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Enantiodivergent Synthesis of Tertiary α-Aryl 1-Indanones: Evidence Toward Disparate Mechanisms in the Palladium-Catalyzed Decarboxylative Asymmetric Protonation

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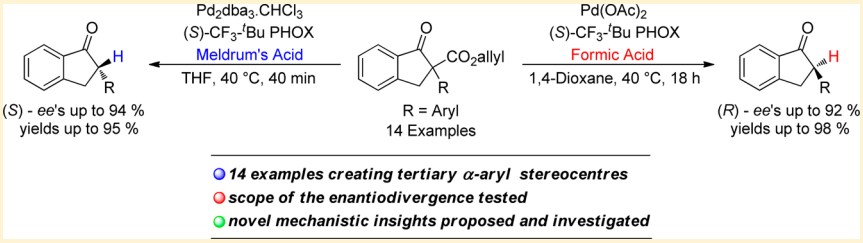
Supporting Information



ABSTRACT: Herein, we describe a study into the scope and origin of an enantiodivergent effect in the palladium-catalyzed decarboxylative asymmetric protonation. By switching the achiral proton source, both enantiomers of a series of tertiary α-aryl-1-indanones are readily accessed from the corresponding α-aryl-β-keto allyl esters. In this example of dual stereocontrol, enantioselectivities up to 94% (*S*) and 92% (*R*) were achieved using Meldrum's acid and formic acid, respectively. In an attempt to rationalize this switch in absolute configuration an investigation of the ambiguous mechanism of the decarboxylative asymmetric protonation was conducted. A novel catalytic cycle for the reaction with formic acid is proposed and subjected to a variety of experimental studies.

INTRODUCTION

Palladium-catalyzed decarboxylative asymmetric protonation (DAP) is a powerful tool for the enantioselective synthesis of tertiary stereocenters adjacent to a carbonyl. Originally, the racemic decarboxylative protonation was developed by Tsuji and co-workers as a mild method of allyl β-keto ester hydrogenolysis to avoid the alternative harsh hydrolysis and decarboxylation conditions.[1] Using a palladium catalyst in the presence of triethylammonium formate, a variety of linear and cyclic tertiary α-alkyl ketones were isolated in excellent yields with ester, ether, and other ketone functionalities well tolerated (Figure 1, A). Several years later an enantioselective variant was reported by Muzart and Hénin using (2-methyl-1-indenyl)-benzyl or allyl carbonates in the presence of a palladium catalyst and chiral proton source (Figure 1, B).[2] With initial *ee*'s up to 40%, further investigation greatly expanded the scope of the reaction to α-alkyl, benzyl, phenyl, and fluorine substituted allyl or benzyl β-keto esters.[3] Subsequently, Stoltz and co-workers reported the DAP of allyl β-keto esters using a chiral palladium-PHOX system and formic acid (Figure 1, C).[4] A variety of monocyclic and fused aromatic compounds with α-alkyl, fluoro, allyl, and benzyl substituents were accessed in excellent *ee*'s up to 94%. A homogeneous variant using Meldrum's acid as the proton source was developed shortly thereafter to avoid the substrate-dependent optimization of the amount of sieves and acid required in the heterogeneous formic acid reaction.[5] In this case, the terms homo- and heterogeneous only refer to the presence of molecular sieves in the reaction mixture and are not a comment on the nature of the reaction. Similar monocyclic and fused aromatic compounds bearing α-alkyl, silyl ether, allyl, and benzyl substituents were accessed in comparable yields but slightly lower *ee*'s to those obtained with formic acid.

Recently our laboratory utilized the DAP for the preparation of tertiary α-aryl stereocenters in the first catalytic asymmetric synthesis of isoflavanones.[6] In contrast to other enantioselective approaches to tertiary α-aryl ketones, the best results were obtained with very sterically hindered di-*ortho* substituted arenes with *ee*'s up to 92%.[7] Interestingly, further investigation of the model α-arylated isoflavanone revealed a novel enantiodivergent effect based on the choice of proton source (Figure 1, D).[8] Enantiodivergent methodology, wherein enantioselectivity is determined by a factor other than the supposed chiral promoter, is an attractive route to both product enantiomers, particularly when both enantiomers of the required chiral ligand are not readily available.[9] Interestingly, Stoltz had observed no such effect in their studies with α-alkyl, allyl, or benzyl substituents. Based on the mechanistic ambiguity of the DAP, it was speculated the enantiodivergence may result from a change in pathway depending on the proton source used. Our research group conducted preliminary testing of the enantiodivergent methodology in the synthesis of tertiary

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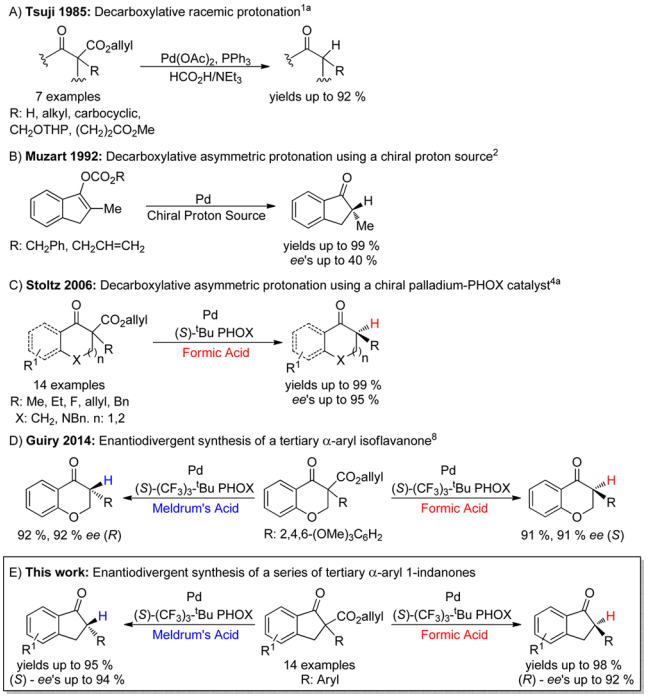


Figure 1. Development of the enantiodivergent decarboxylative asymmetric protonation.

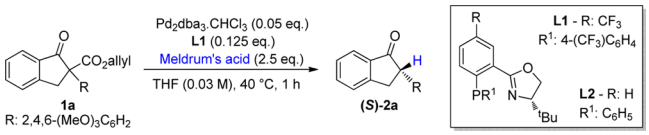
α-aryl aliphatic monocyclic ketones.[10] Disappointingly, the opposite enantiomers were obtained in just two of the seven α-aryl substrates investigated. However, based on the low enantioselectivities of the products with formic acid (0–63% *ee*) and limited number of substrates examined, further testing across a range of substrates was deemed necessary before the synthetic utility of the methodology is accurately determined. Furthermore, we aimed to elucidate a definitive mechanism for the heterogeneous DAP in an attempt to explain the acid-dependent enantiodivergence.

In choosing an appropriate molecular scaffold for our investigation we became interested in the synthesis of tertiary α-aryl 1-indanones due to their prevalence as, and as precursors for, a range of pharmaceuticals[11] and other useful materials such as dyes.[12] The enantioselective synthesis of α-substituted-tertiary-1-indanones has been investigated previously but with a limited substrate scope.[2,3a,4a,5a,13] Only two examples of α-arylated products were found with phenyl- and *para*-methoxyphenyl-substituted products synthesized in moderate *ee*'s.[14]

RESULTS AND DISCUSSION

Reaction Condition Optimization. Our study commenced with the synthesis of allyl β-keto ester model substrate **1a**. α-Acylation of 1-indanone using sodium hydride and diallyl carbonate was followed by α-arylation with the corresponding aryllead triacetate reagent.[15] The 2,4,6-trimethoxyphenyl-substituted β-keto allyl ester **1a** was chosen as the model substrate for reaction optimization. After some experimentation, a combination of $Pd_2dba_3{\cdot}CHCl_3$, the chiral P,N-ligand **L1** and Meldrum's acid in THF at 40 °C produced the optimal result, delivering (*S*)-**2a** in an *ee* of 93% and 92% isolated yield within 1 h (Table 1, entry 1).[16] Variation of the solvent had a deleterious effect upon the enantioselectivity of the product (Table 1, entries 2–4). Similarly, a drop in *ee* was observed

Table 1. Screening of Reaction Conditions[a]



entry	deviation from standard conditions[b]	conversion (%)[c]	*ee* (%)[d]
1	none	>99 (92)	93 (*S*)
2	2-(Me)-THF	>99	85 (*S*)
3	MTBE	>99	44 (*S*)
4	1,4-dioxane	>99	89 (*S*)
5	**L2** instead of **L1**, 1,4-dioxane	>99	80 (*S*)
6	7 °C	>99	88 (*S*)
7	0.015 M	>99	78 (*S*)
8	0.06 M	>99	93 (*S*)
9	$(\eta^3\text{-}C_3H_5)_2Pd_2Cl_2$	>99	0 (*S*)
10	half catalytic loading	47	92 (*S*)
11	formic acid (6 equiv)	>99	50 (*R*)
12	formic acid, $Pd(OAc)_2$, dioxane, 4 Å m·s	>99 (86)	89 (*R*)
13	$Pd(OAc)_2$, dioxane, 4 Å m·s	39	8 (*S*)

[a]See the Supporting Information for complete optimization results (Table S1, Figure S1). [b]Entries 2–13 tested after 18 h. [c]Determined by ^1H NMR spectroscopy of the crude product, isolated yields in parentheses. [d]Determined by supercritical fluid chromatography using a chiral stationary phase.

with (*S*)-*t*Bu PHOX (**L2**) indicating that the electron deficient nature of the ligand is crucial for optimal enantioinduction (Table 1, entry 5). Reducing the temperature and concentration had a negative effect (Table 1, entries 6–7) while increasing the concentration produced no change in *ee* (Table 1, entry 8). While full conversion was seen using $(\eta^3\text{-}C_3H_5)_2Pd_2Cl_2$, the product formed was racemic (Table 1, entry 9). A drop in conversion was seen upon halving the catalyst loading (Table 1, entry 10). Gratifyingly, upon switching to formic acid as the proton source the enantiomeric product was formed in an *ee* of 50% (Table 1, entry 11) indicating that in the case of this indanone substrate the absolute configuration of the product was acid dependent. The *ee* increased significantly to 89% when the previously optimized reaction conditions for formic acid were applied (Table 1, entry 12).[8] The (*S*)-enantiomer was formed once again using Meldrum's acid under these optimized heterogeneous conditions, albeit in a reduced conversion (39%) and an *ee* of only 8%.

Scope of the Enantiodivergent Protonation. A series of α-aryl-β-keto allyl esters **1b–n** were readily accessed in low to good yields using aryllead triacetate reagents (Scheme 1).[17] The aryllead triacetate reagents may be synthesized via direct plumbation or transmetalation methods. Upon application of the established homogeneous and heterogeneous reaction conditions to substrates **1a–1n**, the corresponding products were obtained in good to excellent yields and low to excellent enantioselectivities (Scheme 2). In all cases where the reactions led to product enantioenrichment, either enantiomer could be selectively obtained by judicious choice of the proton source. In addition to the effect that the level of electron density of the aryl substituent had on the reaction, the exact substituent pattern had a marked effect on the level of enantioselectivity achieved. To our delight, good to excellent enantioselectivities were observed for both enantiomeric series with other di-*ortho* substituted electron rich aryl substituents, such as **1a–d**.

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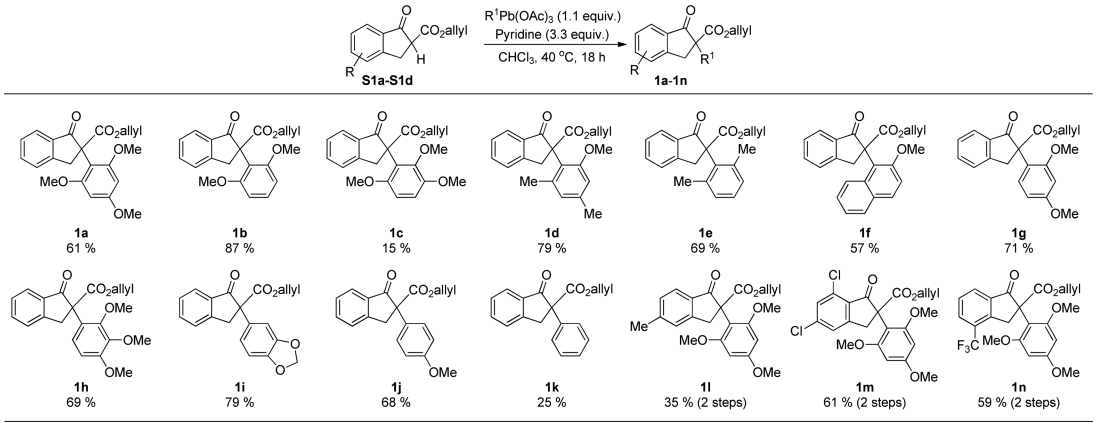
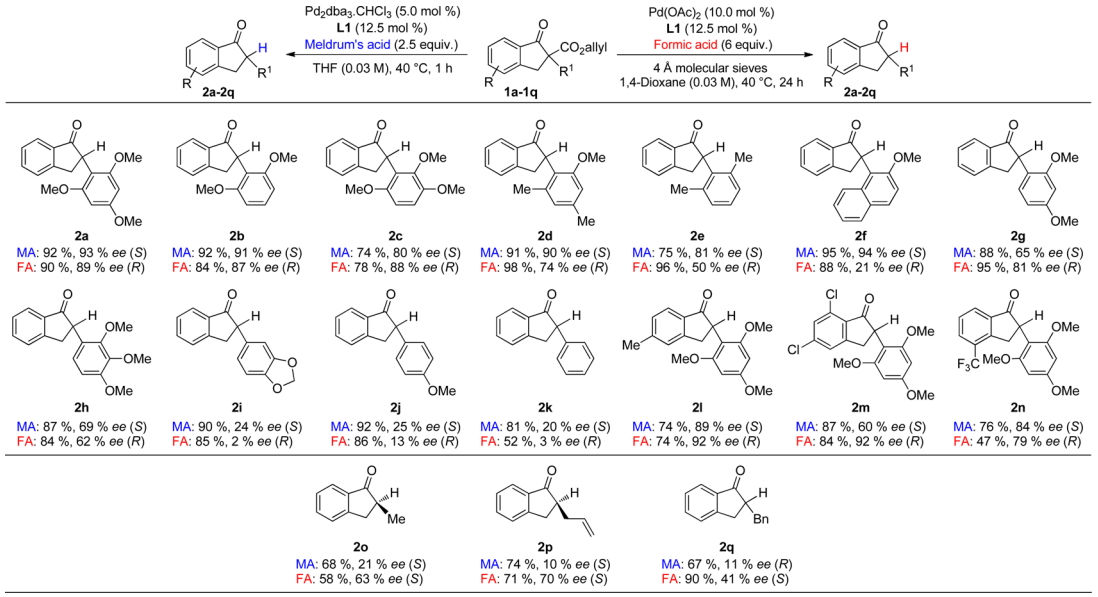
Scheme 1. Synthesis of Substrates



Scheme 2. Substrate Scope[a]



[a]The absolute configurations of **2b**–**2n** were tentatively assigned by analogy to the model substrate. The absolute configurations of **2o**–**2q** were tentatively assigned by comparing the sign of optical rotation to literature values. MA = reaction performed with Meldrum's acid, FA = reaction performed with formic acid.

Moderate to good *ee*'s were seen with a comparatively electron poor aryl group in **2e**. While the methoxy-substituted naphthalene system **2f** was formed in an excellent *ee* using the homogeneous reaction conditions, an *ee* of only 21% was obtained using formic acid. A drop in the enantioselectivity was observed for mono-*ortho* substituted products **2g** and **2h**. Furthermore, products **2i**–**k** lacked *ortho* substitution completely and were synthesized in poor enantioselectivities. The results demonstrate the importance of *ortho* methoxy-substitution on the aryl ring to obtain high levels of enantioinduction. We believe, the stereoelectronic effect of the *ortho* substituent may prohibit a planar orientation of the indanone enolate and aryl ring. This may lead to higher enantioselectivities by introducing a steric effect in the transition state of the protonation or by prohibiting conjugation, leading to an unstabilized enolate. While, methyl- and trifluoromethyl-substitution on the indanone backbone of the model substrate were well tolerated (**2l**, **2n**), a drop in *ee* was seen for dichlorinated **2m** in the homogeneous reaction. Significantly higher *ee*'s were achieved using Meldrum's acid in the case of products **2d**, **2e**, **2f**, **2i**, **2j**, and **2k** while the opposite trend was observed with **2g** and **2m**.

To investigate the scope of the enantiodivergence, α-methyl, allyl, and benzyl substrates were also subjected to the optimized conditions (Scheme 2).[18] No switch in absolute configuration was observed for alkyl and allyl products **2o** and **2p**. The opposite enantiomers were obtained for α-benzyl 1-indanone **2q** indicating the switch in absolute configuration of the product is dependent upon a sterically hindered α-substituent.

Mechanistic Background of the DAP. With the successful application of the enantiodivergent protonation to a range of substrates, we began an investigation to explain the switch in selectivity for the α-aryl substrates. The absolute configuration of the protonated products was shown to be acid-dependent. Therefore, we hypothesized the contrasting selectivities may be due to a change in mechanism upon switching the proton source. We began by examining the various mechanisms proposed throughout the development of the DAP. Although the racemic decarboxylative protonation was reported over three decades ago, a definitive mechanism

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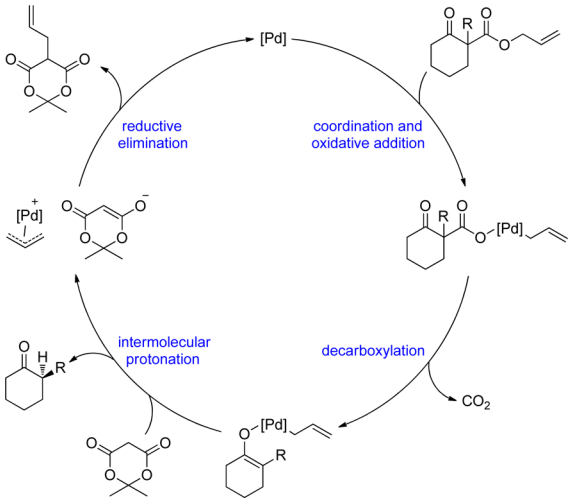
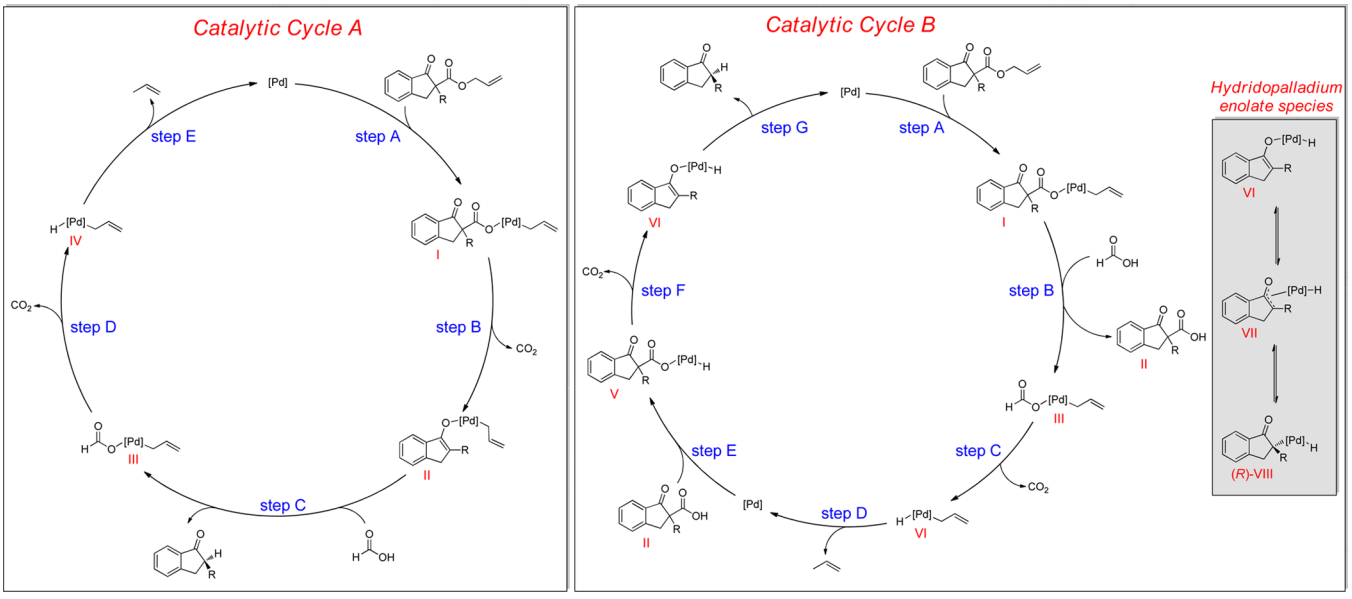
Scheme 3. Proposed Catalytic Cycle for the Protonation by Meldrum's Acid



has not been elucidated. Tsuji proposed a metal-assisted decarboxylative pathway to form a palladium enolate which is subsequently protonated to yield the desired ketone.[19] Shimizu favored an anion exchange pathway to form a β-keto acid *in situ* which undergoes decarboxylation and tautomerisation to yield the product.[20] Likewise, asymmetric protonations have also been subject to investigation without conclusive elucidation of a catalytic cycle. UV and IR spectroscopic analysis of Muzart's enantioselective reaction using benzyl β-keto esters also indicated the formation of β-keto acid *in situ*.[21] The subsequent decarboxylation and tautomerisation appears to be catalyzed by the chiral proton source. In 2006, Stoltz and co-workers investigated the mechanism of the heterogeneous DAP via deuterium-labeling studies.[4a] The results were inconclusive and a catalytic cycle remained ambiguous. Further deuterium-labeling studies by our research group were similarly inconclusive.[8] In 2008, Stoltz and co-workers did propose a plausible catalytic cycle for the homogeneous protonation (Scheme 3) based on the similarity of the kinetics to their extensively investigated decarboxylative asymmetric allylic alkylation.[19] The mechanism features protonation of an oxygen-bound palladium enolate by Meldrum's acid directed by a chiral palladium-PHOX system. The isolation of C-allylated Meldrum's acid is indicative of soft nucleophilic attack by the conjugate base on the allyl fragment, releasing the palladium catalyst back into the cycle.

Plausible Catalytic Cycles for the Heterogeneous DAP. With a catalytic cycle for the homogeneous protonation already proposed, we began a mechanistic investigation of the heterogeneous protonation. Stoltz and co-workers suggested a very similar mechanism with formic acid to that with Meldrum's acid based on similar patterns of selectivity.[22] Such a catalytic cycle was not disclosed at the time, but is now illustrated below (Scheme 4, Catalytic Cycle A). Upon oxidative addition of the palladium catalyst to the substrate and decarboxylation (steps A, B), intermolecular protonation of palladium enolate **II** by formic acid yields the desired product and allyl palladium formate complex **III** (step C). The Pd^0 catalyst, CO_2 and propene are released by decarboxylation and reductive elimination (step D, E).[23] However, our enantiodivergent results led us to re-evaluate this mechanistic proposal in a bid to explain the curious switch in selectivity. Hence, a novel alternative catalytic cycle was envisaged and must also be considered (Scheme 4, Catalytic Cycle B). As a hard oxo-nucleophile it is known formate may coordinate to palladium directly.[1b] Catalytic cycle B begins in the same manner as before with oxidative addition of the palladium catalyst to the substrate. However, on this occasion formate coordinates to palladium before decarboxylation may occur, thereby displacing β-keto acid **II** (step B). Upon fragmentation of intermediate **III** (steps C, D) the catalyst is regenerated. Expelled β-keto acid **II** undergoes a second oxidative addition by the active palladium species (step E) and decarboxylation (step F) to form hydridopalladum species **VI**.[24] In contrast to the homogeneous protonation, the protonated product is formed via intramolecular reductive elimination (step G). Such a fundamentally different enantiodetermining step to the proposed homogeneous protonation may explain the switch in selectivity we have

Scheme 4. Plausible Catalytic Cycles A and B for DAP with Formic Acid as a Proton Source



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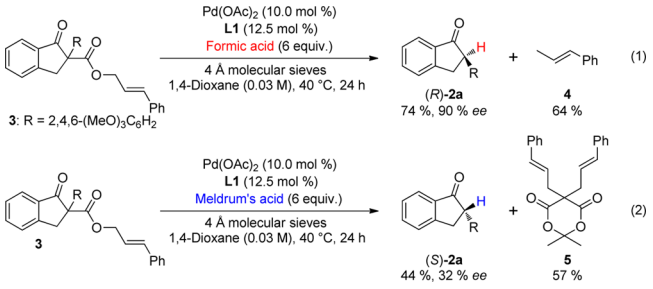
observed. However, a definitive stereochemical rationale would also require determination of the regioselectivity of the hydridopalladium enolate (Scheme 4, far right).[25]

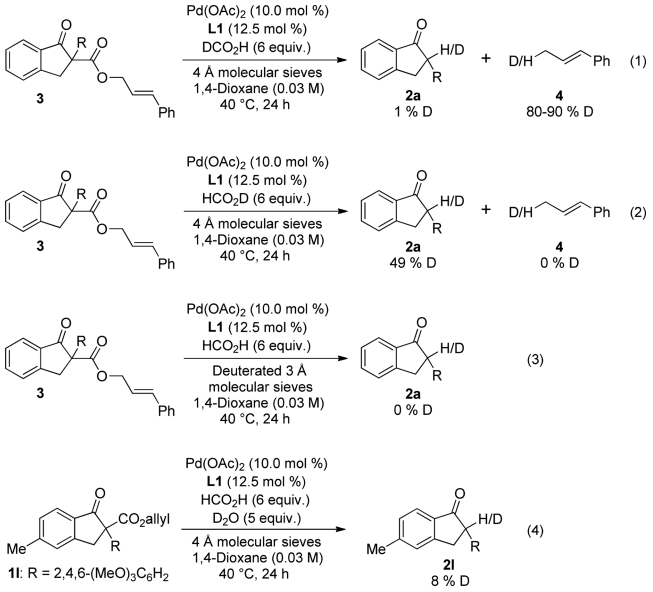
Identification of Divergent Byproducts. Due to the general uncertainty regarding the mechanism of the heterogeneous DAP, initial experiments were designed to test our overall mechanistic hypothesis. In both heterogeneous catalytic cycle A and B (Scheme 4), the allyl group of the starting material is ultimately expelled as propene. To avoid the difficult isolation and quantification of the proposed gaseous byproduct, phenylated substrate **3** was applied in the reaction (Scheme 5, eq 1). Under the optimized heterogeneous conditions, the propene surrogate *trans*-β-methylstyrene **4** was formed in a 64% yield. Testing the reaction without the metal−ligand complex gave only recovered starting material. In contrast, in the proposed homogeneous mechanism the allyl fragment is sequestered by deprotonated Meldrum's acid. Consequently, upon switching to the organic proton source with the same conditions, no *trans*-β-methylstyrene **4** was observed (Scheme 5, eq 2). Instead, the corresponding diallylated Meldrum's acid **5** was isolated along with the enantioenriched (*S*)-**2a**.

Scheme 5. Identification of Divergent By-Products in the DAP



Deuterium-Labeling Studies. Previous reports measured the incorporation of the oxygen-bound deuterium (38−35% D-incorporation) and formyl deuterium (<1% D-incorporation) into the α-stereocenter of the ketone product using isotopically labeled formic acids.[4a,8] The somewhat low levels of the oxygen-D incorporation indicated the presence of an additional unidentified protonating agent while the fate of the formyl-D was not resolved. Formic acid's ability to provide a hydride which may subsequently add to a chiral palladium enolate complex was noted but not tested. Using phenylated substrate **3**, deuterium incorporation into both the final product and expelled propene surrogate, *trans*-β-methylstyrene **4**, could now be quantified for the first time (Scheme 6). In both catalytic cycle A and B the oxygen-bound hydrogen is incorporated into the final product and the formyl hydrogen is transferred to the propene byproduct. Gratifyingly, using DCO_2H, NMR analysis revealed <1% D-incorporation in the product and 80−90% in the isolated *trans*-β-methylstyrene **4** (Scheme 6, eq 1). Switching to HCO_2D, 49% D-incorporation was observed in the product and 0% in the isolated *trans*-β-methylstyrene **4** (Scheme 6, eq 2). The specific patterns of deuteration observed in the two experiments are in accordance with the proposed mechanisms and explain the previously ambiguous fate of the formyl proton. However, 49% deuterium incorporation into the product using HCO_2D was still surprisingly low due to the rigorous drying procedures and anhydrous solvents utilized. To test for the possibility of residual water in the molecular sieves as the alternative source of the α-proton, the DAP was

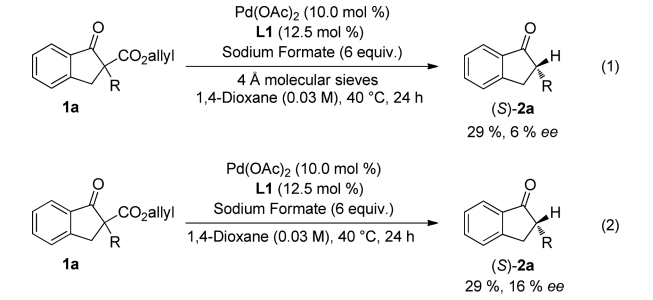
Scheme 6. Deuterium-Labeling Studies



conducted with HCO_2H and deuterated molecular sieves. No D-incorporation into the product was observed (Scheme 6, eq 3). Furthermore, only 8% D-incorporation was found with the addition of D_2O to the reaction mixture (5 equiv., Scheme 6, eq 4), corresponding with previous deuterium labeling studies.[8]

To test for traces of water from the formic acid as the proton source, sodium formate was applied in the reaction. The product (*S*)-**2a** was isolated in a 29% yield (Scheme 7, eq 1) providing further indication of an alternative proton source to the acidic proton of formic acid. Residual water from the molecular sieves was tested for once again by their removal (Scheme 7, eq 2). Again, the product was isolated in a 29% yield and the alternative source of the α-proton remains unidentified.

Scheme 7. Investigation of an Unidentified Proton Source



Investigation of a β-Keto Acid Intermediate. In an attempt to distinguish between the possible catalytic cycles for the heterogeneous DAP we investigated the formation of a β-keto acid intermediate (Scheme 8), as proposed in Catalytic Cycle B. However, none of the corresponding β-keto methyl ester **6** was isolated upon cooling the reaction mixture and addition of ten equivalents of trimethylsilyldiazomethane.

The transient nature of the β-keto acid intermediate may limit the possibility of formation of β-keto methyl ester **6**. The rapid degradation of intermediate **II** may also disfavor the possibility of oxidative addition to afford intermediate **V**, as proposed in Catalytic Cycle B. However, this appears to be the

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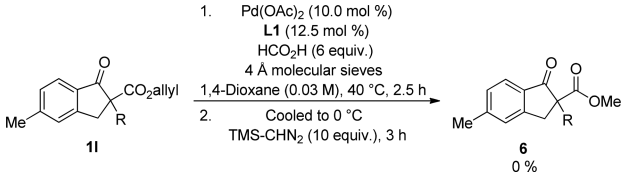
Scheme 8. Investigation of a β-Keto Acid Intermediate



only means to access the hydridopalladium enolate intermediate **VI**, which as noted previously, may be key to the observed enantiodivergence. Further studies are required before the comprehensive mechanism of the DAP with formic acid is elucidated.

CONCLUSIONS

In summary, we have developed an efficient enantiodivergent synthesis of sterically hindered tertiary α-aryl-1-indanones from the corresponding α-aryl-β-keto allyl esters. In contrast to our previous results, both enantiomers of a variety of substrates were readily obtained in high enantioselectivities. Particularly excellent *ee*'s were achieved with sterically hindered aryl groups, providing a complementary route to existing α-arylation methodologies. Based on the experimental evidence outlined above, we believe the decarboxylative asymmetric protonation with formic acid may proceed via one of two distinct catalytic cycles. Further studies are currently underway to elucidate the correct mechanism and the reason for the enantiodivergence with sterically hindered α-substituents.

EXPERIMENTAL SECTION

General Information: 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 using anhydrous solvents. Reactions were heated using an oil bath. 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. Aryllead triacetate reagents and (*S*)-$(CF_3)_3$-*tert*-Bu-PHOX were prepared according to the previously reported procedures.[6a] All anhydrous solvents were obtained from commercial sources and used as received with the following exceptions: diethyl ether (Et_2O), dichloromethane (CH_2Cl_2), and toluene ($PhCH_3$) were dried by passing through activated alumina columns. Tris(dibenzylideneacetone)dipalladium(0) chloroform adduct was prepared via the method of Zalesskiy et al.[26] $Pd(OAc)_2$ was purchased from Strem. Powdered activated 4 Å molecular sieves were purchased from Sigma-Aldrich and were stored in an oven at 120 °C. *In vacuo* refers to the evaporation of solvent under reduced pressure on a rotary evaporator. Thin-layer chromatography (TLC) was performed on aluminum plates precoated with silica gel F254. They were visualized with UV-light (254 nm) fluorescence quenching, or by charring with an acidic vanillin solution (vanillin, H_2SO_4 in ethanol). Flash column chromatography was carried out using 40−63 μm, 230−400 mesh silica gel.

Instrumentation. ^1H NMR spectra were recorded on a 300, 400, or 500 MHz spectrometer. ^{13}C NMR spectra were recorded on a 400 or 500 MHz spectrometer at 101 or 126 MHz. ^{19}F NMR spectra were recorded on a 400 MHz spectrometer at 376 MHz. Chemical shifts (δ) are reported in parts per million (ppm) downfield from tetramethylsilane and for ^1H NMR are referenced to residual proton in the NMR solvent ($CDCl_3$ = δ 7.26 ppm). ^{13}C NMR are referenced to the residual solvent peak ($CDCl_3$ = δ 77.16 ppm). All ^{13}C spectra are ^1H decoupled. NMR data are represented as follows: chemical shift (δ ppm), integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = double doublet, m = multiplet, app. d = apparent doublet, app. t. = apparent triplet), coupling constant (*J*) in Hertz (Hz). High-resolution mass spectra [electrospray ionization (ESI-TOF)] (HRMS) were measured on a micromass LCT orthogonal 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 of wavenumbers (ν_{max}) with units of reciprocal centimeters (cm^{-1}). Microwave experiments were conducted in a CEM Discover S-class microwave reactor with controlled irradiation at 2.45 GHz using standard sealed microwave process Pyrex vials and an external surface sensor to monitor the temperature. (Note: The microwave reactor was only used to further dry molecular sieves during some deuterium labeling experiments.) Optical rotation (α) values were measured at room temperature and specific rotation ($[\alpha]_D^{20}$) values are given in $deg{\cdot}dm^{-1}{\cdot}cm^3{\cdot}g^{-1}$. Melting points were determined in open capillary tubes. Supercritical fluid chromatography (SFC) was performed on a Waters UPC^2 system using a Chiralpak IA-3, IC-3, or ID-3 column.

Typical Procedure A: Preparation of β-Keto Esters S1a−S1d. Acylation procedure was adapted from the literature.[27] A flask was charged with NaH (60% dispersion in mineral oil, 2.5 equiv). THF (1.92 M) was added and the resultant solution cooled to 0 °C (ice/H_2O bath). A solution of 1-indanone (1.0 equiv) in THF (3.20 M) was added dropwise. The solution was allowed to warm to room temperature. After 15 min, diallyl carbonate (1.5 equiv) was added dropwise. After 16 h, the solution was quenched with saturated aqueous NH_4Cl and extracted with EtOAc (3 × 20 mL). The combined organics were dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. In the case of **S1a** the crude product was purified via silica gel column chromatography (pentane/Et_2O, 85:15). For **S1b**, **S1c**, and **S 1d** the crude product was washed through a pad of silica using Et_2O.

Allyl 1-oxo-2,3-Dihydro-1H-indene-2-carboxylate (S1a). Prepared according to typical procedure **A** using 1-indanone (7.4 g, 56 mmol). The product was isolated as a brown oil (7.5 g, 62%). Spectroscopic analysis is in good accordance to literature.[27]

Allyl 5-Methyl-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (S1b). Prepared according to typical procedure **A** using 5-methyl-1-indanone (1.0 g, 6.8 mmol). The isolated crude orange oil was used in the next step without further purification.

Allyl 5,7-Dichloro-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (S1c). Prepared according to typical procedure **A** using 5,7-dichloro-1-indanone (1.0 g, 5.0 mmol). The isolated crude brown oil was used in the next step without further purification.

Allyl 1-oxo-4-(Trifluoromethyl)-2,3-dihydro-1H-indene-2-carboxylate (S1d). Prepared according to typical procedure **A** using 4-trifluoromethyl-1-indanone (1.0 g, 5.0 mmol). The isolated crude colorless oil was used in the next step without further purification.

Typical Procedure B: Preparation of α-Aryl-β-keto Allyl Esters 1a−1n. Arylation procedure was adapted from the literature.[10] To a stirred solution of β-keto allyl ester (1 equiv) and aryllead triacetate (1.1 equiv) in $CHCl_3$ (0.6 M) in a Schlenk flask (25 mL), was added dropwise pyridine (3.3 equiv). The resulting mixture was heated at 40 °C for 18 h, filtered through a plug of Celite, and washed with $CHCl_3$. The organic layer was washed with 6% H_2SO_4 (2 × 50 mL), extracted with $CHCl_3$ (2 × 50 mL), and the combined organic extracts were washed with water (2 × 50 mL) and brine (50 mL), dried over anhydrous Na_2SO_4, and filtered. The solvent was reduced *in vacuo* and resulting residue purified via silica gel column chromatography (pentane/Et_2O or pentane/EtOAc).

Allyl 1-oxo-2-(2,4,6-Trimethoxyphenyl)-2,3-dihydro-1H-inden-2-carboxylate (1a). Prepared according to typical procedure **B** using β-keto allyl ester **S1a** (1.63 g, 7.54 mmol) to afford the product as an orange solid (1.77 g, 61%). Column chromatography conditions = pentane/EtOAc, 80:20; R_f = 0.26 (30% EtOAc in pentane); mp =111−113 °C; IR (NaCl): ν = 3054 (C═C−H), 1721 (Ketone: C═O), 1590 (Aromatic C═C) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.84−7.74 (1H, app. d, *J* = 7.4 Hz), 7.55 (1H, app. t, *J* = 7.4 Hz), 7.42 (1H, app. d, *J* = 7.4 Hz), 7.35 (1H, app. t, *J* = 7.4 Hz), 6.12 (2H, s), 5.95−5.79 (1H, m), 5.24−5.14 (2H, m), 4.70−4.53 (2H, m), 4.35 (1H, d, *J* = 17.1 Hz), 3.76 (3H, s), 3.60 (6H, s), 3.00 (1H, d, *J* = 17.1 Hz) ppm; $^{13}C\{^1H\}$NMR (101 MHz, $CDCl_3$) δ 200.3, 170.1, 160.7,

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158.4, 152.2, 135.4, 134.6, 132.4, 127.3, 126.2, 124.3, 118.1, 111.8, 92.3, 66.6, 61.7, 55.8, 55.5, 39.9 ppm; HRMS (ESI-TOF): calcd. for $C_{22}H_{21}O_6$ [M−H$^+$] 381.1338; found 381.1329.

Allyl 2-(2,6-Dimethoxyphenyl)-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (1b). Prepared according to typical procedure **B** using β-keto allyl ester **S1a** (0.500 g, 2.31 mmol) to afford the product as a brown solid (0.709 g, 87%). Column chromatography conditions = pentane/EtOAc, 75:25; R_f = 0.37 (30% EtOAc in pentane); mp =131−132 °C; IR (NaCl): ν = 3054 (C═C−H), 1720 (Ketone: C═O), 1606 (Aromatic C═C) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) 7.79 (1H, app. d, *J* = 7.7 Hz), 7.52 (1H, app. t, *J* = 7.4, 1.3 Hz), 7.39 (1H, app. d, *J* = 7.7 Hz), 7.33 (1H, app. t, *J* = 7.4 Hz), 7.15 (1H, t, *J* = 8.3 Hz), 6.52 (2H, d, *J* = 8.3 Hz), 5.97−5.72 (1H, m), 5.31−5.02 (2H, m), 4.73−4.48 (2H, m), 4.37 (1H, d, *J* = 17.1 Hz), 3.70−3.48 (6H, s), 3.02 (1H, d, *J* = 17.1 Hz) ppm; ^{13}C{^{1}H}NMR (101 MHz, $CDCl_3$) δ 199.6, 169.7, 157.5, 151.7, 135.2, 134.4, 132.0, 128.5, 127.1, 125.9, 123.9, 118.9, 117.8, 105.5, 104.7, 66.2, 61.5, 55.6, 39.4 ppm; HRMS (ESI-TOF): calcd. for $C_{21}H_{20}O_5Na$ [M+Na$^+$] 375.1208; found 375.1209.

Allyl 1-oxo-2-(2,3,6-Trimethoxyphenyl)-2,3-dihydro-1H-indene-2-carboxylate (1c). Prepared according to typical procedure **B** using β-keto allyl ester **S1a** (0.290 g, 1.34 mmol) to afford the product as an orange oil (0.079 g, 15%). Column chromatography conditions = pentane/EtOAc, 80:20; R_f = 0.40 (30% Et_2O in pentane); IR (NaCl): ν = 3055 (Aromatic C−H), 2992 (sp^{3}C−H), 1714 (Ketone: C═O) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 (1H, app. d, *J* = 7.6 Hz), 7.54 (1H, app. t, *J* = 7.6 Hz), 7.45−7.30 (2H, m), 6.77 (1H, d, *J* = 9.0 Hz), 6.56 (1H, d, *J* = 9.0 Hz), 5.96−5.80 (1H, m), 5.31−5.08 (2H, m), 4.81−4.47 (2H, m), 4.38 (1H, d, *J* = 17.1 Hz), 3.75 (3H, s), 3.60 (6H, s), 3.05 (1H, d, *J* = 17.1 Hz) ppm; ^{13}C{^{1}H}NMR (101 MHz, $CDCl_3$) δ 199.4, 169.6, 151.4, 147.4, 135.4, 134.6, 132.2, 127.4, 126.1, 125.2, 124.1, 117.8, 112.0, 106.1, 66.5, 61.9, 60.3, 56.3, 56.0, 40.1 ppm; HRMS (ESI-TOF): calcd. for $C_{22}H_{22}O_6Na$ [M+Na$^+$] 405.1314; found 405.1316.

Allyl 2-(2-Methoxy-4,6-dimethylphenyl)-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (1d). Prepared according to typical procedure **B** using β-keto allyl ester **S1a** (0.500 g, 2.31 mmol) to afford the product as a yellow solid (0.698 g, 79%). Column chromatography conditions = pentane/EtOAc, 80:20; R_f = 0.27 (30% Et_2O in pentane); mp =116−117 °C; IR (NaCl): ν = 3073 (Aromatic C−H), 3055 (C═C−H), 1722 (Ketone: C═O) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 (1H, app. d, *J* = 7.6 Hz), 7.56 (1H, app. t, *J* = 7.4 Hz), 7.43 (1H, app. d, *J* = 7.6 Hz), 7.36 (1H, app. t, *J* = 7.4 Hz), 6.62 (1H, s), 6.57 (1H, s), 5.92−5.79 (1H, m), 5.30−5.09 (2H, m), 4.70−4.55 (2H, m), 4.42 (1H, d, *J* = 17.1 Hz), 3.56 (3H, s), 3.05 (1H, d, *J* = 17.1 Hz), 2.26 (3H, s), 2.11 (3H, s) ppm; ^{13}C{^{1}H}NMR (101 MHz, $CDCl_3$) δ 200.3, 170.5, 157.1, 152.4, 137.9, 137.4, 135.4, 134.9, 131.9, 127.6, 126.6, 126.3, 125.7, 124.6, 118.7, 111.1, 66.9, 64.6, 55.5, 39.9, 21.9, 21.3 ppm; HRMS (ESI-TOF): calcd. for $C_{22}H_{23}O_4$ [M+H$^+$] 351.1596; found 351.1607.

Allyl 2-(2,6-Dimethylphenyl)-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (1e). Prepared according to typical procedure **B** using β-keto allyl ester **S1a** (0.400 g, 1.85 mmol) to afford the product as a yellow oil (0.407 g, 69%). Column chromatography conditions = pentane/EtOAc, 80:20; R_f = 0.61 (30% Et_2O in pentane); IR (NaCl): ν = 3064 (Aromatic C−H), 3016 (C═C−H), 1747 (Ester C═O) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (1H, app. d, *J* = 7.7 Hz), 7.61 (1H, app. t, *J* = 7.5 Hz), 7.50 (1H, app. d, *J* = 7.7 Hz), 7.39 (1H, app. t, *J* = 7.5 Hz), 7.11−6.97 (3H, m), 5.94−5.77 (1H, m), 5.27−5.10 (2H, m), 4.71−4.56 (2H, m), 4.50 (1H, d, *J* = 17.2 Hz), 3.18 (1H, d, *J* = 17.2 Hz), 2.18 (6H, s) ppm; ^{13}C{^{1}H}NMR (101 MHz, $CDCl_3$) δ 200.4, 170.7, 153.2, 138.8, 137.0, 135.5, 135.2, 131.3, 130.0, 128.0, 127.0, 126.3, 125.3, 119.1, 68.3, 67.2, 40.0, 23.2 ppm; HRMS (ESI-TOF): calcd. for $C_{21}H_{21}O_3$ [M+H$^+$] 321.1491; found 321.1501.

Allyl 2-(2-Methoxynaphthalen-1-yl)-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (1f). Prepared according to typical procedure **B** using β-keto allyl ester **S1a** (0.200 g, 0.925 mmol) to afford the product as a yellow solid (0.197 g, 57%). Column chromatography conditions = pentane/EtOAc, 80:20; R_f = 0.39 (25% EtOAc in pentane); mp =104−105 °C; IR (NaCl): ν = 3051 (Aromatic C−H), 2997 (C═C−H), 1698 (Ketone: C═O) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 (1H, app. d, *J* = 7.5 Hz), 7.82−7.76 (2H, m), 7.63 (1H, app. t, *J* = 7.5 Hz), 7.56−7.31 (5H, m), 7.21 (1H, d, *J* = 9.0 Hz), 5.78−5.64 (1H, m), 5.14−5.00 (2H, m), 4.72−4.48 (3H, m), 3.67 (3H, s), 3.31 (1H, d, *J* = 17.0 Hz) ppm; ^{13}C{^{1}H}NMR (101 MHz, $CDCl_3$) δ 200.0, 171.3, 154.2, 151.4, 135.7, 134.9, 132.8, 131.6, 130.5, 130.1, 129.1, 127.7, 126.6, 126.4, 124.4, 123.9, 123.7, 123.6, 118.5, 115.5, 66.9, 64.1, 56.6, 40.3 ppm; HRMS (ESI-TOF): calcd. for $C_{24}H_{20}O_4Na$ [M+Na$^+$] 395.1259; found 395.1268.

Allyl 2-(2,4-Dimethoxyphenyl)-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (1g). Prepared according to typical procedure **B** using β-keto allyl ester **S1a** (0.400 g, 1.85 mmol) to afford the product as an orange oil (0.461 g, 71%). Column chromatography conditions = pentane/EtOAc, 80:20; R_f = 0.25 (30% Et_2O in pentane); IR (NaCl): ν = 3078 (Aromatic C−H), 2941 (sp^{3}C−H), 1747 (Ester C═O) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77 (1H, app. d, *J* = 7.7 Hz), 7.54 (1H, app. t, *J* = 7.5 Hz), 7.46−7.36 (2H, m), 7.04 (1H, d, *J* = 8.5 Hz), 6.48 (1H, d, *J* = 2.5 Hz), 6.39 (1H, dd, *J* = 8.5, 2.5 Hz), 5.88−5.76 (1H, m), 5.24−5.06 (2H, m), 4.76−4.55 (2H, m), 4.14 (1H, d, *J* = 17.3 Hz), 3.77 (3H, s), 3.75 (3H, s), 3.59 (1H, d, *J* = 17.3 Hz) ppm; ^{13}C{^{1}H}NMR (101 MHz, $CDCl_3$) δ 201.4, 170.2, 160.4, 158.3, 153.5, 135.7, 135.3, 132.1, 128.0, 127.7, 126.5, 124.8, 122.2, 118.2, 103.8, 99.6, 66.4, 64.0, 55.5, 41.1 ppm; HRMS (ESI-TOF): calcd. for $C_{21}H_{21}O_5$ [M+H$^+$] 353.1389; found 353.1395.

Allyl 1-oxo-2-(2,3,4-Trimethoxyphenyl)-2,3-dihydro-1H-indene-2-carboxylate (1h). Prepared according to typical procedure **B** using β-keto allyl ester **S1a** (0.400 g, 1.85 mmol) to afford the product as an orange oil (0.488 g, 69%). Column chromatography conditions = pentane/EtOAc, 75:25; R_f = 0.45 (25% EtOAc in pentane); IR (NaCl): ν = 3054 (C═C−H), 1712 (Ketone: C═O), 1603 (Aromatic C═C) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 (1H, app. d, *J* = 7.6 Hz), 7.62 (1H, app. t, *J* = 7.6 Hz), 7.50−7.30 (2H, m), 6.80 (1H, d, *J* = 8.7 Hz), 6.53 (1H, d, *J* = 8.7 Hz), 5.92−5.80 (1H, m), 5.32−5.07 (2H, m), 4.78−4.55 (2H, m), 4.37 (1H, d, *J* = 17.5 Hz), 3.87−3.76 (9H, m), 3.20 (1H, d, *J* = 17.5 Hz) ppm; ^{13}C{^{1}H}NMR (101 MHz, $CDCl_3$) δ 201.0, 169.9, 153.7, 152.9, 151.6, 142.0, 135.6, 135.2, 131.8, 127.7, 127.0, 126.4, 124.7, 122.0, 118.4, 106.3, 66.6, 64.4, 60.6, 60.3, 56.1, 41.5 ppm; HRMS (ESI-TOF): calcd. for $C_{22}H_{22}O_6Na$ [M+Na$^+$] 405.1314; found 405.1319.

Allyl 2-(Benzo[d][1,3]dioxol-5-yl)-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (1i). Prepared according to typical procedure **B** using β-keto allyl ester **S1a** (0.400 g, 1.85 mmol) to afford the product as an orange oil (0.491 g, 79%). Column chromatography conditions = pentane/Et_2O, 70:30; R_f = 0.33 (30% Et_2O in pentane); IR (NaCl): ν = 3080 (Aromatic C−H), 3016 (C═C−H), 1745 (Ester C═O) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 (1H, app. d, *J* = 7.7 Hz), 7.62 (1H, app. t, *J* = 7.4 Hz), 7.47 (1H, app. d, *J* = 7.7 Hz), 7.39 (1H, app. t, *J* = 7.4 Hz), 6.98 (1H, d, *J* = 2.0 Hz), 6.91−6.83 (1H, dd, *J* = 8.2, 2.0 Hz), 6.73 (1H, d, *J* = 8.2 Hz), 5.90 (2H, s), 5.86−5.77 (1H, m), 5.30−5.10 (2H, m), 4.67−4.57 (2H, m), 4.16 (1H, d, *J* = 17.3 Hz), 3.56 (1H, d, *J* = 17.3 Hz) ppm; ^{13}C{^{1}H}NMR (101 MHz, $CDCl_3$) δ 200.0, 170.3, 151.9, 147.9, 147.0, 135.7, 135.0, 131.9, 131.4, 128.0, 126.2, 125.1, 120.7, 118.5, 108.4, 108.2, 101.2, 66.5, 64.9, 40.8 ppm; HRMS (ESI-TOF): calcd. for $C_{20}H_{17}O_5$ [M+H$^+$] 337.1076; found 337.1091.

Allyl 2-(4-Methoxyphenyl)-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (1j). Prepared according to typical procedure **B** using β-keto allyl ester **S1a** (0.400 g, 1.85 mmol) to afford the product as an orange oil (0.403 g, 68%). Column chromatography conditions = pentane/Et_2O, 85:15; R_f = 0.32 (30% Et_2O in pentane); IR (NaCl): ν = 3073 (Aromatic C−H), 3039 (C═C−H), 1745 (Ester C═O) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (1H, app. d, *J* = 7.6 Hz), 7.51 (1H, app. t, *J* = 7.1 Hz), 7.49 (1H, app. d, *J* = 7.6 Hz), 7.45−7.33 (3H, m), 6.90−6.83 (2H, m), 5.92−5.74 (1H, m), 5.24−5.03 (2H, m), 4.68−4.59 (2H, m), 4.14 (1H, d, *J* = 17.4 Hz), 3.67 (3H, s), 3.59 (1H, d, *J* = 17.4 Hz) ppm; ^{13}C{^{1}H}NMR (101 MHz, $CDCl_3$) δ 200.4, 170.6, 159.0, 152.1, 135.6, 135.1, 131.6, 130.3, 128.7, 128.1, 126.3, 125.2, 118.5, 114.1, 66.4, 64.7, 55.4, 40.7 ppm; HRMS (ESI-TOF): calcd. for $C_{20}H_{19}O_4$ [M+H$^+$] 323.1283; found 323.1294.

Allyl 1-oxo-2-Phenyl-2,3-dihydro-1H-indene-2-carboxylate (1k). Procedure was adapted from the literature.[28] To a mixture of

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phenylboronic acid (1.08 g, 8.89 mmol), lead tetraacetate (3.94 g, 8.89 mmol), and mercury(II) acetate (0.283 g, 0.889 mmol) was added $CHCl_3$ (13.3 mL) under nitrogen atmosphere. After stirring for 1 h at 40 °C a solution of β-keto allyl ester **S1a** (1.75 g, 8.08 mmol) in pyridine (1.9 mL, 24.3 mmol) was added and stirred for 18 h at 40 °C. The reaction mixture was allowed to cool to ambient temperature, filtered through plug of Celite and washed with $CHCl_3$ (2 × 15 mL). The organic layer was washed with aq. sulfuric acid (3 M, 25 mL) and the aq. layer was extracted with $CHCl_3$ (2 × 15 mL). The combined organic layers were washed with water (25 mL), dried over anhydrous Na_2SO_4, filtered, and the solvent was removed *in vacuo*. The resulting residue was purified via silica gel column chromatography (pentane/Et_2O) to yield the product as a yellow oil (0.580 g, 25%). Column chromatography conditions = pentane/Et_2O, 99:1; R_f = 0.25 (30% Et_2O in pentane); IR (NaCl): ν = 3059 (C═C−H), 3026 (Aromatic C−H), 1709 (Ester C═O), 1604 (Aromatic C═C) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.84 (1H, app. d, J = 7.7 Hz), 7.64 (1H, td, J = 7.5, 1.2 Hz), 7.49 (1H, app. d, J = 7.7 Hz), 7.45−7.38 (3H, m), 7.36−7.30 (2H, m), 7.30−7.23 (1H, m), 5.88−5.73 (1H, m), 5.31−5.09 (2H, m), 4.72−4.55 (2H, m), 4.22 (1H, d, J = 17.3 Hz), 3.60 (1H, d, J = 17.3 Hz) ppm; $^{13}C\{^1H\}$NMR (101 MHz, $CDCl_3$) δ 200.1, 170.4, 152.2, 138.7, 135.7, 135.2, 131.5, 128.8, 128.1, 127.7, 127.5, 126.3, 125.3, 118.6, 66.6, 65.5, 40.9 ppm; HRMS (ESI-TOF): calcd. for $C_{19}H_{16}O_3Na$ [M+Na$^+$] 315.0997; found 315.0986.

Allyl 5-Methyl-1-oxo-2-(2,4,6-trimethoxyphenyl)-2,3-dihydro-1H-indene-2-carboxylate ***(1l)***. Prepared according to typical procedure **B** using crude β-keto allyl ester **S1b** (0.689 g) to afford the product as a colorless solid (0.936 g, 35% over two steps). Column chromatography conditions = pentane/EtOAc, 85:15; R_f = 0.29 (15% EtOAc in pentane); mp =123−124 °C; IR (NaCl): ν = 3004 (Aromatic C−H), 1714 (Ester C═O), 1607, 1585 (Aromatic C═C), 1120 (C−O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.69 (1H, d, J = 7.8 Hz), 7.23 (1H, app. s, 1H), 7.17 (1H, dd, J = 7.8, 0.5 Hz), 6.12 (2H, s), 5.95−5.75 (1H, m), 5.31−5.08 (2H, m), 4.68−4.50 (2H, m), 4.28 (1H, d, J = 17.0 Hz), 3.78 (3H, s), 3.61 (6H, s), 2.95 (1H, d, J = 17.0 Hz), 2.42 (3H, s) ppm; $^{13}C\{^1H\}$NMR (101 MHz, $CDCl_3$) δ 199.7, 170.3, 160.6, 158.5, 152.6, 145.7, 133.1, 132.4, 128.6, 126.6, 124.2, 118.1, 111.8, 92.3, 66.5, 61.9, 55.8, 55.5, 39.6, 22.2 ppm; HRMS (ESI-TOF): calcd. for $C_{23}H_{24}O_6Na$ [M+Na$^+$] 419.1471; found 419.1452.

Allyl 5,7-Dichloro-1-oxo-2-(2,4,6-trimethoxyphenyl)-2,3-dihydro-1H-indene-2-carboxylate ***(1m)***. Prepared according to typical procedure **B** using crude β-keto allyl ester **S1c** (1.074 g) to afford the product as a colorless solid (1.383 g, 61% over two steps). Column chromatography conditions = pentane/EtOAc, 85:15; R_f = 0.32 (15% EtOAc in pentane); mp =119−120 °C; IR (NaCl): ν = 3075 (C═C−H), 3029 (Aromatic C−H), 2980, 1440 (sp^{3}C−H), 1721 (Ester C═O), 1607, 1581 (Aromatic C═C), 1121 (C−O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.34−7.31 (1H, m), 7.30−7.27 (1H, m), 6.11 (2H, s), 5.93−5.81 (1H, m), 5.31−5.11 (2H, m), 4.68−4.57 (2H, m), 4.31 (1H, d, J = 17.5 Hz), 3.77 (3H, s), 3.65 (6H, s), 2.96 (1H, d, J = 17.5 Hz) ppm; $^{13}C\{^1H\}$NMR (101 MHz, $CDCl_3$) δ 195.8, 170.0, 160.8, 158.3, 155.0, 140.5, 132.8, 132.2, 130.5, 129.2, 125.0, 118.2, 111.8, 92.4, 66.7, 62.2, 56.1, 55.5, 39.3 ppm; HRMS (ESI-TOF): calcd. for $C_{22}H_{20}O_6Cl_2Na$ [M+Na$^+$] 473.0535; found 473.0554.

Allyl 1-oxo-4-(Trifluoromethyl)-2-(2,4,6-trimethoxyphenyl)-2,3-dihydro-1H-indene-2-carboxylate ***(1n)***. Prepared according to typical procedure **B** using crude β-keto allyl ester **S 1d** (1.021 g) to afford the product as a colorless solid (1.319 g, 59% over two steps). Column chromatography conditions = pentane/EtOAc, 85:15; R_f = 0.29 (15% EtOAc in pentane); mp =96−97 °C; IR (NaCl): ν = 3081, 947 (C═C−H), 3016 (Aromatic C−H), 2982 (sp^{3}C−H), 1735 (Ketone C═O), 1713 (Ester C═O), 1601, 1592 (Aromatic C═C), 1124 (C−O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.98 (1H, app. d, J = 7.6 Hz), 7.84 (1H, app. d, J = 7.6 Hz), 7.51 (1H, t, J = 7.6 Hz), 6.13 (2H, s), 5.97−5.76 (1H, m), 5.32−5.09 (2H, m), 4.69−4.48 (3H, m), 3.79 (3H, s), 3.62 (6H, s), 3.13 (1H, d, J = 17.9 Hz) ppm; $^{13}C\{^1H\}$NMR (101 MHz, $CDCl_3$) δ 199.0, 169.6, 161.0, 158.4, 149.6, 137.0, 132.2, 131.3 (q, J = 4.7 Hz), 128.1 (q, J = 32.4 Hz), 127.8, 127.8, 124.0 (q, J = 273.4 Hz), 118.4, 111.1, 92.3, 66.8, 61.3, 55.8, 55.6, 38.7 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ −62.2 ppm; HRMS (ESI-TOF): calcd. for $C_{23}H_{21}O_6F_3Na$ [M+Na$^+$] 473.1188; found 473.1165.

Typical Procedure C: Preparation of α-Substituted-β-keto Allyl Esters 1o−1q. Alkylation/benzylation/allylation of **S1a** was adapted from the literature.[18] β-Keto allyl ester **S1a** (1 equiv) was added to a suspension of anhydrous K_2CO_3 (2.0 equiv) in acetone (0.75 M) in a round-bottom flask (25 mL). To the reaction mixture was added the electrophile (2.0 equiv) and the reaction mixture was then heated to 50 °C for 14 h. The mixture was cooled, filtered, and the solids washed with acetone. The filtrate was concentrated and the resulting residue purified via silica gel column chromatography (pentane/Et_2O, 90:10).

Allyl 2-Methyl-1-oxo-2,3-dihydro-1H-indene-2-carboxylate ***(1o)***. Prepared according to typical procedure **C** using β-keto allyl ester **S1a** (0.973 g, 4.50 mmol) and iodomethane as the electrophile to afford the product as a yellow oil (0.681 g, 66%). Spectroscopic analysis is in good accordance to literature.[18]

Allyl 2-Allyl-1-oxo-2,3-dihydro-1H-indene-2-carboxylate ***(1p)***. Prepared according to typical procedure **C** using β-keto allyl ester **S1a** (0.973 g, 4.50 mmol) and allyl bromide as the electrophile to afford the product as a brown oil (0.846 g, 73%). R_f = 0.42 (20% Et_2O in pentane); IR (NaCl): ν = 3078 (Aromatic C−H), 2981, 2928, 1417 (sp^{3}C−H), 1740 (Ester C═O), 1707 (Ketone C═O), 1606, 1589 (Aromatic C═C), 1152 (C−O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.77 (1H, app. d, J = 7.7 Hz), 7.62 (1H, td, J = 7.7, 1.1 Hz), 7.47 (1H, app. d, J = 7.7 Hz), 7.39 (1H, app. t, J = 7.7 Hz), 5.92−5.74 (1H, m), 5.72−5.53 (1H, m), 5.29−4.98 (4H, m), 4.60 (2H, dt, J = 5.5, 1.4 Hz), 3.66 (1H, d, J = 17.4 Hz), 3.16 (1H, d, J = 17.4 Hz), 2.96−2.82 (1H, m), 2.71−2.54 (1H, m) ppm; $^{13}C\{^1H\}$NMR (101 MHz, $CDCl_3$) δ 202.1, 170.6, 153.2, 135.6, 135.3, 132.8, 131.7, 127.9, 126.5, 124.9, 119.5, 118.4, 66.2, 60.2, 39.2, 36.1 ppm; HRMS (ESI-TOF): calcd. for $C_{16}H_{16}O_3Na$ [M+Na$^+$] 279.0997; found 279.0999.

Allyl 2-Benzyl-1-oxo-2,3-dihydro-1H-indene-2-carboxylate ***(1q)***. Prepared according to typical procedure **C** using β-keto allyl ester **S1a** (0.973 g, 4.50 mmol) and benzyl bromide as the electrophile to afford the product as a yellow oil (0.906 g, 66%). Spectroscopic analysis is in good accordance to literature.[18]

Substrate Preparation for the Identification of Divergent Byproducts. *Cinnamyl 1H-Imidazole-1-carboxylate* ***(S2)***. Procedure was adapted from the literature.[29] To a 250 mL flask with a magnetic stirring bar was added 1,1′-carbonyldiimidazole (2.43 g, 15.0 mmol) and 100 mL THF. The flask was cooled in an ice−water bath. A solution of cinnamyl alcohol (1.34 g, 10.0 mmol) in 30 mL dichloromethane was added slowly and stirred for 2 h. The solvent was reduced *in vacuo* and resulting residue purified via silica gel column chromatography (pentane/EtOAc) to afford the product as a colorless solid (1.47 g, 64%). Spectroscopic analysis is in good accordance to literature.[29]

Cinnamyl 1-oxo-2,3-Dihydro-1H-indene-2-carboxylate ***(S3)***. *n*-Butylithium (2 mL, 2.5 M in hexanes, 5 mmol) was added dropwise to a well stirred solution of HMDS (1 mL, 5 mmol) in THF (24 mL) at 0 °C in a round-bottom flask (100 mL, 2-neck). The solution was stirred for 30 min then cooled to −78 °C. 1-Indanone (0.489 g, 3.70 mmol) in THF (17 mL) was then added dropwise. After 1 h cinnamyl 1*H*-imidazole-1-carboxylate **S2** in THF (3 mL) was added dropwise and the reaction mixture stirred at −78 °C for 1 h. The reaction was warmed to rt, stirred for 16 h and quenched with saturated aqueous NH_4Cl solution (70 mL). The mixture was then extracted with Et_2O (3 × 35 mL), the combined organic layers dried over anhydrous Na_2SO_4, filtered, and the solvent was removed *in vacuo*. The resulting residue was purified via silica gel column chromatography (pentane/Et_2O, 90:10 to 80:20) to afford the product as a clear oil (0.832 g, 77%). R_f = 0.37 (15% Et_2O in pentane); IR (NaCl): ν = 3077 (C═C−H), 3000 (Aromatic C−H), 1711 (Ester C═O), 1606 (Aromatic C═C) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.79 (1H, d, J = 7.5 Hz), 7.68−7.61 (1H, m), 7.52−7.47 (1H, m), 7.45−7.29 (6H, m), 6.70 (1H, app. d, J = 15.8 Hz), 6.31 (1H, dt, J = 15.8, 6.4 Hz), 4.86 (2H, dd, J = 6.4, 1.2 Hz), 3.78 (1H, dd, J = 8.3, 4.1 Hz), 3.59 (1H, dd, J = 17.2, 4.1 Hz), 3.40 (1H, dd, J = 17.2, 8.3 Hz) ppm; $^{13}C\{^1H\}$NMR (101 MHz, $CDCl_3$) δ 199.4, 169.1, 153.7, 136.3, 135.6, 135.4, 134.8, 129.6,

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128.7, 128.3, 128.0, 126.8, 126.7, 124.9, 122.8, 120.9, 66.4, 53.5, 30.5 ppm; HRMS (ESI-TOF): calcd. for $C_{19}H_{16}O_3Na$ [M+Na$^+$] 315.0997; found 315.0998.

Cinnamyl 1-oxo-2-(2,4,6-Trimethoxyphenyl)-2,3-dihydro-1H-indene-2-carboxylate (3). Prepared according to typical procedure **B** using cinnamyl 1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate **S3** (0.792 g, 2.71 mmol) to afford the product as an colorless oil (1.113 g, 90%). Column chromatography conditions = pentane/EtOAc, 90:10; R_f = 0.33 (30% EtOAc in pentane); IR (NaCl): ν = 3079 (C═C−H), 3011 (Aromatic C−H), 1707 (Ester C═O), 1605, 1588 (Aromatic C═C), 1118 (C−O) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 (1H, d, J = 7.6 Hz), 7.61−7.52 (1H, m), 7.43 (1H, d, J = 7.6 Hz), 7.40−7.16 (6H, m), 6.57 (1H, d, J = 15.9 Hz), 6.27 (1H, dt, J = 15.9, 6.3 Hz), 6.11 (2H, s), 4.88−4.67 (2H, m), 4.37 (1H, d, J = 17.1 Hz), 3.77 (3H, s), 3.58 (6H, s), 3.01 (1H, d, J = 17.1 Hz) ppm; ^{13}C{^{1}H}NMR (101 MHz, $CDCl_3$) δ 200.3, 170.3, 160.7, 158.4, 152.2, 136.5, 135.4, 134.7, 133.8, 128.6, 127.9, 127.3, 126.7, 126.2, 124.4, 123.6, 111.7, 92.3, 66.5, 61.8, 55.9, 55.5, 39.9 ppm; HRMS (ESI-TOF): calcd. for $C_{28}H_{26}O_6Na$ [M+Na$^+$] 481.1627; found 481.1633.

Typical Procedure D: Racemic Decarboxylative Asymmetric Protonation. Racemic protonation of α-substituted-β-keto allyl esters **1a**−**1q** was adapted from the literature.[10] $Pd(OAc)_2$ (0.10 equiv) and dppe (0.125 equiv) were added to a Schlenk flask (25 mL), and 1,4-dioxane (2.5 mL) was added. The suspension was stirred at 40 °C for 60 min, and formic acid (6.00 equiv) was added, followed immediately by α-substituted-β-keto allyl ester (1.00 equiv) in 1,4-dioxane (2.5 mL) from a round-bottom flask (25 mL, 2-neck). The reaction mixture was stirred at 40 °C for 10 h, cooled to room temperature, 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).

2-(2,4,6-Trimethoxyphenyl)-1-indanone (2a). Prepared according to typical procedure **D** using α-aryl-β-keto allyl ester **1a** (50.0 mg, 0.131 mmol) to afford the product as an orange solid (23.5 mg, 60%). Column chromatography conditions = pentane/Et_2O, 95:5 to 80:20; R_f = 0.63 (50% EtOAc in pentane); mp =124−125 °C; IR (NaCl): ν = 3054 (Aromatic C−H), 2988 (sp^{3}C−H), 1713 (Ketone: C═O) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (1H, app. d, J = 7.6 Hz), 7.58 (1H, app. t, J = 7.3 Hz), 7.45 (1H, app. d, J = 7.6 Hz), 7.37 (1H, app. t, J = 7.3 Hz), 6.19 (1H, s), 6.09 (1H, s), 4.34−4.26 (1H, m), 3.82 (3H, s), 3.80 (3H, s), 3.49−3.38 (4H, m), 3.08 (1H, dd, J = 16.7, 5.1 Hz) ppm; ^{13}C{^{1}H}NMR (101 MHz, $CDCl_3$) δ 207.9, 160.4, 159.2, 158.6, 153.2, 137.0, 133.9, 126.8, 126.1, 123.6, 109.4, 91.3, 90.9, 55.9, 55.4, 55.4, 43.3, 34.3 ppm; HRMS (ESI-TOF): calcd. for $C_{18}H_{19}O_4$ [M +H$^+$] 299.1283; found 299.1284.

2-(2,6-Dimethoxyphenyl)-1-indanone (2b). Prepared according to typical procedure **D** using α-aryl-β-keto allyl ester **1b** (52.9 mg, 0.150 mmol) to afford the product as an orange solid (18.9 mg, 47%). Column chromatography conditions = pentane/Et_2O, 95:5 to 80:20; R_f = 0.25 (30% Et_2O in pentane); mp =159−160 °C; IR (NaCl): ν = 2937, 1473 (sp3C−H), 1706 (Ketone: C═O), 856 (Aromatic C−H) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (1H, app. d, J = 7.6 Hz), 7.59 (1H, app. t, J = 7.5), 7.46 (1H, app. d, J = 7.6 Hz), 7.39 (1H, app. t, J = 7.5 Hz), 7.20 (1H, t, J = 8.3 Hz), 6.61 (1H, d, J = 8.3 Hz), 6.51 (1H, d, J = 8.3 Hz), 4.39 (1H, dd, J = 8.4, 5.2 Hz), 3.85 (3H, s), 3.54−3.44 (4H, m), 3.11 (1H, dd, J = 16.7, 5.2 Hz) ppm; ^{13}C{^{1}H}NMR (101 MHz, $CDCl_3$) δ 207.5, 158.7, 158.0, 153.1, 137.0, 134.0, 128.2, 126.9, 126.1, 123.6, 117.0, 104.5, 104.1, 56.0, 55.5, 43.5, 34.2 ppm; HRMS (ESI-TOF): calcd. for $C_{17}H_{16}O_3$ [M$^+$] 268.1099; found 268.1106.

2-(2,3,6-Trimethoxyphenyl)-1-indanone (2c). Prepared according to typical procedure **D** using α-aryl-β-keto allyl ester **1c** (34.0 mg, 0.089 mmol) to afford the product as a brown oil (19.1 mg, 72%). Column chromatography conditions = pentane/Et_2O, 95:5 to 80:20; R_f = 0.17 (30% Et_2O in pentane); IR (NaCl): ν = 3054 (Aromatic C−H), 2988 (sp3C−H), 1711 (Ketone: C═O) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (1H, app. t, J = 7.4 Hz), 7.59 (1H, app. t, J = 7.4 Hz), 7.46 (1H, app. d, J = 7.4 Hz), 7.39 (1H, app. t, J = 7.4 Hz), 6.79 (1H, d, J = 8.9 Hz), 6.60 (0.5H, d, J = 8.9 Hz), 6.54 (0.5H, d, J = 8.9 Hz), 4.37−4.27 (1H, m), 3.92−3.73 (6H, m, J = 31.3, 13.6 Hz), 3.59−3.40 (4H, m), 3.19 (0.5H, dd, J = 16.8, 4.7 Hz), 3.09 (0.5H, dd, J = 16.8, 4.7 Hz). ^{13}C{^{1}H}NMR (101 MHz, $CDCl_3$) δ 208.0, 207.2, 153.4, 153.3, 152.5, 151.9, 149.0, 147.6, 147.4, 147.1, 137.0, 134.3, 127.1, 126.4, 126.3, 123.8, 123.7, 112.0, 111.3, 106.6, 105.7, 61.8, 59.6, 56.4, 55.9, 44.8, 44.0, 4.5, 34.5 ppm; HRMS (ESI-TOF): calcd. for $C_{18}H_{18}O_4$ [M$^+$] 298.1205; found 298.1197.

2-(2-Methoxy-4,6-dimethylphenyl)-1-indanone (2d). Prepared according to typical procedure **D** using α-aryl-β-keto allyl ester **1d** (52.6 mg, 0.150 mmol) to afford the product as a colorless solid (17.0 mg, 43%). Column chromatography conditions = pentane/Et_2O, 75:25; R_f = 0.33 (30% Et_2O in pentane); mp =133−134 °C; IR (NaCl): ν = 3055 (Aromatic C−H), 2987 (sp3C−H), 1712 (Ketone: C═O) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (1H, app. d, J = 7.6 Hz), 7.60 (1H, app. t, J = 7.4 Hz), 7.47 (1H, app. d, J = 7.6 Hz), 7.40 (1H, app. t, J = 7.4 Hz), 6.73−6.50 (2H, m), 3.91 (1H, dd, J = 8.3, 5.2 Hz), 3.55−3.42 (4H, m), 3.13 (1H, dd, J = 16.7, 5.2 Hz), 2.38 (3H, s), 2.31 (3H, s) ppm; ^{13}C{^{1}H}NMR (101 MHz, $CDCl_3$) δ 207.5, 157.1, 152.9, 138.1, 137.7, 137.1, 134.2, 127.1, 126.3, 124.9, 123.9, 123.9, 110.4, 55.4, 47.5, 34.3, 21.6, 20.3 ppm; HRMS (ESI-TOF): calcd. for $C_{18}H_{18}O_2$ [M$^+$] 266.1307; found 266.1315.

2-(2,6-Dimethylphenyl)-1-indanone (2e). Prepared according to typical procedure **D** using α-aryl-β-keto allyl ester **1e** (48.1 mg, 0.150 mmol) to afford the product as a colorless solid (27.4 mg, 77%). Column chromatography conditions = pentane/Et_2O, 93:7; R_f = 0.58 (30% Et_2O in pentane); mp =142−143 °C; IR (NaCl): ν = 3056 (Aromatic C−H), 2985 (sp3C−H), 1717 (Ketone: C═O) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (1H, app. d, J = 7.5 Hz), 7.67 (1H, app. t, J = 7.5 Hz), 7.54 (1H, app. d, J = 7.5 Hz), 7.47 (1H, app. t, J = 7.5 Hz), 7.15−7.07 (2H, m), 7.03 (1H, dd, J = 8.3, 4.7 Hz), 4.27 (1H, dd, J = 8.5, 5.5 Hz), 3.69 (1H, dd, J = 17.4, 8.5 Hz), 3.16 (1H, dd, J = 17.4, 5.5 Hz), 2.46 (3H, s), 1.91 (3H, s) ppm; ^{13}C{^{1}H}NMR (101 MHz, $CDCl_3$) δ 206.5, 152.6, 137.8, 137.0, 136.5, 136.4, 134.9, 129.5, 128.3, 127.9, 127.2, 126.6, 124.3, 50.2, 34.1, 21.4, 20.9 ppm; HRMS (ESI-TOF): calcd. for $C_{17}H_{16}O$ [M$^+$] 236.1201; found 236.1192.

2-(2-(Methoxy)naphthalen-1-yl)-1-indanone (2f). Prepared according to typical procedure **D** using α-aryl-β-keto allyl ester **1f** (34.1 mg, 0.092 mmol) to afford the product as an orange solid (23.5 mg, 89%). Column chromatography conditions = pentane/Et_2O, 95:5 to 90:10; R_f = 0.28 (30% Et_2O in pentane); mp =136−138 °C; IR (NaCl): ν = 3055 (Aromatic C−H), 2987 (sp3C−H), 1712 (Ketone: C═O) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (0.7H, d, J = 8.5 Hz), 7.95 (0.2H, d, J = 7.4 Hz), 7.90 (0.7H, d, J = 7.6 Hz), 7.87−7.76 (2H, m), 7.71 (0.3H, t, J = 7.4 Hz), 7.64 (0.7H, t, J = 7.2 Hz), 7.60−7.30 (3.9H, m), 7.30−7.25 (0.7H, m), 7.22−7.15 (0.3H, m), 6.92 (0.3H, d, J = 8.5 Hz), 5.10 (0.3H, dd, J = 8.4, 5.3 Hz), 4.51 (0.7H, dd, J = 8.4, 5.3 Hz), 3.97 (0.8H, s), 3.69 (1H, dd, J = 17.1, 8.4 Hz), 3.61 (2.2H, s), 3.41 (0.3H, dd, J = 17.1, 5.3 Hz), 3.21 (0.7H, dd, J = 17.1, 5.3 Hz) ppm; ^{13}C{^{1}H}NMR (101 MHz, $CDCl_3$) δ 207.4, 154.4, 152.8, 137.1, 134.9, 134.4, 133.9, 129.8, 129.6, 129.2, 129.2, 128.9, 127.8, 127.3, 127.0, 126.9, 126.4, 124.5, 123.9, 123.7, 123.5, 122.9, 122.6, 114.2, 113.7, 57.3, 56.2, 46.2, 45.7, 35.3, 34.4 ppm; HRMS (ESI-TOF): calcd. for $C_{20}H_{16}O_2$ [M$^+$] 288.1150; found 288.1156.

2-(2,4-Dimethoxyphenyl)-1-indanone (2g). Prepared according to typical procedure **D** using α-aryl-β-keto allyl ester **1g** (46.2 mg, 0.131 mmol) to afford the product as a colorless solid (22.2 mg, 63%). Column chromatography conditions = pentane/Et_2O, 95:5 to 80:20; R_f = 0.22 (30% Et_2O in pentane); mp =119−120 °C; IR (NaCl): ν = 3054 (Aromatic C−H), 2982 (sp3C−H), 1712 (Ketone: C═O) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 (1H, app. d, J = 7.5 Hz), 7.63 (1H, app. t, J = 7.5 Hz), 7.48 (1H, app. d, J = 7.5 Hz), 7.42 (1H, app. t, J = 7.5 Hz), 7.08 (1H, d, J = 8.9 Hz), 6.52−6.43 (2H, m), 3.89 (1H, dd, J = 8.3, 4.9 Hz), 3.81 (3H, s), 3.68−3.49 (4H, m), 3.17 (1H, dd, J = 17.0, 4.9 Hz) ppm; ^{13}C{^{1}H}NMR (101 MHz, $CDCl_3$) δ 207.3, 160.3, 158.2, 153.4, 136.9, 134.6, 130.9, 127.3, 126.4, 124.1, 121.3, 104.5, 99.4, 55.5, 55.5, 50.1, 35.3 ppm; HRMS (ESI-TOF): calcd. for $C_{17}H_{16}O_3$ [M$^+$] 268.1099; found 268.1088.

(2,3,4-Trimethoxyphenyl)-1-indanone (2h). Prepared according to typical procedure **D** using α-aryl-β-keto allyl ester **1h** (34.0 mg, 0.089 mmol) to afford the product as an orange oil (14.8 mg, 56%). Column chromatography conditions = pentane/Et_2O, 95:5 to 80:20; R_f = 0.16

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(30% Et_2O in pentane); IR (NaCl): ν = 3054 (Aromatic C−H), 2985 (sp3C−H), 1710 (Ketone: C═O) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.83 (1H, app. d, J = 7.6 Hz), 7.62 (1H, app. t, J = 7.5 Hz), 7.48 (1H, app. d, J = 7.6 Hz), 7.41 (1H, app. t, J = 7.5 Hz), 6.83 (1H, d, J = 8.5 Hz), 6.62 (1H, d, J = 8.5 Hz), 3.89−3.76 (7H, m), 3.68 (3H, s), 3.59 (1H, dd, J = 17.1, 6.7 Hz), 3.14 (1H, dd, J = 17.1, 4.7 Hz) ppm; $^{13}C\{^1H\}$NMR (101 MHz, $CDCl_3$) δ 207.4, 153.4, 153.4, 151.7, 142.4, 136.8, 134.7, 127.5, 127.0, 126.5, 124.5, 124.1, 107.2, 60.8, 60.5, 56.2, 50.3, 36.2 ppm; HRMS (ESI-TOF): calcd. for $C_{18}H_{18}O_4$ $[M^+]$ 298.1205; found 298.1213.

2-(Benzo[d][1,3]dioxol-5-yl)-1-indanone ***(2i)***. Prepared according to typical procedure **D** using α-aryl-β-keto allyl ester **1i** (33.0 mg, 0.098 mmol) to afford the product as an orange oil (20.3 mg, 82%). Column chromatography conditions = pentane/Et_2O, 92:8; R_f = 0.35 (30% Et_2O in pentane); IR (NaCl): ν = 3055 (Aromatic C−H), 2987 (sp3C−H), 1711 (Ketone: C═O) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.79 (1H, d, J = 7.7 Hz), 7.63 (1H, td, J = 7.5, 1.2 Hz), 7.52−7.48 (1H, m), 7.43−7.38 (1H, m), 6.74 (1H, d, J = 7.8 Hz), 6.66 (1H, dd, J = 7.8, 1.8 Hz), 6.61 (1H, d, J = 1.8 Hz), 5.90 (2H, s), 3.79 (1H, dd, J = 8.3, 4.0 Hz), 3.65 (1H, dd, J = 17.4, 8.3 Hz), 3.19 (1H, dd, J = 17.4, 4.0 Hz); $^{13}C\{^1H\}$NMR (101 MHz, $CDCl_3$) δ 206.09, 153.65, 148.14, 146.76, 136.29, 135.19, 133.50, 127.90, 126.56, 124.70, 121.34, 108.66, 108.21, 101.16, 53.23, 36.11 ppm; HRMS (ESI-TOF): calcd. for $C_{16}H_{12}O_3$ $[M^+]$ 252.0786; found 252.0774.

2-(4-Methoxyphenyl)-1-indanone ***(2j)***. Prepared according to typical procedure **D** using α-aryl-β-keto allyl ester **1j** (42.0 mg, 0.130 mmol) to afford the product as an orange solid (27.0 mg, 87%). Column chromatography conditions = pentane/Et_2O, 95:5; spectroscopic analysis is in good accordance to literature.[30]

2-(Phenyl)-1-indanone ***(2k)***. Prepared according to typical procedure **D** using α-aryl-β-keto allyl ester **1k** (43.9 mg, 0.150 mmol) to afford the product as a brown solid (23.3 mg, 75%). Column chromatography conditions = pentane/Et_2O, 95:5; spectroscopic analysis is in good accordance to literature.[31]

5-Methyl-2-(2,4,6-trimethoxyphenyl)-1-indanone ***(2l)***. Prepared according to typical procedure **D** using α-aryl-β-keto allyl ester **1l** (59.5 mg, 0.150 mmol) to afford the product as a colorless solid (40.3 mg, 86%). Column chromatography conditions = pentane/EtOAc, 85:15; R_f = 0.43 (30% EtOAc in pentane); mp =151−152 °C; IR (NaCl): ν = 2995, 801 (Aromatic C−H), 2961, 1454 (sp^3C−H), 1704 (Ketone: C═O), 1111 (C−O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.70 (1H, d, J = 7.8 Hz), 7.24 (1H, app. s), 7.18 (1H, app. d, J = 7.8 Hz), 6.18 (1H, s), 6.09 (1H, s), 4.27 (1H, dd, J = 8.4, 5.2 Hz), 3.82 (3H, s), 3.80 (3H, s), 3.53−3.32 (4H, m), 3.03 (1H, dd, J = 16.7, 5.2 Hz), 2.45 (3H, s) ppm; $^{13}C\{^1H\}$NMR (101 MHz, $CDCl_3$) δ 207.6, 160.5, 159.3, 158.8, 153.8, 145.0, 134.9, 128.2, 126.6, 123.6, 109.7, 91.5, 91.0, 56.0, 55.6, 55.5, 43.6, 34.3, 22.2 ppm; HRMS (ESI-TOF): calcd. for $C_{19}H_{20}O_4Na$ $[M+Na^+]$ 335.1259; found 335.1271.

5,7-Dichloro-2-(2,4,6-trimethoxyphenyl)-1-indanone ***(2m)***. Prepared according to typical procedure **D** using α-aryl-β-keto allyl ester **1m** (67.7 mg, 0.150 mmol) to afford the product as a colorless solid (33.2 mg, 60%). Column chromatography conditions = pentane/EtOAc, 85:15; R_f = 0.58 (30% EtOAc in pentane); mp =159−160 °C; IR (NaCl): ν = 3061 (Aromatic C−H), 2961, 1442 (sp^3C−H), 1721 (Ketone: C═O), 1585, 1569 (Aromatic C═C), 1113 (C−O), 807 (C−Cl) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.33 (2H, s), 6.15 (1H, s), 6.09 (1H, s), 4.31 (1H, dd, J = 8.6, 5.4 Hz), 3.79 (6H, s), 3.51 (3H, s), 3.37 (1H, dd, J = 17.1, 8.6 Hz), 3.03 (1H, dd, J = 17.1, 5.4 Hz) ppm; $^{13}C\{^1H\}$NMR (101 MHz, $CDCl_3$) δ 203.2, 160.7, 159.3, 158.6, 156.6, 140.1, 132.4, 131.6, 128.9, 125.1, 108.9, 91.4, 91.1, 56.0, 55.8, 55.5, 44.0, 33.5 ppm; HRMS (ESI-TOF): calcd. for $C_{18}H_{16}O_4Cl_2Na$ $[M+Na^+]$ 389.0323; found 389.0312.

4-(Trifluoromethyl)-2-(2,4,6-trimethoxyphenyl)-1-indanone ***(2n)***. Prepared according to typical procedure **D** using α-aryl-β-keto allyl ester **1n** (67.6 mg, 0.150 mmol) to afford the product as an orange oil (42.3 mg, 77%). Column chromatography conditions = pentane/EtOAc, 85:15; R_f = 0.48 (30% EtOAc in pentane); IR (NaCl): ν = 3061 (Aromatic C−H), 2921, 2852, 1442 (sp^3C−H), 1728 (Ketone: C═O), 1612, 1594 (Aromatic C═C), 1113 (C−O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.98 (1H, app. d, J = 7.6 Hz), 7.85 (1H, app. d, J = 7.6 Hz), 7.51 (1H, app. t, J = 7.6 Hz), 6.19 (1H, s), 6.09 (1H, s), 4.34 (1H, dd, J = 8.5, 5.1 Hz), 3.83 (3H, s), 3.80 (3H, s), 3.69 (1H, dd, J = 17.1, 8.5 Hz), 3.46 (3H, s), 3.19 (1H, dd, J = 17.1, 5.1 Hz) ppm; $^{13}C\{^1H\}$NMR (101 MHz, $CDCl_3$) δ 206.6, 160.8, 159.3, 158.5, 150.6 (q, J = 2.1 Hz), 138.6, 130.7 (q, J = 4.7 Hz), 128.0 (q, J = 32.1 Hz), 127.4, 127.2, 124.1 (q, J = 273.3 Hz), 108.8, 91.4, 91.1, 56.0, 55.5, 43.0, 33.3 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ −62.3 ppm; HRMS (ESI-TOF): calcd. for $C_{19}H_{17}O_4F_3Na$ $[M+Na^+]$ 389.0977; found 389.0979.

2-Methyl-1-indanone ***(2o)***. Prepared according to typical procedure **D** using α-methyl-β-keto allyl ester **1o** (34.5 mg, 0.150 mmol) to afford the product as a yellow oil (20.3 mg, 91%). Column chromatography conditions = pentane/EtOAc, 95:5; spectroscopic analysis is in good accordance to literature.[4a]

2-Allyl-1-indanone ***(2p)***. Prepared according to typical procedure **D** using α-allyl-β-keto allyl ester **1p** (38.4 mg, 0.150 mmol) to afford the product as a brown oil (10.1 mg, 39%). Column chromatography conditions = pentane/EtOAc, 95:5; spectroscopic analysis is in good accordance to literature.[32]

2-Benzyl-1-indanone ***(2q)***. Prepared according to typical procedure **D** using α-benzyl-β-keto allyl ester **1q** (46.0 mg, 0.150 mmol) to afford the product as a yellow oil (25.5 mg, 77%). Column chromatography conditions = pentane/EtOAc, 95:5; spectroscopic analysis is in good accordance to literature.[33]

Typical Procedure E: Homogeneous Decarboxylative Asymmetric Protonation. Homogeneous protonation of α-substituted-β-keto allyl esters **1a−1q** was adapted from the literature.[10] Pd_2dba_3·$CHCl_3$ (0.05 equiv) and (*S*)-$(CF_3)_3$-*t*-Bu PHOX (0.125 equiv) were dissolved in THF in a Schlenk flask (25 mL) and stirred at 40 °C for 30 min. α-Substituted-β-keto allyl ester (1 equiv) and Meldrum's acid (2.5 equiv) were dissolved in THF (0.03 M) in a round-bottom flask (25 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 1 h, cooled to room temperature, 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).

(S)-2-(2,4,6-Trimethoxyphenyl)-1-indanone ***((S)-2a)***. Prepared according to typical procedure **E** using α-aryl-β-keto allyl ester **1a** (50.0 mg, 0.131 mmol) to afford the product (34.0 mg, 87%), identical in all respects to the previously prepared racemic sample, with the exception of $[\alpha]_D^{20}$ = −50.1 (*c* 0.30, $CHCl_3$); SFC (see Table S1).

(S)-2-(2,6-Dimethoxyphenyl)-1-indanone ***((S)-2b)***. Prepared according to typical procedure **E** using α-aryl-β-keto allyl ester **1b** (50.0 mg, 0.142 mmol) to afford the product (35.7 mg, 94%), identical in all respects to the previously prepared racemic sample, with the exception of $[\alpha]_D^{20}$ = −48.1 (*c* 1.00, $CHCl_3$); SFC (see Table S1).

(S)-2-(2,3,6-Trimethoxyphenyl)-1-indanone ***((S)-2c)***. Prepared according to typical procedure **E** using α-aryl-β-keto allyl ester **1c** (24.5 mg, 0.064 mmol) to afford the product (13.8 mg, 72%), identical in all respects to the previously prepared racemic sample, with the exception of $[\alpha]_D^{20}$ = −11.8 (*c* 0.40, $CHCl_3$); SFC (see Table S1).

(S)-2-(2-Methoxy-4,6-dimethylphenyl)-1-indanone ***((S)-2d)***. Prepared according to typical procedure **E** using α-aryl-β-keto allyl ester **1d** (50.0 mg, 0.143 mmol) to afford the product (35.3 mg, 93%), identical in all respects to the previously prepared racemic sample, with the exception of $[\alpha]_D^{20}$ = −47.3 (*c* 0.40, $CHCl_3$); SFC (see Table S1).

(S)-2-(2,6-Dimethylphenyl)-1-indanone ***((S)-2e)***. Prepared according to typical procedure **E** using α-aryl-β-keto allyl ester **1e** (48.1 mg, 0.150 mmol) to afford the product (26.1 mg, 74%), identical in all respects to the previously prepared racemic sample, with the exception of $[\alpha]_D^{20}$ = −47.1 (*c* 2.20, $CHCl_3$); SFC (see Table S1).

(S)-2-(2-(Methoxy)naphthalen-1-yl)-1-indanone ***((S)-2f)***. Prepared according to typical procedure **E** using α-aryl-β-keto allyl ester **1f** (55.9 mg, 0.150 mmol) to afford the product (41.2 mg, 95%), identical in all respects to the previously prepared racemic sample, with the exception of $[\alpha]_D^{20}$ = −63.9 (*c* 1.60, $CHCl_3$); SFC (see Table S1).

(S)-2-(2,4-Dimethoxyphenyl)-1-indanone ***((S)-2g)***. Prepared according to typical procedure **E** using α-aryl-β-keto allyl ester **1g** (52.9 mg, 0.150 mmol) to afford the product (37.7 mg, 94%), identical in all

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respects to the previously prepared racemic sample, with the exception of $[\alpha]_D^{20} = -1.61$ (*c* 1.30, $CHCl_3$); SFC (see Table S1).

(S)-(2,3,4-Trimethoxyphenyl)-1-indanone ***((S)-2h).*** Prepared according to typical procedure **E** using α-aryl-β-keto allyl ester **1h** (50.0 mg, 0.131 mmol) to afford the product (29.6 mg, 76%), identical in all respects to the previously prepared racemic sample, with the exception of $[\alpha]_D^{20} = -16.0$ (*c* 0.40, $CHCl_3$); SFC (see Table S1).

(S)-2-(Benzo[d][1,3]dioxol-5-yl)-1-indanone ***((S)-2i).*** Prepared according to typical procedure **E** using α-aryl-β-keto allyl ester **1i** (50.5 mg, 0.150 mmol) to afford the product (23.6 mg, 62%), identical in all respects to the previously prepared racemic sample, with the exception of $[\alpha]_D^{20} = +34.7$ (*c* 0.60, $CHCl_3$); SFC (see Table S1).

(S)-2-(4-Methoxyphenyl)-1-indanone ***((S)-2j).*** Prepared according to typical procedure **E** using α-aryl-β-keto allyl ester **1j** (48.4 mg, 0.150 mmol) to afford the product (25.1 mg, 70%), identical in all respects to the previously prepared racemic sample, with the exception of $[\alpha]_D^{20} = +24.2$ (*c* 1.70, $CHCl_3$); SFC (see Table S1).

(S)-2-(Phenyl)-1-indanone ***((S)-2k).*** Prepared according to typical procedure **E** using α-aryl-β-keto allyl ester **1k** (43.9 mg, 0.150 mmol) to afford the product (26.3 mg, 84%), identical in all respects to the previously prepared racemic sample, with the exception of $[\alpha]_D^{20} = +6.4$ (*c* 0.12, $CHCl_3$); SFC (see Table S1).

(S)-5-Methyl-2-(2,4,6-trimethoxyphenyl)-1-indanone ***((S)-2l).*** Prepared according to typical procedure **E** using α-aryl-β-keto allyl ester **1l** (59.5 mg, 0.150 mmol) to afford the product (34.7 mg, 74%), identical in all respects to the previously prepared racemic sample, with the exception of $[\alpha]_D^{20} = -37.8$ (*c* 0.21, $CHCl_3$); SFC (see Table S1).

(S)-5,7-Dichloro-2-(2,4,6-trimethoxyphenyl)-1-indanone ***((S)-2m).*** Prepared according to typical procedure **E** using α-aryl-β-keto allyl ester **1m** (67.7 mg, 0.150 mmol) to afford the product (48.0 mg, 87%), identical in all respects to the previously prepared racemic sample, with the exception of $[\alpha]_D^{20} = -174.3$ (*c* 0.11, $CHCl_3$); SFC (see Table S1).

(S)-4-(Trifluoromethyl)-2-(2,4,6-trimethoxyphenyl)-1-indanone ***((S)-2n).*** Prepared according to typical procedure **E** using α-aryl-β-keto allyl ester **1n** (67.6 mg, 0.150 mmol) to afford the product (41.9 mg, 76%), identical in all respects to the previously prepared racemic sample, with the exception of $[\alpha]_D^{20} = -48.1$ (*c* 0.11, $CHCl_3$); SFC (see Table S1).

(S)-2-Methyl-1-indanone ***((S)-2o).*** Prepared according to typical procedure **E** using α-methyl-β-keto allyl ester **1o** (34.5 mg, 0.150 mmol) to afford the product (20.7 mg, 95%), identical in all respects to the previously prepared racemic sample, with the exception of $[\alpha]_D^{20} = +15.0$ (*c* 0.05, $CHCl_3$); SFC (see Table S1). The absolute configuration was established by comparison of the optical rotation to the literature value for (*R*)-2-methyl-1-indanone: $[\alpha]_D^{22} - 42$ (c 1.72, *p*-dioxane).[34]

(S)-2-Allyl-1-indanone ***((S)-2p).*** Prepared according to typical procedure **E** using α-allyl-β-keto allyl ester **1p** (38.4 mg, 0.150 mmol) to afford the product (19.2 mg, 74%), identical in all respects to the previously prepared racemic sample, with the exception of $[\alpha]_D^{20} = +6.6$ (*c* 0.86, $CHCl_3$); SFC (see Table S1). The absolute configuration was established by comparison of the optical rotation to the literature value for (*R*)-2-allyl-1-indanone: $[\alpha]_D^{24} = +95.8$ (c = 4.0, CH_2Cl_2, 81% ee).[32]

(R)-2-Benzyl-1-indanone ***((R)-2q).*** Prepared according to typical procedure **E** using α-benzyl-β-keto allyl ester **1q** (46.0 mg, 0.150 mmol) to afford the product (22.4 mg, 67%), identical in all respects to the previously prepared racemic sample, with the exception of $[\alpha]_D^{20} = -19.2$ (*c* 0.89, $CHCl_3$); SFC (see Table S1). The absolute configuration was established by comparison of the optical rotation to the literature value for (*S*)-2-benzyl-1-indanone: $[\alpha]_D^{20} = +162$ (c = 0.1, $CHCl_3$, 52% ee).[35]

Typical Procedure F: Heterogeneous Decarboxylative Asymmetric Protonation. Heterogeneous protonation of α-substituted-β-keto allyl esters **1a**−**1q** was adapted from the literature.[8] Powdered 4 Å molecular sieves (270 mg) were added to a Schlenk flask (25 mL). The flask and molecular sieves were flame-dried and backfilled with N_2 three times. Once the flask had cooled to ambient temperature under N_2, $Pd(OAc)_2$ (3.4 mg, 0.015 mmol), (*S*)-$(CF_3)_3$-*t*-Bu-PHOX (11.1 mg, 0.01875 mmol), and 1,4-dioxane (2.5 mL) were added. The mixture was stirred at 40 °C for 30 min prior to the addition of formic acid (34 μL, 0.90 mmol) followed immediately by a solution of α-substituted-β-keto allyl ester (0.15 mmol) in 1,4-dioxane (2.5 mL) from a round-bottom flask (25 mL, 2-neck). The reaction mixture was stirred at 40 °C for 18 h, filtered through a plug of Celite, and washed with Et_2O. The filtrate was concentrated *in vacuo* and purified by silica gel column chromatography (pentane/Et_2O).

(R)-2-(2,4,6-Trimethoxyphenyl)-1-indanone ***((R)-2a).*** Prepared according to typical procedure **F** using α-aryl-β-keto allyl ester **1a** (57.4 mg, 0.150 mmol) to afford the product (36.2 mg, 81%), identical in all respects to the previously prepared racemic sample, with the exception of $[\alpha]_D^{20} = +24.6$ (*c* 2.11, $CHCl_3$); SFC (see Table S1).

(R)-2-(2,6-Dimethoxyphenyl)-1-indanone ***((R)-2b).*** Prepared according to typical procedure **F** using α-aryl-β-keto allyl ester **1b** (52.9 mg, 0.150 mmol) to afford the product (33.8 mg, 84%), identical in all respects to the previously prepared racemic sample, with the exception of $[\alpha]_D^{20} = +36.0$ (*c* 1.79, $CHCl_3$); SFC (see Table S1).

(R)-2-(2,3,6-Trimethoxyphenyl)-1-indanone ***((R)-2c).*** Prepared according to typical procedure **F** using α-aryl-β-keto allyl ester **1c** (57.4 mg, 0.150 mmol) to afford the product (35.4 mg, 79%), identical in all respects to the previously prepared racemic sample, with the exception of $[\alpha]_D^{20} = +26.8$ (*c* 1.56, $CHCl_3$); SFC (see Table S1).

(R)-2-(2-Methoxy-4,6-dimethylphenyl)-1-indanone ***((R)-2d).*** Prepared according to typical procedure **F** using α-aryl-β-keto allyl ester **1d** (52.6 mg, 0.150 mmol) to afford the product (38.9 mg, 97%), identical in all respects to the previously prepared racemic sample, with the exception of $[\alpha]_D^{20} = +27.6$ (*c* 1.67, $CHCl_3$); SFC (see Table S1).

(R)-2-(2,6-Dimethylphenyl)-1-indanone ***((R)-2e).*** Prepared according to typical procedure **F** using α-aryl-β-keto allyl ester **1e** (48.1 mg, 0.150 mmol) to afford the product (34.0 mg, 96%), identical in all respects to the previously prepared racemic sample, with the exception of $[\alpha]_D^{20} = +0.3$ (*c* 1.38, $CHCl_3$); SFC (see Table S1).

(R)-2-(2-(Methoxy)naphthalen-1-yl)-1-indanone ***((R)-2f).*** Prepared according to typical procedure **F** using α-aryl-β-keto allyl ester **1f** (55.9 mg, 0.150 mmol) to afford the product (38.3 mg, 88%), identical in all respects to the previously prepared racemic sample, with the exception of $[\alpha]_D^{20} = +22.9$ (*c* 1.64, $CHCl_3$); SFC (see Table S1).

(R)-2-(2,4-Dimethoxyphenyl)-1-indanone ***((R)-2g).*** Prepared according to typical procedure **F** using α-aryl-β-keto allyl ester **1g** (52.9 mg, 0.150 mmol) to afford the product (37.8 mg, 94%), identical in all respects to the previously prepared racemic sample, with the exception of $[\alpha]_D^{20} = +2.8$ (*c* 2.36, $CHCl_3$); SFC (see Table S1).

(R)-(2,3,4-Trimethoxyphenyl)-1-indanone ***((R)-2h).*** Prepared according to typical procedure **F** using α-aryl-β-keto allyl ester **1h** (57.4 mg, 0.150 mmol) to afford the product (37.9 mg, 85%), identical in all respects to the previously prepared racemic sample, with the exception of $[\alpha]_D^{20} = -1.7$ (*c* 0.51, $CHCl_3$); SFC (see Table S1).

(R)-2-(Benzo[d][1,3]dioxol-5-yl)-1-indanone ***((R)-2i).*** Prepared according to typical procedure **F** using α-aryl-β-keto allyl ester **1i** (50.5 mg, 0.150 mmol) to afford the product (32.0 mg, 85%), identical in all respects to the previously prepared racemic sample, with the exception of $[\alpha]_D^{20} = -18.7$ (*c* 0.82, $CHCl_3$); SFC (see Table S1).

(R)-2-(4-Methoxyphenyl)-1-indanone ***((R)-2j).*** Prepared according to typical procedure **F** using α-aryl-β-keto allyl ester **1j** (48.4 mg, 0.150 mmol) to afford the product (29.7 mg, 83%), identical in all respects to the previously prepared racemic sample, with the exception of $[\alpha]_D^{20} = +4.0$ (*c* 0.18, $CHCl_3$); SFC (see Table S1).

(R)-2-(Phenyl)-1-indanone ***((R)-2k).*** Prepared according to typical procedure **F** using α-aryl-β-keto allyl ester **1k** (43.9 mg, 0.150 mmol) to afford the product (18.2 mg, 58%), identical in all respects to the previously prepared racemic sample, with the exception of $[\alpha]_D^{20} = +1.1$ (*c* 0.97, $CHCl_3$); SFC (see Table S1).

(R)-5-Methyl-2-(2,4,6-trimethoxyphenyl)-1-indanone ***((R)-2l).*** Prepared according to typical procedure **F** using α-aryl-β-keto allyl ester **1l** (59.5 mg, 0.150 mmol) to afford the product (34.8 mg, 74%), identical in all respects to the previously prepared racemic sample, with the exception of $[\alpha]_D^{20} = +13.8$ (*c* 1.45, $CHCl_3$); SFC (see Table S1).

(R)-5,7-Dichloro-2-(2,4,6-trimethoxyphenyl)-1-indanone ***((R)-2m).*** Prepared according to typical procedure **F** using α-aryl-β-keto

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allyl ester **1m** (67.5 mg, 0.150 mmol) to afford the product (46.3 mg, 84%), identical in all respects to the previously prepared racemic sample, with the exception of $[\alpha]_D^{20}$ = +65.9 (*c* 0.32, $CHCl_3$); SFC (see Table S1).

(R)-4-(Trifluoromethyl)-2-(2,4,6-trimethoxyphenyl)-1-indanone ((R)-2n). Prepared according to typical procedure **F** using α-aryl-β-keto allyl ester **1n** (67.6 mg, 0.150 mmol) to afford the product (26.4 mg, 48%), identical in all respects to the previously prepared racemic sample, with the exception of $[\alpha]_D^{20}$ = +3.1 (*c* 0.81, $CHCl_3$); SFC (see Table S1).

(S)-2-Methyl-1-indanone ((S)-2o). Prepared according to typical procedure **F** using α-methyl-β-keto allyl ester **1o** (34.5 mg, 0.150 mmol) to afford the product (15.6 mg, 71%), identical in all respects to the previously prepared racemic sample, with the exception of $[\alpha]_D^{20}$ = +6.3 (*c* 0.10, $CHCl_3$); SFC (see Table S1).

(S)-2-Allyl-1-indanone ((S)-2p). Prepared according to typical procedure **F** using α-allyl-β-keto allyl ester **1p** (38.4 mg, 0.150 mmol) to afford the product (18.3 mg, 71%), identical in all respects to the previously prepared racemic sample, with the exception of $[\alpha]_D^{20}$ = +81.9 (*c* 0.80, $CHCl_3$); SFC (see Table S1).

(S)-2-Benzyl-1-indanone ((S)-2q). Prepared according to typical procedure **F** using α-benzyl-β-keto allyl ester **1q** (46.0 mg, 0.150 mmol) to afford the product (30.1 mg, 90%), identical in all respects to the previously prepared racemic sample, with the exception of $[\alpha]_D^{20}$ = +64.0 (*c* 1.12, $CHCl_3$); SFC (see Table S1).

Identification of Divergent Byproducts. Eq 1. The reaction was performed using α-aryl-β-keto allyl ester **S4** (0.229 g, 0.500 mmol) according to typical procedure **F**. **2a** was isolated (109 mg, 73%) with an *ee* of (*R*)-90%. *trans*-β-Methylstyrene **4** was isolated (0.038 g, 64%) with spectroscopic analysis in good accordance to literature.[36]

Reaction without the Metal–Ligand Complex. The reaction was performed using α-aryl-β-keto allyl ester **S4** (69 mg, 0.15 mmol) according to typical procedure **F** except no palladium or ligand was added. As per the standard conditions, the reaction mixture was stirred at 40 °C for 18 h, cooled to room temperature, and filtered through a plug of Celite, and washed with Et_2O. The crude product was analyzed by SFC and no product **2a** or *trans*-β-methylstyrene **4** formation was observed. Subsequently, the solvent was removed *in vacuo*, and the resulting residue was purified by silica gel column chromatography (pentane/Et_2O, 95:5 to 80:20) with α-aryl-β-keto allyl ester **S4** isolated (26 mg, 0.057 mmol).

Eq 2. The reaction was performed using α-aryl-β-keto allyl ester **S4** (0.115 g, 0.250 mmol) as in eq 1 but Meldrum's acid was added (with the substrate as in typical procedure **E**) in place of formic acid. **2a** was isolated (0.033 g, 44%) with an *ee* of (*S*)-32%. 5,5-dicinnamyl-2,2-dimethyl-1,3-dioxane-4,6-dione **5** was isolated (0.027 g, 57%) with spectroscopic analysis in good accordance to literature.[37]

Deuterium-Labeling Studies. Prior to use, 4 Å molecular sieves (270 mg) were heated in the microwave to 280 °C for 5 min (200 W) then immediately transferred to a flame-dried Schlenk flask (25 mL) containing a magnetic stir bar. The flask and molecular sieves were then flame-dried and backfilled with N_2 three times. Once the flask had cooled to ambient temperature under N_2, $Pd(OAc)_2$ (3.4 mg, 0.015 mmol), (*S*)-$(CF_3)_3$-*t*-Bu-PHOX (11.1 mg, 0.01875 mmol), and 1,4-dioxane (2.5 mL) were added. The mixture was stirred at 40 °C for 30 min prior to the addition of formic acid (34 μL, 0.90 mmol) followed immediately by a solution of α-aryl-β-keto allyl ester **S4** (68.8 mg, 0.150 mmol) in 1,4-dioxane (2.5 mL) from a round-bottom flask (25 mL, 2-neck). The reaction mixture was stirred at 40 °C for 18 h, filtered through a plug of Celite and washed with Et_2O. The filtrate was concentrated *in vacuo* and purified by silica gel column chromatography (pentane/Et_2O, 100:0 to 90:10). The *ee* of the product was determined by SFC under the standard conditions. Deuterium incorporation was determined by comparison of the ^1H NMR integration to the previously isolated product **2a** using unlabeled formic acid as the proton source. Spectra were recorded using a 600 MHz spectrometer with a 25 s relaxation delay.

Eq 1. Reaction performed using DCO_2H. **2a** was isolated (23.9 mg, 53%). ^1H NMR integration indicates 1% deuterium incorporation at the α-position (observed at δ 4.31 ppm). *trans*-β-Methylstyrene **4** was also isolated (7.4 mg, 42%). ^1H NMR integration indicates 80–90% deuterium incorporation at the methyl-position (observed at δ 1.90 ppm).

Eq 2. Reaction performed using HCO_2D. **2a** was isolated (36.2 mg, 81%). ^1H NMR integration indicates 49% deuterium incorporation at the α-position (observed at δ 4.28 ppm). *trans*-β-Methylstyrene **4** was also isolated (7.1 mg, 40%). ^1H NMR integration indicates 0% deuterium incorporation at the methyl-position (observed at δ 1.91 ppm).

Eq 3. Reaction performed using 3 Å molecular sieves and HCO_2H. **2a** was isolated (29.5 mg, 66%). ^1H NMR integration indicates 0% deuterium incorporation at the α-position (observed at δ 4.28 ppm).

Eq 4. Reaction performed with the addition of D_2O (13.5 μL, 0.75 mmol) immediately prior to HCO_2H. **2a** was isolated (32.6 mg, 70%). ^1H NMR integration indicates 8% deuterium incorporation at the α-position (observed at δ 4.30–4.25 ppm).

Investigation of an Unidentified Proton Source. Eq 1. Powdered 4 Å molecular sieves (180 mg) were added to a flame-dried Schlenk flask (25 mL). The flask and molecular sieves were flame-dried and backfilled with N_2 three times. Once the flask had cooled to ambient temperature under N_2, $Pd(OAc)_2$ (3.4 mg, 0.010 mmol), (*S*)-$(CF_3)_3$-*t*-Bu-PHOX (11.1 mg, 0.0125 mmol), and 1,4-dioxane (2.5 mL) were added. The mixture was stirred at 40 °C for 30 min. Sodium formate (61.2 mg, 0.900 mmol) and α-aryl-β-keto allyl ester **1a** (57.4 mg, 0.150 mmol) were dried under vacuum for 1 h in a flame-dried round-bottom flask (2-neck 25 mL), dissolved in 1,4-dioxane (2.5 mL) and the solution transferred to the Schlenk flask via a cannula. The reaction mixture was stirred at 40 °C for 18 h, filtered through a plug of Celite and washed with Et_2O. The filtrate was concentrated in vacuo and purified by silica gel column chromatography (pentane/Et_2O, 95:5 to 80:20). **2a** was isolated (13.0 mg, 29%) with an *ee* of (*S*)-6%.

Eq 2. The reaction carried out as described for eq 1, except no molecular sieves were included. **2a** was isolated (13.2 mg, 29%) with an *ee* of (*S*)-16%.

Investigation of a β-Keto Acid Intermediate. The reaction was set up according to typical procedure **F** using α-aryl-β-keto allyl ester **1l** (59.5 mg, 0.150 mmol). At 2.5 h the reaction was analyzed by TLC. With evidence of some product formation, the reaction mixture was cooled to 0 °C, filtered through a plug of Celite and washed with Et_2O (100 mL) into a 2-neck round-bottom flask. The filtrate was cooled to 0 °C and the flask flushed with N_2. Trimethylsilyldiazomethane (1.5 mL, 2.0 M solution in ether, 3.0 mmol) was added dropwise and the reaction mixture warmed to rt and stirred for 2 h. The solution was cooled again to 0 °C and acetic acid (5 mL) added dropwise. The reaction mixture was stirred for 2 h, washed with H_2O (3 × 100 mL) and then ether (100 mL). The organic layers were combined and washed with saturated Na_2CO_3 solution (100 mL), dried over Na_2SO_4, and concentrated *in vacuo*. No evidence of the formation of **6** was observed via TLC and ^1H NMR spectroscopic analysis of the crude reaction mixture.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.7b00303.

Full optimization results (Table S1, Figure S1); ^1H NMR, ^{13}C NMR, and ^{19}F NMR spectra of new compounds; ^1H NMR spectra for deuterium-labeling studies; and the methods for the determination of enantiomeric excess and SFC chromatograms of racemic and enantioenriched compounds (PDF)

X-ray crystallographic information for compound (*S*)-**2a** (CIF)

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Notes

The authors declare no competing financial interest.

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