Catalytic Asymmetric Synthesis of Sterically Hindered Tertiary α-Aryl Ketones
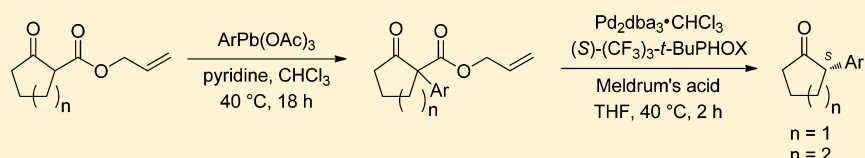
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ⓢ *Supporting Information*

ABSTRACT: The catalytic asymmetric synthesis of a series of tertiary α-aryl cyclopentanones and cyclohexanones has been accomplished via a Pd-catalyzed decarboxylative protonation of the corresponding α-aryl-β-keto allyl esters. Enantioselectivities of up to 92% *ee* and 74% *ee* were achieved for cyclopentanone and cyclohexanone substrates, respectively. The route described gives access to these important structural motifs in moderate to high levels of enantioselectivity. In particular, this is only the second direct approach for the preparation of tertiary α-aryl cyclopentanones. The synthetic approach allows for simple modification of the aryl group. Significantly, substrates containing sterically hindered aryl groups gave the highest levels of enantioselectivity, and these aryl groups were readily installed by a Pb-mediated arylation of a β-keto allyl ester.

INTRODUCTION

Enantioenriched tertiary α-aryl carbonyls represent an important class of organic compounds. They are prevalent structural motifs in many biologically active molecules and pharmaceuticals, such as naproxen and clopidogrel.[1] They are also important intermediates in the synthesis of many medicinally important molecules. As a result, the asymmetric synthesis of compounds possessing this structural motif has received a great deal of attention, particularly in the past decade.

A number of approaches have been developed for the catalytic asymmetric synthesis of quaternary α-aryl carbonyl containing compounds. However, the vast majority of the reports to date necessitate the use of basic conditions. Therefore, these methods are unsuitable for the synthesis of tertiary α-aryl carbonyls due to the acidity of a tertiary α-aryl carbonyl proton. Excellent progress has been made in recent years in the realization of a catalytic asymmetric synthesis of tertiary α-aryl carbonyls. Jørgensen and co-workers developed an organocatalytic enantioselective α-arylation of aldehydes with quinones.[2] Fu and co-workers reported Ni-catalyzed Kumada and Negishi coupling reactions using bisoxazoline ligands to generate α-aryl ketones.[3] MacMillan described enantioselective α-arylations of aldehydes with diaryliodonium salts in the presence of an organocatalyst.[4] Also, MacMillan and Gaunt and co-workers independently reported the enantioselective Cu-catalyzed α-arylation of silyl-*N*-acyloxazolidinones with diaryliodonium salts using bisoxazoline ligands.[5] Zhou and colleagues reported the Pd-catalyzed α-arylation of silyl ketene acetals to form tertiary α-aryl esters[6] and, more recently, the arylation of Sn- or Li-enolates to access α-aryl ketones[7] or lactones.[8]

All of the above methods introduce the aryl group during the enantiodetermining step. An alternative strategy would be to already have the aryl group in place and to generate the tertiary stereocenter via an asymmetric protonation of an enolate complex. This was first realized by the pioneering work of Yamamoto in this area with the use of Lewis acid assisted chiral Brønsted acid (LBA) catalysts in the enantioselective synthesis of α-aryl cyclohexanones. Initially developed with the use of stoichiometric quantities of a BINOL–SnCl₄ catalyst for the asymmetric protonation of silyl enol ethers,[9] the extensive development of this reaction has resulted in a catalytic variant with an achiral proton donor[10] and expansion of the scope to include tertiary α-aryl carboxylic acids.[11] Further improvement was made with the development of a metal-free *N*-triflyl thiophosphoramide BINOL derived proton source[12] and, more recently, a Lewis base tolerant chiral LBA.[13]

A number of other asymmetric enolate protonation reactions have been described using chiral proton sources in the synthesis of α-aryl cyclohexanones. These include the stoichiometric use of chiral diols[14] and α-sulfinyl alcohols.[15] Other catalytic approaches involve the use of a BINAP–AgF complex with MeOH as the achiral proton source,[16] a chiral sulfonamide/achiral sulfonic acid system,[17] and a cationic BINAP–Au complex that also was extended to acyclic tertiary α-aryl ketones.[18] Enantioenriched 2-aryl-cyclohexanones have also been accessed by oxidative kinetic resolution of secondary alcohols, kinetic resolution of racemic 2-arylcyclohexanones via an asymmetric Bayer–Villiger oxidation,[19] and by arylation

with diaryliodonium salts and desymmetrization with a chiral Li-base.[20]

Despite the number of reports of the asymmetric synthesis of tertiary α-aryl cyclohexanones, there have only been three reports that describe the asymmetric synthesis of tertiary α-aryl cyclopentanones. The first of these was reported by Shi and colleagues via asymmetric epoxidation of benzylidene cyclobutanes and epoxide rearrangement in a subsequent step.[21] Bäckvall and co-workers used a dynamic kinetic resolution of allylic alcohols—allylic substitution—oxidative cleavage sequence to access 2-phenylcyclopentanone.[22] The first direct catalytic asymmetric synthesis of tertiary α-aryl ketones was recently described by Kingsbury and co-workers using a series of Sc-catalyzed diazoalkane—carbonyl homologations with bis/tris oxazoline ligands.[23]

The Pd-catalyzed asymmetric decarboxylative protonation reaction was developed by Stoltz to generate tertiary α-alkyl/benzyl ketones. The first report used formic acid, in the presence of molecular sieves, as the proton source to intercept the intermediate generated from a decarboxylative allylation reaction and form a tertiary stereocenter in the α-position with ee's with up to 94%.[24] Subsequently, homogeneous conditions were developed by Stoltz and co-workers using Meldrum's acid as the proton source.[25] Recently, we exploited this methodology for the first catalytic asymmetric synthesis of isoflavanones, a class of tertiary α-aryl ketones, via Pb-mediated arylation to generate **1**, followed by an asymmetric palladium-catalyzed decarboxylative asymmetric protonation to generate the chiral center in **2** (Scheme 1) using modified conditions.[26]

Scheme 1. Catalytic Asymmetric Synthesis of Isoflavanones
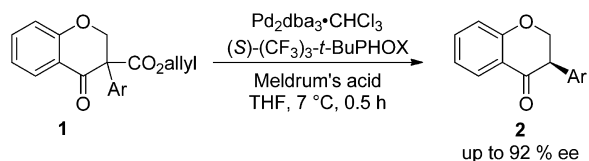

Having applied this methodology to the construction of several non-natural isoflavanones, we achieved the first asymmetric synthesis of naturally occurring isoflavanones sativanone and 3-o-methylviolanone, which feature oxygenation at the 7-position.[27] During the course of this work, we observed an interesting switch in enantioselectivity when the achiral proton source was changed (Scheme 2).

We now wish to expand the scope of this work to the catalytic asymmetric synthesis of tertiary α-aryl cyclohexanones and, in particular, cyclopentanones given the dearth of reported methods for their direct asymmetric synthesis to date. These substrates are readily accessible and would enable us to develop general catalytic conditions that could be applied to more complex systems in the future, in particular those containing ortho-substituted aryls.

■ RESULTS AND DISCUSSION

The synthesis of a series of α-aryl-β-keto allyl esters was accomplished by first preparing cyclopentanone and cyclohexanone β-keto allyl esters **7** and **8** (Scheme 3). This was achieved via Dieckmann condensation of commercially available diallyl adipate using NaH as the base to generate cyclopentanone β-keto allyl ester **7** in 73% yield. Similarly, diallyl pimelate, prepared by transesterification of pimelic acid

Scheme 2. Enantiodivergence Observed with Different H⁺ Sources[a]
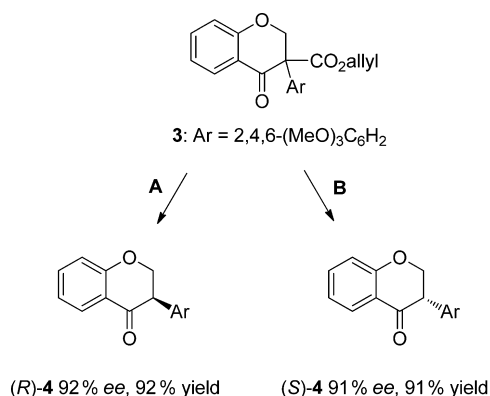
[a] A: Pd₂dba₃·CHCl₃, (S)-(CF₃)₃-t-BuPHOX, Meldrum's acid, THF, 7 °C, 0.5 h. B: Pd(OAc)₂, (S)-(CF₃)₃-t-BuPHOX, formic acid, 4 Å mol. sieves, 1,4-dioxane, 40 °C, 10 h.

Scheme 3. Synthesis of Cyclic β-Keto Allyl Esters
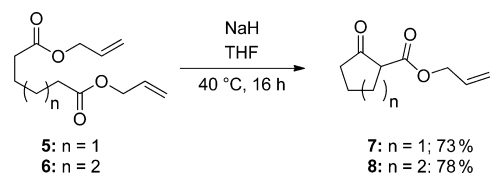
with allyl alcohol, was cyclized in the same manner to yield cyclohexanone β-keto allyl ester **8** in 78% yield over two steps using a previously reported method.[28]

The next step was to generate a series of α-aryl-β-keto allyl esters from the cyclopentanone and cyclohexanone β-keto allyl esters. This could be achieved by the use of aryllead triacetates under relatively mild conditions of 40 °C in the presence of pyridine. These reagents have shown a remarkable ability for the α-arylation of β-keto esters, particularly impressive is their ability to introduce sterically bulky aryl groups generating a quaternary center in very high yields.[26,29]

A total of 11 aryllead triacetates were prepared according to previously reported methods.[26] We chose a number of sterically demanding, electron-rich aryl groups as we knew from our previous report that this was important to achieve reasonable levels of enantioinduction.[26] These were successfully used in the arylation of the cyclopentanone and cyclohexanone β-keto allyl esters in moderate to excellent yields, with the exception of the 2,6-dimethylphenyl group. The aryl groups utilized and the yields for the various α-arylation reactions are summarized in Table 1.

We chose the cyclopentanone α-aryl-β-keto allyl ester (**9a**) bearing a 2,4,6-trimethoxyphenyl group as the model substrate to assess the viability of our previously optimized conditions for the Pd-catalyzed decarboxylative asymmetric protonation protocol on these types of substrates (Table 2). Thus, we attempted the reaction using Pd₂dba₃·CHCl₃, (S)-(CF₃)₃-t-BuPHOX as the chiral P,N-ligand, and Meldrum's acid as the proton source at 7 °C in THF (Table 2, entry 1). Promisingly, the reaction went with full conversion, although the level of enantioselectivity was poor at 28% ee. We then lowered the temperature to −20 °C, and surprisingly, this led to formation of the opposite enantiomer (R) of tertiary α-aryl cyclopentanone **11a**, albeit with low enantioselectivity and

Table 1. Synthesis of α-Aryl-β-keto Allyl Esters

substrate	Ar	yield (%) 9	yield (%) 10
a	2,4,6-(MeO)$_3$C$_6$H$_2$	80	60
b	2,4-(MeO)$_2$C$_6$H$_3$	77	90
c	2,6-(MeO)$_2$C$_6$H$_3$	84	61
d	2,3,4-(MeO)$_3$C$_6$H$_2$	91	94
e	2,3,6-(MeO)$_3$C$_6$H$_2$	91	85
f	4-MeOC$_6$H$_4$	61	92
g	2-MeOC$_{10}$H$_6$	62	89
h	3,4−(OCH$_2$O)−C$_6$H$_3$	89	86
i	2-BnOC$_{10}$H$_6$	67	79
j	2-MeO-4,6-Me$_2$C$_6$H$_2$	90	90
k	2,6-Me$_2$C$_6$H$_3$	36	n.d.[a]

[a]n.d. = not determined; due to poor yield for arylation and moderate *ee* for the same aryl group in the cyclopentanone series.

Table 2. Optimization of Conditions for the Decarboxylative Asymmetric Protonation[l]

entry	solvent	T (°C)	conv. (%)[a]	ee (%)[b]
1	THF	7	100	28
2	THF	−20	18	20 (R)
3	toluene	−20	60	10 (R)
4	THF	23	100(61)	36
5	1,4-dioxane	23	100(69)	51
6	2-Me-THF	23	100(61)	26
7	toluene	23	100	42
8	Et$_2$O	23	100	17
9	1,4-dioxane	40	100	75
10	**THF**	**40**	**100(91)**	**82 (1.5 h)**
11	THF	30	100	82 (19 h)
12	THF	50	100	73
13	2:1 THF/benzene	40	100	58
14[c]	THF	40	100	62
15[d]	THF	40	100	81
16[e]	THF	40	100	76
17[f]	THF	40	100	70
18[g]	THF	40	100	80
19[h]	THF	40	100	70
20[i]	THF	40	100	74
21[j]	THF	40	100	73
22[k]	THF	40	100	8

[a]% conversion determined by chiral HPLC analysis. Yields in parentheses. [b]% ee values determined by chiral SFC analysis. [c]Using commercial Pd$_2$dba$_3$. [d]1.0 equiv of Meldrum's acid. [e]5.0 equiv of Meldrum's acid. [f]0.025 M THF. [g]0.10 M THF. [h]Meldrum's acid added during complex formation. [i]Meldrum's acid/substrate solution added dropwise. [j]0.10 M THF, 1 equiv of Meldrum's acid. [k]Using (S)-t-BuPHOX. [l]Reactions carried out with 5 mol % Pd$_2$dba$_3$·CHCl$_3$ and 12.5 mol % ligand in 0.20 M substrate concentration unless otherwise stated.

conversion (Table 2, entries 2 and 3). Carrying out the reaction at 23 °C increased the *ee* slightly to 36% of the (S)-enantiomer (Table 2, entry 4). A number of solvents were then screened with 1,4-dioxane, leading to an increase in enantioselectivity up to 51% *ee* (Table 2, entry 5). Encouraged by this, we decided to increase the temperature to 40 °C as we had seen a slight increase going from 7 to 23 °C. This resulted in further increase in enantioinduction up to 75% *ee* (Table 2, entry 9). We then re-examined THF at this higher temperature, and this further increased the *ee* to 82% with a yield of 91% (Table 2, entry 10). For completeness, we carried out the reaction at 30 °C and achieved the same level of enantioselectivity, albeit with a longer reaction time (Table 2, entry 11). At 50 °C, the *ee* drops to 73%, possibly due to the instability of the catalyst at this elevated temperature (Table 2, entry 12).

Further attempts were made to improve the level of enantioselectivity. Surprisingly, using only 1.0 equiv of Meldrum's acid did not result in the formation of the competitive allylation product and had no effect on the enantioselectivity (Table 2, entry 14). Increasing this to 5.0 equiv had a detrimental effect on the enantioselectivity (Table 2, entry 15). To ensure complete protonation for both the cyclopentanone and cyclohexanone motifs with the various aryl groups, we chose to use 2.5 equiv of Meldrum's acid in the optimized conditions. Forming the complex in the presence of Meldrum's acid also had a negative effect on enantioselectivity (Table 2, entry 19), as did the slow addition of the solution of Meldrum's acid/substrate solution (Table 2, entry 20). Also, decreasing the concentration of THF lowered the *ee*, whereas increasing the concentration did not have a significant effect (Table 2, entries 17 and 18, respectively). The optimum conditions chosen were in THF (1.5 mL for 0.15 mmol) at 40 °C with a one-portion addition of the substrate and Meldrum's acid (2.5 equiv).

It is worth noting that, during the course of optimization of the reaction conditions, we found that the *ee* values would slowly increase over time when the reaction was carried out at 23 and 7 °C despite complete reaction of all of the starting material upon initial sampling of the reaction. The level of increase in *ee* observed was significantly greater than 10%, suggesting that the intermediate is not a monomeric Pd-bound species. A previous report by Stoltz and co-workers suggested that the reaction proceeded via a ligand-bound Pd-enolate complex.[25] For example, in Table 2, entry 19, the *ee* after 30 min was 30% with no starting material remaining. When this was sampled after 2 h, the *ee* had increased to 70% and was unchanged thereafter. Previous work carried out during the development of conditions for the catalytic asymmetric synthesis of isoflavanones showed a similar trend.[30] During the course of that study, we showed that the process was not dynamic; i.e., the protonated product was not deprotonated under the reaction conditions. This led us to the conclusion that a long-lived intermediate was being slowly protonated over time. We believed that, when the reaction was sampled for chromatographic analysis, this intermediate was quenched on silica. In order to prove this, we carried out the reaction where we replaced Meldrum's acid with silica gel, and this resulted in formation of the racemic protonated product in 78% yield. Unfortunately, we have been unable to establish a potential structure for this postulated intermediate.

This observed increase in *ee* over time might explain why, in the case of the cyclopentanone substrate, the level of enantioselectivity increased as the temperature was increased.

At temperatures lower than 30 °C, the intermediate may not have enough reactivity to be asymmetrically protonated by Meldrum's acid, and hence, the lower *ee* value could be more truly viewed as a lower conversion. It should also be noted that this process is difficult to observe when the THF used for the reaction is of high purity with the asymmetrically protonated product formed in as little as 30 min. The use of dry, degassed, and peroxide-free THF is crucial to obtaining good, reproducible levels of enantioselectivity in this reaction.

An example of the importance of the solvent purity was the formation of an unexpected impurity during the first few attempts at this reaction. The formation of lactone **12c**, albeit in low yields, is likely to have resulted from oxygen insertion (Scheme 4).[31] The only reasonable source of this is dissolved

**Scheme 4. Proposed Mechanism for the Formation of Lactone 12c**
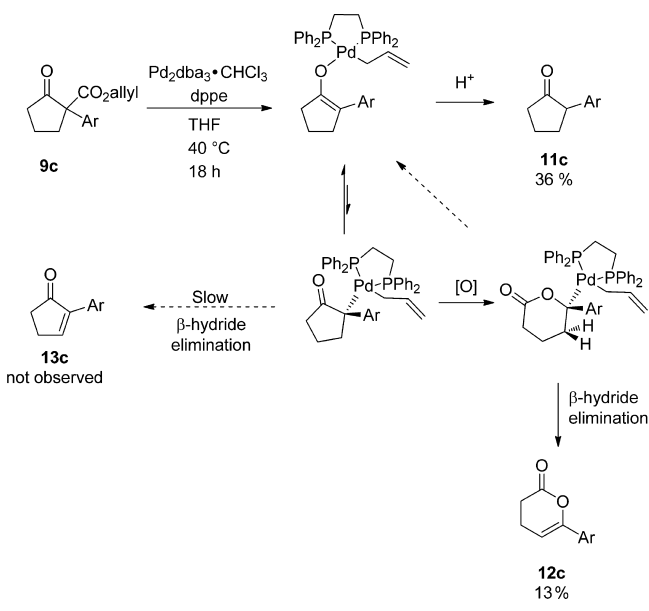
oxygen in the solvent THF or peroxides. It should be noted that this impurity was generated when a Na/benzophenone still was used. The still, however, was freshly setup and had not been refluxed for a sufficient time to allow complete degassing of the solvent, evident by the deep blue color, which indicates that the THF is relatively dry; however, a deep purple color indicates that the solvent is also degassed. Perhaps the most significant observation in the formation of this impurity is the unsaturation of the lactone. This is potentially as a result of β-hydride elimination from a carbopalladated species. Against this argument would be the lack of a detectable quantity of cyclopentanone **13c** in any of the reactions carried out. It is perhaps plausible that there may be equilibrium between a carbopalladated species and a Pd-enolate, which may account for the observed product distribution (Scheme 5). In order to investigate this further, we synthesized a cyclopentanone substrate that contained a *gem*-dimethyl substituent in the β-position (Scheme 6).[32] An alkene product, as observed in the formation of **13c**, is not possible with this substrate due to the absence of a β-hydrogen. We have previously exploited this approach in our use of 2,2-dimethyl-2,3-dihydrofuran as a substrate in intermolecular asymmetric Heck reactions to afford one regioisomeric product.[33] We did not observe the formation of a lactone byproduct with this substrate. We, subsequently,

Scheme 5. β-*gem*-Dimethyl Substituted Cyclopentanone Analogue
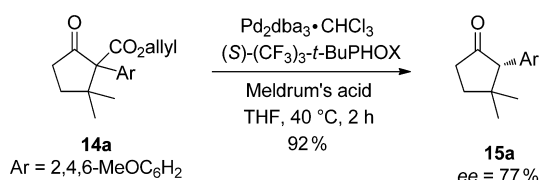
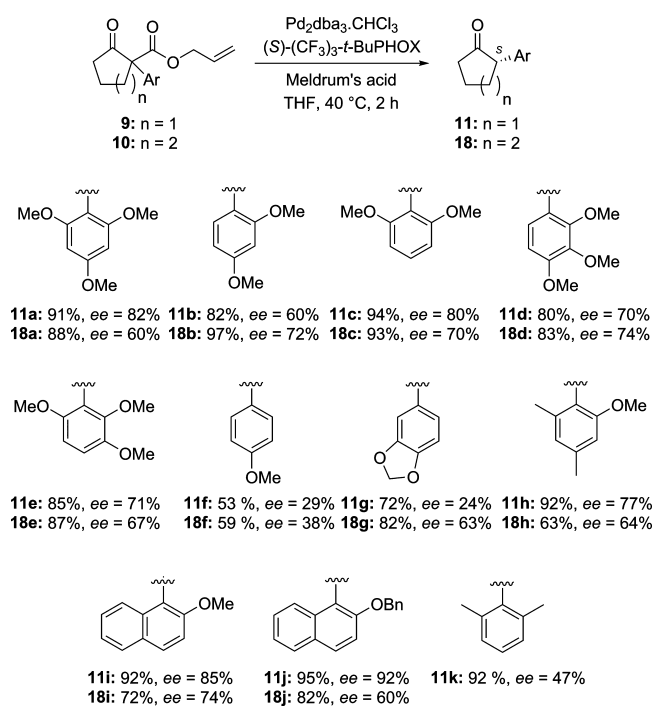**Scheme 6. Formation of Byproduct of Pd₂dba₃ and Meldrum's Acid**
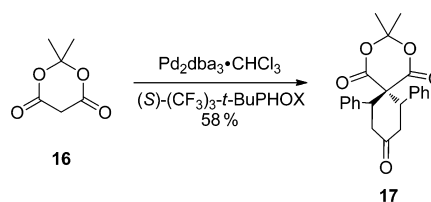
concluded that degassed and peroxide-free THF prevented the formation of lactone **12c**.

Another minor byproduct was also formed during this study due to a side reaction between dibenzylideneacetone, a ligand from the Pd⁰ precursor, and Meldrum's acid in the presence of (S)-(CF₃)₃-*t*-BuPHOX (Scheme 6). The double Michael addition of Meldrum's acid to dba formed spirocyclic compound **17**, which is a known reaction, but has not been reported as a byproduct from Pd₂dba₃.[34]

We then subjected the collection of cyclopentanone and cyclohexanone substrates to the optimized reaction conditions, and the enantioselectivities obtained are summarized in Scheme 7. The highest level of enantioselectivity was observed for the bulky 2-benzyloxynaphthyl substituted cyclopentanone substrate (**11j**, 92% *ee*). This high *ee* was unfortunately not

Scheme 7. Scope and Enantioselectivity of Tertiary α-Aryl Cyclopentanones and Cyclohexanones

11a: 91%, *ee* = 82%   **11b:** 82%, *ee* = 60%   **11c:** 94%, *ee* = 80%   **11d:** 80%, *ee* = 70%
18a: 88%, *ee* = 60%   **18b:** 97%, *ee* = 72%   **18c:** 93%, *ee* = 70%   **18d:** 83%, *ee* = 74%

11e: 85%, *ee* = 71%   **11f:** 53 %, *ee* = 29%   **11g:** 72%, *ee* = 24%   **11h:** 92%, *ee* = 77%
18e: 87%, *ee* = 67%   **18f:** 59 %, *ee* = 38%   **18g:** 82%, *ee* = 63%   **18h:** 63%, *ee* = 64%

11i: 92%, *ee* = 85%   **11j:** 95%, *ee* = 92%   **11k:** 92 %, *ee* = 47%
18i: 72%, *ee* = 74%   **18j:** 82%, *ee* = 60%

transferred to the cyclohexanone substrate (**18j**), which had a more moderate *ee* of 60%. In most cases, the cyclopentanone substrates resulted in a higher level of enantioinduction compared to their cyclohexanone counterpart. The best *ee* achieved in the cyclohexanone series was 74% for both the 2,3,4-trimethoxyphenyl and the 2-methoxynaphthyl substituents, **18d** and **18i**, respectively. The tertiary α-aryl ketones were obtained in moderate to excellent yields, particularly given the scale of the reactions. In line with our previous report, the presence of substitution in the ortho position of the aryl group is crucial to achieve reasonable levels of stereoselectivity. For example, the 4-methoxyphenyl group gave low *ee* values of 29% and 38% for the cyclopentanone and cyclohexanone substrates, **11f** and **18f**, respectively. It should also be noted the importance of the presence of an oxygen-containing substituent, as evidenced by the drop in enantioselectivity for the 2,6-dimethylphenyl substituted cyclopentanone (**11k**) to 47% ee. Comparatively, the 2-methoxy-4,6-dimethylphenyl group (**11h**) gave a much higher *ee* of 77% on the cyclopentanone substrate. This is likely due to an interaction between the oxygen of the methoxy group and the palladium center. The presence of steric bulk in the β-position had little effect on the level of enantioselectivity, as observed with the β-*gem*-dimethyl substituted cyclopentanone analogue (**15a**, Scheme 5). With a 2,4,6-trimethoxyphenyl group, an *ee* of 77% was observed compared to 82% in the absence of substitution in the β-position.

As noted earlier, a switch in enantioselectivity was observed for isoflavanone substrate **2** when the proton source was switched to formic acid. The heterogeneous reaction conditions, also developed by Stoltz and co-workers,[24] were applied to the cyclopentanone and cyclohexanone substrates to ascertain if we would observe a similar switch in enantioselectivity with these substrates (Scheme 8). The results obtained

Scheme 8. Scope of the Switch in Enantioselectivity Using Formic Acid
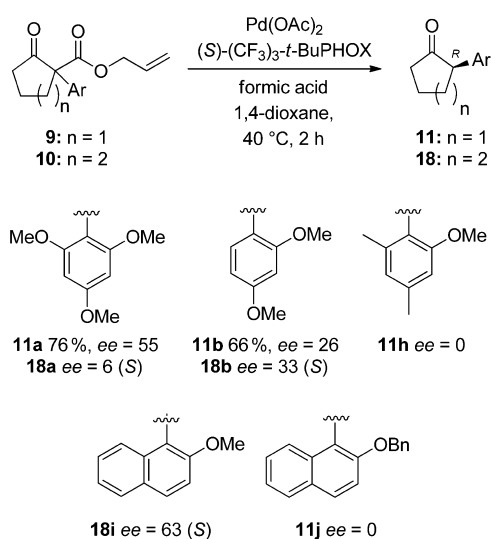
products resulting from the three cyclohexanone substrates screened (**11a**, **11b**, and **11i**) were formed in moderate to good enantioselectivities, however, preferentially forming the same enantiomer as when Meldrum's acid was used. This goes to underlie the apparent mechanistic differences when using an oxo-acid, formic acid, compared to a carbon acid, Meldrum's acid. It also shows how subtle the interactions are between the substrate, catalyst, and proton source given the large changes in selectivity observed. Attempts to understand the differences between these two mechanisms are currently under investigation, and any significant results will be reported in due course.

CONCLUSION

In conclusion, we have described the catalytic asymmetric synthesis of a series of tertiary α-aryl cyclopentanones and cyclohexanones. This offers a new route to access these important structural motifs with moderate to good levels of enantioselectivity. This is only the second report of the direct catalytic asymmetric synthesis of tertiary α-aryl cyclopentanones. A major advantage of this methodology is the ability to insert a number of different aryl groups prior to the enantiodetermining step by Pb-mediated arylation of a β-keto allyl ester. In particular, this allows the insertion of bulky aryl groups where the new stereocenter is generated. Furthermore, the conditions developed for the decarboxylative asymmetric protonation reaction achieved good levels of enantioselectivity for mono- and di-ortho-substituted aryl groups.

EXPERIMENTAL SECTION

Materials and Methods. Unless otherwise noted, reactions were performed with rigorous exclusion of air and moisture, under an inert atmosphere of nitrogen in flame-dried glassware with magnetic stirring. N_2-flushed stainless steel cannulas or plastic syringes were used to transfer air- and moisture-sensitive reagents. All reagents were obtained from commercial sources and used without further purification unless otherwise stated. Anhydrous tetrahydrofuran (THF) and dichloromethane were obtained from a dry solvent dispenser with activated alumina columns. All other anhydrous solvents were obtained from commercial sources and used as received. For stated reactions, THF was freshly distilled under N_2 from sodium/benzophenone ketyl. Anhydrous 1,4-dioxane was purchased from Sigma-Aldrich and dried over molecular sieves (3 Å beads, 20 g/100 mL for 3 days). Pd(OAc)$_2$ was purchased from Strem. Powdered activated 4 Å molecular sieves were purchased from Sigma-Aldrich and were stored in a desiccator. Tris(dibenzylideneacetone)dipalladium(0) chloroform adduct was prepared via the method of Zalesskiy et al.[35] *In vacuo* refers to the evaporation of solvent under reduced pressure on a rotary evaporator. Thin-layer chromatography (TLC) was performed on aluminum plates precoated with silica gel F254. They were visualized with UV-light (254 nm) fluorescence quenching, or by charring with an acidic vanillin solution (vanillin, H_2SO_4 in ethanol). Flash column chromatography was carried out using 40−63 μm, 230−400 mesh silica gel.

Instrumentation. ^{1}H NMR spectra were recorded on a 300, 400, 500, or 600 MHz spectrometer. ^{13}C NMR spectra were recorded on a 400, 500, or 600 MHz spectrometer at 101, 126, or 151 MHz, respectively. Chemical shifts (δ) are reported in parts per million (ppm) downfield from tetramethylsilane and are referenced to residual proton in the NMR solvent (CDCl$_3$ = δ 7.26 ppm, (CD$_3$)$_2$CO = δ 2.05 ppm). ^{13}C NMR are referenced to the residual solvent peak (CDCl$_3$ = δ 77.16 ppm, (CD$_3$)$_2$CO = δ 206.26 ppm). All ^{13}C spectra are ^{1}H decoupled. NMR data are represented as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = double doublet, m = multiplet, app. dd, = apparent doublet of doublets, app. t, = apparent triplet), coupling constant (*J*) in hertz

showed that only two of the cyclopentanone substrates demonstrated a switch in the sense of enantioinduction with *ee*'s of 55% and 26% (*R*) for the 2,4,6-trimethoxyphenyl and 2,4-dimethoxyphenyl substrates **11a** and **11b**, respectively. Both the 2-methoxy-4,6-dimethylphenyl and 2-benzyloxynaphthyl substrates, **11h** and **11j**, formed only racemic products. The

(Hz), integration. High-resolution mass spectra [electrospray ionization (ESI-TOF)] (HRMS) were measured on a time-of-flight mass spectrometer with leucine enkephalin (Tyr-Gly-Phe-Leu) as an internal lock mass. Infrared spectra were recorded on an FT-IR spectrometer and are reported in terms wavenumbers (ν_{max}) with units of reciprocal centimeters (cm^{-1}). Optical rotation (α) values were measured at room temperature, and specific rotation ($[\alpha]_D^{20}$) values are given in degrees (deg). Melting points were determined in open capillary tubes. Supercritical fluid chromatography (SFC) was performed using a Chiralcel-IA3, IB3, IC3, or ID3 column.

Allyl 2-Oxocyclopentanecarboxylate (7).[28] NaH (793 mg, 19.84 mmol, 60% dispersion in mineral oil) was suspended in anhydrous THF (15 mL) in a flame-dried Schlenk flask. Diallyl adipate (1) (4.0 mL, 18.04 mmol) in THF (3 mL) was added dropwise to the stirred suspension, and the reaction mixture was stirred at 40 °C for 16 h. The reaction mixture was allowed to cool to room temperature, quenched by the slow addition of 1 M HCl (20 mL), and extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with brine (100 mL) and dried over anhydrous Na$_2$SO$_4$. The solvent was removed *in vacuo*, and the resulting oil was purified by silica gel column chromatography (20% EtOAc in pentane) to yield the product as a pale pink oil (2.21 g, 73%). ^{1}H NMR (300 MHz, CDCl$_3$, mixture of keto and enol tautomers; 90% keto): δ 10.34 (s, 0.1H, enol), 5.92 (ddt, J = 17.2, 10.4, 5.6 Hz, 1H), 5.34 (dq, J = 17.2, 1.5 Hz, 1H), 5.24 (dq, J = 10.4, 1.5 Hz, 1H), 4.71−4.58 (m, 2H), 3.19 (t, J = 9.2 Hz, 1H), 2.58−2.48 (m, 0.3H), 2.37−2.25 (m, 4H), 2.22−2.08 (m, 1H), 1.97−1.80 (m, 1H). All other physical data were identical to those previously reported.[36]

Allyl 2,2-Dimethyl-5-oxocyclopentanecarboxylate (21).[37] β-Keto methyl ester (20) (500 mg, 2.94 mmol), which was synthesized according to a previously reported method,[38] was suspended in toluene (5 mL) and 3 Å molecular sieves (500 mg). Allyl alcohol (0.60 mL, 8.81 mmol) and DMAP (538 mg, 4.41 mmol) were successively added, and the reaction mixture was heated to reflux and stirred for 14 h. The reaction mixture was allowed to cool to room temperature, quenched by the slow addition of 1 M HCl (5 mL), and extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine (40 mL) and dried over anhydrous Na$_2$SO$_4$. The solvent was removed *in vacuo*, and the resulting oil was purified by silica gel column chromatography (20% EtOAc in pentane) to yield the product as a colorless oil (311 mg, 54%). R_f = 0.38 (40% Et$_2$O in pentane); IR (thin film) ν_{max} 2963, 1735, 1726 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$, mixture of keto and enol tautomers, keto ≈85%): δ 10.70 (s, 0.15H), 5.98−5.82 (m, 1H), 5.36−5.27 (m, 1H), 5.25−5.19 (m, 1H), 4.65−4.55 (m, 2H), 2.90 (s, 1H), 2.52−2.33 (m, 2H), 2.04−1.94 (m, 1H), 1.80−1.71 (m, 1H), 1.19 (s, 3H), 1.08 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ 212.9, 168.5, 131.9, 118.9, 65.8, 65.6, 41.0, 36.8, 36.1, 29.1, 24.1

General Procedure for the Preparation of α-Aryl-β-keto Allyl Esters (9 and 10). Aryllead triacetate (1.2 equiv) and β-keto allyl ester (1.0 equiv, X) were dissolved in anhydrous CHCl$_3$ (10X) in a flame-dried Schlenk flask. Anhydrous pyridine (3.6 equiv) was added dropwise, and the reaction mixture was stirred at 40 °C for 18 h. The reaction mixture was then filtered through Celite to remove Pb(OAc)$_2$ precipitate and washed with CHCl$_3$ (30X). The filtrate was transferred to a separatory funnel and washed twice with 3 M H$_2$SO$_4$ (40X) with vigorous shaking to quench unreacted aryllead triacetate. The aqueous layers were re-extracted with CHCl$_3$ (40X), and the combined organic layers were washed with water (60X), dried over anhydrous Na$_2$SO$_4$, and filtered. The solvent was removed *in vacuo*, and the resulting oil was purified by silica gel column chromatography (pentane/Et$_2$O or EtOAc).

Allyl 2,2-Dimethyl-5-oxo-1-(2,4,6-trimethoxyphenyl)cyclopentanecarboxylate (14a). The title compound was prepared according to the general procedure using β-keto allyl ester (21) (291 mg, 1.48 mmol) and 2,4,6-trimethoxyphenyllead triacetate (979 mg, 1.78 mmol) to yield the product as a white solid (439 mg, 82%). R_f = 0.22 (40% Et$_2$O in pentane); IR (thin solid film) ν_{max} 2940, 1748, 1715, 1608 cm^{-1}; M.P. = 92−93 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 6.10 (s, 2H), 5.82 (ddt, J = 17.2, 10.5, 5.8 Hz, 1H), 5.22−5.15 (m,

1H), 5.15−5.07 (m, 1H), 4.56 (ddt, J = 13.2, 5.8, 1.4 Hz, 1H), 4.45 (ddt, J = 13.2, 5.9, 1.4 Hz, 1H), 3.78 (s, 3H), 3.65 (s, 6H), 2.71 (ddd, J = 20.0, 14.8, 9.3 Hz, 1H), 2.45−2.34 (m, 2H), 1.72−1.63 (m, 1H), 1.41 (s, 3H), 0.83 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ 211.9, 169.1, 160.4, 159.5, 158.3, 132.6, 117.8, 109.8, 92.0, 91.9, 68.6, 65.8, 55.6, 55.4, 55.2, 45.9, 37.4, 35.3, 27.1, 25.2; HRMS: (ESI-TOF) calculated for C$_{20}$H$_{26}$O$_6$Na [M + Na$^+$] 385.1627, found 385.1614.

Allyl 2-Oxo-1-(2,4,6-trimethoxyphenyl)cyclopentanecarboxylate (9a). The title compound was prepared according to the general procedure using β-keto allyl ester (7) (600 mg, 3.57 mmol) and 2,4,6-trimethoxyphenyllead triacetate (2.361 g) to yield the product as a white solid (951 mg, 80%). R_f = 0.15 (40% Et$_2$O in pentane); IR (thin solid film) ν_{max} 2942, 1748, 1722, 1608, 1588 cm^{-1}; M.P. = 74−75 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 6.10 (s, 2H), 5.93−5.80 (m, 1H), 5.28−5.20 (m, 1H), 5.16−5.11 (m, 1H), 4.67−4.54 (m, 2H), 3.77 (s, 3H), 3.67 (s, 6H), 2.98−2.87 (m, 1H), 2.61−2.50 (m, 1H), 2.33−2.21 (m, 1H), 2.10−1.92 (m, 2H), 1.91−1.79 (m, 1H); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ 212.8, 170.7, 160.5, 158.1, 132.5, 117.9, 112.1, 92.2, 66.1, 61.4, 55.9, 55.5, 38.7, 36.0, 20.4; HRMS: (ESI-TOF) calculated for C$_{18}$H$_{22}$O$_6$Na [M + Na$^+$] 357.1314, found 357.1326.

Allyl 1-(2,4-Dimethoxyphenyl)-2-oxocyclopentanecarboxylate (9b). The title compound was prepared according to the general procedure using β-keto allyl ester (7) (250 mg, 1.49 mmol) and 2,4-dimethoxyphenyllead triacetate (932 mg, 1.79 mmol) to yield the product as a white solid (349 mg, 77%). R_f = 0.30 (40% Et$_2$O in pentane); IR (thin solid film) ν_{max} 2958, 1751, 1724, 1613 cm^{-1}; M.P. = 74−76 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 6.85 (d, J = 8.5 Hz, 1H), 6.46 (d, J = 2.5 Hz, 1H), 6.41 (dd, J = 8.5, 2.5 Hz, 1H), 5.91−5.79 (m, 1H), 5.24 (dd, J = 17.2, 1.6 Hz, 1H), 5.17 (dd, J = 10.5, 1.3 Hz, 1H), 4.71−4.56 (m, 2H), 3.78 (s, 3H), 3.73 (s, 3H), 2.91 (dt, J = 13.5, 6.8 Hz, 1H), 2.46 (t, J = 7.5 Hz, 2H), 2.29 (dt, J = 13.4, 6.8 Hz, 1H), 2.06−1.94 (m, 1H), 1.90−1.78 (m, 1H); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ 214.1, 170.4, 160.4, 157.8, 132.1, 128. 1, 121.1, 118.3, 104.0, 99.9, 66.2, 64.3, 55.5, 55.5, 38.7, 35.4, 19.9; HRMS: (ESI-TOF) calculated for C$_{17}$H$_{20}$O$_5$Na [M + Na$^+$] 327.1208, found 327.1197.

Allyl 1-(2,6-Dimethoxyphenyl)-2-oxocyclopentanecarboxylate (9c). The title compound was prepared according to the general procedure using β-keto allyl ester (7) (320 mg, 1.90 mmol) and 2,6-dimethoxyphenyllead triacetate (932 mg, 1.79 mmol) to yield the product as a white solid (511 mg, 88%). R_f = 0.32 (40% Et$_2$O in pentane); IR (thin solid film) ν_{max} 2957, 1750, 1723, 1613 cm^{-1}; M.P. = 74−75 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.18 (t, J = 8.3 Hz, 1H), 6.54 (d, J = 8.3 Hz, 1H), 5.93−5.80 (m, 1H), 5.23 (dd, J = 17.2, 1.4 Hz, 1H), 5.14 (dd, J = 10.5, 1.4 Hz, 1H), 4.67−4.56 (m, 2H), 3.70 (s, 6H), 2.97 (ddd, J = 13.3, 8.4, 6.8 Hz, 1H), 2.65−2.54 (m, 1H), 2.35−2.23 (m, 1H), 2.14−1.95 (m, 2H), 1.94−1.81 (m, 1H); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ 212. 6, 170.5, 157.5, 132.5, 128.7, 119.6, 117.9, 105.6, 66.2, 61.6, 55.9, 38.7, 35.9, 20.5; HRMS: (ESI-TOF) calculated for C$_{17}$H$_{20}$O$_5$Na [M + Na$^+$] 327.1208, found 327.1201.

Allyl 2-Oxo-1-(2,3,4-trimethoxyphenyl)cyclopentanecarboxylate (9d). The title compound was prepared according to the general procedure using β-keto allyl ester (7) (250 mg, 1.49 mmol) and 2,3,4-trimethoxyphenyllead triacetate (986 mg, 1.79 mmol) to yield the product as a white solid (453 mg, 91%). R_f = 0.27 (40% Et$_2$O in pentane); IR (thin solid film) ν_{max} 2947, 1753, 1724 cm^{-1}; M.P. = 50−52 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 6.62 (d, J = 8.7 Hz, 1H), 6.53 (d, J = 8.7 Hz, 1H), 5.93−5.79 (m, 1H), 5.25 (dq, J = 17.2, 1.5 Hz, 1H), 5.17 (dq, J = 10.4, 1.5 Hz, 1H), 4.70−4.57 (m, 2H), 3.80 (s, 6H), 3.78 (s, 3H), 2.92−2.82 (m, 1H), 2.48−2.39 (m, 2H), 2.23 (ddd, J = 13.0, 8.2, 6.9 Hz, 1H), 2.03−1.83 (m, 2H); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ 213.3, 170.0, 153.5, 151.2, 142.2, 131.8, 126.0, 122.0, 118.5, 106.3, 66.2, 64.5, 60.5, 60.0, 56.0, 38.2, 36.2, 19.8; HRMS: (ESI-TOF) calculated for C$_{18}$H$_{22}$O$_6$Na [M + Na$^+$] 357.1314, found 357.1310.

Allyl 2-Oxo-1-(2,3,6-trimethoxyphenyl)cyclopentanecarboxylate (9e). The title compound was prepared according to the general procedure using β-keto allyl ester (7) (250 mg, 1.49 mmol) and 2,3,6-trimethoxyphenyllead triacetate (986 mg, 1.79 mmol) to yield the product as a colorless oil (454 mg, 91%). R_f = 0.23 (40% Et$_2$O in pentane); IR (thin film) ν_{max} 2944, 1746, 1724 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$): δ 6.78 (d, J = 8.9 Hz, 1H), 6.56 (d, J = 8.9 Hz, 1H),

5.88 (ddt, J = 17.2, 10.5, 5.5 Hz, 1H), 5.25 (dq, J = 17.2, 1.5 Hz, 1H), 5.15 (dq, J = 10.5, 1.5 Hz, 1H), 4.71−4.57 (m, 2H), 3.81 (s, 3H), 3.68 (s, 3H), 3.65 (s, 3H), 2.93 (ddd, J = 13.0, 9.6, 6.5 Hz, 1H), 2.62 (dddd, J = 18.1, 8.5, 4.87, 1.8 Hz, 1H), 2.26 (dt, J = 18.1, 8.5 Hz, 1H), 2.13 (dddd, J = 13.0, 6.5, 4.7, 1.8 Hz, 1H), 2.02−1.93 (m, 1H), 1.90−1.78 (m, 1H); ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$): δ 211.6, 170.3, 151.0, 147.0, 147.0, 132.4, 125.2, 117.5, 111.3, 110.0, 106.4, 66.0, 62.1, 59.9, 56.1, 55.8, 38.5, 36.0, 20.1; HRMS: (ESI-TOF) calculated for C$_{18}$H$_{22}$O$_6$Na [M + Na$^+$] 357.1314, found 357.1305.

Allyl 1-(4-Methoxyphenyl)-2-oxocyclopentanecarboxylate (9f). The title compound was prepared according to the general procedure using β-keto allyl ester (7) (250 mg, 1.49 mmol) and 4-methoxyphenyllead triacetate (879 mg, 1.79 mmol) to yield the product as a colorless oil (247 mg, 61%). R$_f$ = 0.41 (40% Et$_2$O in pentane); IR (thin film) ν_{max} 2957, 1749, 1730 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.36−7.32 (m, 2H), 6.90−6.86 (m, 2H), 5.88−5.78 (m, 1H), 5.22 (dq, J = 17.2, 1.4 Hz, 1H), 5.18 (dq, J = 10.5, 1.4 Hz, 1H), 4.60 (dt, J = 5.5, 1.4 Hz, 2H), 3.78 (s, 3H), 2.89−2.80 (m, 1H), 2.58−2.43 (m, 2H), 2.38−2.30 (m, 1H), 2.06−1.87 (m, 2H); ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$): δ 212.0, 170.6, 159.1, 131.5, 128.6, 127.6, 118.3, 113.9, 66.1, 64.2, 55.2, 37.6, 34.7, 19.3; HRMS: (ESI-TOF) calculated for C$_{16}$H$_{18}$O$_4$Na [M + Na$^+$] 297.1103, found 297.1100.

Allyl 1-(2-Methoxynaphthalen-1-yl)-2-oxocyclopentanecarboxylate (9g). The title compound was prepared according to the general procedure using β-keto allyl ester (7) (250 mg, 1.49 mmol) and 2-methoxynaphthyllead triacetate (968 mg, 1.79 mmol) to yield the product as a white solid (303 mg, 62%). R$_f$ = 0.32 (40% Et$_2$O in pentane); IR (thin solid film) ν_{max} 2948, 1744, 1716 cm^{-1}; M.P. = 83−85 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.81−7.74 (m, 2H), 7.54 (d, J = 8.7 Hz, 1H), 7.45−7.36 (m, 1H), 7.39−7.30 (m, 1H), 7.22 (d, J = 9.0 Hz, 1H), 5.66 (ddt, J = 17.3, 10.0, 5.6 Hz, 1H), 5.08−4.97 (m, 2H), 4.63−4.51 (m, 2H), 3.76 (s, 3H), 3.19 (ddd, J = 13.0, 11.2, 6.7 Hz, 1H), 2.73 (dddd, J = 18.0, 8.4, 3.3, 2.1 Hz, 1H), 2.48−2.31 (m, 2H), 2.12−2.02 (m, 1H), 1.94−1.79 (m, 1H); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ 211.8, 172.4, 154.0, 132.6, 131.8, 130.9, 130.2, 129.1, 126.7, 124.0, 123.9, 123.8, 118.1, 116.0, 66.5, 63.9, 57.3, 57.3, 39.0, 36.7, 20.5; HRMS: (ESI-TOF) calculated for C$_{20}$H$_{20}$O$_4$Na [M + Na$^+$] 347.1259, found 347.1265.

Allyl 1-(Benzo[d][1,3]dioxol-5-yl)-2-oxocyclopentanecarboxylate (9h).[39] The title compound was prepared according to the general procedure using β-keto allyl ester (7) (250 mg, 1.49 mmol) and 3,4-methylenedioxyphenyllead triacetate (902 mg, 1.79 mmol) to yield the product as a colorless oil (382 mg, 89%). R$_f$ = 0.45 (40% Et$_2$O in pentane); IR (thin film) ν_{max} 2890, 1751, 1730 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$): δ 6.94 (d, J = 1.9 Hz, 1H), 6.84 (dd, J = 8.2, 1.9 Hz, 1H), 6.76 (d, J = 8.2 Hz, 1H), 5.92 (q, J = 1.5 Hz, 2H), 5.83 (ddt, J = 17.2, 10.5, 5.5 Hz, 1H), 5.23 (dq, J = 17.2, 1.5 Hz, 1H), 5.18 (dq, J = 10.5, 1.5 Hz, 1H), 4.59 (dt, J = 5.5, 1.5 Hz, 2H), 2.86−2.78 (m, 1H), 2.52−2.42 (m, 2H), 2.38−2.28 (m, 1H), 2.03−1.87 (m, 2H); ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$): δ 211.6, 170.4, 147.1, 147.1, 131.5, 129.4, 120.7, 118.4, 108.3, 108.1, 101.2, 66.2, 64.4, 37.6, 34.9, 19.2; HRMS: (ESI-TOF) calculated for C$_{16}$H$_{16}$O$_5$Na [M + Na$^+$] 311.0895, found 311.0903.

Allyl 1-(2-(Benzyloxy)naphthalen-1-yl)-2-oxocyclopentanecarboxylate (9i). The title compound was prepared according to the general procedure using β-keto allyl ester (7) (250 mg, 1.49 mmol) and 2-benzyloxynaphthyllead triacetate (1.104 g, 1.79 mmol) to yield the product as a white solid (399 mg, 67%). R$_f$ = 0.56 (40% Et$_2$O in pentane); IR (thin solid film) ν_{max} 2948, 1743, 1715 cm^{-1}; M.P. = 121−123 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.79 (dd, J = 8.0, 1.5 Hz, 1H), 7.75 (d, J = 8.9 Hz, 1H), 7.57 (dd, J = 8.6, 1.0 Hz, 1H), 7.50−7.45 (m, 2H), 7.45−7.33 (m, 5H), 7.27 (d, J = 8.9 Hz, 1H), 5.68 (dddt, J = 16.5, 10.9, 8.6, 5.6 Hz, 1H), 5.11−4.97 (m, 4H), 4.67−4.52 (m, 2H), 3.20 (ddd, J = 12.7, 10.9, 6.7 Hz, 1H), 2.44 (dddd, J = 12.7, 5.9, 3.4, 2.0 Hz, 1H), 2.34 (dddd, J = 18.0, 8.2, 3.4, 2.0 Hz, 1H), 2.19 (ddd, J = 18.0, 9.9, 8.2 Hz, 1H), 2.06−1.96 (m, 1H), 1.92−1.79 (m, 1H); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ 211.9, 172.3, 153.3, 136.4, 132.7, 131.8, 130.8, 130.1, 129.1, 128.7, 128.3, 128.3, 126.7, 124.1, 123.9, 123.9, 118.1, 116.7, 72.8, 66.5, 64.1, 39.0, 36.7, 20.5; HRMS:

(ESI-TOF) calculated for C$_{26}$H$_{24}$O$_4$Na [M + Na$^+$] 423.1572, found 423.1567.

Allyl 1-(2-Methoxy-4,6-dimethylphenyl)-2-oxocyclopentanecarboxylate (9j). The title compound was prepared according to the general procedure using β-keto allyl ester (7) (250 mg, 1.49 mmol) and 2-methoxy-4,6-dimethylphenyllead triacetate (929 mg, 1.79 mmol) to yield the product as a colorless oil (404 mg, 90%). R$_f$ = 0.43 (40% Et$_2$O in pentane); IR (thin film) ν_{max} 2971, 1748, 1720 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$): δ 6.63 (s, 1H), 6.56 (s, 1H), 5.94−5.83 (m, 1H), 5.27 (dt, J = 17.2, 1.4 Hz, 1H), 5.18 (dt, J = 10.5, 1.4 Hz, 1H), 4.71−4.58 (m, 2H), 3.65 (s, 3H), 3.06−2.99 (m, 1H), 2.68−2.58 (m, 1H), 2.35−2.24 (m, 4H), 2.14−1.99 (m, 5H), 1.94−1.84 (m, 1H); ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$): δ 211.9, 171.2, 156.4, 137.8, 137.7, 131.9, 127.3, 126.1, 118.6, 111.9, 66.5, 64.0, 55.9, 38.7, 36.4, 21.2, 20.7, 20.4; HRMS: (ESI-TOF) calculated for C$_{18}$H$_{22}$O$_4$Na [M + Na$^+$] 325.1416, found 325.1420.

Allyl 1-(2,6-Dimethylphenyl)-2-oxocyclopentanecarboxylate (9k). The title compound was prepared according to the general procedure using β-keto allyl ester (7) (250 mg, 1.49 mmol) and 2,6-dimethylphenyllead triacetate (875 mg, 1.79 mmol) to yield the product as a colorless oil (146 mg, 36%). R$_f$ = 0.63 (40% Et$_2$O in pentane); IR (thin film) ν_{max} 2969, 1748, 1716 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.04 (dd, J = 8.5, 6.4 Hz, 1H), 6.99−6.94 (m, 2H), 5.85 (ddt, J = 17.2, 10.4, 5.7 Hz, 1H), 5.25 (dq, J = 17.2, 1.4 Hz, 1H), 5.18 (dq, J = 10.4, 1.4 Hz, 1H), 4.70−4.55 (m, 2H), 3.24−3.14 (m, 1H), 2.78−2.67 (m, 1H), 2.56−2.46 (m, 1H), 2.33−2.14 (m, 8H), 2.09−1.97 (m, 1H); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ 214.0, 170.8, 139.3, 136.4, 131.4, 130.1, 126.9, 118.9, 67.9, 66.8, 39.1, 36.4, 23.1, 19.8; HRMS: (ESI-TOF) calculated for C$_{17}$H$_{20}$O$_3$Na [M + Na$^+$] 295.1310, found 295.1323.

Allyl 2-Oxo-1-(2,4,6-trimethoxyphenyl)cyclohexanecarboxylate (10a). The title compound was prepared according to the general procedure using β-keto allyl ester (8) (450 mg, 2.47 mmol) and 2,4,6-trimethoxyphenyllead triacetate (1.635 g, 2.96 mmol) to yield the product as a colorless oil (518 mg, 60%). R$_f$ = 0.10 (40% Et$_2$O in pentane); IR (thin film) ν_{max} 2940, 1729, 1718, 1607 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$): δ 6.13 (s, 2H), 5.91−5.81 (m, 1H), 4.66 (dd, J = 13.7, 5.4 Hz, 1H), 4.56 (dd, J = 13.7, 5.4 Hz, 1H), 3.78 (s, 3H), 3.68 (s, 6H), 2.66−2.51 (m, 2H), 2.48−2.40 (m, 1H), 2.37−2.29 (m, 1H), 1.89−1.74 (m, 3H), 1.66−1.57 (m, 1H); ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$): δ 205.6, 170.8, 160.4, 158.6, 132.3, 117.5, 111.2, 92.4, 65.7, 62.6, 55.9, 55.3, 40.5, 34.8, 25.6, 21.9; HRMS: (ESI-TOF) calculated for C$_{19}$H$_{24}$O$_6$Na [M + Na$^+$] 371.1471, found 371.1480.

Allyl 1-(2,4-Dimethoxyphenyl)-2-oxocyclohexanecarboxylate (10b). The title compound was prepared according to the general procedure using β-keto allyl ester (8) (250 mg, 1.37 mmol) and 2,4-dimethoxyphenyllead triacetate (857 mg, 1.64 mmol) to yield the product as a colorless oil (394 mg, 90%). R$_f$ = 0.23 (40% Et$_2$O in pentane); IR (thin film) ν_{max} 2940, 1732, 1715, 1612 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.08−7.00 (m, 1H), 6.52−6.46 (m, 2H), 5.84 (ddt, J = 17.1, 10.7, 5.5 Hz, 1H), 5.22−5.13 (m, 2H), 4.68−4.55 (m, 2H), 3.80 (s, 3H), 3.71 (s, 3H), 2.65−2.43 (m, 4H), 1.95−1.79 (m, 2H), 1.78−1.63 (m, 2H); ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$): δ 206.74, 171.52, 160.45, 158.70, 132.00, 127.98, 120.18, 117.97, 104.68, 99.96, 65.70, 64.26, 55.69, 55.41, 40.50, 35.44, 27.80, 21.86; HRMS: (ESI-TOF) calculated for C$_{18}$H$_{22}$O$_5$Na [M + Na$^+$] 341.1365, found 341.1375.

Allyl 1-(2,6-Dimethoxyphenyl)-2-oxocyclohexanecarboxylate (10c). The title compound was prepared according to the general procedure using β-keto allyl ester (8) (250 mg, 1.37 mmol) and 2,4-dimethoxyphenyllead triacetate (857 mg, 1.64 mmol) to yield the product as a colorless oil (268 mg, 61%). R$_f$ = 0.19 (40% Et$_2$O in pentane); IR (thin film) ν_{max} 2940, 1719, 1736, 1587 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.19 (t, J = 8.3 Hz, 1H), 6.56 (d, J = 8.3 Hz, 2H), 5.86 (ddt, J = 17.2, 10.5, 5.5 Hz, 1H), 5.20 (dq, J = 17.2, 1.5 Hz, 1H), 5.13 (dq, J = 10.5, 1.5 Hz, 1H), 4.67 (ddt, J = 13.5, 5.5, 1.5 Hz, 1H), 4.56 (ddt, J = 13.5, 5.5, 1.5 Hz, 1H), 3.69 (s, 6H), 2.69−2.58 (m, 1H), 2.55−2.43 (m, 2H), 2.39−2.30 (m, 1H), 1.90−1.77 (m, 3H), 1.68−1.57 (m, 1H); ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$): δ 205.2, 170.6, 157.8, 132.3, 128.8, 119.0, 117.7, 106.0, 65.8, 62.7, 56.0, 40.6,

34.7, 25.2, 21.9; HRMS: (ESI-TOF) calculated for $C_{18}H_{22}O_5Na$ [M + Na$^+$] 341.1365, found 341.1353.

Allyl 2-Oxo-1-(2,3,4-trimethoxyphenyl)cyclohexanecarboxylate (10d). The title compound was prepared according to the general procedure using β-keto allyl ester (**8**) (250 mg, 1.37 mmol) and 2,3,4-trimethoxyphenyllead triacetate (907 mg, 1.64 mmol) to yield the product as a colorless oil (447 mg, 94%). R_f = 0.24 (40% Et$_2$O in pentane); IR (thin film) ν_{max} 2945, 1733, 1712 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$): δ 6.83 (d, J = 8.8 Hz, 1H), 6.64 (d, J = 8.8 Hz, 1H), 5.84 (ddt, J = 17.1, 10.4, 5.6 Hz, 1H), 5.23−5.11 (m, 2H), 4.67−4.56 (m, 2H), 3.85 (s, 3H), 3.83 (s, 3H), 3.77 (s, 3H), 2.60−2.52 (m, 3H), 2.50−2.42 (m, 1H), 1.89−1.81 (m, 2H), 1.70−1.63 (m, 2H); ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$): δ 206.5, 171.4, 153.6, 152.4, 142.4, 132.0, 125.0, 121.4, 118.3, 106.8, 65.9, 64.4, 60.6, 56.0, 56.0, 40.6, 35.7, 28.0, 21.7; HRMS: (ESI-TOF) calculated for $C_{19}H_{24}O_6Na$ [M + Na$^+$] 371.1471, found 371.1480.

Allyl 2-Oxo-1-(2,3,6-trimethoxyphenyl)cyclohexanecarboxylate (10e). The title compound was prepared according to the general procedure using β-keto allyl ester (**8**) (250 mg, 1.37 mmol) and 2,3,6-trimethoxyphenyllead triacetate (907 mg, 1.64 mmol) to yield the product as a white solid (405 mg, 85%). R_f = 0.21 (40% Et$_2$O in pentane); IR (thin solid film) ν_{max} 2942, 1736, 1731 cm^{-1}; M.P. = 74−75 °C; ^{1}H NMR (500 MHz, CDCl$_3$): δ 6.82 (d, J = 9.0 Hz, 1H), 6.61 (d, J = 9.0 Hz, 1H), 5.88 (ddt, J = 17.2, 10.5, 5.5 Hz, 1H), 5.22 (dq, J = 17.2, 1.5 Hz, 1H), 5.14 (dq, J = 10.5, 1.5 Hz, 1H), 4.71 (ddt, J = 13.4, 5.5, 1.5 Hz, 1H), 4.57 (ddt, J = 13.4, 5.5, 1.5 Hz, 1H), 3.82 (s, 3H), 3.68 (s, 3H), 3.64 (s, 3H), 2.74−2.63 (m, 2H), 2.47 (ddd, J = 13.9, 7.9, 3.7 Hz, 1H), 2.43−2.34 (m, 1H), 1.88−1.72 (m, 3H), 1.63−1.54 (m, 1H); ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$): δ 204.9, 170.6, 151.6, 147.8, 147.5, 132.3, 124.6, 117.7, 111.8, 107.3, 66.0, 63.4, 60.8, 56.2, 56.2, 40.8, 34.7, 25.4, 21.8; HRMS: (ESI-TOF) calculated for $C_{19}H_{24}O_6Na$ [M + Na$^+$] 371.1471, found 371.1472.

Allyl 1-(4-Methoxyphenyl)-2-oxocyclohexanecarboxylate (10f). The title compound was prepared according to the general procedure using β-keto allyl ester (**8**) (250 mg, 1.37 mmol) and 4-methoxyphenyllead triacetate (808 mg, 1.64 mmol) to yield the product as a colorless oil (362 mg, 92%). R_f = 0.41 (40% Et$_2$O in pentane); IR (thin film) ν_{max} 2941, 1735, 1713 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.18−7.13 (m, 2H), 6.91−6.86 (m, 2H), 5.85 (ddt, J = 17.0, 10.2, 5.6 Hz, 1H), 5.25−5.15 (m, 2H), 4.67−4.58 (m, 2H), 3.78 (s, 3H), 2.80−2.71 (m, 1H), 2.54 (app. t, J = 6.6 Hz, 2H), 2.41−2.33 (m, 1H), 2.02−1.90 (m, 1H), 1.88−1.71 (m, 3H); ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$): δ 206.8, 171.2, 159.0, 131.6, 129.0, 128.5, 118.5, 113.9, 66.0, 66.0, 55.2, 40.6, 35.1, 27.8, 22.1; HRMS: (ESI-TOF) calculated for $C_{17}H_{20}O_4Na$ [M + Na$^+$] 311.1259, found 311.1264.

Allyl 1-(2-Methoxynaphthalen-1-yl)-2-oxocyclohexanecarboxylate (10g). The title compound was prepared according to the general procedure using β-keto allyl ester (**8**) (250 mg, 1.37 mmol) and 2-methoxynaphthyllead triacetate (890 mg, 1.64 mmol) to yield the product as a colorless oil (412 mg, 89%). R_f = 0.29 (40% Et$_2$O in pentane); IR (thin film) ν_{max} 2940, 1734, 1710 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.79 (d, J = 8.8 Hz, 2H), 7.56 (dd, J = 8.8, 1.2 Hz, 1H), 7.42−7.33 (m, 1H), 7.36−7.30 (m, 1H), 7.23 (d, J = 9.0 Hz, 1H), 5.79 (ddt, J = 17.2, 10.4, 5.6 Hz, 1H), 5.19−5.06 (m, 2H), 4.73 (ddt, J = 13.4, 5.6, 1.4 Hz, 1H), 4.58 (ddt, J = 13.4, 5.6, 1.5 Hz, 1H), 3.78 (s, 3H), 2.87−2.73 (m, 2H), 2.73−2.64 (m, 1H), 2.55 (ddd, J = 14.9, 8.4, 5.9 Hz, 1H), 1.99−1.78 (m, 3H), 1.50−1.38 (m, 1H); ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$): δ 205.8, 171.9, 154.7, 132.0, 131.9, 130.8, 130.4, 129.2, 126.0, 124.4, 123.6, 123.2, 118.1, 115.9, 77.4, 77.2, 76.9, 66.2, 64.6, 57.5, 40.7, 35.3, 25.0, 21.3; HRMS: (ESI-TOF) calculated for $C_{21}H_{22}O_4Na$ [M + Na$^+$] 361.1416, found 361.1416.

Allyl 1-(Benzo[d][1,3]dioxol-5-yl)-2-oxocyclohexanecarboxylate (10h). The title compound was prepared according to the general procedure using β-keto allyl ester (**8**) (250 mg, 1.37 mmol) and 3,4-methylenedioxyphenyllead triacetate (828 mg, 1.64 mmol) to yield the product as a white solid (356 mg, 86%). R_f = 0.47 (40% Et$_2$O in pentane); IR (thin solid film) ν_{max} 2944, 1733, 1713 cm^{-1}; M.P. = 76−78 °C; ^{1}H NMR (500 MHz, CDCl$_3$): δ 6.79 (d, J = 8.2 Hz, 1H), 6.75 (d, J = 1.9 Hz, 1H), 6.70 (dd, J = 8.2, 1.9 Hz, 1H), 5.95 (s, 2H), 5.87

(ddt, J = 17.3, 10.4, 5.6 Hz, 1H), 5.29−5.18 (m, 2H), 4.68−4.59 (m, 2H), 2.79−2.69 (m, 1H), 2.55 (app. t, J = 6.6 Hz, 2H), 2.37−2.28 (m, 1H), 2.01−1.91 (m, 1H), 1.88−1.68 (m, 3H); ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$): δ 206.7, 171.1, 147.9, 147.1, 131.6, 130.2, 121.2, 118.8, 108.7, 108.2, 101.3, 66.2, 66.1, 40.7, 35.3, 27.7, 22.2; HRMS: (ESI-TOF) calculated for $C_{17}H_{18}O_5Na$ [M + Na$^+$] 325.1052, found 325.1046.

Allyl 1-(2-(Benzyloxy)naphthalen-1-yl)-2-oxocyclohexanecarboxylate (10i). The title compound was prepared according to the general procedure using β-keto allyl ester (**8**) (250 mg, 1.37 mmol) and 2-benzyloxynaphthyllead triacetate (1.015 g, 1.64 mmol) to yield the product as a white solid (448 mg, 79%). R_f = 0.52 (40% Et$_2$O in pentane); IR (thin solid film) ν_{max} 2942, 1732, 1718 cm^{-1}; M.P. = 84−87 °C; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.77 (dd, J = 8.1, 1.5 Hz, 1H), 7.74 (d, J = 8.9 Hz, 1H), 7.58 (d, J = 8.6 Hz, 1H), 7.45−7.40 (m, 2H), 7.40−7.35 (m, 3H), 7.35−7.29 (m, 2H), 7.23 (d, J = 8.9 Hz, 1H), 5.75 (ddt, J = 17.2, 10.4, 5.6 Hz, 1H), 5.15−5.05 (m, 2H), 5.02 (s, 2H), 4.65 (ddt, J = 13.3, 5.6, 1.4 Hz, 1H), 4.46 (ddt, J = 13.3, 5.6, 1.4 Hz, 1H), 2.82−2.74 (m, 1H), 2.74−2.66 (m, 1H), 2.62 (dt, J = 15.4, 6.0 Hz, 1H), 2.46−2.36 (m, 1H), 1.87−1.70 (m, 3H), 1.47−1.37 (m, 1H); ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$): δ 205.7, 171.9, 154.1, 136.6, 132.1, 131.9, 130.9, 130.3, 129.2, 128.6, 128.2, 128.1, 126.1, 124.4, 123.8, 123.7, 118.3, 117.3, 73.3, 66.3, 64.8, 40.9, 35.4, 24.7, 21.3; HRMS: (ESI-TOF) calculated for $C_{27}H_{26}O_4Na$ [M + Na$^+$] 437.1729, found 437.1707.

Allyl 1-(2-(Methoxy)-4,6-dimethylphenyl)-2-oxocyclohexanecarboxylate (10j). The title compound was prepared according to the general procedure using β-keto allyl ester (**8**) (250 mg, 1.37 mmol) and 2-methoxy-4,6-dimethylphenyllead triacetate (854 mg, 1.64 mmol) to yield the product as a colorless oil (390 mg, 90%). R_f = 0.37 (40% Et$_2$O in pentane); IR (thin film) ν_{max} 2935, 1721, 1711, 1612 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$): δ 6.60 (s, 1H), 6.58 (s, 1H), 5.84 (ddt, J = 17.2, 10.6, 5.5 Hz, 1H), 5.20 (dq, J = 17.2, 1.6 Hz, 1H), 5.13 (dq, J = 10.6, 1.4 Hz, 1H), 4.69 (ddt, J = 13.5, 5.5, 1.4 Hz, 1H), 4.55 (ddt, J = 13.5, 5.5, 1.4 Hz, 1H), 3.66 (s, 3H), 2.68−2.57 (m, 1H), 2.51−2.40 (m, 2H), 2.40−2.30 (m, 1H), 2.26 (s, 3H), 2.16 (s, 3H), 1.91−1.81 (m, 3H), 1.66−1.56 (m, 1H); ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$): δ 205.4, 171.0, 157.1, 137.3, 137.3, 117.9, 111.9, 65.9, 64.7, 55.9, 40.4, 35.5, 25.9, 22.2, 21.7, 21.1, 14.1; HRMS: (ESI-TOF) calculated for $C_{19}H_{24}O_4Na$ [M + Na$^+$] 339.1572, found 339.1576.

General Procedure for the Racemic Decarboxylative Protonation Reaction (11 and 18). Pd(OAc)$_2$ (3.4 mg, 0.015 mmol) and dppe (7.5 mg, 0.019 mmol) were added to a flame-dried Schlenk flask (10 mL), and 1,4-dioxane (1.5 mL) was added. The suspension was stirred at 40 °C for 90 min, and formic acid (34 μL, 0.90 mmol) was added, followed immediately by α-aryl-β-keto allyl ester (0.15 mmol) in 1,4-dioxane (1.5 mL) from a flame-dried round-bottom flask (10 mL, 2-neck). The reaction mixture was stirred at 40 °C for 10 h, cooled to room temperature, and filtered through a plug of Celite and washed with Et$_2$O. The solvent was removed *in vacuo*, and the resulting residue was purified by silica gel column chromatography (pentane/Et$_2$O).

3,3-Dimethyl-2-(2,4,6-trimethoxyphenyl)cyclopentanone (rac-15a). The title compound was prepared according to the general procedure using α-aryl-β-keto allyl ester (**14a**) to yield the product as a pale yellow oil (14.5 mg, 35%). R_f = 0.15 (40% Et$_2$O in pentane); IR (thin film) ν_{max} 2953, 1739, 1608 cm^{-1}; M.P. = 87−89 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 6.11 (d, J = 2.3 Hz, 1H), 6.08 (d, J = 2.3 Hz, 1H), 3.77 (s, 3H), 3.73 (s, 3H), 3.64 (s, 3H), 3.50 (d, J = 1.4 Hz, 1H), 2.55−2.43 (m, 1H), 2.35 (dddd, J = 18.1, 8.4, 5.0, 1.4 Hz, 1H), 1.90 (ddd, J = 12.4, 8.4, 5.0 Hz, 1H), 1.77−1.66 (m, 1H), 1.13 (s, 3H), 0.79 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ 220.4, 160.4, 159.9, 158.5, 107.7, 91.4, 91.1, 55.8, 55.7, 55.5, 55.4, 55.4, 41.7, 37.7, 37.0, 30.9, 24.1; HRMS: (ESI-TOF) calculated for $C_{16}H_{22}O_4Na$ [M + Na$^+$] 301.1416, found 301.1405.

2-(2,4,6-Trimethoxyphenyl)cyclopentanone (rac-11a). The title compound was prepared according to the general procedure using α-aryl-β-keto allyl ester (**9a**) to yield the product as an off-white solid (24 mg, 64%). R_f = 0.15 (40% Et$_2$O in pentane); IR (thin solid film) ν_{max} 2960, 1738, 1609 cm^{-1}; M.P. = 87−89 °C; ^{1}H NMR (400 MHz,

CDCl$_3$): δ 6.12 (s, 2H), 3.78 (s, 3H), 3.73 (s, 6H), 3.71–3.64 (m, 1H), 2.44–2.31 (m, 2H), 2.28–2.18 (m, 1H), 2.17–2.00 (m, 2H), 1.90–1.77 (m, 1H); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ 220.8, 160.4, 158.7, 109.5, 91.3, 55.7, 55.5, 45.2, 38.2, 30.0, 21.9; HRMS: (ESI-TOF) calculated for C$_{14}$H$_{18}$O$_4$Na [M + Na$^+$] 273.1103, found 273.1111.

2-(2,4-Dimethoxyphenyl)cyclopentanone (rac-11b). The title compound was prepared according to the general procedure using α-aryl-β-keto allyl ester (**9b**) to yield the product as a pale yellow oil (24 mg, 67%). R$_f$ = 0.26 (40% Et$_2$O in pentane); IR (thin film) ν_{max} 2960, 1739, 1614 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$): δ 6.97 (d, J = 7.9 Hz, 1H), 6.47–6.42 (m, 2H), 3.78 (s, 3H), 3.74 (s, 3H), 3.30 (dd, J = 10.9, 9.0 Hz, 1H), 2.45–2.28 (m, 3H), 2.17–2.04 (m, 2H), 1.92–1.80 (m, 1H); ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$): δ 219.8, 160.2, 157.9, 130.9, 120.8, 104.6, 99.4, 55.5, 55.4, 52.0, 38.3, 31.3, 21.5; HRMS: (ESI-TOF) calculated for C$_{13}$H$_{16}$O$_3$Na [M + Na$^+$] 243.0997, found 243.0990.

2-(2,6-Dimethoxyphenyl)cyclopentanone (rac-11c). The title compound was prepared according to the general procedure using α-aryl-β-keto allyl ester (**9c**) to yield the product as an off-white solid (28 mg, 78%). R$_f$ = 0.29 (40% Et$_2$O in pentane); IR (thin solid film) ν_{max} 2961, 1739, 1594 cm^{-1}; M.P. = 52–54 °C; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.16 (t, J = 8.3 Hz, 1H), 6.54 (d, J = 8.3 Hz, 2H), 3.84–3.70 (m, 7H), 2.49–2.31 (m, 2H), 2.30–2.21 (m, 1H), 2.19–2.06 (m, 2H), 1.92–1.81 (m, 1H); ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$): δ 220.4, 158.1, 128.2, 117.0, 104.5, 55.8, 45.4, 38.2, 29.9, 22.1; HRMS: (ESI-TOF) calculated for C$_{13}$H$_{16}$O$_3$Na [M + Na$^+$] 243.0997, found 243.0997.

2-(2,3,4-Trimethoxyphenyl)cyclopentanone (rac-11d). The title compound was prepared according to the general procedure using α-aryl-β-keto allyl ester (**9d**) to yield the product as a pale yellow oil (32 mg, 85%). R$_f$ = 0.24 (40% Et$_2$O in pentane); IR (thin film) ν_{max} 2960, 1739, 1602 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ 6.74 (d, J = 8.5 Hz, 1H), 6.59 (d, J = 8.5 Hz, 1H), 3.84 (s, 3H), 3.82 (s, 3H), 3.81 (s, 3H), 3.32–3.23 (m, 1H), 2.47–2.29 (m, 3H), 2.17–2.00 (m, 2H), 1.93–1.79 (m, 1H); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ 219.7, 153.2, 151.5, 142.3, 126.2, 124.4, 107.2, 60.7, 60.2, 56.1, 52.2, 38.3, 32.3, 21.4; HRMS: (ESI-TOF) calculated for C$_{14}$H$_{18}$O$_4$Na [M + Na$^+$] 273.1103, found 273.1104.

2-(2,3,6-Trimethoxyphenyl)cyclopentanone (rac-11e). The title compound was prepared according to the general procedure using α-aryl-β-keto allyl ester (**9e**) to yield the product as a pale yellow oil (32 mg, 86%). R$_f$ = 0.24 (40% Et$_2$O in pentane); IR (thin film) ν_{max} 2959, 1739 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$): δ 6.75 (d, J = 8.9 Hz, 1H), 6.54 (d, J = 8.9 Hz, 1H), 3.80 (s, 3H), 3.77 (s, 3H), 3.74–3.67 (m, 1H), 3.70 (s, 3H), 2.48–2.33 (m, 2H), 2.32–2.22 (m, 1H), 2.19–2.07 (m, 2H), 1.94–1.80 (m, 1H); ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$): δ 220.2, 151.7, 147.2, 125.6, 123.6, 111.4, 106.1, 56.3, 56.0, 46.2, 38.2, 30.7, 22.0. HRMS: (ESI-TOF) calculated for C$_{14}$H$_{18}$O$_4$Na [M + Na$^+$] 273.1103, found 273.1104.

2-(4-Methoxyphenyl)cyclopentanone (rac-11f).[21] The title compound was prepared according to the general procedure using α-aryl-β-keto allyl ester (**9f**) to yield the product as a pale yellow oil (22 mg, 77%). R$_f$ = 0.37 (40% Et$_2$O in pentane); IR (thin film) ν_{max} 2927, 1706, 1668, 1601, 1511 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.15–7.08 (m, 2H), 6.90–6.85 (m, 2H), 3.79 (s, 3H), 3.31–3.22 (m, 1H), 2.52–2.41 (m, 2H), 2.34–2.22 (m, 1H), 2.16–2.02 (m, 2H), 1.99–1.87 (m, 1H); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ 218.5, 158.6, 130.6, 129.2, 114.2, 55.4, 54.7, 38.4, 31.9, 20.9; HRMS: (ESI-TOF) calculated for C$_{12}$H$_{14}$O$_2$Na [M + Na$^+$] 213.0891, found 213.0901.

2-(2-Methoxynaphthalen-1-yl)cyclopentanone (rac-11g). The title compound was prepared according to the general procedure using α-aryl-β-keto allyl ester (**9g**) to yield the product as an off-white solid (24 mg, 65%). R$_f$ = 0.26 (40% Et$_2$O in pentane); IR (thin solid film) ν_{max} 2962, 1740 cm^{-1}; M.P. = 115–118 °C; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.84 (br s, 1H), 7.81–7.74 (m, 2H), 7.49–7.43 (m, 1H), 7.35–7.31 (m, 1H), 7.25 (d, J = 9.0 Hz, 1H), 3.92 (br s, 1H), 3.84 (s, 3H), 2.66–2.52 (m, 1H), 2.52–2.37 (m, 2H), 2.29–2.15 (m, 2H), 2.05–1.90 (m, 1H); ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$): δ 219.9, 129.7, 129.1, 128.8, 126.8, 123.6, 122.6, 114.2, 56.2, 47.9, 38.3, 30.9,

22.2; HRMS: (ESI-TOF) calculated for C$_{16}$H$_{16}$O$_2$Na [M + Na$^+$] 263.1048, found 263.1058.

2-(Benzo[d][1,3]dioxol-5-yl)cyclopentanone (rac-11h).[39] The title compound was prepared according to the general procedure using α-aryl-β-keto allyl ester (**9h**) to yield the product as a pale yellow oil (29 mg, 95%). R$_f$ = 0.14 (40% Et$_2$O in pentane); IR (thin film) ν_{max} 2922, 1733, 1674 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$): δ 6.77 (d, J = 8.0 Hz, 1H), 6.70–6.66 (m, 1H), 6.66–6.62 (m, 1H), 5.93 (s, 2H), 3.30–3.17 (m, 1H), 2.53–2.38 (m, 2H), 2.33–2.21 (m, 1H), 2.20–2.10 (m, 1H), 2.10–1.99 (m, 1H), 1.97–1.85 (m, 1H); ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$): δ 218.2, 148.0, 146.6, 132.2, 132.2, 121.4, 108.7, 108.5, 101.1, 55.2, 38.4, 32.0, 20.8; HRMS: (ESI-TOF) calculated for C$_{12}$H$_{13}$O$_3$ [M + H$^+$] 205.0865, found 205.0867.

2-(2-(Benzyloxy)naphthalen-1-yl)cyclopentanone (rac-11i). The title compound was prepared according to the general procedure using α-aryl-β-keto allyl ester (**9i**) to yield the product as an off-white solid (44 mg, 93%). R$_f$ = 0.41 (40% Et$_2$O in pentane); IR (thin solid film) ν_{max} 2958, 1739, 1593 cm^{-1}; M.P. = 114–116 °C; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.86 (br s, 1H), 7.78 (d, J = 8.2 Hz, 1H), 7.75 (d, J = 8.2 Hz, 1H), 7.50–7.25 (m, 8H), 5.12 (d, J = 11.0 Hz, 1H), 5.04 (d, J = 11.0 Hz, 1H), 3.90 (br s, 1H), 2.43–2.30 (m, 1H), 2.29–2.15 (m, 2H), 2.11–1.94 (m, 2H), 1.92–1.78 (m, 1H); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ 219.8, 153.1, 136.6, 133.7, 129.7, 129.0, 128.8, 128.7, 128.4, 128.3, 126.8, 123.6, 122.6, 114.6, 71.4, 48.1, 38.2, 30.7, 22.0; HRMS: (ESI-TOF) calculated for C$_{22}$H$_{20}$O$_2$Na [M + Na$^+$] 339.1361, found 339.1356.

2-(2-Methoxy-4,6-dimethylphenyl)cyclopentanone (rac-11j). The title compound was prepared according to the general procedure using α-aryl-β-keto allyl ester (**9j**) to yield the product as a pale yellow oil (28 mg, 88%). R$_f$ = 0.33 (40% Et$_2$O in pentane); IR (thin film) ν_{max} 2958, 1739, 1612, 1581 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ 6.63 (s, 1H), 6.55 (s, 1H), 3.70 (s, 3H), 3.34 (br s, 1H), 2.53–2.04 (m, 11H), 1.94–1.79 (m, 1H); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ 220.2, 156.6, 137.8, 137.5, 124.0, 110.4, 55.3, 49.0, 38.0, 29.9, 22.0, 21.5, 20.1; HRMS: (ESI-TOF) calculated for C$_{14}$H$_{18}$O$_2$Na [M + Na$^+$] 241.1204, found 241.1215.

2-(2,6-Dimethylphenyl)cyclopentanone (rac-11k). The title compound was prepared according to the general procedure using α-aryl-β-keto allyl ester (**9k**) to yield the product as a pale yellow oil (26 mg, 92%). R$_f$ = 0.44 (40% Et$_2$O in pentane); IR (thin film) ν_{max} 2960, 1738 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.08–7.00 (m, 3H), 3.66–3.59 (m, 1H), 2.56–2.05 (m, 11H), 2.03–1.90 (m, 1H); ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$): δ 218.9, 135.8, 127.0, 52.8, 38.1, 29.6, 21.6, 21.4; HRMS: (ESI-TOF) calculated for C$_{13}$H$_{16}$ONa [M + Na$^+$] 211.1099, found 211.1107.

2-(2,4,6-Trimethoxyphenyl)cyclohexanone (rac-18a).[40] The title compound was prepared according to the general procedure using α-aryl-β-keto allyl ester (**10a**) to yield the product as an off-white solid (17 mg, 45%). R$_f$ = 0.17 (40% Et$_2$O in pentane); IR (thin solid film) ν_{max} 2939, 1710, 1608 cm^{-1}; M.P. = 109–111 °C; ^{1}H NMR (500 MHz, CDCl$_3$): δ 6.14 (s, 2H), 3.89 (dd, J = 12.3, 6.6 Hz, 1H), 3.79 (s, 3H), 3.74 (s, 6H), 2.62–2.55 (m, 1H), 2.37–2.26 (m, 1H), 2.18–2.08 (m, 1H), 2.07–2.01 (m, 1H), 2.00–1.89 (m, 2H), 1.85–1.74 (m, 1H), 1.74–1.63 (m, 1H); ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$): δ 209.92, 160.12, 158.54, 110.29, 91.35, 55.81, 55.39, 46.19, 41.56, 31.29, 25.40, 25.30; HRMS: (ESI-TOF) calculated for C$_{15}$H$_{20}$O$_4$Na [M + Na$^+$] 287.1259, found 287.1266.

2-(2,4-Dimethoxyphenyl)cyclohexanone (rac-18b). The title compound was prepared according to the general procedure using α-aryl-β-keto allyl ester (**10b**) to yield the product as an off-white solid (34 mg, 97%). R$_f$ = 0.30 (40% Et$_2$O in pentane); IR (thin solid film) ν_{max} 2937, 1712, 1613, 1588 cm^{-1}; M.P. = 92–93 °C; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.00 (d, J = 8.2 Hz, 1H), 6.51–6.44 (m, 2H), 3.85 (dd, J = 13.0, 5.4 Hz, 1H), 3.79 (s, 3H), 3.74 (s, 3H), 2.55–2.42 (m, 2H), 2.22–2.10 (m, 2H), 2.05–1.93 (m, 2H), 1.87–1.71 (m, 2H); ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$): δ 210.4, 159.8, 157.9, 129.1, 120.4, 104.2, 98.7, 55.5, 55.4, 50.6, 42.4, 33.7, 27.7, 25.9; HRMS: (ESI-TOF) calculated for C$_{14}$H$_{18}$O$_3$Na [M + Na$^+$] 257.1154, found 257.1162.

2-(2,6-Dimethoxyphenyl)cyclohexanone (rac-18c). The title compound was prepared according to the general procedure using α-aryl-β-keto allyl ester (**10c**) to yield the product as a pale yellow oil (33 mg, 94%). R_f = 0.43 (40% Et$_2$O in pentane); IR (thin film) ν_{max} 2938, 1711, 1594 cm^{-1}; M.P. = 79−81 °C; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.18 (t, J = 8.3 Hz, 1H), 6.56 (d, J = 8.3 Hz, 2H), 4.00 (dd, J = 11.9, 6.8 Hz, 1H), 3.76 (s, 6H), 2.65−2.57 (m, 1H), 2.39−2.30 (m, 1H), 2.19−2.09 (m, 1H), 2.09−1.97 (m, 2H), 1.97−1.91 (m, 1H), 1.88−1.77 (m, 1H), 1.77−1.63 (m, 1H); ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$): δ 209.7, 157.9, 128.0, 125.6, 117.9, 104.5, 55.8, 46.3, 41.5, 31.0, 25.2, 25.2; HRMS: (ESI-TOF) calculated for C$_{14}$H$_{18}$O$_3$Na [M + Na$^+$] 257.1154, found 257.1157.

2-(2,3,4-Trimethoxyphenyl)cyclohexanone (rac-18d).[41] The title compound was prepared according to the general procedure using α-aryl-β-keto allyl ester (**10d**) to yield the product as a pale yellow oil (39 mg, 98%). R_f = 0.23 (40% Et$_2$O in pentane); IR (thin film) ν_{max} 2936, 1711, 1604 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$): δ 6.78 (d, J = 8.6 Hz, 1H), 6.65 (d, J = 8.6 Hz, 1H), 3.85 (s, 3H), 3.84 (s, 4H), 3.83−3.80 (m, 1H), 3.80 (s, 3H), 2.57−2.43 (m, 2H), 2.21−2.12 (m, 2H), 2.03−1.93 (m, 2H), 1.86−1.73 (m, 2H); ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$): δ 210.4, 152.7, 151.6, 142.0, 125.5, 123.4, 107.2, 60.9, 60.7, 56.0, 51.2, 42.3, 34.2, 27.6, 25.8, 15.4; HRMS: (ESI-TOF) calculated for C$_{15}$H$_{20}$O$_4$Na [M + Na$^+$] 287.1259, found 287.1253.

2-(2,3,6-Trimethoxyphenyl)cyclohexanone (rac-18e). The title compound was prepared according to the general procedure using α-aryl-β-keto allyl ester (**10e**) to yield the product as a pale yellow oil (37 mg, 93%). R_f = 0.23 (40% Et$_2$O in pentane); IR (thin film) ν_{max} 2939, 1709 cm^{-1}; M.P. = 97−100 °C; ^{1}H NMR (500 MHz, CDCl$_3$): δ 6.76 (d, J = 8.9 Hz, 1H), 6.58 (d, J = 8.9 Hz, 1H), 3.93 (dd, J = 12.1, 6.7 Hz, 1H), 3.81 (s, 3H), 3.76 (s, 3H), 3.71 (s, 3H), 2.65−2.58 (m, 1H), 2.35 (dddd, J = 16.3, 13.1, 6.2, 1.2 Hz, 1H), 2.22−2.09 (m, 1H), 2.10−1.98 (m, 2H), 1.98−1.90 (m, 1H), 1.88−1.76 (m, 1H), 1.75−1.65 (m, 1H); ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$): δ 209.8, 151.6, 147.7, 147.2, 124.2, 111.2, 106.3, 60.7, 56.3, 56.1, 47.3, 41.4, 31.5, 25.2, 25.1; HRMS: (ESI-TOF) calculated for C$_{15}$H$_{20}$O$_4$Na [M + Na$^+$] 287.1259, found 287.1255.

2-(4-Methoxyphenyl)cyclohexanone (rac-18f).[9] The title compound was prepared according to the general procedure using α-aryl-β-keto allyl ester (**10f**) to yield the product as an off-white solid (30 mg, 97%). R_f = 0.36 (40% Et$_2$O in pentane); IR (thin solid film) ν_{max} 2926, 1704 cm^{-1}; M.P. = 86−88 °C; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.06 (d, J = 8.6 Hz, 2H), 6.88 (d, J = 8.6 Hz, 2H), 3.79 (s, 3H), 3.56 (dd, J = 12.4, 5.4 Hz, 1H), 2.56−2.48 (m, 1H), 2.48−2.39 (m, 1H), 2.29−2.20 (m, 1H), 2.18−2.09 (m, 1H), 2.04−1.93 (m, 2H), 1.87−1.75 (m, 2H); ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$): δ 210.8, 158.5, 131.0, 129.5, 113.9, 56.7, 55.3, 42.3, 35.4, 28.0, 25.5; HRMS: (ESI-TOF) calculated for C$_{13}$H$_{16}$O$_2$Na [M + Na$^+$] 227.1048, found 227.1041.

2-(2-Methoxynaphthalen-1-yl)cyclohexanone (rac-18g). The title compound was prepared according to the general procedure using α-aryl-β-keto allyl ester (**10g**) to yield the product as an off-white solid (33 mg, 87%). R_f = 0.28 (40% Et$_2$O in pentane); IR (thin solid film) ν_{max} 2937, 1708, 1596 cm^{-1}; M.P. = 116−118 °C; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.81−7.75 (m, 2H), 7.71 (d, J = 8.6 Hz, 1H), 7.45−7.40 (m, 1H), 7.33−7.29 (m, 1H), 7.27 (d, J = 9.0 Hz, 1H), 4.27 (dd, J = 12.4, 6.6 Hz, 1H), 3.87 (s, 3H), 2.77−2.70 (m, 1H), 2.52−2.41 (m, 1H), 2.28−2.17 (m, 1H), 2.17−2.10 (m, 2H), 2.05−1.89 (m, 2H), 1.84−1.73 (m, 1H); ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$): δ 209.8, 154.1, 132.4, 129.8, 129.0, 128.9, 126.4, 123.3, 123.1, 114.0, 56.5, 48.4, 41.5, 31.8, 25.2, 25.1; HRMS: (ESI-TOF) calculated for C$_{17}$H$_{18}$O$_2$Na [M + Na$^+$] 277.1204, found 277.1196.

2-(Benzo[d][1,3]dioxol-5-yl)cyclohexanone (rac-18h). The title compound was prepared according to the general procedure using α-aryl-β-keto allyl ester (**10h**) to yield the product as an off-white solid (12 mg, 37%). R_f = 0.37 (40% Et$_2$O in pentane); IR (thin solid film) ν_{max} 2930, 1710 cm^{-1}; M.P. = 88−90 °C; ^{1}H NMR (500 MHz, CDCl$_3$): δ 6.76 (d, J = 8.0 Hz, 1H), 6.64 (d, J = 1.7 Hz, 1H), 6.57 (dd, J = 8.0, 1.7 Hz, 1H), 5.93 (s, 2H), 3.56−3.50 (m, 1H), 2.55−2.49 (m, 1H), 2.48−2.39 (m, 1H), 2.28−2.21 (m, 1H), 2.19−2.10 (m, 1H), 2.04−1.91 (m, 2H), 1.87−1.73 (m, 2H); ^{13}C{^{1}H} NMR (126 MHz,

CDCl$_3$): δ 210.6, 147.7, 146.6, 132.7, 121.7, 109.1, 108.3, 101.1, 57.3, 42.3, 35.5, 27.9, 25.6; HRMS: (ESI-TOF) calculated for C$_{13}$H$_{15}$O$_3$ [M + H$^+$] 219.1021, found 219.1019.

2-(2-(Benzyloxy)naphthalen-1-yl)cyclohexanone (rac-18i). The title compound was prepared according to the general procedure using α-aryl-β-keto allyl ester (**10i**) to yield the product as an off-white solid (26 mg, 52%). R_f = 0.40 (40% Et$_2$O in pentane); IR (thin solid film) ν_{max} 2937, 1707, 1595 cm^{-1}; M.P. = 129−130 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.84−7.74 (m, 3H), 7.49−7.32 (m, 8H), 5.19 (d, J = 11.2 Hz, 1H), 5.11 (d, J = 11.2 Hz, 1H), 4.32−4.18 (m, 1H), 2.59−2.49 (m, 1H), 2.43−2.31 (m, 1H), 2.30−2.17 (m, 1H), 2.16−2.05 (m, 1H), 2.00−1.89 (m, 2H), 1.79−1.66 (m, 1H), 1.65−1.52 (m, 1H); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ 209.7, 153.4, 137.1, 132.6, 129.9, 129.0, 128.9, 128.6, 128.2, 128.2, 126.5, 123.5, 123.4, 123.1, 115.0, 71.5, 48.7, 41.6, 31.6, 25.1, 24.7; HRMS: (ESI-TOF) calculated for C$_{23}$H$_{23}$O$_2$ [M + H$^+$] 331.1698, found 331.1693.

2-(2-Methoxy-4,6-dimethylphenyl)cyclohexanone (rac-18j). The title compound was prepared according to the general procedure using α-aryl-β-keto allyl ester (**10j**) to yield the product as a pale yellow oil (28 mg, 80%). R_f = 0.37 (40% Et$_2$O in pentane); IR (thin film) ν_{max} 2935, 1710, 1580 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$): δ 6.63 (s, 1H), 6.58 (s, 1H), 3.73 (s, 3H), 3.66−3.58 (m, 1H), 2.65 (dddd, J = 16.5, 4.6, 2.7, 1.8 Hz, 1H), 2.40−2.31 (m, 1H), 2.30 (s, 3H), 2.22 (s, 3H), 2.11−1.93 (m, 4H), 1.90−1.79 (m, 1H), 1.74−1.63 (m, 1H); ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$): δ 209.9, 156.8, 137.3, 136.9, 125.6, 124.0, 110.4, 55.5, 49.5, 41.3, 31.1, 25.1, 25.0, 21.5, 20.3; HRMS: (ESI-TOF) calculated for C$_{15}$H$_{21}$O$_2$ [M + H$^+$] 233.1542, found 233.1544.

General Procedure for the Decarboxylative Asymmetric Protonation. Pd$_2$dba$_3$·CHCl$_3$ (7.8 mg, 0.0075 mmol) and (*S*)-(CF$_3$)$_3$-*t*-BuPHOX (11.1 mg, 0.0188 mmol) were dissolved in freshly distilled THF in a flame-dried Schlenk flask and stirred at 40 °C for 30 min. α-Aryl-β-keto allyl ester (0.15 mmol) and Meldrum's acid (0.375 mmol) were dissolved in THF in a flame-dried round-bottom flask (10 mL, 2-neck) and added to the Pd-complex solution, maintained at 40 °C, in one portion. The reaction mixture was stirred at 40 °C for 2 h, filtered through a bed of charcoal on a plug of Celite, and washed with EtOAc. The filtrate was concentrated *in vacuo* and purified by silica gel column chromatography (pentane/Et$_2$O).

(S)-3,3-Dimethyl-2-(2,4,6-trimethoxyphenyl)cyclopentanone ((S)-15a). The title compound was prepared according to the general procedure using α-aryl-β-keto allyl ester (**14a**) to yield the product as a pale yellow oil (38 mg, 92%, 77% ee), identical in all respects to the previously prepared racemic sample, with the exception of $[\alpha]_D^{20}$ = −33.4 (*c* 1.0, CHCl$_3$); SFC (Chiralcel IA-3, scCO$_2$/2-propanol, 99/1 to 70/30 gradient over 5 min, 3 mL/min): R_t = 2.67 (major) and 3.70 min.

(S)-2-(2,4,6-Trimethoxyphenyl)cyclopentanone ((S)-11a). The title compound was prepared according to the general procedure using α-aryl-β-keto allyl ester (**9a**) to yield the product as an off-white solid (34 mg, 91%, 82% ee), identical in all respects to the previously prepared racemic sample, with the exception of $[\alpha]_D^{20}$ = −53.3 (*c* 1.7, CH$_2$Cl$_2$); SFC (Chiralcel IC-3, scCO$_2$/MeOH, 99/1 to 60/40 gradient over 4 min, 3 mL/min): R_t = 2.78 (major) and 2.43 min.

(S)-2-(2,4-Dimethoxyphenyl)cyclopentanone ((S)-11b). The title compound was prepared according to the general procedure using α-aryl-β-keto allyl ester (**9b**) to yield the product as an off-white solid (27 mg, 82%, 60% ee), identical in all respects to the previously prepared racemic sample, with the exception of $[\alpha]_D^{20}$ = −51.0 (*c* 1.0, CHCl$_3$); SFC (Chiralcel IC-3, scCO$_2$/MeOH, 99/1 to 60/40 gradient over 4 min, 3 mL/min): R_t = 2.56 (major) and 2.44 min.

(S)-2-(2,6-Dimethoxyphenyl)cyclopentanone ((S)-11c). The title compound was prepared according to the general procedure using α-aryl-β-keto allyl ester (**9c**) to yield the product as an off-white solid (31 mg, 94%, 80% ee), identical in all respects to the previously prepared racemic sample, with the exception of $[\alpha]_D^{20}$ = −70.0 (*c* 1.0, CHCl$_3$); SFC (Chiralcel IC-3, scCO$_2$/MeOH, 99/1 to 70/30 gradient over 5 min, 3 mL/min): R_t = 3.88 (major) and 3.75 min.

(S)-2-(2,3,4-Trimethoxyphenyl)cyclopentanone ((S)-11d). The title compound was prepared according to the general procedure using α-aryl-β-keto allyl ester (**9d**) to yield the product as an off-white

solid (30 mg, 80%, 70% *ee*), identical in all respects to the previously prepared racemic sample, with the exception of $[\alpha]_D^{20} = -60.5$ (*c* 1.0, CHCl$_3$); SFC (Chiralcel IC-3, scCO$_2$/MeCN, 99/1 to 70/30 gradient over 5 min, 3 mL/min): R$_t$ = 3.92 (major) and 4.51 min.

(S)-2-(2,3,6-Trimethoxyphenyl)cyclopentanone ((S)-11e). The title compound was prepared according to the general procedure using α-aryl-β-keto allyl ester (**9e**) to yield the product as an off-white solid (32 mg, 85%, 71% *ee*), identical in all respects to the previously prepared racemic sample, with the exception of $[\alpha]_D^{20} = -52.3$ (*c* 1.0, CHCl$_3$); SFC (Chiralcel IB-3, scCO$_2$/MeCN, 99/1 to 70/30 gradient over 5 min, 3 mL/min): R$_t$ = 2.74 (major) and 3.07 min.

(S)-2-(4-Methoxyphenyl)cyclopentanone ((S)-11f). The title compound was prepared according to the general procedure using α-aryl-β-keto allyl ester (**9f**) to yield the product as an off-white solid (15 mg, 53%, 29% *ee*),[42] identical in all respects to the previously prepared racemic sample, with the exception of SFC (Chiralcel IC-3, scCO$_2$/2-propanol, 99/1 to 70/30 gradient over 5 min, 3 mL/min): R$_t$ = 3.25 (major) and 2.88 min.

(S)-2-(2-Methoxynaphthalen-1-yl)cyclopentanone ((S)-11g). The title compound was prepared according to the general procedure using α-aryl-β-keto allyl ester (**9g**) to yield the product as an off-white solid (33 mg, 92%, 85% *ee*), identical in all respects to the previously prepared racemic sample, with the exception of $[\alpha]_D^{20} = -92.2$ (*c* 1.0, CHCl$_3$); SFC (Chiralcel IB-3, scCO$_2$/MeOH, 99/1 to 70/30 gradient over 5 min, 3 mL/min): R$_t$ = 2.86 (major) and 3.17 min.

(S)-2-(Benzo[d][1,3]dioxol-5-yl)cyclopentanone ((S)-11h). The title compound was prepared according to the general procedure using α-aryl-β-keto allyl ester (**9h**) to yield the product as an off-white solid (22 mg, 72%, 24% *ee*), identical in all respects to the previously prepared racemic sample, with the exception of $[\alpha]_D^{20} = -2.2$ (*c* 1.0, CHCl$_3$); SFC (Chiralcel IC-3, scCO$_2$/2-propanol, 99/1 to 70/30 gradient over 5 min, 3 mL/min): R$_t$ = 2.93 (major) and 2.72 min.

(S)-2-(2-(Benzyloxy)naphthalen-1-yl)cyclopentanone ((S)-11i). The title compound was prepared according to the general procedure using α-aryl-β-keto allyl ester (**9i**) to yield the product as an off-white solid (45 mg, 95%, 92% *ee*), identical in all respects to the previously prepared racemic sample, with the exception of $[\alpha]_D^{20} = 30.6$ (*c* 1.0, CHCl$_3$); SFC (Chiralcel IC-3, scCO$_2$/MeOH, 99/1 to 70/30 gradient over 5 min, 3 mL/min): R$_t$ = 5.73 (major) and 6.64 min.

(S)-2-(2-Methoxy-4,6-dimethylphenyl)cyclopentanone ((S)-11j). The title compound was prepared according to the general procedure using α-aryl-β-keto allyl ester (**9j**) to yield the product as an off-white solid (30 mg, 92%, 77% *ee*), identical in all respects to the previously prepared racemic sample, with the exception of $[\alpha]_D^{20} = -88.4$ (*c* 1.0, CHCl$_3$); SFC (Chiralcel IC-3, scCO$_2$/MeOH, 99/1 to 70/30 gradient over 5 min, 3 mL/min): R$_t$ = 2.83 (major) and 2.61 min.

(S)-2-(2,6-Dimethylphenyl)cyclopentanone ((S)-11k). The title compound was prepared according to the general procedure using α-aryl-β-keto allyl ester (**9k**) to yield the product as an off-white solid (26 mg, 92%, 47% *ee*), identical in all respects to the previously prepared racemic sample, with the exception of $[\alpha]_D^{20} = -88.4$ (*c* 1.0, CHCl$_3$); SFC (Chiralcel IC-3, scCO$_2$/MeCN, 99/1 to 70/30 gradient over 5 min, 3 mL/min): R$_t$ = 2.52 (major) and 2.39 min.

(S)-2-(2,4,6-Trimethoxyphenyl)cyclohexanone ((S)-18a). The title compound was prepared according to the general procedure using α-aryl-β-keto allyl ester (**10a**) to yield the product as an off-white solid (35 mg, 88%, 60% *ee*), identical in all respects to the previously prepared racemic sample, with the exception of $[\alpha]_D^{20} = -19.6$ (*c* 0.5, CHCl$_3$); SFC (Chiralcel IC-3, scCO$_2$/MeOH, 99/1 to 70/30 gradient over 5 min, 3 mL/min): R$_t$ = 3.85 (major) and 3.62 min.

(S)-2-(2,4-Dimethoxyphenyl)cyclohexanone ((S)-18b). The title compound was prepared according to the general procedure using α-aryl-β-keto allyl ester (**10b**) to yield the product as an off-white solid (34 mg, 97%, 72% *ee*), identical in all respects to the previously prepared racemic sample, with the exception of $[\alpha]_D^{20} = -20.9$ (*c* 1.0, CHCl$_3$); SFC (Chiralcel IB-3, scCO$_2$/MeCN, 99/1 to 70/30 gradient over 5 min, 3 mL/min): R$_t$ = 2.90 (major) and 3.29 min.

(S)-2-(2,6-Dimethoxyphenyl)cyclohexanone ((S)-18c). The title compound was prepared according to the general procedure using α-aryl-β-keto allyl ester (**10c**) to yield the product as an off-white solid (33 mg, 93%, 70% *ee*), identical in all respects to the previously prepared racemic sample, with the exception of $[\alpha]_D^{20} = -21.3$ (*c* 1.0, CHCl$_3$); SFC (Chiralcel IB-3, scCO$_2$/MeCN, 99/1 to 70/30 gradient over 5 min, 3 mL/min): R$_t$ = 3.64 (major) and 4.10 min.

(S)-2-(2,3,4-Trimethoxyphenyl)cyclohexanone ((S)-18d). The title compound was prepared according to the general procedure using α-aryl-β-keto allyl ester (**10d**) to yield the product as an off-white solid (33 mg, 83%, 74% *ee*), identical in all respects to the previously prepared racemic sample, with the exception of $[\alpha]_D^{20} = -25.1$ (*c* 1.0, CHCl$_3$); SFC (Chiralcel IC-3, scCO$_2$/2-propanol, 99/1 to 70/30 gradient over 5 min, 3 mL/min): R$_t$ = 2.86 (major) and 3.28 min.

(S)-2-(2,3,6-Trimethoxyphenyl)cyclohexanone ((S)-18e). The title compound was prepared according to the general procedure using α-aryl-β-keto allyl ester (**10e**) to yield the product as an off-white solid (34 mg, 87%, 67% *ee*), identical in all respects to the previously prepared racemic sample, with the exception of $[\alpha]_D^{20} = -36.7$ (*c* 0.25, CHCl$_3$); SFC (Chiralcel IB-3, scCO$_2$/MeCN, 99/1 to 70/30 gradient over 5 min, 3 mL/min): R$_t$ = 4.12 (major) and 5.55 min.

(S)-2-(4-Methoxyphenyl)cyclohexanone ((S)-18f). The title compound was prepared according to the general procedure using α-aryl-β-keto allyl ester (**10f**) to yield the product as an off-white solid (18 mg, 59%, 38% *ee*), identical in all respects to the previously prepared racemic sample, with the exception of $[\alpha]_D^{20} = -49.3$ (*c* 1.0, CHCl$_3$); SFC (Chiralcel IB-3, scCO$_2$/MeCN, 99/1 to 70/30 gradient over 5 min, 3 mL/min): R$_t$ = 3.25 (major) and 3.40 min.

(S)-2-(2-Methoxynaphthalen-1-yl)cyclohexanone ((S)-18g). The title compound was prepared according to the general procedure using α-aryl-β-keto allyl ester (**10g**) to yield the product as an off-white solid (28 mg, 72%, 74% *ee*), identical in all respects to the previously prepared racemic sample, with the exception of $[\alpha]_D^{20} = -36.8$ (*c* 1.0, CHCl$_3$); SFC (Chiralcel IC-3, scCO$_2$/MeCN, 99/1 to 70/30 gradient over 5 min, 3 mL/min): R$_t$ = 4.94 (major) and 5.30 min.

(S)-2-(Benzo[d][1,3]dioxol-5-yl)cyclohexanone ((S)-18h). The title compound was prepared according to the general procedure using α-aryl-β-keto allyl ester (**10h**) to yield the product as an off-white solid (27 mg, 82%, 63% *ee*), identical in all respects to the previously prepared racemic sample, with the exception of $[\alpha]_D^{20} = -49.3$ (*c* 1.0, CHCl$_3$); SFC (Chiralcel ID-3, scCO$_2$/MeCN, 70/30, 3 mL/min): R$_t$ = 2.52 (major) and 2.74 min.

(S)-2-(2-(Benzyloxy)naphthalen-1-yl)cyclohexanone ((S)-18i). The title compound was prepared according to the general procedure using α-aryl-β-keto allyl ester (**10i**) to yield the product as an off-white solid (40 mg, 82%, 60% *ee*), identical in all respects to the previously prepared racemic sample, with the exception of $[\alpha]_D^{20} = -6.6$ (*c* 1.0, CHCl$_3$); SFC (Chiralcel IC-3, scCO$_2$/2-propanol, 70/30, 3 mL/min): R$_t$ = 5.84 (major) and 7.39 min.

(S)-2-(2-Methoxy-4,6-dimethylphenyl)cyclohexanone ((S)-18j). The title compound was prepared according to the general procedure using α-aryl-β-keto allyl ester (**10j**) to yield the product as an off-white solid (22 mg, 63%, 64% *ee*), identical in all respects to the previously prepared racemic sample, with the exception of $[\alpha]_D^{20} = -30.6$ (*c* 1.0, CHCl$_3$); SFC (Chiralcel IC-3, scCO$_2$/2-propanol, 80/20, 3 mL/min): R$_t$ = 1.69 (major) and 1.54 min.

(R)-2-(2,4,6-Trimethoxyphenyl)cyclopentanone ((R)-11a). Powdered 4 Å molecular sieves (270 mg) were added to a flame-dried 10 mL Schlenk flask with a Teflon-coated magnetic stir bar. The flask and molecular sieves were flame-dried and backfilled with N$_2$ three times. Once the flask had cooled to ambient temperature under N$_2$, Pd(OAc)$_2$ (3.4 mg, 0.015 mmol), (*S*)-(CF$_3$)$_3$-*t*-Bu-PHOX (11.1 mg, 0.0188 mmol), and anhydrous 1,4-dioxane (1.5 mL) were added. The mixture was stirred vigorously at 40 °C for 30 min prior to the addition of formic acid (34 μL, 0.90 mmol) and followed immediately by a solution of β-ketoester **7a** (50 mg, 0.15 mmol) in anhydrous 1,4-dioxane (1.5 mL) [in a flame-dried, 2-neck, 10 mL round-bottom flask under N$_2$]. The reaction mixture was stirred at 40 °C for 10 h and filtered through Celite, and the solvent was removed *in vacuo*. The resulting solid was then purified by silica gel column chromatography (40% Et$_2$O in pentane) to yield the product as a white solid (29 mg, 76%, 55% *ee*). All physical data were identical in all respects to the previously prepared racemic sample, with the exception of $[\alpha]_D^{20} = 45.4$

(*c* 1.0, CHCl$_3$); SFC (Chiralcel IA-3, scCO$_2$/2-propanol, 99/1 to 70/30 gradient over 5 min, 3 mL/min): R$_t$ = 2.39 (major) and 2.71 min.

(R)-2-(2,4-Dimethoxyphenyl)cyclopentanone ((R)-11b). Reaction carried out according to the same procedure as for (*R*)-**11a** using Pd(OAc)$_2$ (3.4 mg, 0.015 mmol), (*S*)-(CF$_3$)$_3$-*t*-Bu-PHOX (11.1 mg, 0.0188 mmol), formic acid (34 μL, 0.90 mmol), and β-ketoester **7b** (46 mg, 0.15 mmol) to yield the product as a white solid (22 mg, 66%, 26% *ee*). All physical data were identical in all respects to the previously prepared racemic sample, with the exception of [α]$^{20}_D$ = 22.2 (*c* 1.0, CHCl$_3$); SFC (Chiralcel IC-3, scCO$_2$/MeOH, 99/1 to 60/40 gradient over 4 min, 3 mL/min): R$_t$ = 2.41 (major) and 2.54 min.

6-(2,6-Dimethoxyphenyl)-3,4-dihydro-2H-pyran-2-one (12c). Pd$_2$dba$_3$·CHCl$_3$ (8.5 mg, 0.0082 mmol) and dppe (8.2 mg, 0.0205 mmol) were dissolved in THF (2 mL, fresh Na/benzophenone still, indicator blue) in a flame-dried Schlenk flask and stirred at 40 °C for 30 min. α-Aryl-β-keto allyl ester (50 mg, 0.164 mmol) and Meldrum's acid (59 mg, 0.410 mmol) were dissolved in THF (2 mL) in a flame-dried round-bottom flask (10 mL, 2-neck) and added to the Pd-complex solution, maintained at 40 °C, in one portion. The reaction mixture was stirred at 40 °C for 2 h, filtered through a bed of charcoal on a plug of Celite, and washed with EtOAc. The filtrate was concentrated *in vacuo* and purified by silica gel column chromatography (pentane/Et$_2$O). IR (thin film) ν$_{max}$ 2925, 1704, 1594 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.27 (t, *J* = 8.4 Hz, 1H), 6.55 (d, *J* = 8.4 Hz, 2H), 5.34 (t, *J* = 4.6 Hz, 1H), 3.80 (s, 6H), 2.71 (t, *J* = 7.6 Hz, 2H), 2.50 (td, *J* = 7.6, 4.6 Hz, 2H). ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ 169.99, 158.97, 145.13, 130.82, 112.34, 106.68, 104.01, 56.19, 28.69, 19.57. HRMS: (ESI-TOF) calculated for C$_{13}$H$_{15}$O$_4$ [M + H$^+$] 235.0970, found 235.0971.

3,3-Dimethyl-7,11-diphenyl-2,4-dioxaspiro[5.5]undecane-1,5,9-trione (17). Pd$_2$dba$_3$·CHCl$_3$ (39 mg, 0.038 mmol) and Meldrum's acid (270 mg, 1.87 mmol) were dissolved in THF (7.5 mL) and stirred at 40 °C for 12 h. The solvent was removed *in vacuo*, and the resulting residue was purified by silica gel column chromatography (10% Et$_2$O in pentane) to yield the product as a white solid (25 mg, 58%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.37–7.22 (m, 10H), 4.02 (dd, *J* = 14.4, 4.3 Hz, 2H), 3.73 (t, *J* = 14.4 Hz, 2H), 2.65 (dd, *J* = 14.4, 4.3 Hz, 2H), 0.55 (s, 6H). All other physical data were identical to those previously reported.[34b]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H and ^{13}C NMR spectra of all new compounds, SFC chromatograms of new chiral compounds, and X-ray crystal structure of compounds **11a** and **18b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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(32) Please see the Supporting Information for the synthesis of this substrate.

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