Article

Catalytic Asymmetric Synthesis of Sterically Hindered Tertiary alpha-Aryl Ketones

Robert Doran, and Patrick Jerome Guiry

J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/jo5014806 • Publication Date (Web): 03 Sep 2014

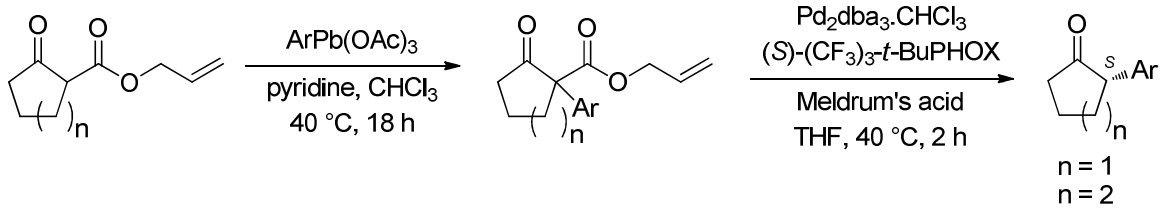
Catalytic Asymmetric Synthesis of Sterically Hindered Tertiary α-Aryl Ketones

Robert Doran and Patrick J. Guiry*

Centre for Synthesis and Chemical Biology, School of Chemistry and Chemical Biology, University College Dublin, Belfield, Dublin 4, Ireland.

*E-mail: patrick.guiry@ucd.ie.

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 and, 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 last decade.

A number of approaches have been developed for the catalytic asymmetric synthesis of quaternary α-aryl carbonyl containing compounds. However, the basic conditions employed in 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 developed an organocatalytic enantioselective α-arylation of

aldehydes with quinones.[2] Fu 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 independently reported the enantioselective Cu-catalyzed α-arylation of silyl-N-acyloxazolidinones with diaryliodonium salts using bisoxazoline ligands.[5] Zhou 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]

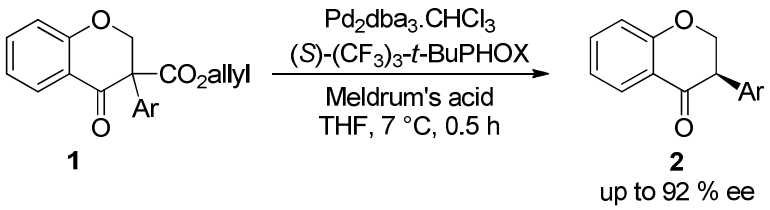
All of the above methods introduce the aryl group during the enantiodetermining step. An alternative strategy would be to already have the aryl group in place and to generate the tertiary stereocentre via an asymmetric protonation of an enolate complex. This was first realized by the pioneering work 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-$SnCl_4$ 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 which 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 desymmetrisation 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 which describe the asymmetric synthesis of tertiary α-aryl cyclopentanones. The first of these was reported by Shi via asymmetric epoxidation of benzylidene cyclobutanes and epoxide rearrangement in a subsequent step.[21] Bäckvall 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 using a series of Sc-catalyzed diazoalkane-carbonyl homologations with bis/tris oxazoline ligands.[23]

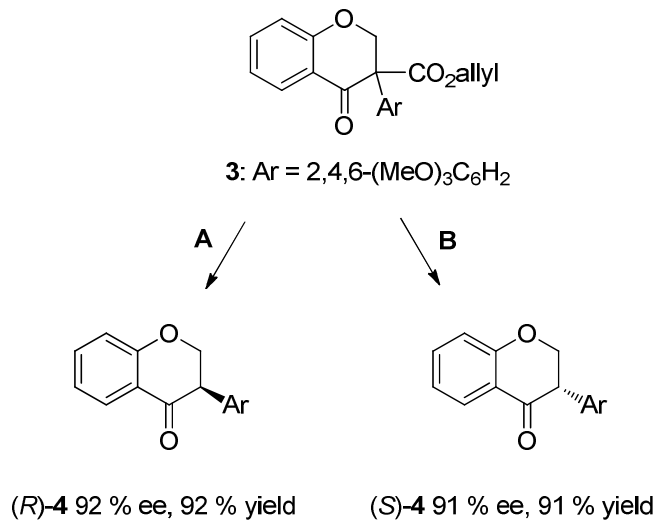
The Pd-catalyzed asymmetric decarboxylative protonation reaction was developed by Stoltz to generate tertiary α-alkyl/benzyl ketones. The first report used formic acid, in the presence of molecular sieves, as the proton source to intercept the intermediate generated from a decarboxylative allylation reaction and form a tertiary stereocentre in the α-position with *ee*'s with up to 94 %.[24] Subsequently homogeneous conditions were developed by Stoltz 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 centre 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. Enantiodivergence observed with different H^+ sources. A: $Pd_2dba_3.CHCl_3$, (*S*)-$(CF_3)_3$-*t*-BuPHOX, Meldrum's acid, THF, 7 °C, 0.5 h. **B**: $Pd(OAc)_2$, (*S*)-$(CF_3)_3$-*t*-BuPHOX, formic acid, 4 Å mol. sieves, 1,4-dioxane, 40 °C, 10 h.

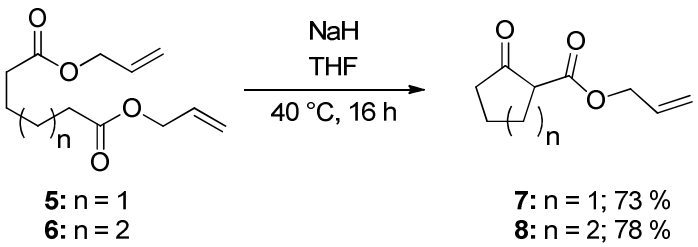


We now wish to expand the scope of this work to the catalytic asymmetric synthesis of tertiary α-aryl cyclohexanones and, in particular, cyclopentanones given the dearth of reported methods for their direct asymmetric synthesis to date. These substrates are readily accessible and would enable us to develop general catalytic conditions which could be applied to more complex systems in 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 with allyl alcohol, was cyclized in the same manner to yield cyclohexanone β-keto allyl ester **8** in 74 % yield over 2 steps using a previously reported method.[28]

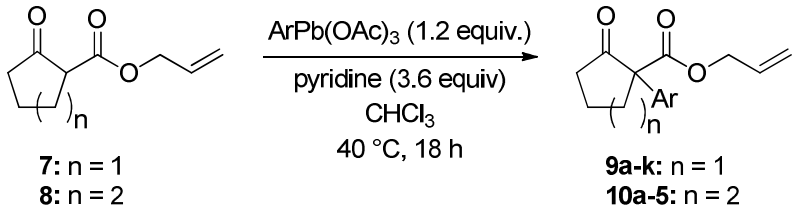
Scheme 3. Synthesis of cyclopentanone β-keto allyl ester.



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 centre 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.

Table 1. Synthesis of α-aryl-β-keto allyl esters.



7: n = 1
8: n = 2

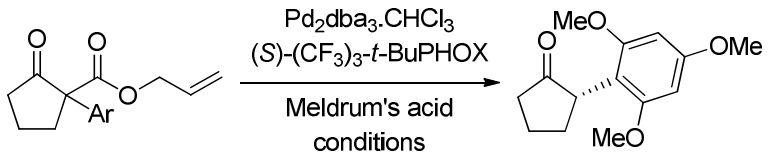
9a-k: n = 1
10a-5: n = 2

Substrate	Ar	Yield (%) **9**	Yield (%) **10**
a	2,4,6-$(MeO)_3C_6H_2$	80	60
b	2,4-$(MeO)_2C_6H_3$	77	90
c	2,6-$(MeO)_2C_6H_3$	84	61
d	2,3,4-$(MeO)_3C_6H_2$	91	94
e	2,3,6-$(MeO)_3C_6H_2$	91	85
f	4-$MeOC_6H_4$	61	92
g	2-$MeOC_{10}H_6$	62	89
h	3,4−(OCH_2O)−C_6H_3	89	86
i	2-$BnOC_{10}H_6$	67	79
j	2-MeO-4,6-$Me_2C_6H_2$	90	90
k	2,6-$Me_2C_6H_3$	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.

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 $Pd_2dba_3.CHCl_3$, (*S*)-$(CF_3)_3$-*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 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 °C to 23 °C. This resulted in further increase in enantioinduction up to 75 % *ee* (Table 2, entry 9). We then re-examined THF at

Table 2. Optimization of conditions for the decarboxylative asymmetric protonation.



9a **11a**

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_2O	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

Reactions carried out with 5 mol % $Pd_2dba_3.CHCl_3$ and 12.5 mol % ligand in 0.20 M substrate concentration unless otherwise stated. [a] % conversion determined by chiral HPLC analysis. Yields in parentheses. [b] % ee values determined by chiral SFC analysis. [c] Using commercial Pd_2dba_3. [d] 1.0 equiv. Meldrum's acid. [e] 5.0 equiv. 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. Meldrum's acid. [k] Using (*S*)-*t*-BuPHOX.

this higher temperature and this further increased the *ee* to 82 % with an 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).

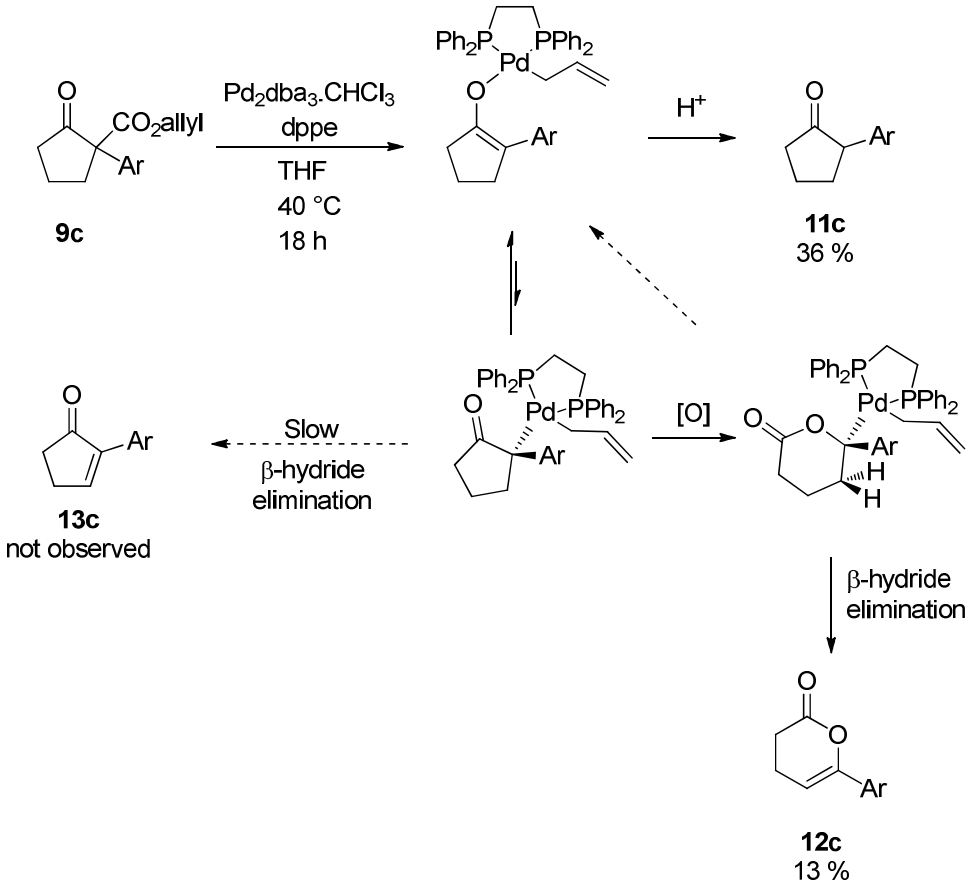
Further attempts were made to improve the level of enantioselectivity. Surprisingly, using only 1.0 equivalent of Meldrum's acid did not result in the formation of the competitive allylation product and had no effect on the enantioselectivity (Table 2, entry 14). Increasing this to 5.0 equivalents had 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 equivalents 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 during the course of optimization of the reaction conditions we found the *ee* values would slowly increase over time when the reaction was carried out at 23 °C 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 the intermediate is not a monomeric Pd-bound species. A previous report by Stoltz and co-workers suggested 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 been deprotonated under the reaction conditions. This led us to the conclusion that a long-lived intermediate was being slowly protonated over time. We believed when the reaction was sampled for chromatographic analysis this intermediate was been 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.

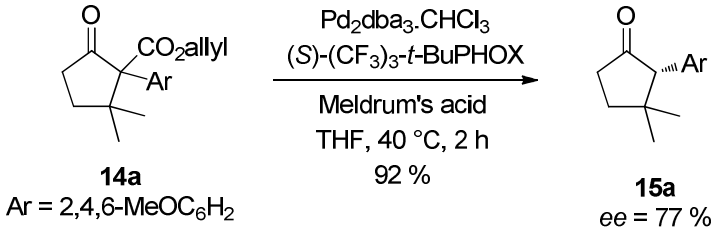
Scheme 4. Proposed mechanism for the formation of lactone 12c.



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 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 set-up and had not been refluxed for a sufficient time to allow complete degassing of the solvent, evident by the deep blue color which indicates the THF is relatively dry however, a deep purple color indicates 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 which 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 by-product with this substrate. We subsequently concluded that degassed and peroxide free THF prevented the formation of lactone **12c**.

Scheme 5. β-g*em*-Dimethyl substituted cyclopentanone analogue.

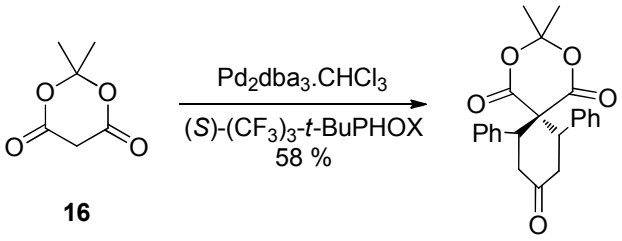


14a
Ar = 2,4,6-MeOC$_6$H$_2$

15a
ee = 77 %

Another minor by-product was also during this study due to a side reaction between dibenzylideneacetone, a ligand from the Pd^0 precursor, and Meldrum's acid in the presence of (*S*)-$(CF_3)_3$-*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 by-product from Pd_2dba_3.[34]

Scheme 6. Formation of by-product of Pd_2dba_3 and Meldrum's acid.



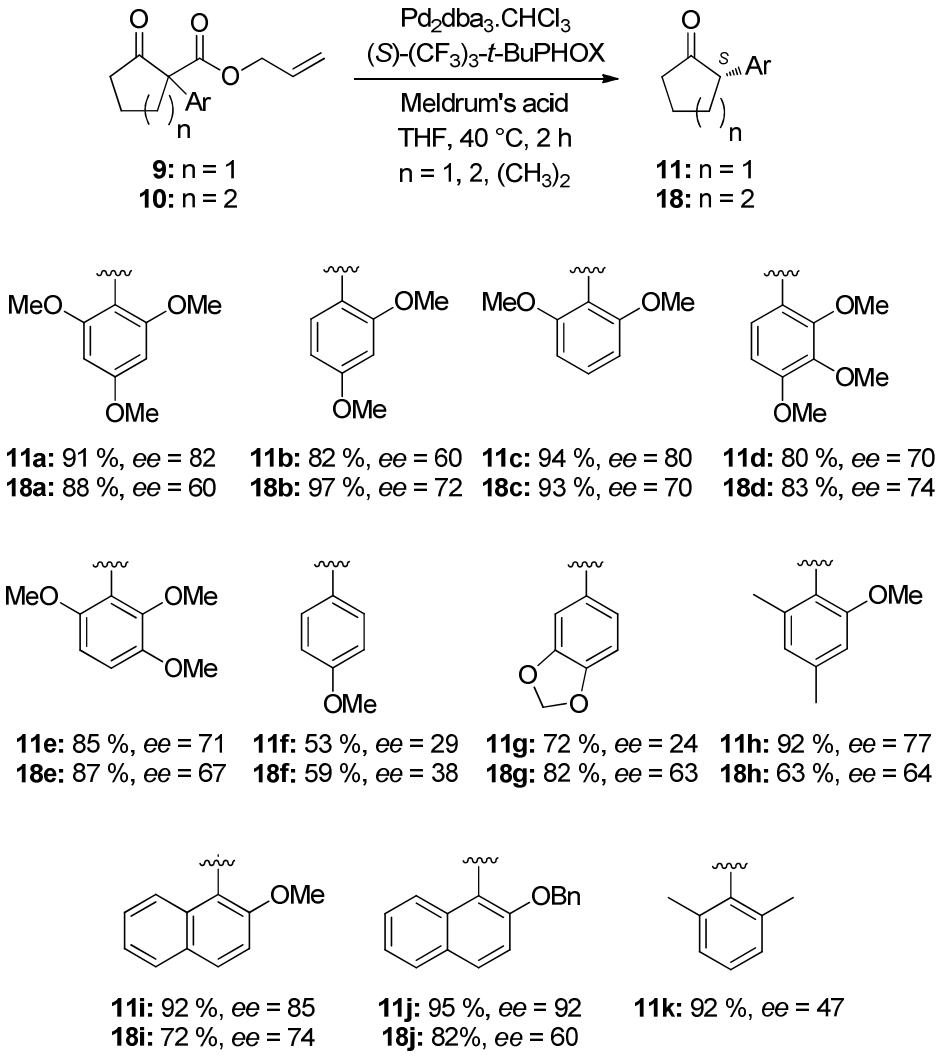
16

17

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 (**11i**, 92 % *ee*). This high *ee* was unfortunately not transferred to the cyclohexanone substrate (**18i**) 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 **18g**, 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 (**11j**) 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 centre. The presence of steric bulk in the β position had little effect on the level of enantioselectivity as observed with the β-g*em*-dimethyl substituted cyclopentanone analogue (**15a**, Scheme 5). With a 2,4,6-trimethoxypheny group an *ee* of 77 % was observed compared with 82 % in the absence of substitution in the β-position.

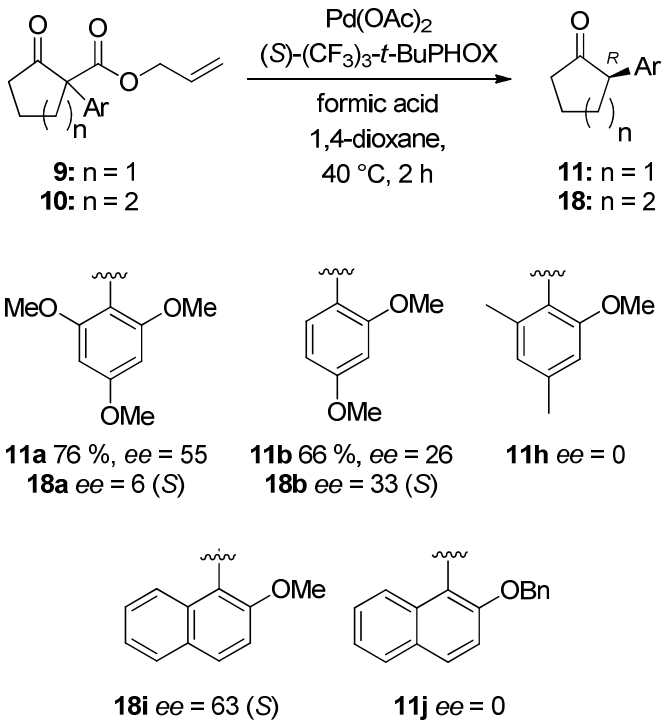
Scheme 7. Scope and enantioselectivity of tertiary α-aryl cyclopentanones and cyclohexanones.



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,[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 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 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.

Scheme 8. Scope of the switch in enantioselectivity using formic acid.



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 stereocentre 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 (3Å beads, 20 g/100 mL for 3 d). $Pd(OAc)_2$ was purchased from Strem. Powdered activated 4Å 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 aluminium plates pre-coated with silica gel F254. They were visualised 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, $(CD_3)_2CO$ = δ 2.05 ppm). ^{13}C-NMR are referenced to the residual solvent peak ($CDCl_3$ = δ 77.16 ppm, $(CD_3)_2CO$ = 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 (Hz), integration. High resolution mass spectra [electrospray ionisation (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 a FT-IR spectrometer and are reported in terms wavenumbers (ν_{max}) with units of reciprocal centimetres (cm^{-1}). Optical rotation (α) values were measured at room temperature and specific rotation ($[\alpha]_D^{20}$) values are given in degrees (°). 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_2SO_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 was 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_2SO_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 colourless oil (311 mg, 54 %). R_f = 0.38 (40 % Et_2O 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_2SO_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_2SO_4 and filtered. The solvent was removed *in vacuo* and the resulting oil was purified by silica gel column chromatography (pentane/Et_2O 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_2O in pentane); IR (thin solid film) ν_{max} 2940, 1748, 1715, 1608 cm^{-1}; M.P. = 92-93 °C; ^1H 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); $^{13}C\{^1H\}$ 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 $C_{20}H_{26}O_6Na$ [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_2O in pentane); IR (thin solid film) ν_{max} 2942, 1748, 1722, 1608, 1588 cm^{-1}; M.P. = 74-75 °C; ^1H 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); $^{13}C\{^1H\}$ 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 $C_{18}H_{22}O_6Na$ [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_2O in pentane); IR (thin solid film) ν_{max} 2958, 1751, 1724, 1613 cm^{-1}; M.P. = 74-76 °C; ^1H 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 $C_{17}H_{20}O_5Na$ [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_2O 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 $C_{17}H_{20}O_5Na$ [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_2O 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 $C_{18}H_{22}O_6Na$ [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 colourless oil (454 mg, 91 %). R_f = 0.23 (40 % Et_2O 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 $C_{18}H_{22}O_6Na$ [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 colourless oil (247 mg, 61 %). R_f = 0.41 (40 % Et_2O in pentane); IR (thin film) ν_{max} 2957, 1749, 1730 cm^{-1}; ^1H 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); $^{13}C\{^1H\}$ 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 $C_{16}H_{18}O_4Na$ [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_2O in pentane); IR (thin solid film) ν_{max} 2948, 1744, 1716 cm^{-1}; M.P. = 83-85 °C; ^1H 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); $^{13}C\{^1H\}$ 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 $C_{20}H_{20}O_4Na$ [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 colourless oil (382 mg, 89 %). R_f = 0.45 (40 % Et_2O in pentane); IR (thin film) ν_{max} 2890, 1751, 1730 cm^{-1}; ^1H 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); $^{13}C\{^1H\}$ 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 $C_{16}H_{16}O_5Na$ [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_2O in pentane); IR (thin solid film) ν_{max} 2948, 1743, 1715 cm^{-1}; M.P. = 121-123 °C; ^1H 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); $^{13}C\{^1H\}$ 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 $C_{26}H_{24}O_4Na$ [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 colourless oil (404 mg, 90 %). R_f = 0.43 (40 % Et_2O in pentane); IR (thin film) ν_{max} 2971, 1748, 1720 cm^{-1}; ^1H 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); $^{13}C\{^1H\}$ 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 $C_{18}H_{22}O_4Na$ [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 colourless oil (146 mg, 36 %). R_f = 0.63 (40 % Et_2O in pentane); IR (thin film) ν_{max} 2969, 1748, 1716 cm^{-1}; ^1H 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); $^{13}C\{^1H\}$ 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 $C_{17}H_{20}O_3Na$ [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 colourless oil (518 mg, 60 %). R_f = 0.10 (40 % Et_2O in pentane); IR (thin film) ν_{max} 2940, 1729, 1718, 1607 cm^{-1}; ^1H 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); $^{13}C\{^1H\}$ 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 $C_{19}H_{24}O_6Na$ [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 colourless oil (394 mg, 90 %). R_f = 0.23 (40 % Et_2O in pentane); IR (thin film) ν_{max} 2940, 1732, 1715, 1612 cm^{-1}; ^1H 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); $^{13}C\{^1H\}$ 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 $C_{18}H_{22}O_5Na$ [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 colourless oil (268 mg, 61 %). R_f = 0.19 (40 % Et_2O in pentane); IR (thin film) ν_{max} 2940, 1719, 1736, 1587 cm^{-1}; ^1H 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); $^{13}C\{^1H\}$ 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 colourless oil (447 mg, 94 %). R_f = 0.24 (40 % Et_2O in pentane); IR (thin film) ν_{max} 2945, 1733, 1712 cm^{-1}; ^1H 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); $^{13}C\{^1H\}$ 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_2O 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 colourless oil (362 mg, 92 %). R_f = 0.41 (40 % Et_2O 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 colourless oil (412 mg, 89 %). R_f = 0.29 (40 % Et_2O 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_2O 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_2O in pentane); IR (thin solid film) ν_{max} 2942, 1732, 1718 cm^{-1}; M.P. = 84-87 °C; ^1H 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); $^{13}C\{^1H\}$ 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 colourless oil (390 mg, 90 %). R_f = 0.37 (40 % Et_2O in pentane); IR (thin film) ν_{max} 2935, 1721, 1711, 1612 cm^{-1}; ^1H 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); $^{13}C\{^1H\}$ 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_2O. The solvent was removed *in vacuo* and the resulting residue was purified by silica gel column chromatography (pentane/Et_2O).

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 an pale yellow oil (14.5 mg, 35 %). R_f = 0.15 (40 % Et_2O in pentane); IR (thin film) ν_{max} 2953, 1739, 1608 cm^{-1}; M.P. = 87-89 °C; ^1H 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); $^{13}C\{^1H\}$ 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_2O in pentane); IR (thin solid film) ν_{max} 2960, 1738, 1609 cm^{-1}; M.P. = 87-89 °C; ^1H 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); $^{13}C\{^1H\}$ 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 $C_{14}H_{18}O_4Na$ [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_2O in pentane); IR (thin film) ν_{max} 2960, 1739, 1614 cm^{-1}; ^1H 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); $^{13}C\{^1H\}$ 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 $C_{13}H_{16}O_3Na$ [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_2O in pentane); IR (thin solid film) ν_{max} 2961, 1739, 1594 cm^{-1}; M.P. = 52-54 °C; ^1H 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); $^{13}C\{^1H\}$ 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 $C_{13}H_{16}O_3Na$ [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_2O in pentane); IR (thin film) ν_{max} 2960, 1739, 1602 cm^{-1}; ^1H 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); $^{13}C\{^1H\}$ 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 $C_{14}H_{18}O_4Na$ [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_2O in pentane); IR (thin film) ν_{max} 2959, 1739 cm^{-1}; ^1H 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); $^{13}C\{^1H\}$ 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 $C_{14}H_{18}O_4Na$ [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_2O in pentane); IR (thin film) ν_{max} 2927, 1706, 1668, 1601, 1511 cm^{-1}; ^1H 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); $^{13}C\{^1H\}$ 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 $C_{12}H_{14}O_2Na$ [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_2O in pentane); IR (thin solid film) ν_{max} 2962, 1740 cm^{-1}; M.P. = 115-118 °C; ^1H 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); $^{13}C\{^1H\}$ 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 $C_{16}H_{16}O_2Na$ [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_2O in pentane); IR (thin film) ν_{max} 2922, 1733, 1674 cm^{-1}; ^1H 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); $^{13}C\{^1H\}$ 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_2O in pentane); IR (thin solid film) ν_{max} 2958, 1739, 1593 cm^{-1}; M.P. = 114-116 °C; ^1H 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); $^{13}C\{^1H\}$ 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 $C_{22}H_{20}O_2Na$ [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_2O in pentane); IR (thin film) ν_{max} 2958, 1739, 1612, 1581 cm^{-1}; ^1H 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); $^{13}C\{^1H\}$ 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 $C_{14}H_{18}O_2Na$ [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_2O in pentane); IR (thin film) ν_{max} 2960, 1738 cm^{-1}; ^1H 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); $^{13}C\{^1H\}$ 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_2O in pentane); IR (thin solid film) ν_{max} 2939, 1710, 1608 cm^{-1}; M.P. = 109-111 °C; ^1H 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); $^{13}C\{^1H\}$ 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 $C_{15}H_{20}O_4Na$ [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_2O in pentane); IR (thin solid film) ν_{max} 2937, 1712, 1613, 1588 cm^{-1}; M.P. = 92-93 °C; ^1H 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 $C_{14}H_{18}O_3Na$ [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_2O in pentane); IR (thin film) ν_{max} 2938, 1711, 1594 cm^{-1}; M.P. = 79-81 °C; ^1H 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 $C_{14}H_{18}O_3Na$ [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_2O in pentane); IR (thin film) ν_{max} 2936, 1711, 1604 cm^{-1}; ^1H 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 $C_{15}H_{20}O_4Na$ [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_2O in pentane); IR (thin film) ν_{max} 2939, 1709 cm^{-1}; M.P. = 97-100 °C; ^1H 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 $C_{15}H_{20}O_4Na$ [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_2O in pentane); IR (thin solid film) ν_{max} 2926, 1704 cm^{-1}; M.P. = 86-88 °C; ^1H 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 $C_{13}H_{16}O_2Na$ [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_2O in pentane); IR (thin solid film) ν_{max} 2937, 1708, 1596 cm^{-1}; M.P. = 116-118 °C; ^1H 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); $^{13}C\{^1H\}$ 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 $C_{17}H_{18}O_2Na$ [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_2O in pentane); IR (thin solid film) ν_{max} 2930, 1710 cm^{-1}; M.P. = 88-90 °C; ^1H 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); $^{13}C\{^1H\}$ 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_2O in pentane); IR (thin solid film) ν_{max} 2937, 1707, 1595 cm^{-1}; M.P. = 129-130 °C; ^1H 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); $^{13}C\{^1H\}$ 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_2O in pentane); IR (thin film) ν_{max} 2935, 1710, 1580 cm^{-1}; ^1H 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); $^{13}C\{^1H\}$ 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. $Pd_2dba_3 \cdot CHCl_3$ (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_2O).

(*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_2Cl_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 stirbar. The flask and molecular sieves were flame dried and back-filled 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_2O in pentane) to yield the product as a white solid (29 mg, 76 %, 55 % *ee*). All physical data 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 identical in all respects to the previously prepared racemic sample, with the exception of $[\alpha]_D^{20}$ = 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). $Pd_2dba_3 \cdot CHCl_3$ (8.5 mg, 0.0082 mmol) and dppe (8.2 mg, 0.0205 mmol) were dissolved 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_2O). IR (thin film) ν_{max} 2925, 1704, 1594 cm^{-1}; ^1H 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). $^{13}C\{^1H\}$ 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). $Pd_2dba_3.CHCl_3$ (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_2O in pentane) to yield the product as a white solid (25 mg, 58 %). ^1H 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 was identical to those previously reported.[34b]

Author Information

Corresponding Author: *Fax: (+353) 1-7162501. E-mail: patrick.guiry@ucd.ie.

Acknowledgements

RD is grateful for the award of an Irish Research Council (IRC) EMBARK Initiative PhD Scholarship. We acknowledge facilities provided by the Centre for Synthesis and Chemical Biology

(CSCB), funded by the Higher Education Authority's Programme for Research in Third-Level Institutions (PRTLI).

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.

References

1. (a) Roszkowski, A. P.; Rooks, W. H.; Tomolonis, A. J.; Miller, L. M., *J. Pharmacol. Exp. Ther.* **1971,** *179*, 114-123; (b) Aubert, D.; Ferrand, C.; Maffrand, J.-P. (*Sanofi S.A.*). *Thieno [3,2-c] pyridine derivatives and their therapeutic application.* US Patent 4529596, Jul 16, 1985.
2. Alemán, J.; Cabrera, S.; Maerten, E.; Overgaard, J.; Jørgensen, K. A., *Angew. Chem., Int. Ed.* **2007,** *46*, 5520-5523.
3. (a) Lundin, P. M.; Esquivias, J.; Fu, G. C., *Angew. Chem., Int. Ed.* **2009,** *48*, 154-156; (b) Lou, S.; Fu, G. C., *J. Am. Chem. Soc.* **2010,** *132*, 1264-1266.
4. Allen, A. E.; MacMillan, D. W. C., *J. Am. Chem. Soc.* **2011,** *133*, 4260-4263.
5. (a) Harvey, J. S.; Simonovich, S. P.; Jamison, C. R.; MacMillan, D. W. C., *J. Am. Chem. Soc.* **2011,** *133*, 13782-13785; (b) Bigot, A.; Williamson, A. E.; Gaunt, M. J., *J. Am. Chem. Soc.* **2011,** *133*, 13778-13781.
6. Huang, Z.; Liu, Z.; Zhou, J., *J. Am. Chem. Soc.* **2011,** *133*, 15882-15885.
7. Huang, Z.; Lim, L. H.; Chen, Z.; Li, Y.; Zhou, F.; Su, H.; Zhou, J., *Angew. Chem., Int. Ed.* **2013,** *52*, 4906-4911.
8. Huang, Z.; Chen, Z.; Lim, L. H.; Quang, G. C. P.; Hirao, H.; Zhou, J., *Angew. Chem., Int. Ed.* **2013,** *52*, 5807-5812.
9. Ishihara, K.; Kaneeda, M.; Yamamoto, H., *J. Am. Chem. Soc.* **1994,** *116*, 11179-11180.
10. Ishihara, K.; Nakamura, S.; Kaneeda, M.; Yamamoto, H., *J. Am. Chem. Soc.* **1996,** *118*, 12854-12855.
11. Nakamura, S.; Kaneeda, M.; Ishihara, K.; Yamamoto, H., *J. Am. Chem. Soc.* **2000,** *122*, 8120-8130.
12. Cheon, C. H.; Yamamoto, H., *J. Am. Chem. Soc.* **2008,** *130*, 9246-9247.
13. Cheon, C. H.; Imahori, T.; Yamamoto, H., *Chem. Commun.* **2010,** *46*, 6980-6982.
14. Nakamura, Y.; Takeuchi, S.; Ohgo, Y.; Yamaoka, M.; Yoshida, A.; Mikami, K., *Tetrahedron Lett.* **1997,** *38*, 2709-2712.
15. Nakamura, Y.; Takeuchi, S.; Ohgo, Y.; Yamaoka, M.; Yoshida, A.; Mikami, K., *Tetrahedron* **1999,** *55*, 4595-4620.
16. Yanagisawa, A.; Touge, T.; Arai, T., *Angew. Chem., Int. Ed.* **2005,** *44*, 1546-1548.
17. (a) Asensio, G.; Cuenca, A.; Rodriguez, N.; Medio-Simón, M., *Tetrahedron: Asymm.* **2003,** *14*, 3851-3855; (b) Asensio, G.; Cuenca, A.; Gaviña, P.; Medio-Simón, M., *Tetrahedron Lett.* **1999,** *40*, 3939-3940.
18. Cheon, C. H.; Kanno, O.; Toste, F. D., *J. Am. Chem. Soc.* **2011,** *133*, 13248-13251.
19. Zhou, L.; Liu, X.; Ji, J.; Zhang, Y.; Hu, X.; Lin, L.; Feng, X., *J. Am. Chem. Soc.* **2012,** *134*, 17023-17026.
20. Aggarwal, V. K.; Olofsson, B., *Angew. Chem., Int. Ed.* **2005,** *44*, 5516-5519.
21. Shen, Y.-M.; Wang, B.; Shi, Y., *Angew. Chem., Int. Ed.* **2006,** *45*, 1429-1432.
22. Warner, M. C.; Nagendiran, A.; Bogár, K.; Bäckvall, J.-E., *Org. Lett.* **2012,** *14*, 5094-5097.
23. Rendina, V. L.; Kaplan, H. Z.; Kingsbury, J. S., *Synthesis* **2012**, 686-693.

24. Mohr, J. T.; Nishimata, T.; Behenna, D. C.; Stoltz, B. M., *J. Am. Chem. Soc.* **2006,** *128*, 11348-11349.
25. Marinescu, S. C.; Nishimata, T.; Mohr, J. T.; Stoltz, B. M., *Org. Lett.* **2008,** *10*, 1039-1042.
26. Carroll, M. P.; Muller-Bunz, H.; Guiry, P. J., *Chem. Commun.* **2012,** *48*, 11142-11144.
27. Doran, R.; Carroll, M. P.; Akula, R.; Hogan, B. F.; Martins, M.; Fanning, S.; Submitted Publication.
28. Mohr, J. T.; Krout, M. R.; Stoltz, B. M., *Org. Synth.* **2009,** *86*, 194-211.
29. Pinhey, J.; Rowe, B., *Aust. J. Chem.* **1980,** *33*, 113-120.
30. Carroll, M. P. Development of a Catalytic Asymmetric Synthesis of Isoflavanones. PhD Thesis, University College Dublin, 2012.
31. The lactone by-product was also observed when the aryl group was a 2,4,6-trimethoxypheyl however it was not isolable from the protonated product 11a.
32. Please see supporting information for the synthesis of this substrate.
33. (a) Kilroy, T. G.; Hennessy, A. J.; Connolly, D. J.; Malone, Y. M.; Farrell, A.; Guiry, P. J., *J. Mol. Catal. A: Chem.* **2003,** *196*, 65-81; (b) Hennessy, A. J.; Connolly, D. J.; Malone, Y. M.; Guiry, P. J., *Tetrahedron Lett.* **2000,** *41*, 7757-7761; (c) Hennessy, A. J.; Malone, Y. M.; Guiry, P. J., *Tetrahedron Lett.* **2000,** *41*, 2261-2264; (d) Hennessy, A. J.; Malone, Y. M.; Guiry, P. J., *Tetrahedron Lett.* **1999,** *40*, 9163-9166.
34. (a) Ramachary, D. B.; Chowdari, N. S.; Barbas, C. F., *Angew. Chem., Int. Ed.* **2003,** *42*, 4233-4237; (b) Chande, M. S.; Khanwelkar, R. R., *Tetrahedron Lett.* **2005,** *46*, 7787-7792.
35. Zalesskiy, S. S.; Ananikov, V. P., *Organometallics* **2012,** *31*, 2302-2309.
36. Back, T. G.; Gladstone, P. L.; Parvez, M., *J. Org. Chem.* **1996,** *61*, 3806-3814.
37. Boddaert, T.; Coquerel, Y.; Rodriguez, J., *Eur. J. Org. Chem.* **2011,** *2011*, 5061-5070.
38. Zou, Y.; Millar, J. G., *J. Org. Chem.* **2009,** *74*, 7207-7209.
39. Suginome, H.; Ishikawa, M.; Yorita, K.; Shimoyama, N.; Sasaki, T.; Orito, K., *J. Org. Chem.* **1995,** *60*, 3052-3064.
40. Murthi, K. K.; Dubay, M.; McClure, C.; Brizuela, L.; Boisclair, M. D.; Worland, P. J.; Mansuri, M. M.; Pal, K., *Bioorg. Med. Chem. Lett.* **2000,** *10*, 1037-1041.
41. Ginsburg, D.; Pappo, R., *J. Am. Chem. Soc.* **1953,** *75*, 1094-1097.
42. Enantiomeric excess obtained for crude sample of the reaction mixture. Product racemised during purification.