.1, 2.9 Hz, 1 H), 7.05 (d, *J* = 2.4 Hz, 1 H), 6.87 (dd, *J* = 2.4, 8.2 Hz, 1 H), 6.69 (dd, *J* = 1.4, 5.0 Hz, 1 H), 4.98 (d, *J* = 1.8 Hz, 1 H), 3.84 (s, 3 H), 3.74 (s, 3 H) **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 164.6, 159.3, 142.2, 141.8, 141.5, 140.9, 138.1, 126.7, 125.3, 124.9, 121.8, 114.6, 108.3, 55.4, 51.5, 49.9. **IR**: 3103 (w), 2949 (w), 2835 (w), 1705 (s) cm^{-1}. **HRMS (EI)** m/z: $[M]^+$ Calcd. for $C_{16}H_{14}O_3S$ 286.0664; Found 286.0662.

*Methyl 6-(thiophen-2-yl)-4H-cyclopenta[b]thiophene-5-carboxylate (**5ah-I**)*

The general procedure F was followed using allylic alcohol **4ah** (71 mg, 0.255 mmol) in benzene (5.1 mL), $Ca(NTf_2)_2$ (15.3 mg, 0.026 mmol), *n*-Bu_4NPF_6 (9.9 mg, 0.026 mmol). After work up and purification, (20% EtOAc/Hexanes, R_f = 0.692), compound **5ah-I** was afforded as a reddish-brown oil (44.2 mg, 66% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.99 (d, *J* = 3.66 Hz, 1 H) 7.51 (d, *J* = 5.19 Hz, 1 H), 7.47 (dd, *J* = 4.88, 0.61 Hz, 1 H), 7.15 - 7.19 (m, 1 H), 7.11 (d, *J* = 4.88 Hz, 1 H), 3.82 (d, *J* = 0.61 Hz, 3 H), 3.75 (s, 2 H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 164.9, 148.7, 146.0, 142.1, 134.9, 131.0, 130.4, 128.6, 127.3, 126.9, 122.3, 51.3, 37.3. **IR**: 3099 (w), 2945 (w), 1692 (s) cm^{-1}. **HRMS (EI)** m/z: $[M]^+$ Calcd. for $C_{13}H_{10}O_2S_2$ 262.0122; Found 262.0127.

*Methyl (E)-6-styryl-4H-cyclopenta[b]thiophene-5-carboxylate (**5ai-I**)*

The general procedure F was followed using allylic alcohol **4ai** (45.8 mg, 0.153 mmol) in benzene (3.1 mL), $Ca(NTf_2)_2$ (9.2 mg, 0.015 mmol), *n*-Bu_4NPF_6 (5.9 mg, 0.015 mmol). After work up and purification, (15% EtOAc/Hexanes, R_f = 0.411), compound **5ai-I** was afforded as a yellow solid (9.4 mg, 22% yield). [m.p. = 96-101 ˚C] **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.29 (d, *J* = 16.48 Hz, 1 H) 7.65 (d, *J* = 7.63 Hz, 2 H) 7.50 (d, *J* = 4.88 Hz, 1 H) 7.37 - 7.42 (m, 3 H) 7.33 - 7.35 (m, 1 H) 7.13 (d, J = 4.88 Hz, 1 H) 3.86 (s, 3 H) 3.68 (s, 2 H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 165.5, 149.2, 147.4, 142.2, 136.6, 136.5, 130.2, 130.1, 128.9, 128.8, 127.4, 122.1, 121.3, 51.3, 36.5. **IR**: 3059 (w), 3024 (w), 2949 (w), 2845 (w), 1690 (s) cm^{-1}. **HRMS (EI)** m/z: $[M]^+$ Calcd. for $C_{17}H_{14}O_2S$ 282.0715; Found 282.0718.

*Methyl 6-(naphthalen-2-yl)-6H-cyclopenta[b]thiophene-5-carboxylate (**5aj**)*

The general procedure F was followed using allylic alcohol **4aj** (27.4 mg, 0.085 mmol) in benzene (1.7 mL), $Ca(NTf_2)_2$ (5.1 mg, 0.008 mmol), *n*-Bu_4NPF_6 (3.3 mg, 0.008 mmol). After work up and purification, (20% EtOAc/Hexanes, R_f = 0.48), a four compound isomeric mixture was afforded as a reddish-brown oil (18.4 mg, 71% yield). (Isomeric Ratio = 20 : 7.0 : 3.5: 1; Alkene ratio = 2.0:1 trisubstituted (**5aj-II**/**5aj-IV**) to tetrasubstituted (**5aj-I**/**5aj-III**)) **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.17 (s, .36 H), 7.94 - 7.89 (m, 1.21 H), 7.87 (dd, *J* = 4.9, 8.2 Hz, 2.56 H), 7.80 (d, *J* = 1.8 Hz, 1.02 H), 7.75 (dd, *J* = 1.8, 8.5 Hz, 0.49 H), 7.71 (d, *J* = 8.2 Hz, 1.13 H), 7.66 (d, *J* = 8.2 Hz, 1.12 H), 7.56 - 7.50 (m, 1.07 H), 7.48 (d, *J* = 4.9 Hz, 0.40 H), 7.43 (ddd, *J* = 1.2, 6.7, 7.9 Hz, 1.32 H), 7.36 (ddd, *J* = 1.2, 6.7, 8.2 Hz, 1.20 H), 7.33 - 7.31 (m, 0.21 H), 7.18 (dd, *J* = 1.4, 2.9 Hz, 1.01 H), 7.13 (dd, *J* = 3.1, 4.9 Hz, 1.01 H), 7.01 (dd, *J* = 1.8, 8.5 Hz, 0.06 H), 6.90 - 6.89 (m, 0.04 H), 6.87 (dd, *J* = 1.4, 5.0 Hz, 0.04 H), 6.64 (dd, *J* = 1.4, 5.0 Hz, 0.98 H), 5.39 (d, *J* = 1.8 Hz, 1.00 H), 5.06 - 5.04 (m, 0.04 H), 3.96 (s, 0.34 H), 3.81 (s, 0.73 H), 3.78 (s, 2.96 H), 3.72 (s, 0.97 H), 3.71 (s, 0.51 H), 3.66 (s, 0.13 H) **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 165.0, 164.4, 150.2, 148.8, 147.4, 146.0, 142.9, 141.5, 140.9, 139.0, 138.9, 137.5, 133.5, 133.4, 133.2, 132.9, 131.8, 130.4, 129.6, 129.4, 129.1, 128.8, 128.8, 128.4, 128.2, 127.8, 127.7, 127.5, 127.1, 126.8, 126.6, 126.2, 126.2, 126.0, 125.7, 125.3, 125.2, 124.0, 123.3, 122.8, 122.7, 122.2, 121.2, 51.5, 51.3, 51.2, 50.5, 39.9, 37.2. **IR**: 3103 (w), 3055 (w), 2947 (w), 2843 (w), 1703 (s) cm^{-1}. **HRMS (EI)** m/z: $[M]^+$ Calcd. for $C_{19}H_{14}O_2S$ 306.0715; Found 306.0713.

*Methyl 3-phenyl-1H-benzo[b]cyclopenta[d]thiophene-2-carboxylate (**5ba-I**)*

The general procedure was followed using allylic alcohol **4ba** (54 mg, 0.167 mmol) in benzene (3.3 mL), $Ca(NTf_2)_2$ (10 mg, 0.017 mmol), *n*-Bu_4NPF_6 (6.5 mg, 0.017 mmol). After work up and purification, (25% EtOAc/Hexanes, R_f = 0.673), compound **5ba-I** was afforded as a yellow solid (26.8 mg, 53% yield). [m.p. = 104-113 ˚C] **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.81 - 7.86 (m, 2 H), 7.71 (dd, *J* = 7.93, 1.53 Hz, 2 H), 7.40 - 7.52 (m, 4 H), 7.31 - 7.36 (m, 1 H), 3.96 (s, 2 H), 3.76 (s, 3 H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 164.7, 150.8, 146.9, 144.6, 143.7, 134.4, 133.8, 130.0, 129.0, 128.8, 128.0, 124.9, 124.5, 123.8, 121.8, 51.3, 36.9. **IR**: 3057 (w), 2949 (w), 2845 (w), 1701 (s) cm^{-1}. **HRMS (EI)** m/z: $[M]^+$ Calcd. for $C_{19}H_{14}O_2S$ 306.0715; Found 306.0708.

*Methyl 1-phenyl-1H-cyclopenta[b]naphthalene-2-carboxylate (**5da-II**)*

The general procedure F was followed using allylic alcohol **4da** (99 mg, 0.311 mmol) in benzene (6.2 mL), $Ca(NTf_2)_2$ (18.7 mg, 0.031 mmol), *n*-Bu_4NPF_6 (12.0 mg, 0.031 mmol). After work up and purification, (15% EtOAc/Hexanes, R_f = 0.404), compound **5da-II** was afforded as a white solid (69.6 mg, 75% yield). [m.p. = 145-147 ˚C] **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.90 (d, *J* = 8.24 Hz, 2 H) 7.88 (d, *J* = 1.83 Hz, 1 H) 7.70 (d, *J* = 8.54 Hz, 2 H) 7.43 (ddd, *J* = 8.16, 6.79, 1.22 Hz, 1 H) 7.35 (ddd, *J* = 8.32, 6.94, 1.22 Hz, 1 H) 7.21 - 7.30 (m, 3 H) 7.16 - 7.19 (m, 2 H) 5.22 (d, *J* = 1.83 Hz, 1 H) 3.77 (s, 3 H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 164.3, 146.9, 142.7, 141.1, 139.4, 138.1, 133.5, 129.3, 128.8, 128.7, 128.5, 128.4, 126.8, 126.6, 125.9, 123.9, 121.1, 55.6, 51.4. **IR**: 3055 (w), 3026 (w), 2949 (w), 1705 (s) cm^{-1}. **HRMS (EI)** m/z: $[M]^+$ Calcd. for $C_{21}H_{16}O_2$ 300.1150; Found 300.1148.

*Methyl 5-methoxy-1-phenyl-1H-indene-2-carboxylate (**5ea-II**)*

The general procedure F was followed using allylic alcohol **4ea** (73 mg, 0.245 mmol) in benzene (4.9 mL), $Ca(NTf_2)_2$ (14.7 mg, 0.024 mmol), *n*-Bu_4NPF_6 (9.5 mg, 0.024 mmol). After work up and purification, (15% EtOAc/Hexanes, R_f = 0.320), compound **5ea-II** was afforded as an off-white solid (52.6 mg, 77% yield). [m.p. = 131-137 ˚C] **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.77 (d, *J* = 1.8 Hz, 1 H), 7.30 - 7.23 (m, 3 H), 7.15 - 7.08 (m, 4 H), 6.87 (dd, *J* = 2.4, 8.2 Hz, 1 H), 4.84 (d, *J* = 1.8 Hz, 1 H), 3.86 (s, 3 H), 3.73 (s, 3 H) **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 164.6, 159.3, 142.8, 142.6, 142.4, 141.4, 138.6, 128.5, 127.8, 126.8, 125.0, 114.7, 108.2, 55.5, 54.9, 51.5. **IR**: 3028 (w), 2953 (w), 2835 (w), 1707 (s) cm^{-1}. **HRMS (EI)** m/z: $[M]^+$ Calcd. for $C_{18}H_{16}O_3$ 280.1099; Found 280.1098.

*Methyl 5,6-dimethoxy-1-phenyl-1H-indene-2-carboxylate (**5fa-II**)*

The general procedure F was followed using allylic alcohol **4fa** (50 mg, 0.152 mmol) in benzene (3.1 mL), $Ca(NTf_2)_2$ (9.1 mg, 0.015 mmol), *n*-Bu_4NPF_6 (5.9 mg, 0.015 mmol). After work up and purification, (20% EtOAc/Hexanes, R_f = 0.24), compound **5fa-II** was afforded as a colorless oil (32.3 mg, 68% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.73 (d, *J* = 1.53 Hz, 1 H) 7.22 - 7.30 (m, 3 H) 7.10 (d, *J* = 6.71 Hz, 2 H) 7.06 (s, 1 H) 6.77 (s, 1 H) 4.79 (d, *J* = 1.22 Hz, 1 H) 3.95 (s, 3 H) 3.82 (s, 3 H) 3.70 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 164.6, 150.2, 148.9, 144.1, 141.7, 140.1, 138.7, 133.5, 128.5, 127.9, 126.8, 107.5, 105.9, 56.1, 55.6, 51.3. **IR**: 2949 (w), 2833 (w), 1701 (s) cm^{-1}. **HRMS (EI)** m/z: $[M]^+$ Calcd. for $C_{19}H_{18}O_4$ 310.1205; Found 310.1201.

4.7. Attempted [4+2] cycloadditions.

General Procedure *G*: To a round bottom flask charged with a magnetic stir bar under nitrogen atmosphere was added a solution of **5aa-I** (1.0 equiv.) in solvent (0.2 to 0.5 M) at room temperature. Alkene or diene (1 to 1.8 equiv.) was then added. The reaction stirred at reflux for 18 h and was allowed to cool to room temperature. An aliquot of the reaction was taken and concentrated under reduced pressure. A crude NMR was obtained of the reaction mixture.

Rxn 1: General procedure G was followed using **5aa-I** (1.0 equiv., 73 mg), maleic anhydride (1.8 equiv., 54 mg), and toluene (0.5 M, 0.55 mL). No product formed.

Rxn 2: General procedure G was followed using **5aa-I** (1.0 equiv., 108 mg), *n*-butyl vinyl ether (1.0 equiv., 0.6 mL), and benzene (0.2 M, 2.1 mL). No product formed.

Rxn 3: General procedure G was followed using **5aa-I** (1.0 equiv., 73 mg), 2,5-dimethylfuran (1.8 equiv., 0.6 mL), and toluene (0.2 M, 1.5 mL). No product formed.

4.8. Isomerization probing.

Procedure: Two flasks (5 mL) containing stir bars were put under a nitrogen atmosphere. To one was added 10 mol % $HNTf_2$ and to each 1 mL of benzene was added. They were then heated to 40 ˚C with stirring. To each was added a 2.2:1 ratio of 5aa-I to 5aa-II dissolved in benzene, enough to make two 3 mL, 0.1 M solutions when added to their flasks. The reactions were allowed to stir for two hours, with aliquots of 0.15 mL being taken every 15 minutes. Each aliquot was immediately cooled to room temperature while being concentrated under reduced pressure. Once all aliquots had been taken, each was dissolved in $CDCl_3$ and an NMR was taken immediately without further purification. Ratios of products were determined by NMR.

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