Tandem Decarboxylative Allylation and Fragmentation of Allyl Benzocyclobutenyl Carbonates: Access to *ortho*-Functionalized Aryls from Aryl Bromides

David Rosa, Andrei Chtchemelinine, Arturo Orellana*

Department of Chemistry, York University, 4700 Keele Street, Toronto, ON, M3J 1P3, Canada
Fax +1(416)7365936; E-mail: aorellan@yorku.ca

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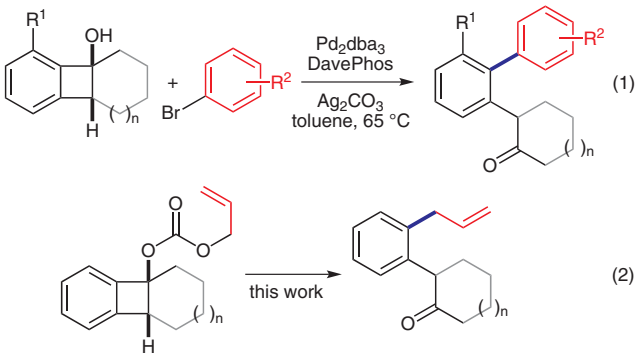
Abstract: Allyl benzocyclobutyl carbonates yield *ortho*-allyl α-aryl ketones through a palladium-catalyzed decarboxylative allylation, fragmentation, and cross-coupling process.

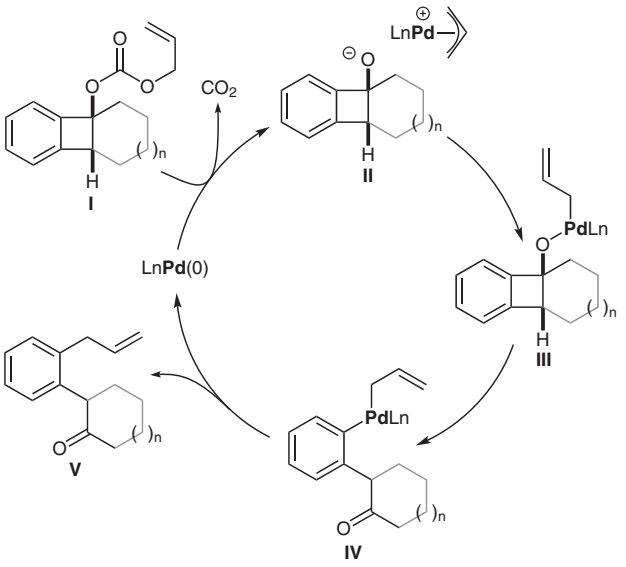
Key words: benzocyclobutenol, decarboxylative allylation, palladium, fragmentation, strain release

Due to their inherent reactivity, highly strained carbocyclic systems provide unusual opportunities for synthesis. Transition-metal catalysts are capable of modulating the reactivity of such systems, thereby furnishing useful products with a good degree of selectivity and in good yields. We have been interested in developing reactions in which the palladium-catalyzed β-carboelimination[1] of tertiary alcohols is a key design element.[2] Recently we reported the selective and high-yielding cross-coupling reaction of benzocyclobutenols with aryl bromides[3] (Scheme 1, equation 1). Here we extend this chemistry to the use of allyl benzocyclobutenyl carbonates, and show that these substrates undergo a decarboxylative allylation and fragmentation reaction to yield *ortho*-allyl α-arylated ketones (Scheme 1, equation 2).



Scheme 1

We envisioned that allyl benzocyclobutenyl carbonates would participate in a tandem reaction combining the palladium-catalyzed decarboxylative allylation chemistry of allyl carbonate[4] functions with the selective, palladium-catalyzed cleavage[5] of benzocyclobutenols.[6] Such a process would result in the preparation of *ortho*-functionalized aryl rings bearing allyl and ketone groups.[7] A plausible catalytic cycle for this transformation would involve palladium-catalyzed ionization of the allyl benzocyclobutenyl carbonate, followed by decarboxylation to generate an ion pair consisting of a cationic allylpalladium intermediate and an alkoxide anion (**I** to **II**, Scheme 2). Coordination of palladium to the alkoxide oxygen (**II** to **III**), selective β-carboelimination (**III** to **IV**), and reductive elimination (**IV** to **V**) would furnish the allylated product.



Scheme 2 Plausible catalytic cycle for the proposed tandem decarboxylative allylation and fragmentation reaction

Benzocyclobutenols[8] have featured in complex molecule synthesis[9] and a number of synthetic methods. Their generation via nucleophilic addition to the corresponding benzocyclobutenone is a common preparative method, however the preparation of the benzocyclobutenone[10] moiety itself suffers from lengthy reaction sequences that often require the use of *ortho*-difunctionalized aryl substrates.[11] With the aim of developing a streamlined synthetic method, we decided to prepare substrates for the proposed reaction from the corresponding bromobenzenes. Durst has shown that treatment of bromo- and iodobenzenes with a strong, non-nucleophilic base in the presence of a ketone results in the formation of benzocyclobutenols.[12,13] Addition of the ketone enolate to the benzyne generated in situ results in the formation of an aryl anion that undergoes a subsequent 1,2-addition to the ke-

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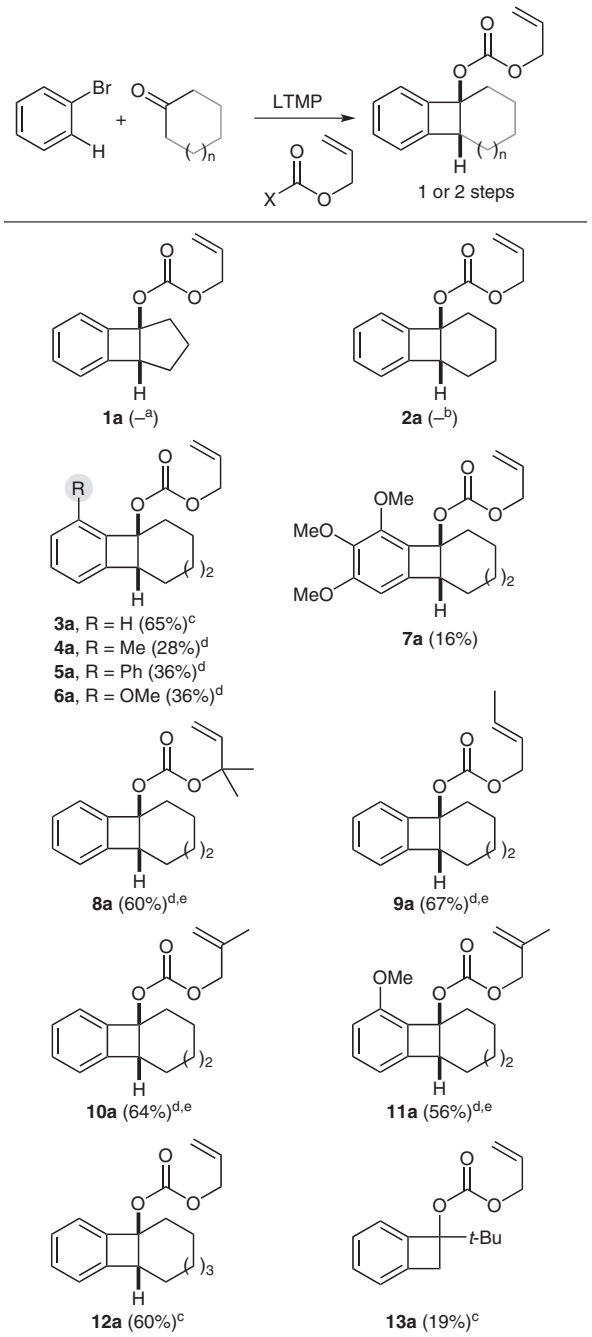
tone function. Simply quenching the reaction mixture with allyl chloroformate or allyl imidazolide[14] results in the formation of the desired substrates (Scheme 3).



Scheme 3 Preparation of allyl benzocyclobutenyl carbonates from aryl bromides. [a] Not isolated; the corresponding benzocyclobutenol was isolated in 36% yield. [b] Not isolated; the corresponding benzocyclobutenol was isolated in 53% yield. [c] Overall yield for a one-pot process. [d] Prepared in two steps, overall yield. [e] Prepared using the corresponding allyl imidazolide.

Although the desired carbonates could all be prepared in a one-pot process, in most cases it was difficult to isolate them from the reaction mixture. This required us to isolate the benzocyclobutenol and install the allyl carbonate function in a separate operation in the case of **4a**–**11a** (Scheme 3). Curiously, consistent with Durst's report we were able to prepare benzocyclobutenols using cyclopentanone and cyclohexanone, however attempts to prepare the corresponding allyl benzocyclobutenyl carbonates **1a** and **2a** in one or two steps failed. In contrast, the use of cycloheptanone in combination with a variety of substituted bromobenzenes provided the desired benzocyclobutenols **3a**–**11a**. Similarly, the use of a cyclooctanone and an acyclic ketone provided the desired substrates **12a** and **13a**, respectively, in practical yields. We also prepared substrates bearing 1,1-dimethylallyl **8a**, crotyl **9a**, and methallyl groups **10a** and **11a** on the carbonate function by simply quenching the corresponding alkoxide anions with the corresponding allyl imidazolides. It is clear that in a number of cases the yields of allylbenzocyclobutenyl carbonates are poor, nevertheless this unoptimized protocol provided access to practical amounts of substrates for the present study.

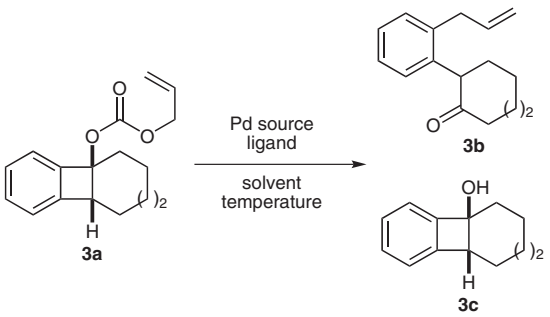
Optimization of the reaction was conducted with substrate **3a** (Table 1). We were happy to observe that treatment of a toluene solution of this substrate with 10% palladium(II) acetate and triphenylphosphine provided the desired product **3b** in 75% yield (entry 1). The use of tris(dibenzylideneacetone)dipalladium(0) (Pd_2dba_3, 10% Pd basis) and triphenylphosphine provided similar yield of the coupled product along with some of the corresponding benzocyclobutenol **3c** (entry 2). Increased yields of the desired product **3b** were obtained with a range of biarylphosphine (Buchwald) ligands and Pd_2dba_3, with S-Phos providing the best result (entries 3–6). The use of bidentate phosphine ligands provided diminished yields of the coupled product along with the benzocyclobutenol **3c** (entries 7–9). Reduction of the palladium loading to 5% and 2% did not affect the isolated yields significantly (entries 10 and 11). While the use of tetrahydrofuran and acetonitrile as solvents gave similar results (entries 12 and 13), more polar solvents provided diminished yields of the coupled product, along with significant amounts of the free alcohol (entries 14–17). An excellent yield of the coupled product was also obtained at reduced temperature (entry 18).

With optimized reaction conditions in hand we set out to test the scope of the reaction (Scheme 4). Substrates **3a**–**7a**, bearing an allyl carbonate function and a fused cycloheptane ring provided the coupled products **3b**–**7b** in uniformly excellent yields.

Substrates **8a** and **9a**, bearing 1,1-dimethylallyl and crotyl carbonate functions respectively, failed to provide any of the possible coupled products, i.e. **8b**/**8c** or **9b**/**9c**. In contrast, substrates **10a** and **11a**, bearing methallyl carbonates, provided the expected coupled product in excellent yields. Similar yields were observed with substrates **12a** and **13a**.

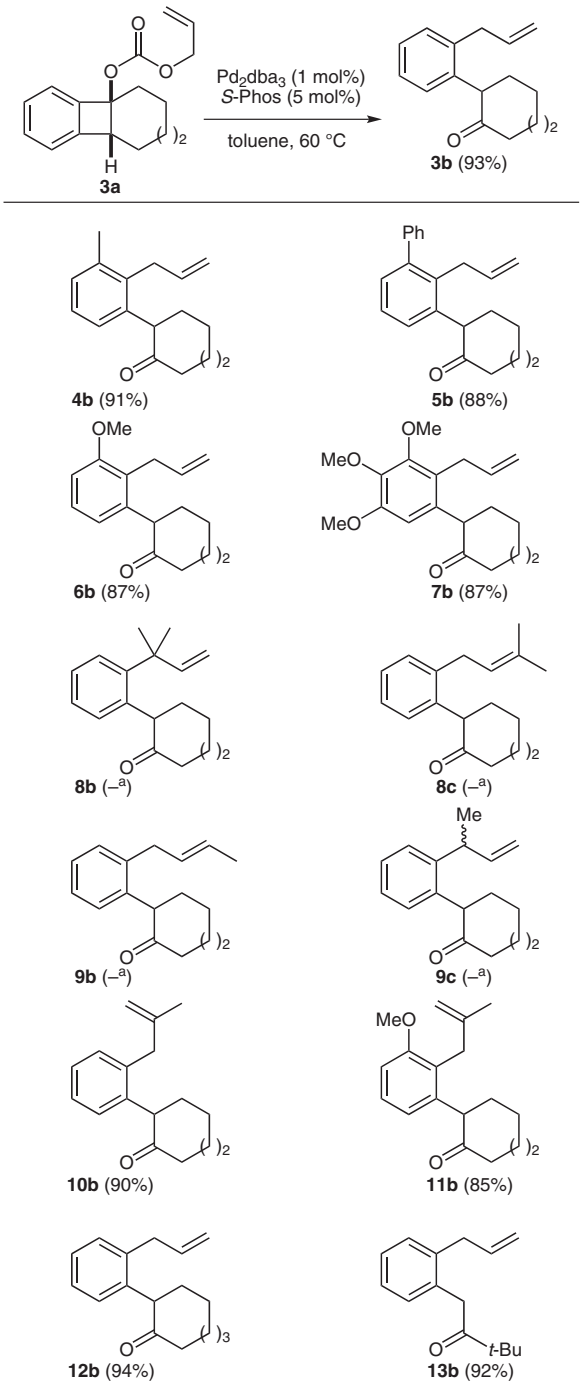
Finally, in order to explore the mechanism proposed in Scheme 2, we conducted a cross-over experiment under optimized conditions using substrates **3a** and **11a** (Scheme 5). Analysis of the crude reaction mixture by ^1H

Table 1 Reaction Optimization[a]



Entry	Pd source	Ligand	Solvent, temp	Yield[b] (%)	
				3b	**3c**
1[c]	$Pd(OAc)_2$	Ph_3P	toluene, 80 °C	75	–
2[d]	Pd_2dba_3	Ph_3P	toluene, 80 °C	72	15
3[d]	Pd_2dba_3	DavePhos	toluene, 80 °C	88	–
4[d]	Pd_2dba_3	X-Phos	toluene, 80 °C	82	–
5[d]	Pd_2dba_3	S-Phos	toluene, 80 °C	93	–
6[d]	Pd_2dba_3	*t*-Bu-X-Phos	toluene, 80 °C	88	–
7[e]	Pd_2dba_3	dppe	toluene, 80 °C	53	39
8[e]	Pd_2dba_3	dppp	toluene, 80 °C	57	21
9[e]	Pd_2dba_3	dppf	toluene, 80 °C	78	9
10[f]	Pd_2dba_3	S-Phos	toluene, 80 °C	93	–
11[g]	Pd_2dba_3	S-Phos	toluene, 80 °C	96	–
12[g]	Pd_2dba_3	S-Phos	THF, 60 °C	88	–
13[g]	Pd_2dba_3	S-Phos	MeCN, 80 °C	93	–
14[g]	Pd_2dba_3	S-Phos	NMP, 80 °C	29	53
16[g]	Pd_2dba_3	S-Phos	DME, 80 °C	41	39
17[g]	Pd_2dba_3	S-Phos	DMA, 80 °C	23	55
18[g]	Pd_2dba_3	S-Phos	toluene, 60 °C	93	–

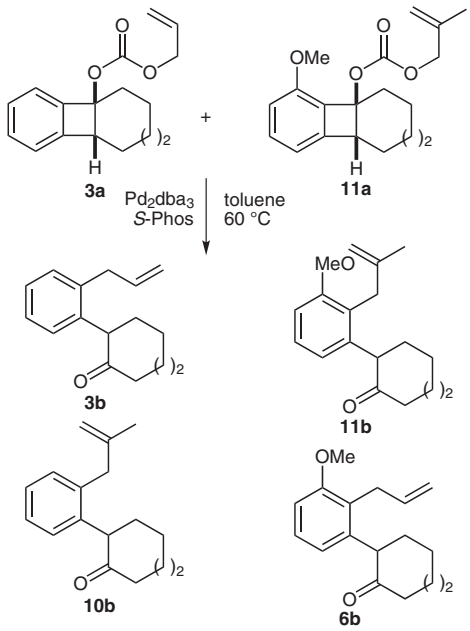
[a] All reactions were conducted at 0.1 M concentration.
[b] Isolated yields.
[c] 10 mol% Pd and 40 mol% Ph_3P.
[d] 10 mol% Pd and 20 mol% ligand.
[e] 10 mol% Pd and 10 mol% ligand.
[f] 5 mol% Pd and 10 mol% ligand.
[g] 2 mol% Pd and 5 mol% ligand.



Scheme 4 Substrate scope study. [a] Not isolated.

NMR and GC-MS revealed that the expected products (i.e., **3b** and **11b**) and the cross-over products (i.e., **6b** and **10b**) were formed in this process, and suggests that the reaction takes place via a solvent separated ion pair (cf. **II**, Scheme 2).

We have shown that the palladium-catalyzed decarboxylative allylation and the selective β-carboelimination of benzocyclobutenols can be incorporated into a tandem reaction leading to *ortho*-functionalized aryl rings. While there is significant room for improvement in the preparation of substrates, the cross-coupling reaction works in excellent yields with allyl and methallyl carbonates. The effect of polar solvents on product distribution, and the results of a cross-over experiment are consistent with a reaction occurring through a solvent separated ion pair.



Scheme 5 Cross-over study

Reactions were conducted in flame- or oven-dried glassware under an atmosphere of argon using freshly distilled solvents unless specified otherwise. Commercial reagents were used as received. Toluene and MeCN were distilled from CaH_2 prior to use. THF was distilled from Na/benzophenone. TLC was performed on Merck silica gel 60 F254 plates. Visualization was carried out using UV light and/or $KMnO_4$, anisaldehyde or $(NH_4)_2Ce(NO_3)_6$ solns. ACS grade hexanes and EtOAc were used as received. Flash column chromatography was carried out using Dynamic Absorbents Inc. Flash silica gel (32–63 μm). ^1H and ^{13}C NMR spectra were recorded on a Bruker 400 AV or 300 AV spectrometer in $CDCl_3$ (99.8% deuterated). Spectra recorded using $CDCl_3$ were calibrated to δ = 7.28 (^1H) and 77.23 (^{13}C). Infrared spectra were recorded as thin films (neat) in NaCl cells using a Mattson Genesis II FT-IR instrument. Mass spectrometry was conducted at the Mass Spectrometry Facility of Queen's University on either a Waters/Micromass GC-TOF instrument with an EI source or an Applied Biosystems/MDS Sciex QStar XL QqTOF instrument with and ESI source.

Allyl 5,6,7,8,9,9a-Hexahydro-4b*H*-benzo[3,4]cyclobuta[1,2]cyclohepten-4b-yl Carbonate (3a); Typical Procedure 1 for the One-Step Preparation of 3a, 12a, and 13a

Following a procedure published by Durst et al.,[12] an oven-dried, 25-mL round-bottomed flask equipped with a stir bar was charged with 2,2,6,6-tetramethylpiperdine (0.724 g, 0.907 mL, 5.4 mmol, 2.0 equiv) and capped with a rubber septum. The reaction vessel was flushed with argon for 10 min at r.t. prior to the addition of THF (8 mL). The resulting soln was cooled to –40 °C using dry ice/EtOH–H_2O (2:1). Once cold, 1.7 M *t*-BuLi soln (5.4 mmol, 2.0 equiv) was added dropwise via syringe. The mixture was stirred for 30 min before a soln of cycloheptanone (0.300 g, 0.315 mL, 2.7 mmol, 1.0 equiv) in THF (2 mL) was added. This was followed by a soln of bromobenzene (0.424 g, 0.284 mL, 2.7 mmol, 1.0 equiv) in THF (2 mL). The reaction was stirred at –40 °C for a further 4 h before neat allyl chloroformate (0.976 g, 0.861 mL, 3.0 equiv) was introduced. After the reaction had warmed to r.t. it was quenched with sat. NH_4Cl soln. The layers were separated and the aqueous layer was extracted with EtOAc (2 ×). The combined organic layers were washed with brine and dried ($MgSO_4$). Filtration and concentration in vacuo gave the crude product, which was purified by flash column chromatography (1% EtOAc–hexanes) to afford carbonate **3a** (0.480 g, 1.8 mmol, 65%) as a clear oil.

IR (thin film): 3079, 2923, 1743, 1648, 1454 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.44 (d, *J* = 7.2 Hz, 1 H), 7.34 (t, *J* = 7.2 Hz, 1 H), 7.26 (t, *J* = 7.2 Hz, 1 H), 7.15 (d, *J* = 7.2 Hz, 1 H), 5.95 (dddd, *J* = 16.4, 10.4, 5.6 Hz, 1 H), 5.36 (dd, *J* = 16.4, 1.2 Hz, 1 H), 5.27 (d, *J* = 10.4 Hz, 1 H), 4.65 (dd, *J* = 12.8, 5.6 Hz, 1 H), 4.60 (dd, *J* = 12.8, 5.6 Hz, 1 H), 3.81 (dd, *J* = 10.0, 4.0 Hz, 1 H), 2.70 (m, 1 H), 2.17 (m, 1 H), 2.03 (m, 1 H), 1.75–1.67 (m, 4 H), 1.57–1.41 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.6, 145.8, 144.3, 131.7, 129.9, 127.4, 124.4, 122.4, 118.6, 90.7, 67.9, 56.7, 32.4, 31.7, 30.0, 27.0, 23.8.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{17}H_{20}O_3$: 272.1412; found: 272.1416.

Carbonate 12a

Chromatography (2% EtOAc–hexanes); colorless oil; yield: 465 mg (1.6 mmol, 60%).

IR (thin film): 3068, 3023, 2926, 1745, 1649, 1460, 951 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.45 (d, *J* = 7.6 Hz, 1 H), 7.33 (t, *J* = 7.6 Hz, 1 H), 7.25 (t, *J* = 7.6 Hz, 1 H), 7.15 (d, *J* = 7.6 Hz, 1 H), 5.95 (dddd, *J* = 17.2, 10.4, 5.2 Hz, 1 H), 5.36 (dd, *J* = 17.2, 1.6 Hz, 1 H), 5.27 (d, *J* = 10.4 Hz, 1 H), 4.66 (dd, *J* = 13.2, 5.2 Hz, 1 H), 4.60 (dd, *J* = 13.2, 5.2 Hz, 1 H), 3.51 (d, *J* = 11.6 Hz, 1 H), 2.90 (dt, *J* = 15.6, 3.6 Hz, 1 H), 2.02 (d, *J* = 14.8 Hz, 1 H), 1.82–1.54 (m, 8 H), 1.41 (m, 1 H), 1.03 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.7, 146.4, 145.0, 131.7, 129.9, 127.5, 124.3, 121.9, 118.6, 88.6, 67.9, 56.2, 29.1, 28.8, 27.7, 25.7, 25.4, 25.1.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{18}H_{22}O_3$: 286.1569; found: 286.1561.

Carbonate 13a

Chromatography (2% EtOAc–hexanes); colorless oil; yield: 136 mg (0.52 mmol, 19%).

IR (thin film): 3065, 2926, 1743, 1645, 1380 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.30–7.23 (m, 3 H), 7.16 (d, *J* = 6.9 Hz, 1 H), 5.95 (dddd, *J* = 17.1, 10.5, 6.0 Hz, 1 H), 5.34 (dd, *J* = 17.1, 1.2 Hz, 1 H), 5.26 (d, *J* = 10.5 Hz, 1 H), 4.55 (d, *J* = 6.0 Hz, 2 H), 3.58 (d, *J* = 14.1 Hz, 1 H), 3.47 (d, *J* = 14.1 Hz, 1 H), 1.04 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.4, 144.7, 141.7, 131.9, 129.6, 126.8, 123.8, 122.7, 118.6, 92.7, 67.8, 39.5, 37.0, 25.2.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{16}H_{20}O_3$: 260.1412; found: 260.1405.

Allyl 4-Methyl-5,6,7,8,9,9a-hexahydro-4b*H*-benzo[3,4]cyclobuta[1,2]cyclohepten-4b-yl Carbonate (4a); Typical Procedure 2 for the Two-Step Preparation of 4a–11a

The required benzocyclobutenols were prepared from the corresponding bromobenzenes and cycloheptanone according to the procedure reported by Durst.[12] An oven-dried, 25-mL round-bottomed flask equipped with a stir bar was capped with a rubber septum and flushed with argon for 10 min at r.t. The flask was charged with *i*-Pr_2NH (0.081 g, 0.81 mmol, 1.3 equiv) and THF (6 mL). The resulting soln was cooled to 0 °C prior to the addition of *n*-BuLi (0.81 mmol, 1.3 equiv) to prepare LDA. After stirring at 0 °C for 30 min, a soln of the required benzocyclobutenol (0.125 g, 0.62 mmol, 1.0 equiv) in THF (2 mL) was added dropwise via syringe. The temperature was maintained at 0 °C for a 2 h, after which neat allyl chloroformate (0.149 g, 1.2 mmol, 2.0 equiv) was added. The resulting mixture was warmed to r.t. over 16 h. Sat. NH_4Cl soln was added and the aqueous layer was extracted with EtOAc (2 ×). The combined organic layers were washed with brine and dried ($MgSO_4$).

Filtration and concentration in vacuo gave the crude product which was purified by flash column chromatography (1% EtOAc–hexanes) to afford carbonate **4a** (0.148 g, 0.52 mmol, 28% overall yield in 2 steps from the bromobenzene) as a clear oil. This protocol was followed for the preparation of substrates **4a**–**7a**. A similar protocol was followed for substrates **8a**–**11a** using the corresponding allyl imidazolide instead of allyl chloroformate. All reported yields are for the two-step process.

IR (thin film): 3063, 3025, 2915, 1747, 1640, 1365, 877 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.24 (t, *J* = 7.6 Hz, 1 H), 7.04 (d, *J* = 7.6 Hz, 1 H), 6.96 (d, *J* = 7.6 Hz, 1 H), 5.95 (dddd, *J* = 17.2, 10.4, 5.2 Hz, 1 H), 5.37 (d, *J* = 17.2 Hz, 1 H), 5.27 (d, *J* = 10.4 Hz, 1 H), 4.64 (dd, *J* = 13.6, 5.2 Hz, 1 H), 4.60 (dd, *J* = 13.6, 5.2 Hz, 1 H), 3.98 (dd, *J* = 6.8, 3.2 Hz, 1 H), 2.64 (t, *J* = 12.4 Hz, 1 H), 2.32 (s, 3 H), 2.23 (m, 2 H), 2.06 (m, 1 H), 1.58–1.76 (m, 3 H), 1.36 (m, 2 H), 0.96 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.8, 145.3, 142.0, 133.6, 131.7, 129.9, 128.6, 119.8, 118.6, 91.9, 67.8, 56.2, 32.8, 31.8, 28.9, 25.9, 24.0, 17.2.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{18}H_{22}O_3$: 286.1569; found: 286.1575.

Carbonate 5a
Chromatography (1% CH_2Cl_2–toluene); colorless oil; yield: 184 mg (0.53 mmol, 36%).

IR (thin film): 3063, 3042, 2910, 1739, 1647, 1412, 928 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.74 (d, *J* = 7.6 Hz, 2 H), 7.46 (m, 4 H), 7.37 (t, *J* = 7.6 Hz, 1 H), 7.13 (m, 1 H), 5.95 (dddd, *J* = 17.2, 10.4, 5.2 Hz, 1 H), 5.40 (d, *J* = 17.2 Hz, 1 H), 5.30 (d, *J* = 10.4 Hz, 1 H), 4.70 (dd, *J* = 13.2, 5.2 Hz, 1 H), 4.65 (dd, *J* = 13.2, 5.2 Hz, 1 H), 4.15 (m, 1 H), 2.43 (t, *J* = 12.8 Hz, 1 H), 2.19 (m, 2 H), 2.07 (m, 1 H), 1.61 (m, 1 H), 1.45 (m, 1 H), 1.30–1.20 (m, 3 H), 0.56 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.8, 146.1, 140.8, 137.7, 137.4, 131.8, 130.4, 128.5, 128.0, 127.5, 126.3, 121.6, 118.6, 92.0, 67.9, 55.9, 32.1, 31.6, 28.6, 25.4, 24.1.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{23}H_{24}O_3$: 348.1725; found: 348.1733.

Carbonate 6a
Chromatography (8% EtOAc–hexanes); colorless oil; yield: 148 mg (0.49 mmol, 36%).

IR (thin film): 3058, 2921, 1743, 1642, 1235 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.31 (t, *J* = 7.6 Hz, 1 H), 6.75 (d, *J* = 7.6 Hz, 1 H), 6.74 (d, *J* = 7.6 Hz, 1 H), 5.95 (ddt, *J* = 16.8, 10.4, 5.6 Hz, 1 H), 5.36 (d, *J* = 16.8 Hz, 1 H), 5.27 (d, *J* = 10.4 Hz, 1 H), 4.62 (d, *J* = 5.6 Hz, 2 H), 4.00 (dd, *J* = 5.2, 3.2 Hz, 1 H), 3.87 (s, 3 H), 2.59 (t, *J* = 12.8 Hz, 1 H), 2.26 (dd, *J* = 13.6, 8.0 Hz, 1 H), 2.12 (m, 2 H), 1.73–1.57 (m, 3 H), 1.29 (m, 2 H), 0.92 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.4, 153.8, 147.1, 131.7, 131.6, 128.4, 118.5, 115.1, 111.6, 91.1, 67.8, 56.1, 55.8, 33.8, 31.6, 28.5, 25.5, 24.3.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{18}H_{22}O_4$: 302.1526; found: 302.1518.

Carbonate 7a
Chromatography (13% EtOAc–hexanes); colorless oil; yield: 175 mg (0.47 mmol, 16%).

IR (thin film): 3061, 2987, 1730, 1648, 1606, 1241, 1045 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 6.41 (s, 1 H), 5.95 (dddd, *J* = 17.2, 13.2, 10.4, 6.0 Hz, 1 H), 5.36 (dd, *J* = 17.2, 1.6 Hz, 1 H), 5.28 (d, *J* = 10.4 Hz, 1 H), 4.65 (dd, *J* = 13.2, 6.0 Hz, 1 H), 4.59 (dd, *J* = 13.2, 6.0 Hz, 1 H), 4.00 (s, 3 H), 3.93 (dd, *J* = 5.6, 3.2 Hz, 1 H), 3.87 (s, 3 H), 3.81 (s, 3 H), 2.65 (dd, *J* = 13.6, 12.0 Hz, 1 H), 2.19–2.07 (m, 3 H), 1.73–1.62 (m, 3 H), 1.27 (m, 2 H), 0.93 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.4, 153.6, 149.7, 140.7, 137.6, 131.6, 119.8, 118.7, 99.8, 91.2, 67.9, 60.9, 58.9, 56.2, 54.4, 35.1, 31.4, 28.3, 25.2, 24.1.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{20}H_{26}O_6$: 362.1729; found: 362.1738.

Carbonate 8a
Chromatography (1% CH_2Cl_2–toluene); colorless oil; yield: 120 mg (0.40 mmol, 60%).

IR (thin film): 3043, 2971, 1745, 1642, 1456, 1083 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.42 (d, *J* = 7.2 Hz, 1 H), 7.32 (t, *J* = 7.2 Hz, 1 H), 7.24 (t, *J* = 7.2 Hz, 1 H), 7.14 (d, *J* = 7.2 Hz, 1 H), 6.13 (dd, *J* = 17.6, 10.8 Hz, 1 H), 5.22 (d, *J* = 17.6 Hz, 1 H), 5.14 (d, *J* = 10.4 Hz, 1 H), 3.80 (dd, *J* = 9.2, 3.6 Hz, 1 H), 2.70 (m, 1 H), 2.16 (m, 1 H), 2.03 (m, 1 H), 1.69 (m, 3 H), 1.57 (s, 3 H), 1.55 (s, 3 H), 1.47–1.28 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.1, 145.8, 144.6, 142.0, 129.7, 127.3, 124.4, 122.3, 113.1, 90.2, 64.0, 56.6, 32.4, 31.7, 29.8, 26.8, 26.7, 26.0, 23.7.

MS: *m*/*z* $[M - C_5H_9 - CO_2]^+$ calcd for $C_{12}H_{13}O$:173.0966; found: 173.13. $[M]^+$ was not observed.

Carbonate 9a
Chromatography (1% CH_2Cl_2–toluene); colorless oil; yield: 126 mg (0.44 mmol, 67%).

IR (thin film): 3067, 2925, 1748, 1633, 1426 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.44 (d, *J* = 7.2 Hz, 1 H), 7.33 (t, *J* = 7.2 Hz, 1 H), 7.26 (t, *J* = 7.2 Hz, 1 H), 7.14 (d, *J* = 7.2 Hz, 1 H), 5.83 (m, 1 H), 5.63 (m, 1 H), 4.55 (m, 2 H), 3.80 (dd, *J* = 10.0, 4.0 Hz, 1 H), 2.70 (m, 1 H), 2.17 (m, 1 H), 2.05 (m, 1 H), 1.69 (m, 7 H), 1.61–1.41 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.7, 145.8, 144.4, 132.0, 129.8, 127.4, 124.6, 124.4, 122.3, 90.6, 67.9, 56.7, 32.4, 31.7, 30.0, 27.0, 23.8, 17.7.

MS: *m*/*z* $[M - C_4H_7 - CO_2]^+$ calcd for $C_{12}H_{13}O$: 173.0966; found: 173.11. $[M]^+$ was not observed.

Carbonate 10a
Chromatography (1% CH_2Cl_2–toluene); colorless oil; yield: 182 mg (0.64 mmol, 64%).

IR (thin film): 3054, 2956, 1742, 1637, 1409, 1076 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.43 (d, *J* = 7.2 Hz, 1 H), 7.33 (t, *J* = 7.2 Hz, 1 H), 7.26 (t, *J* = 7.2 Hz, 1 H), 7.14 (d, *J* = 7.2 Hz, 1 H), 5.02 (s, 1 H), 4.96 (s, 1 H), 4.57 (d, *J* = 12.8 Hz, 1 H), 4.50 (d, *J* = 12.8 Hz, 1 H), 3.81 (dd, *J* = 10.0, 4.0 Hz, 1 H), 2.70 (m, 1 H), 2.17 (m, 1 H), 2.03 (m, 1 H), 1.78 (s, 3 H), 1.74–1.63 (m, 3 H), 1.58–1.43 (m, 3 H), 0.96 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.7, 145.8, 144.3, 139.4, 129.8, 127.4, 124.4, 122.4, 113.2, 90.7, 70.5, 56.7, 32.3, 31.7, 30.0, 26.9, 23.7, 19.3.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{18}H_{22}O_3$: 286.1569; found: 286.1577.

Carbonate 11a
Chromatography (2% EtOAc–hexanes); colorless oil; yield: 0.153 g (0.48 mmol, 56%).

IR (thin film): 3061, 2946, 1725, 1641, 1218, 1046 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.31 (t, *J* = 8.0 Hz, 1 H), 6.76 (d, *J* = 8.0 Hz, 1 H), 6.75 (d, *J* = 8.0 Hz, 1 H), 5.02 (s, 1 H), 4.95 (s, 1 H), 4.54 (m, 2 H), 4.00 (m, 1 H), 3.88 (s, 3 H), 2.60 (t, *J* = 12.8 Hz, 1 H), 2.26 (dd, *J* = 12.8, 8 Hz, 1 H), 2.13 (m, 2 H), 1.78 (s, 3 H), 1.73–1.62 (m, 3 H), 1.29 (m, 2 H), 0.95 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.4, 153.9, 147.1, 139.5, 131.6, 128.4, 115.1, 113.1, 111.6, 91.1, 70.4, 56.1, 55.8, 33.8, 31.6, 28.5, 25.5, 24.3, 19.3.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{19}H_{24}O_4$: 316.1675; found: 316.1683.

2-(2-Allylphenyl)cycloheptanone (3b); Typical Procedure 3 for Palladium-Catalyzed Decarboxylative Allylation and Fragmentation

An oven-dried 15-mL test tube equipped with a stir bar was charged Pd_2dba_3 (0.002 g, 0.002 mmol, 0.01 equiv) and S-Phos (0.003 g, 0.008 mmol, 0.05 equiv). The reaction vessel was sealed with a septum and flushed with argon for 10 min at r.t. Toluene was added (1.0 mL) and the resulting soln stirred at r.t.. To the reaction vessel was added a soln of carbonate **3a** (0.040 g, 0.15 mmol, 1.0 equiv) in toluene (0.5 mL); the vessel was heated to 60 °C (TLC monitoring). Upon completion, the reaction mixture was filtered through a pad of silica gel (EtOAc). The filtrate was concentrated in vacuo and the crude product purified by flash column chromatography (4% EtOAc–hexanes) to give ketone **3b** (33 mg, 0.014 mmol, 93%) as a clear oil.

IR (thin film): 3068, 3021, 2921, 1702, 1637, 1602, 1454 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.22–7.18 (m, 4 H), 5.98 (ddt, *J* = 17.2, 10.4, 6.4 Hz, 1 H), 5.09 (d, *J* = 10.4 Hz, 1 H), 4.98 (d, *J* = 17.2 Hz, 1 H), 3.98 (dd, *J* = 11.2, 2.8 Hz, 1 H), 3.50 (dd, *J* = 16.4, 6.4 Hz, 1 H), 3.39 (dd, *J* = 16.4, 6.4 Hz, 1 H), 2.69 (m, 2 H), 2.08–1.95 (m, 5 H), 1.72 (m, 1 H), 1.63–1.44 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 213.5, 139.8, 137.2, 136.9, 129.9, 127.8, 126.7, 126.5, 115.7, 53.4, 43.7, 37.7, 32.7, 29.7, 29.6, 24.6.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{16}H_{20}O$: 228.1514; found: 228.1519.

2-(2-Allyl-3-methylphenyl)cycloheptanone (4b)

Chromatography (3% EtOAc–hexanes); colorless oil; yield: 33 mg (14 mmol, 91%).

IR (thin film): 3057, 2942, 1701, 1648, 1422 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.16 (t, *J* = 7.6 Hz, 1 H), 7.09 (d, *J* = 7.6 Hz, 1 H), 7.08 (d, *J* = 7.6 Hz, 1 H), 5.95 (ddt, *J* = 17.2, 10.0, 5.6 Hz, 1 H), 5.09 (dd, *J* = 10.0, 1.6 Hz, 1 H), 4.84 (d, *J* = 17.2 Hz, 1 H), 4.04 (dd, *J* = 11.2, 3.2 Hz, 1 H), 3.50 (dd, *J* = 16.8, 5.6 Hz, 1 H), 3.41 (dd, *J* = 16.8, 5.6 Hz, 1 H), 2.70 (m, 2 H), 2.31 (s, 3 H), 2.31–1.94 (m, 5 H), 1.70 (m, 1 H), 1.48 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 213.8, 140.2, 136.9, 135.8, 135.0, 128.7, 126.2, 125.5, 115.2, 53.7, 43.7, 33.1, 33.0, 29.8, 29.6, 24.7, 20.3.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{17}H_{22}O$: 242.1671; found: 242.1681.

2-(2-Allylbiphenyl-3-yl)cycloheptanone (5b)

Chromatography (2% EtOAc–hexanes); colorless oil; yield: 40 mg (0.13 mmol, 88%).

IR (thin film): 3059, 2925, 1697, 1642, 1468 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.27 (m, 7 H), 7.15 (dd, *J* = 6.8, 1.6 Hz, 1 H), 5.96 (ddt, *J* = 17.2, 10.0, 5.2 Hz, 1 H), 5.09 (dd, *J* = 10.0, 1.6 Hz, 1 H), 4.82 (dd, *J* = 17.2, 1.6 Hz, 1 H), 4.17 (dd, *J* = 10.8, 2.0 Hz, 1 H), 3.40 (dd, *J* = 16.8, 5.2 Hz, 1 H), 3.32 (dd, *J* = 16.8, 5.2 Hz, 1 H), 2.70 (m, 2 H), 2.09–1.98 (m, 5 H), 1.74 (m, 1 H), 1.61–1.45 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 213.5, 143.0, 142.4, 140.9, 137.7, 133.7, 129.0, 128.6, 127.7, 127.4, 126.7, 126.0, 115.7, 53.3, 43.9, 34.1, 33.4, 29.8, 29.6, 24.4.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{22}H_{24}O$: 304.1827; found: 304.1836.

2-(2-Allyl-3-methoxyphenyl)cycloheptanone (6b)

Chromatography (2% EtOAc–hexanes); colorless oil; yield: 34 mg (0.13 mmol, 87%).

IR (thin film): 2925, 1695, 1637, 1461, 1257, 1065 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.23 (t, *J* = 8.0 Hz, 1 H), 6.85 (d, *J* = 8.0 Hz, 1 H), 6.80 (d, *J* = 8.0 Hz, 1 H), 5.95 (ddt, *J* = 17.2, 10.4, 6.0 Hz, 1 H), 5.00 (d, *J* = 10.4 Hz, 1 H), 5.01 (dd, *J* = 17.2, 1.2 Hz, 1 H), 4.07 (dd, *J* = 10.8, 2.8 Hz, 1 H), 3.82 (s, 3 H), 3.55 (dd, *J* = 15.6, 6.0 Hz, 1 H), 3.44 (dd, *J* = 15.6, 6.0 Hz, 1 H), 2.71 (m, 2 H), 2.08–1.93 (m, 5 H), 1.71 (m, 1 H), 1.54–1.42 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 213.6, 157.3, 141.4, 136.9, 127.0, 125.7, 120.1, 114.4, 108.8, 55.6, 53.5, 43.8, 32.9, 29.8, 29.7, 29.6, 24.6.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{17}H_{22}O_2$: 258.1620; found: 258.1611.

2-(2-Allyl-3,4,5-trimethoxyphenyl)cycloheptanone (7b)

Chromatography (17% EtOAc–hexanes); colorless oil; yield: 42 mg (0.13 mmol, 87%).

IR (thin film): 3051, 2920, 1700, 1648, 1232, 1215, 1046 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.57 (s, 1 H), 5.95 (ddt, *J* = 17.2, 10.0, 5.2 Hz, 1 H), 5.02 (d, *J* = 10.0 Hz, 1 H), 4.88 (dd, *J* = 17.2, 1.6 Hz, 1 H), 4.03 (dd, *J* = 11.2, 2.4 Hz, 1 H), 3.87 (s, 6 H), 3.84 (s, 3 H), 3.45 (dd, *J* = 15.2, 5.2 Hz, 1 H), 3.37 (dd, *J* = 15.2, 5.2 Hz, 1 H), 2.67 (m, 2 H), 2.04 (m, 4 H), 1.91 (m, 1 H), 1.72 (m, 1 H), 1.55 (m, 1 H), 1.41 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 213.3, 161.6, 151.6, 140.8, 137.5, 135.7, 123.2, 114.7, 107.6, 61.1, 60.6, 55.9, 53.0, 43.9, 33.3, 30.0, 29.7, 29.4, 24.2.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{19}H_{26}O_4$: 318.1831; found: 318.1843.

2-(2-Methallylphenyl)cycloheptanone (10b)

Chromatography (5% EtOAc–hexanes); colorless oil; yield: 33 mg (0.14 mmol, 90%).

IR (thin film): 3072, 2968, 1695, 1649, 1489, 1450, 741 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25 (m, 2 H), 7.21–7.14 (m, 2 H), 4.84 (s, 1 H), 4.52 (s, 1 H), 4.07 (dd, *J* = 10.8, 3.2 Hz, 1 H), 3.43 (d, *J* = 16.0 Hz, 1 H), 3.32 (dd, *J* = 16.0 Hz, 1 H), 2.66 (m, 2 H), 2.00 (m, 5 H), 1.75 (s, 3 H), 1.73 (m, 1 H), 1.49 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 213.3, 144.9, 140.2, 136.7, 130.4, 128.0, 126.5, 126.4, 111.9, 53.1, 43.7, 42.0, 32.9, 29.7, 29.6, 24.5, 22.6.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{17}H_{22}O$: 242.1671; found: 242.1665.

2-(2-Methallyl-3-methoxyphenyl)cycloheptanone (11b)

Chromatography (5% EtOAc–hexanes); colorless oil; yield: 35 mg (0.13 mmol, 85%).

IR (thin film): 2928, 2852, 1698, 1635, 1218, 1032 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.23 (t, *J* = 8.0 Hz, 1 H), 6.88 (d, *J* = 8.0 Hz, 1 H), 6.80 (d, *J* = 8.0 Hz, 1 H), 4.74 (s, 1 H), 4.38 (s, 1 H), 4.03 (dd, *J* = 10.8, 2.4 Hz, 1 H), 3.81 (s, 3 H), 3.49 (d, *J* = 16.4 Hz, 1 H), 3.38 (d, *J* = 16.4 Hz, 1 H), 2.67 (m, 2 H), 2.00 (m, 5 H), 1.80 (s, 3 H), 1.67 (m, 1 H), 1.45 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 213.4, 157.4, 144.8, 141.8, 126.9, 125.8, 120.3, 110.1, 108.8, 55.7, 53.2, 43.8, 33.3, 33.0, 29.7, 29.6, 24.5, 22.9.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{18}H_{24}O_2$: 272.1776; found: 272.1785.

2-(2-Allylphenyl)cyclooctanone (12b)

Chromatography (5% EtOAc–hexanes); colorless oil; yield: 34 mg (0.14 mmol, 94%).

IR (thin film): 3072, 3027, 2968, 1695, 1648, 1450 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.44 (t, *J* = 8.0 Hz, 1 H), 7.36 (d, *J* = 8.0 Hz, 1 H), 7.25 (m, 2 H), 5.82 (dddd, *J* = 17.6, 10.4, 6.4 Hz, 1 H), 5.09 (d, *J* = 17.6 Hz, 1 H), 4.97 (d, *J* = 10.4 Hz, 1 H), 3.45 (m, 1 H), 3.19 (m, 1 H), 2.57 (m, 1 H), 2.48–2.40 (m, 2 H), 1.75–1.49 (m, 5 H), 1.40–1.22 (m, 3 H), 1.16 (m, 1 H), 0.59 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 210.6, 142.4, 141.5, 137.1, 130.4, 126.7, 125.1, 115.7, 44.3, 39.7, 36.1, 35.0, 28.0, 22.7, 21.8, 21.7.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{17}H_{22}O$: 242.1671; found: 242.1663.

1-(2-Allylphenyl)-3,3-dimethylbutan-2-one (13b)
Chromatography (2% EtOAc–hexanes); colorless oil; yield: 28 mg (0.14 mmol, 92%).

IR (thin film): 3065, 2957, 1703, 1623, 1438 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.24–7.18 (m, 3 H), 7.05 (d, *J* = 7.6 Hz, 1 H), 5.98 (ddt, *J* = 17.2, 10.0, 6.0 Hz, 1 H), 5.09 (d, *J* = 10.0 Hz, 1 H), 4.99 (dd, *J* = 17.2, 1.6 Hz, 1 H), 3.89 (s, 2 H), 3.30 (d, *J* = 6.0 Hz, 2 H), 1.27 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 212.7, 138.2, 136.8, 133.5, 130.6, 129.6, 127.1, 126.3, 115.8, 44.4, 40.8, 37.4, 26.6.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{15}H_{20}O$: 216.1514; found: 216.1519.

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Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synthesis.

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