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Enantioselective Synthesis of Chiral 3-Aryl-1-indanones through Rhodium-Catalyzed Asymmetric Intramolecular 1,4-Addition

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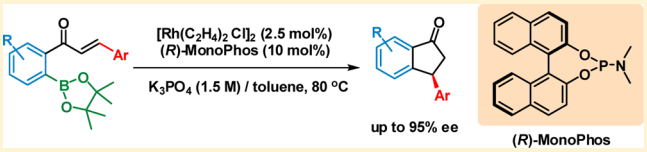
Supporting Information

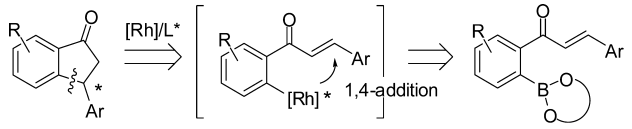
ABSTRACT: Enantioselective synthesis of potentially useful chiral 3-aryl-1-indanones was achieved through a rhodium-catalyzed asymmetric intramolecular 1,4-addition of pinacolborane chalcone derivatives using extraordinary simple MonoPhos as chiral ligand under relatively mild conditions. This novel protocol offers an easy access to a wide variety of enantioenriched 3-aryl-1-indanone derivatives in high yields (up to 95%) with excellent enantioselectivities (up to 95% ee).



Indanone frameworks are commonly found in a wealth of natural products and biologically active compounds.[1] Among them, 1-indanones bearing a stereogenic center at the 3-position are not only particularly important structural components of many pharmaceutical agents but also versatile intermediates in organic synthesis and medicinal chemistry.[2] As a result, methods that enable convenient access to optically active 3-substituted 1-indanones are of great importance. Surprisingly, however, only a limited number of methods for the stereoselective formation of 3-substituted 1-indanones have been developed.[3] Other than Friedel–Crafts cyclization of chiral aryl carboxylic acids[3a] and bakers' yeast reduction of 3-aryl-1-indenones,[3b] the main synthetic protocol for their synthesis relies on transition-metal-catalyzed asymmetric transformations such as rhodium-catalyzed enantioselective addition,[3f,j] rearrangement,[3g] isomerization,[3i] hydroacylation,[3l] and palladium-catalyzed reductive-Heck Reaction.[3m] Although notable successes were achieved by Morehead[3l] and Hayashi,[3f,i] the need to use applicable substrates and nucleophiles led to some limitations. Moreover, there remains a general lack of efficient catalytic asymmetric methods for synthesis of more valuable chiral 3-aryl-1-indanones.[3e,l,m] On the other hand, rhodium-catalyzed asymmetric 1,4-addition of arylboron reagents to α,β-unsaturated carbonyl compounds has been realized as a powerful method for carbon–carbon bond formation.[4,5] In this context, we envisaged that the direct construction of the 1-indanone ring might be expected to be achieved by an intramolecular asymmetric 1,4-addition reaction of chalcones having an ortho-nucleophilic group, wherein the C-3 chirality could be effectively introduced under the rhodium catalysis in the presence of an appropriate chiral ligand (Scheme 1). To our knowledge, utilization of such intramolecular cyclization strategy for synthesis of chiral 1-indanones has not been previously documented. Herein, we reported our successful development of this reaction as a new catalytic enantioselective method for the preparation of chiral 3-aryl-1-indanones.

Our investigations began with constructing proper substrates for the intramolecular 1,4-addition strategy. Considering

Scheme 1. Intramolecular Asymmetric 1,4-Addition Proposal



arylboron reagents' relative insensitivity to air and moisture, low toxicity, as well as their impressive outcomes on metal-catalyzed enantioselective intramolecular ketone hydroarylations,[6] we chose pinacolboron as an ortho-nucleophilic group of chalcone as proposed in Scheme 1. Accordingly, the pinacolborane chalcone derivative **1a** was readily prepared through simple procedures[7] and used as a model substrate for rhodium-catalyzed asymmetric intramolecular 1,4-addition reaction.

Initially, we attempted the cyclization of **1a** with (*R*)-BINAP acting as chiral ligand and using $[Rh(C_2H_4)_2Cl]_2$ (2.5 mol %) as the catalyst in combination with aqueous KOH (1.5 M)/toluene at 100 °C. To our delight, the reaction reached completion within 3 h and furnished the expected 3-phenyl-1-indanone (**2a**) in 80% yield and 54% ee (Table 1, entry 1). Prompted by this result, we undertook an optimization of the reaction conditions. A survey of various solvents suggested that the use of toluene was the best choice (Table 1, entries 1–5). Lowering the reaction temperature to 80 °C gave a very slight improvement of the enantioselectivity, while the yield was not ideal due to the incomplete conversion (Table 1, entry 6). Subsequently, examination of base additives was performed (Table 1, entries 8–12). It was found that considerable yield and enantioselectivity could be gained when aqueous K_3PO_4 (1.5 M) was employed (Table 1, entry 8). Using other bases such as K_2CO_3, Na_2CO_3, and $NaHCO_3$ resulted in slightly better enantioselectivities but with much lower yields (Table 1,

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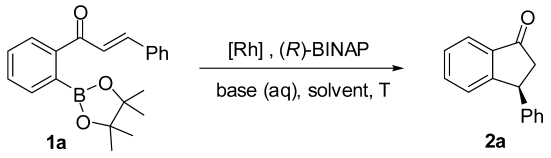
Table 1. Optimization of Reaction Conditions[a]



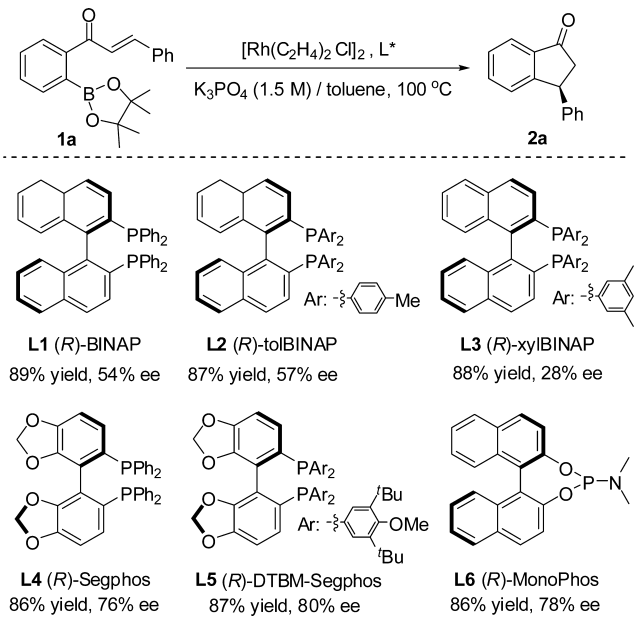
entry	[Rh]	base	temp (°C)	solvent	yield[b] (%)	ee[c] (%)
1	$[Rh(C_2H_4)_2Cl]_2$	KOH	100	toluene	80	54
2	$[Rh(C_2H_4)_2Cl]_2$	KOH	100	dioxane	75	52
3	$[Rh(C_2H_4)_2Cl]_2$	KOH	100	DMF	71	53
4	$[Rh(C_2H_4)_2Cl]_2$	KOH	100	THF	52	48
5	$[Rh(C_2H_4)_2Cl]_2$	KOH	100	*p*-xylene	20	60
6	$[Rh(C_2H_4)_2Cl]_2$	KOH	80	toluene	25	60
7	$[Rh(C_2H_4)_2Cl]_2$	KOH	60	toluene	trace	
8	$[Rh(C_2H_4)_2Cl]_2$	K_3PO_4	100	toluene	89	54
9	$[Rh(C_2H_4)_2Cl]_2$	K_2CO_3	100	toluene	64	56
10	$[Rh(C_2H_4)_2Cl]_2$	Na_2CO_3	100	toluene	61	58
11	$[Rh(C_2H_4)_2Cl]_2$	$NaHCO_3$	100	toluene	24	58
12	$[Rh(C_2H_4)_2Cl]_2$	KF	100	toluene	trace	
13	$[Rh(COE)_2Cl]_2$	K_3PO_4	100	toluene	80	45
14	$[Rh(COD)Cl]_2$	K_3PO_4	100	toluene	64	32
15	$[Rh(COE)_2(acac)]$	K_3PO_4	100	toluene	33	56

[a]The reaction was carried out with 0.2 mmol of **1a** in the presence of 5 mol % of [Rh], 5 mol % of (*R*)-BINAP, and 1.5 M aq base (0.5 equiv) in 2 mL of solvent for 3−5 h, unless otherwise noted. [b]Isolated yield. [c]Determined by chiral HPLC analysis; the absolute configuration was determined to be *S* by comparison with the known data.[3m]

entries 9−11). Ultimately, the use of different rhodium resource was investigated. $[Rh(COE)_2Cl]_2$ and $[Rh(COD)Cl]_2$ showed decreased enantioselectivities (Table 1, entries 13 and 14), whereas $[Rh(COE)_2(acac)]$ afforded **2a** with comparable enantioselectivity in poor yield (Table 1, entry 15). Thus, we decided to use conditions from entry 8 for further ligand screening.

Under the optimal conditions, a range of chiral bisphosphine ligands were evaluated for the intramolecular 1,4-addition reaction, and some representative results are summarized in Scheme 2. Generally, Segphos-type ligands showed better

Scheme 2. Attempts with Chiral Phosphine Ligands



results. Among them, (*R*)-DTBM-Segphos (**L5**) with 3,5-di-*tert*-butyl-4-methoxyphenyl groups on the phosphorus was found to be the most effective ligand, giving the cyclized product **2a** in high yield (87%) with promising enantioselectivity (80% ee). However, further studies revealed that this catalytic system was not applicable to the substrates with bulky substitutents such as 2-naphthyl, 2-methoxylphenyl attached to the double bond of α,β-unsaturated ketone moiety, where very low reaction conversions were observed. As a result of lacking success with bidentate phosphine ligands, we anticipated that BINOL-derived monodonor phosphorus ligands could also be used in the reaction. (*R*)-MonoPhos was first examined under similar conditions. Gratifyingly, the reaction was smoothly catalyzed in the presence of 10 mol % of (*R*)-MonoPhos (**L6**). The enantioselectivity (78%) as high as that obtained with (*R*)-DTBM-Segphos, along with excellent yield (86%), was observed. In comparison with the use of bisphosphine ligands, this result showed the great potential of employing less expensive and more readily available chiral phosphoramidites as ligands for the asymmetric reaction.

To attain higher enantioselectivity of the resulting 3-phenyl-1-indanone **2a**, a variety of chiral (*R*)-BINOL-based phosphoramidite ligands were prepared following the known procedures[8] and tested in the asymmeric cyclization of **1a** (Scheme 3). A survey of different *N*-substituents in place of two methyls identified that bulky groups on the nitrogen atom were not beneficial for the stereoselectivity (**L7**−**10**). Similarly, **L11** and **L12** with cyclic amine units did not induce higher enantioselectivity. To our disappointment, no improvement was observed with the use of 8H-BINOL as the ligand backbone (**L13**). Further ligand architecture modification was carried out by introducing two phenyl substitutents onto the 3- and 3′-positions of the binaphthyl unit, however, with **L14**, the reaction of **1a** failed to produce any of the desired adduct. Fortunately, a subsequent re-evaluation of ligand performance revealed that MonoPhos displayed higher catalytic activity than

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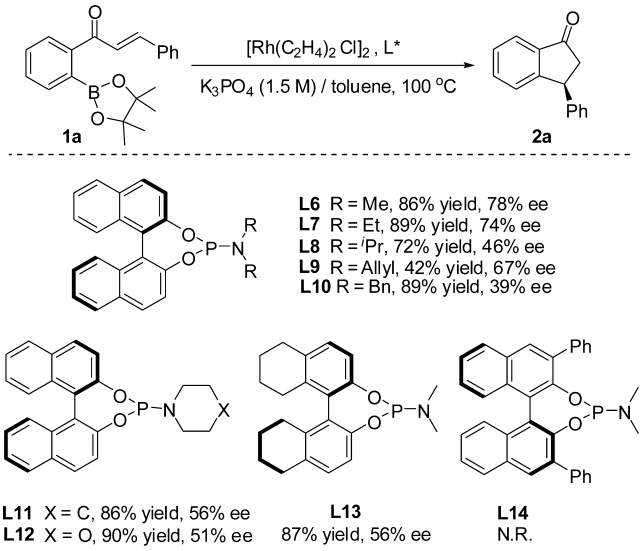
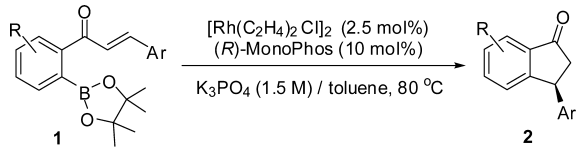
Scheme 3. Ligand Optimization



BINAP, allowing the reaction temperature to be decreased to 80 °C; product **2a** was obtained in 82% yield with improved 82% ee.

Having identified the optimal conditions, we turned our attention to investigate the reaction substrate scope using (*R*)-MonoPhos (**L6**) as chiral ligand. As summarized in Table 2, a variety of pinacolborane chalcone derivatives with diverse steric and electronic properties were examined. In general, all substrates underwent clean reaction to provide the expected optically active 3-aryl-1-indanones **3** in good to excellent yields (82−95%) with high enantioselectivities (81−95% ee) after 3−5 h at 80 °C, regardless of electron-donating or-withdrawing groups substituted on the phenyl rings. It appears that steric effects of the Ar moiety are important for achieving higher stereoselectivity. In most cases, substrates with *para*-substitued Ar provided remarkably higher enatioselectivities compared to those with *orth*- and *meta*-substituted Ar (Table 2, entries 1−12). Substrate **1o**, which bears a methoxy group adjacent to the carbonyl, gave a somewhat lower enantioselectivity (81% ee), albeit with good reactivity (90%, Table 2, entry 15). Notably, these results are generally superior to those previously reported by Buchwald through palladium-catalyzed asymmetric reductive-Heck cyclization of 2′-perfluoroalkylsulfonated aryl *α,β*-unsaturated ketones using (*R*)-3,5-XylMeOBIPHEP as ligand.[3m]

Table 2. $[Rh(C_2H_4)_2Cl]_2$/L6-Catalyzed Asymmeric Intramolecular 1,4-Addition[a]



entry	R	Ar	2	yield[b] (%)	ee[c] (%)
1	H (**1a**)	Ph	**2a**	82	82
2	H (**1b**)	4-FC_6H_4	**2b**	93	88
3	H (**1c**)	4-ClC_6H_4	**2c**	95	94
4	H (**1d**)	3,4-$Cl_2C_6H_3$	**2d**	88	91
5	H (**1e**)	4-$CF_3C_6H_4$	**2e**	80	95
6	H (**1f**)	4-MeC_6H_4	**2f**	90	91
7	H (**1g**)	4-$^tBuC_6H_4$	**2g**	86	89
8	H (**1h**)	4-PhC_6H_4	**2h**	92	95
9	H (**1i**)	2-Naphthyl	**2i**	95	94
10	H (**1j**)	2-$MeOC_6H_4$	**2j**	80	84
11	H (**1k**)	3-$MeOC_6H_4$	**2k**	89	82
12	H (**1l**)	4-$MeOC_6H_4$	**2l**	92	95
13	4-F (**1m**)	4-ClC_6H_4	**2m**	90	94
14	5-F (**1n**)	4-ClC_6H_4	**2n**	92	93
15	5-MeO (**1o**)	4-ClC_6H_4	**2o**	90	81

[a]The reaction was carried out with 0.2 mmol of **1** in the presence of 2.5 mol % of $[Rh(C_2H_4)_2Cl]_2$, (*R*)-MonoPhos (10 mol %), and 1.5 M aq K_3PO_4 (0.5 equiv) in 2 mL of toluene for 3−5 h. [b]Isolated yield. [c]Determined by chiral HPLC analysis.

In summary, we have developed an enantioselective approach for the synthesis of potentially useful chiral 3-aryl-1-indanones through a rhodium-catalyzed asymmetric intramolecular 1,4-addition process. By simple treatment of the corresponding pinacolborane chalcone derivatives with a rhodium/MonoPhos complex under relatively mild conditions, enantioenriched 3-aryl-1-indanone products can be easily prepared in high yields. In contrast to previously reported methods, the asymmetric intramolecular 1,4-addition approach presented herein is general and efficient with respect to substrate scope and reaction stereocontrol. Moreover, the use of extraordinary simple MonoPhos ligand offers notable synthetic and economic advantages over expensive and complex bisphosphine ligands.

EXPERIMENTAL SECTION

General Information. All reactions, unless otherwise stated, were run under an atmosphere of argon or nitrogen. NMR spectra were recorded at ambient temperature on a standard spectrometer operating at 300, 400, and 500 MHz. Chemical shifts are reported in δ ppm referenced to an internal $SiMe_4$ standard for ^1H NMR and chloroform-*d* (δ 77.16) for ^{13}C NMR. The mass analyzer of the HRMS was Q-TOF for ESI and MAT-95 for EI. IR spectra were recorded on a FTIR instrument. Melting points were measured by a melting point apparatus (uncorrected). Optical rotations were measured at 25 °C.

Typical Procedure for Synthesis of Pinacolborane Chalcone Derivatives 1. (1) A solution of 2-bromoacetophenone (1.5 mL, 11.1 mmol) in carbinol (100 mL) was added a solution of NaOH (0.53 g, 13.3 mmol) in H_2O (0.5 mL). After the solution was stirred at room temperature for 0.5 min, benzaldehyde (1.2 mL, 11.1 mmol) was poured into the mixture. The reaction was stirred for 1 h and quenched with HCl (1 M, 14 mL). After solvent removal, the residue was diluted with ethyl acetate and then washed with brine. The organic layer was dried over anhydrous Na_2SO_4 and then concentrated under reduced pressure. The residue was purified by silica gel column chromatography to afford (*E*)-2-Br-chalcone. (2.65 g, 83%). (2) A solution of (*E*)-2-bromochalcone (2.65 g, 9.2 mmol), ethylene glycol (2.6 mL, 46 mmol), and $TsOH·H_2O$ (87.4 mg, 0.46 mmol) was stirred in toluene (60 mL) under reflux for 2 days on a Dean−Stark trap to remove water. The reaction mixture was cooled to room temperature, quenched with water, and extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and then concentrated under reduced pressure. The residue was purified by silica gel column chromatography to afford the corresponding addition product (2.5 g, 80%). (3) *n*-Butyllithium (3.3 mL, 2.5 M solution in hexanes) was added dropwise at −78 °C to a solution of the previous step's product (2.5 g, 7.4 mmol) in THF (50 mL). After the solution was stirred for 0.5 h, isopropenylboronic acid pinacol ester (3.0 mL, 14.8 mmol) was added to the mixture. The reaction mixture was allowed to warm to room temperature and stirred overnight. The reaction was quenched with water and extracted with diethyl ether. The organic layer was dried over anhydrous Na_2SO_4 and then concentrated under reduced pressure. The residue was purified by silica gel column chromatography to afford the corresponding product (2.3 g, 83%). (4) A solution

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of the last step's product and TsOH·H_2O (58.0 mg, 0.31 mmol) in acetone was refluxed overnight. After solvent removal, the residue was purified by recrystallization from EtOAc to give **1a**: yellow solid (1.4 g, 67%); mp 168−170 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 (d, J = 7.6 Hz, 1H), 7.76 (d, J = 15.8 Hz, 1H), 7.68−7.59 (m, 3H), 7.59−7.51 (m, 1H), 7.51−7.37 (m, 5H), 1.42 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.3, 145.6, 142.0, 134.8, 132.9, 131.8, 130.6, 129.0, 128.9, 128.5, 127.5, 121.9, 83.7, 24.9; HRMS (ESI) for $C_{21}H_{23}BO_3Na$ [M + Na]$^+$ calcd 357.1638, found 357.1651.

(*E*)-3-(4-Fluorophenyl)-1-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)prop-2-en-1-one (1b): yellow solid (2.0 g, overall 48%); mp 172−174 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 (d, J = 7.5 Hz, 1H), 7.72 (d, J = 15.8 Hz, 1H), 7.66−7.59 (m, 3H), 7.59−7.51 (m, 1H), 7.51−7.44 (m, 1H), 7.39 (d, J = 15.8 Hz, 1H), 7.16−7.05 (m, 2H), 1.42 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.0, 164.0 (d, $^1J_{CF}$ = 253 Hz), 144.2, 141.9, 132.9, 131.9, 131.1 (d, $^3J_{CF}$ = 3.1 Hz), 130.4 (d, $^3J_{CF}$ = 8.5 Hz), 129.0, 127.5, 121.7, 116.1 (d, $^2J_{CF}$ = 21.2 Hz), 83.7, 24.8; HRMS (ESI) for $C_{21}H_{22}BO_3NaF$ [M + Na]$^+$ calcd 375.1544, found 375.1537.

(*E*)-3-(4-Cchlorophenyl)-1-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)prop-2-en-1-one (1c): yellow solid (2.3 g, overall 53%); mp 182−184 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 (d, J = 7.3 Hz, 1H), 7.68 (d, J = 15.8 Hz, 1H), 7.63 (dd, J = 7.2, 1.4 Hz, 1H), 7.59−7.52 (m, 3H), 7.49 (dd, J = 7.5, 1.5 Hz, 1H), 7.45 (s, 1H), 7.41−7.36 (m, 2H), 1.41 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.0, 144.0, 141.9, 136.4, 133.3, 133.0, 131.9, 129.6, 129.1, 127.6, 122.5, 83.7, 24.8; HRMS (ESI) for $C_{21}H_{22}BO_3NaCl$ [M + Na]$^+$ calcd 391.1248, found 391.1268.

(*E*)-3-(3,4-Dichlorophenyl)-1-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)prop-2-en-1-one (1d): yellow solid (2.1 g, overall 45%); mp 196−198 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 7.6 Hz, 1H), 7.69 (d, J = 2.0 Hz, 1H), 7.64−7.58 (m, 2H), 7.55−7.52 (m, 1H), 7.51−7.47 (m, 1H), 7.47−7.45 (m, 1H), 7.45−7.39 (m, 2H), 1.41 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.6, 142.4, 141.7, 134.8, 134.3, 133.2, 133.0, 132.0, 130.9, 129.8, 129.1, 127.6, 127.4, 123.6, 83.8, 24.8; HRMS (ESI) for $C_{21}H_{21}BO_3NaCl_2$ [M + Na]$^+$ calcd 425.0859, found 425.0842.

(*E*)-1-(2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-phenyl)-3-(4-(trifluoromethyl)phenyl)prop-2-en-1-one (1e): yellow solid (1.4 g, overall 30%); mp 172 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 (d, J = 7.5 Hz, 1H), 7.74 (d, J = 7.5 Hz, 1H), 7.70−7.60 (m, 5H), 7.60−7.50 (m, 2H), 7.50−7.40 (m, 1H), 1.42 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.0, 143.2, 141.8, 138.2, 133.2, 132.0, 131.8 (q, $^2J_{CF}$ = 2.8 Hz), 129.2, 128.5, 127.7, 125.9 (q, $^3J_{CF}$ =3.3 Hz), 123.8 (q, $^1J_{CF}$ = 273.7 Hz), 83.9, 24.8; HRMS (ESI) for $C_{22}H_{22}BO_3NaF_3$ [M + Na]$^+$ calcd 425.1512, found 425.1517.

(*E*)-1-(2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-phenyl)-3-*p*-tolylprop-2-en-1-one (1f): yellow solid (1.6 g, overall 39%); mp 192−194 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 (d, J = 7.7 Hz, 1H), 7.75 (d, J = 15.7 Hz, 1H), 7.62 (d, J = 7.1 Hz, 1H), 7.58−7.38 (m, 5H), 7.21 (d, J = 7.9 Hz, 2H), 2.38 (s, 3H), 1.41 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.3, 145.9, 142.1, 141.2, 132.8, 132.1, 131.8, 129.7, 128.9, 128.5, 127.4, 120.8, 83.6, 24.9, 21.5; HRMS (ESI) for $C_{22}H_{25}BO_3Na$ [M + Na]$^+$ calcd 371.1794, found 371.1783.

(*E*)-3-(4-*tert*-Butylphenyl)-1-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)prop-2-en-1-one (1g): yellow solid (2.3g, overall 51%); mp 132−134 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 7.6 Hz, 1H), 7.78 (d, J = 15.8 Hz, 1H), 7.63 (dd, J = 7.2, 0.8 Hz, 1H), 7.60−7.52 (m, 3H), 7.50−7.41 (m, 4H), 1.43 (s, 12H), 1.34 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.2, 154.3, 145.8, 142.0, 132.8, 132.1, 131.9, 128.9, 128.4, 127.4, 125.9, 120.8, 83.6, 34.9, 31.1, 24.9; HRMS (ESI) for $C_{25}H_{31}BO_3Na$ [M + Na]$^+$ calcd 413.2264, found 413.2264.

(*E*)-3-(Biphenyl-4-yl)-1-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)prop-2-en-1-one (1h): yellow solid (2.1 g, overall 47%); mp 198−200 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 (d, J = 7.6 Hz, 1H), 7.82 (d, J = 15.8 Hz, 1H), 7.74−7.61 (m, 7H), 7.60−7.43 (m, 5H), 7.43−7.33 (m, 1H), 1.44 (d, J = 2.9 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.1, 145.2, 143.3, 142.0, 140.0, 133.7, 132.9, 131.9, 129.0, 128.9, 127.9, 127.5, 127.0, 121.6, 83.6, 24.9; HRMS (ESI) for $C_{27}H_{28}BO_3$ [M + H]$^+$ calcd 411.2132, found 411.2133.

(*E*)-3-(Naphthalen-2-yl)-1-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)prop-2-en-1-one (1i): yellow solid (1.9 g, overall 45%); mp 228−230 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.97−7.76 (m, 6H), 7.70−7.46 (m, 6H), 1.43 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.3, 145.8, 142.1, 134.4, 133.3, 133.0, 132.3, 131.9, 130.8, 129.1, 128.7, 128.6, 127.8, 127.6, 127.4, 126.7, 123.6, 122.1, 83.7, 24.9; HRMS (ESI) for $C_{25}H_{25}BO_3Na$ [M + Na]$^+$ calcd 407.1794, found 407.1782.

(*E*)-3-(2-Methoxyphenyl)-1-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)prop-2-en-1-one (1j): yellow solid (1.3 g, overall 31%); mp 190−192 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08 (d, J = 15.9 Hz, 1H), 7.87 (d, J = 7.4 Hz, 1H), 7.67−7.51 (m, 4H), 7.50−7.42 (m, 1H), 7.42−7.33 (m, 1H), 7.03−6.91 (m, 2H), 3.91 (s, 3H), 1.43 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.6, 158.8, 142.1, 141.6, 132.7, 131.9, 131.8, 129.5, 128.8, 127.5, 123.8, 122.2, 120.7, 111.2, 83.5, 55.5, 24.9; HRMS (ESI) for $C_{22}H_{25}BO_4Na$ [M + Na]$^+$ calcd 387.1744, found 387.1733.

(*E*)-3-(3-Methoxyphenyl)-1-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)prop-2-en-1-one (1k): yellow solid (1.8 g, overall 30%); mp 158−160 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 (d, J = 7.5 Hz, 1H), 7.71 (d, J = 15.8 Hz, 1H), 7.63 (d, J = 7.0 Hz, 1H), 7.59−7.40 (m, 3H), 7.36−7.27 (m, 1H), 7.24−7.18 (m, 1H), 7.13 (s, 1H), 6.95 (d, J = 7.8 Hz, 1H), 3.84 (s, 3H), 1.42 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.3, 159.9, 145.5, 142.1, 136.1, 133.0, 131.8, 129.9, 129.0, 127.6, 122.4, 121.1, 116.4, 113.3, 83.7, 55.3, 24.9; HRMS (ESI) for $C_{22}H_{25}BO_4Na$ [M + Na]$^+$ calcd 387.1744, found 387.1737.

(*E*)-3-(4-Methoxyphenyl)-1-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)prop-2-en-1-one (1l): yellow solid (1.7 g, overall 28%); mp 204−206 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 7.7 Hz, 1H), 7.77 (d, J = 15.7 Hz, 1H), 7.66−7.57 (m, 3H), 7.56−7.51 (m, 1H), 7.47−7.43 (m, 1H), 7.38 (d, J = 15.7 Hz, 1H), 6.97−6.89 (m, 2H), 3.85 (s, 3H), 1.42 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.2, 161.8, 145.9, 142.1, 132.7, 131.9, 130.4, 128.9, 127.5, 127.3, 119.1, 114.4, 83.5; HRMS (ESI) for $C_{22}H_{25}BO_4Na$ [M + Na]$^+$ calcd 387.1744, found 387.1740.

(*E*)-3-(4-Chlorophenyl)-1-(4-fluoro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)prop-2-en-1-one (1m): yellow solid (2.1 g, overall 48%); mp 214−216 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, J = 8.6, 5.0 Hz, 1H), 7.75 (d, J = 15.7 Hz, 1H), 7.56 (d, J = 8.6 Hz, 2H), 7.45 (s, 1H), 7.42−7.36 (m, 2H), 7.26 (dd, J = 8.4, 2.6 Hz, 1H), 7.12 (td, J = 8.4, 2.6 Hz, 1H), 1.43 (s, 12H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.03, 165.44 (d, $^1J_{CF}$ = 258 Hz), 144.6, 137.6, 136.7, 133.1, 130.0 (d, $^3J_{CF}$ = 9.1 Hz), 129.7, 129.2, 121.0, 119.9 (d, $^2J_{CF}$ =21.2 Hz), 115.7 (d, $^2J_{CF}$ = 22.2 Hz), 83.8, 24.9; HRMS (ESI) for $C_{21}H_{22}BO_3FCl$ [M + H]$^+$ calcd 387.1335, found 387.1349.

(*E*)-3-(4-Chlorophenyl)-1-(5-fluoro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)prop-2-en-1-one (1n): yellow solid (2.2 g, overall 52%); mp 204−206 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66−7.56 (m, 2H), 7.53 (d, J = 8.4 Hz, 2H), 7.45 (dd, J = 9.3, 2.4 Hz, 1H), 7.41−7.36 (m, 2H), 7.32−7.19 (m, 2H), 1.37 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.7, 163.4 (d, $^1J_{CF}$ = 253 Hz), 145.0 (d, $^3J_{CF}$ = 6.1 Hz), 144.5, 136.7, 135.4, 135.3, 133.1, 129.6, 129.3, 123.3, 118.4 (d, $^2J_{CF}$ = 20.3 Hz), 114.7 (d, $^2J_{CF}$ = 21.4 Hz), 84.0, 24.8; HRMS (EI) for $C_{21}H_{21}BO_3FCl$ [M]$^+$ calcd 386.1256, found 386.1240.

(*E*)-3-(4-Chlorophenyl)-1-(5-methoxy-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)prop-2-en-1-one (1o): yellow solid (2.1 g, overall 47%); mp 182−184 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 (d, J = 8.2 Hz, 1H), 7.53−7.43 (m, 3H), 7.37 (d, J = 8.4 Hz, 2H), 7.25−7.17 (m, 2H), 7.05 (dd, J = 8.2, 2.4 Hz, 1H), 3.86 (s, 3H), 1.32 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.2, 160.8, 145.3, 143.6, 136.3, 135.3, 133.3, 129.5, 129.2, 125.1, 116.0, 113.5, 83.7, 55.4, 24.8; HRMS (ESI) for $C_{22}H_{25}BO_4Cl$ [M + H]$^+$ calcd 399.1534, found 399.1510.

General Procedures for Rh-Catalyzed Intramolecular 1,4-Addition. Under N_2, a solution of **1** (0.2 mmol), $[RhCl(C_2H_4)_2]_2$ (1.9 mg, 0.01 mmol of Rh), and **L6** (7.3 mg, 0.02 mmol) in toluene (2 mL) was stirred at 80 °C for 30 min. To this mixture was added

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aqueous K_3PO_4 (67 μL, 1.5 M). After being stirred at 40 °C for 3−5 h, the mixture was concentrated under reduced pressure. The residue was purified by silica gel column chromatography to afford the corresponding addition product **2**.

(3*S*)-Phenylindan-1-one (2a):[3m] white solid (34.2 mg, 82%); mp 82−84 °C; $[\alpha]_D$ = +49.7 (c 0.5, $CHCl_3$), 82% ee, determined by HPLC analysis: chiral OD-H column (hexane/2-propanol = 97/3, 0.6 mL/min, 214 nm), *t*(major) = 18.2 min, *t*(minor) = 22.1 min; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.7 Hz, 1H), 7.55 (td, *J* = 4.7, 2.3 Hz, 1H), 7.46−7.37 (m, 1H), 7.36−7.22 (m, 4H), 7.16−7.08 (m, 2H), 4.57 (dd, *J* = 8.0, 3.9 Hz, 1H), 3.21 (dd, *J* = 19.2, 8.0 Hz, 1H), 2.69 (dd, *J* = 19.2, 3.9 Hz, 1H).

(3*S*)-(4-Fluorophenyl)indan-1-one (2b): white solid (42 mg, 93%); mp 138−140 °C; $[\alpha]_D$ = +34.6 (c 0.5, $CHCl_3$); 88% ee, determined by HPLC analysis: chiral OD-H column (hexane/2-propanol = 97/3, 0.6 mL/min, 214 nm), *t*(major) = 18.0 min, *t*(minor) = 21.0 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.7 Hz, 1H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.26 (d, *J* = 7.9 Hz, 1H), 7.12−7.05 (m, 2H), 7.03−6.96 (m, 2H), 4.58 (dd, *J* = 8.0, 3.8 Hz, 1H), 3.23 (dd, *J* = 19.2, 8.1 Hz, 1H), 2.64 (dd, *J* = 19.2, 3.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.7, 161.7 (d, $^1J_{CF}$ = 246 Hz), 157.6, 139.4 (d, *J* = 3.2 Hz), 136.7, 129.1, 129.0, 128.0, 126.7, 123.4, 115.7 (d, $^2J_{CF}$ = 21 Hz), 46.9, 43.6; IR (KBr) ν 3062, 2925, 1703, 1601, 1508, 1462, 768 cm^{-1}; HRMS (EI) for $C_{15}H_{11}OF$ $[M]^+$ calcd 226.0794, found 226.0799;

(3*S*)-(4-Chlorophenyl)indan-1-one (2c):[3m] white solid (46.1 mg, 95%); mp 58 °C; $[\alpha]_D$ = +55.2 (c 0.5, $CHCl_3$); 94% ee, determined by HPLC analysis: chiral OD-H column (hexane/2-propanol = 97/3, 0.6 mL/min, 214 nm), *t*(major) = 19.6 min, *t*(minor) = 22.4 min; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 7.7, 0.6 Hz, 1H), 7.63−7.54 (m, 1H), 7.50−7.39 (m, 1H), 7.33−7.20 (m, 3H), 7.15−7.00 (m, 2H), 4.56 (dd, *J* = 8.0, 3.8 Hz, 1H), 3.23 (dd, *J* = 19.2, 8.1 Hz, 1H), 2.63 (dd, *J* = 19.2, 3.9 Hz, 1H).

(3*S*)-(3,4-Dichlorophenyl)indan-1-one (2d):[9] white solid (48.8 mg, 88%); mp 96−98 °C; $[\alpha]_D$ = +58.0 (c 0.5, $CHCl_3$); 91% ee, determined by HPLC analysis: chiral OD-H column (hexane/2-propanol = 97/3, 0.7 mL/min, 220 nm), *t*(major) = 21.1 min, *t*(minor) = 24.4 min; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.6 Hz, 1H), 7.61 (t, *J* = 6 Hz, 1H), 7.46 (t, *J* = 6 Hz, 1H), 7.41−7.33 (m, 1H), 7.30−7.20 (m, 2H), 6.96 (dd, *J* = 8.3, 2.1 Hz, 1H), 4.55 (dd, *J* = 8.0, 3.7 Hz, 1H), 3.23 (dd, *J* = 19.2, 8.0 Hz, 1H), 2.62 (dd, *J* = 19.2, 3.7 Hz, 1H).

(3*S*)-(4-Trifluoromethylphenyl)indan-1-one (2e): colorless oil (44.2 mg, 80%): $[\alpha]_D$ = +44.9 (*c* = 0.5, $CHCl_3$); 95% ee, determined by HPLC analysis: chiral OD-H column (hexane/2-propanol = 97/3, 0.6 mL/min, 214 nm), *t*(major) = 18.5 min, *t*(minor) = 22.3 min; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.6 Hz, 1H), 7.67−7.53 (m, 3H), 7.46 (t, *J* = 7.3 Hz, 1H), 7.30−7.20 (m, 3H), 4.65 (dd, *J* = 8.2, 4.5 Hz, 1H), 3.27 (dd, *J* = 19.2, 8.2 Hz, 1H), 2.67 (dd, *J* = 19.2 Hz, 4.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.2, 156.9, 147.7, 136.8, 135.3, 129.4 (q, $^2J_{CF}$ = 32.3 Hz), 128.3, 128.0, 126.7, 125.9 (q, $^3J_{CF}$ = 4.0 Hz), 124.0 (q, $^1J_{CF}$ =272.7 Hz), 46.5, 44.2; IR (KBr) ν 3300, 2924, 1716, 1620, 1602, 1464, 1327, 762 cm^{-1}; HRMS (EI) for $C_{16}H_{11}OF_3$ $[M]^+$ calcd 276.0762, found 276.0771.

(3*S*)-(4-Methylphenyl)indan-1-one (2f): colorless oil (40.0 mg, 90%): $[\alpha]_D$ = +62.5 (c 0.5, $CHCl_3$); 91% ee, determined by HPLC analysis: chiral OD-3 column (hexane/2-propanol =99/1, 0.6 mL/min, 214 nm), *t*(major) = 23.6 min, *t*(minor) = 25.1 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.7 Hz, 1H), 7.55 (td, *J* = 7.5, 1.2 Hz, 1H), 7.45−7.36 (m, 1H), 7.29−7.23 (m, 1H), 7.12 (d, *J* = 7.8 Hz, 2H), 7.01 (d, *J* = 8.1 Hz, 2H), 4.54 (dd, *J* = 8.0, 3.8 Hz, 1H), 3.21 (dd, *J* = 19.2, 8.0 Hz, 1H), 2.67 (dd, *J* = 19.2, 3.9 Hz, 1H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.2, 158.1, 140.6, 136.6, 136.5, 135.0, 129.5, 127.7, 127.4, 126.8, 123.3, 46.7, 44.0, 21.0; IR (KBr) ν 3022, 2967, 2922, 2853, 1712, 1600, 1514, 1462, 760 cm^{-1}; HRMS (EI) for $C_{16}H_{14}O$ $[M]^+$ calcd 222.1045, found 222.1045.

(3*S*)-(4-*tert*-Butylphenyl)indan-1-one (2g): white solid (45.4 mg, 86%); mp 106−108 °C; $[\alpha]_D$ = +54.2 (*c* 0.5, $CHCl_3$); 89% ee, determined by HPLC analysis: chiral OD-H column (hexane/2-propanol =97/3, 0.6 mL/min, 214 nm), *t*(major) = 11.7 min, *t*(minor) = 14.8 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.7 Hz, 1H), 7.56 (td, *J* = 7.6, 1.2 Hz, 1H), 7.40 (dd, *J* = 10.8, 4.1 Hz, 1H), 7.36−7.24 (m, 3H), 7.10−7.00 (m, 2H), 4.55 (dd, *J* = 8.0, 3.8 Hz, 1H), 3.21 (dd, *J* = 19.2, 8.0 Hz, 1H), 2.69 (dd, *J* = 19.2, 3.9 Hz, 1H), 1.30 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.2, 158.1, 149.8, 140.5, 136.7, 135.0, 127.7, 127.2, 126.9, 125.7, 123.3, 46.8, 43.9, 34.4, 31.3; IR (KBr) ν 3042, 2962, 2926, 2854, 1703, 1603, 1514, 1464, 1389, 759 cm^{-1}; HRMS (EI) for $C_{19}H_{20}O$ $[M]^+$ calcd 264.1514, found 264.1514.

(3*S*)-(4-Phenylphenyl)indan-1-one (2h): white solid (52.3 mg, 92%); mp 160 °C; $[\alpha]_D$ = +76.9 (*c* 0.5, $CHCl_3$); 95% ee, determined by HPLC analysis: chiral AD-H column (hexane/2-propanol =97/3, 0.7 mL/min, 214 nm), *t*(minor) = 19.9 min, *t*(major) = 21.9 min; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.6 Hz, 1H), 7.62−7.49 (m, 5H), 7.47−7.37 (m, 3H), 7.37−7.27 (m, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 4.62 (dd, *J* = 7.9, 3.6 Hz, 1H), 3.26 (dd, *J* = 19.2, 8.0 Hz, 1H), 2.73 (dd, *J* = 19.2, 3.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.0, 157.9, 143.6, 136.7, 135.0, 128.8, 127.8, 127.6, 126.9, 126.8, 123.3, 46.8, 44.4; IR (KBr) ν 3020, 2991, 2896,1705, 1635, 1608, 1521, 1464, 752 cm^{-1}; HRMS (EI) for $C_{21}H_{16}O$ $[M]^+$ calcd 284.1201, found 284.1193.

(3*S*)-(2-Naphthyl)indan-1-one (2i): white solid (49.0 mg, 95%); mp 152−154 °C; $[\alpha]_D$ = +143.2 (*c* 0.5, $CHCl_3$); 94% ee, determined by HPLC analysis: chiral AD-3 column (hexane/2-propanol =97/3, 0.6 mL/min, 254 nm), *t*(minor) = 23.1 min, *t*(major) = 24.4 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93−7.74 (m, 4H), 7.67 (d, *J* = 1.3 Hz, 1H), 7.56 (td, *J* = 7.7, 1.2 Hz, 1H), 7.51−7.39 (m, 3H), 7.28 (dd, *J* = 7.7, 0.8 Hz, 1H), 7.13 (dd, *J* = 8.5, 1.7 Hz, 1H), 4.73 (dd, *J* = 8.1, 3.9 Hz, 1H), 3.29 (dd, *J* = 19.3, 8.1 Hz, 1H), 2.78 (dd, *J* = 19.3, 3.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.0, 157.8, 140.8, 136.8, 135.1, 133.4, 132.4, 128.9, 127.9, 127.7, 127.6, 126.9, 126.4, 125.8, 125.4, 123.4, 46.7, 44.6; IR (KBr) ν 3053, 2922, 2854, 1703, 1662, 1602, 1508, 750 cm^{-1}; HRMS (EI) for $C_{19}H_{14}O$ $[M]^+$ calcd 258.1045, found 258.1045.

(3*S*)-(2-Methoxy)indan-1-one (2j): colorless oil (30.1 mg, 80%); $[\alpha]_D$ = +23.0 (*c* 0.5, $CHCl_3$); 84% ee, determined by HPLC analysis: chiral OJ-H column (hexane/2-propanol = 97/3, 0.6 mL/min, λ = 220 nm), *t*(major) = 32.4 min, *t*(minor) = 40.8 min; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.6 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.30 (d, *J* = 7.7 Hz, 1H), 7.26−7.17 (m, 1H), 6.95 (d, *J* = 7.3 Hz, 1H), 6.91−6.81 (m, 2H), 4.89 (dd, *J* = 8.1, 3.5 Hz, 1H), 3.74 (s, 3H), 3.17 (dd, *J* = 19.2, 8.1 Hz, 1H), 2.69 (dd, *J* = 19.2, 3.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.6, 128.3, 128.1, 127.4, 126.6, 123.2, 120.7, 110.8, 55.3, 45.1; IR (KBr) ν 3050, 2987, 2923, 2846, 1712, 1601, 1493, 1462, 756 cm^{-1}; HRMS (EI) for $C_{16}H_{14}O_2$ $[M]^+$ calcd 238.0994, found 238.1003.

(3*S*)-(3-Methoxy)indan-1-one (2k): colorless oil (33.5 mg, 89%): $[\alpha]_D$ = +52.5 (*c* 0.5, $CHCl_3$); 82% ee, determined by HPLC analysis: chiral OD-H column (hexane/2-propanol =97/3, 0.6 mL/min, 214 nm), *t*(major) = 12.5 min, *t*(minor) = 19.9 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.7 Hz, 1H), 7.57 (td, *J* = 7.6, 1.2 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.30 (dd, *J* = 7.7, 0.8 Hz, 1H), 7.26−7.20 (m, 1H), 6.79 (dd, *J* = 8.3, 2.5 Hz, 1H), 6.72 (d, *J* = 7.6 Hz, 1H), 6.67−6.63 (m, 1H), 4.55 (dd, *J* = 8.0, 3.8 Hz, 1H), 3.76 (s, 3H), 3.22 (dd, *J* = 19.2, 8.0 Hz, 1H), 2.70 (dd, *J* = 19.2, 3.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.0, 160.0, 157.7, 145.3, 136.7, 135.1, 129.9, 127.9, 126.9, 123.4, 120.0, 113.6, 111.9, 55.2, 46.7, 44.4; IR (KBr) ν 3381, 2954, 2924, 2852, 1714, 1600, 1585, 1464, 762 cm^{-1}; HRMS (EI) for $C_{16}H_{14}O_2$ $[M]^+$ calcd 238.0994, found 238.0994.

(3*S*)-(4-Methoxy)indan-1-one (2l):[3m] white solid (34.6 mg, 92%); mp 108 °C; $[\alpha]_D$ = +69.0 (*c* 0.5, $CHCl_3$); 95% ee, determined by HPLC analysis: chiral OJ-H column (hexane/2-propanol = 95/5, 1.0 mL/min, 220 nm), *t*(minor) = 22.7 min, *t*(major) = 33.1 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.7 Hz, 1H), 7.57 (td, *J* = 7.6, 1.2 Hz, 1H), 7.46−7.36 (m, 1H), 7.31−7.24 (m, 1H), 7.14−7.00 (m, 2H), 6.92−6.79 (m, 2H), 4.53 (dd, *J* = 8.0, 3.9 Hz, 1H), 3.79 (s, 3H), 3.22 (dd, *J* = 19.2, 8.0 Hz, 1H), 2.65 (dd, *J* = 19.2, 3.9 Hz, 1H).

(3*S*)-(4-Chlorophenyl)-5-fluoroindan-1-one (2m): white solid (46.8 mg, 90%); mp 118 °C; $[\alpha]_D$ = +61.6 (c 0.5, $CHCl_3$); 94% ee, determined by HPLC analysis: chiral AD-3 column (hexane/2-propanol = 97/3, 0.7 mL/min, λ = 220 nm), *t*(minor) = 15.8 min,

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t(major) = 17.8 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 8.4, 5.3 Hz, 1H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.13 (td, *J* = 8.6, 2.0 Hz, 1H), 7.06 (d, *J* = 8.4 Hz, 2H), 6.89 (dd, *J* = 8.4, 1.3 Hz, 1H), 4.53 (dd, *J* = 8.1, 3.9 Hz, 1H), 3.25 (dd, *J* = 19.2, 8.1 Hz, 1H), 2.66 (dd, *J* = 19.2, 3.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.4, 167.3 (d, $^1J_{CF}$ = 259 Hz), 160.2 (d, $^3J_{CF}$ = 9.5 Hz), 141.3, 133.1, 129.2, 128.9, 125.9 (d,$^3J_{CF}$ = 10.4 Hz), 116.5 (d, $^2J_{CF}$ = 24.2 Hz), 113.3 (d, $^2J_{CF}$ = 22.5 Hz), 46.8, 43.6; IR (KBr) ν 3310, 2920, 2856, 1714, 1614, 1591, 1493, 835 cm^{-1}; HRMS (EI) for $C_{15}H_{10}OFCl$ [M]$^+$ calcd 260.0404, found 260.0400.

(3*S*)-(4-Chlorophenyl)-7-fluoroindan-1-one (2n): white solid (47.8 mg, 92%); mp 55 °C; $[\alpha]_D$ = +53.0 (*c* 0.5, $CHCl_3$); 93% ee, determined by HPLC analysis: chiral OD-H column (hexane/2-propanol = 97/3, 0.6 mL/min, 214 nm), *t*(major) = 22.6 min, *t*(minor) = 27.1 min; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 (dd, *J* = 7.4, 2.5 Hz, 1H), 7.35−7.15 (m, 4H), 7.05 (d, *J* = 8.2 Hz, 2H), 4.54 (dd, *J* = 8, 3.8 Hz, 1H), 3.28 (dd, *J* = 19.3, 8.0 Hz, 1H), 2.67 (dd, *J* = 19.3, 3.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.3, 162.6 (d, $^1J_{CF}$ = 250 Hz), 152.8, 141.8, 138.5 (d, $^3J_{CF}$ = 7.3 Hz), 133.0, 129.1, 128.9, 128.3 (d, $^3J_{CF}$ = 8.1 Hz), 122.9 (d, $^2J_{CF}$ = 24.3 Hz), 109.4, 109.3 (d, $^2J_{CF}$ = 22.0 Hz), 47.4, 43.3; IR (KBr) ν 3073, 2924, 2852, 1705, 1614, 1485, 1440, 852 cm^{-1}; HRMS (EI) for $C_{15}H_{10}OFCl$ [M]$^+$ calcd 260.0404, found 260.0406.

(3*S*)-(4-Chlorophenyl)-7-methoxyindan-1-one (2o): white solid (42.7 mg, 90%); mp 118 °C; $[\alpha]_D$ = +52.0 (*c* 0.5, $CHCl_3$); 81% ee, determined by HPLC analysis: chiral AD-3 column (hexane/2-propanol = 97/3, 0.7 mL/min, λ = 220 nm), *t*(major) = 19.7 min, *t*(minor) = 22.0 min; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34−7.21 (m, 3H), 7.20−7.10 (m, 2H), 7.09−7.00 (m, 2H), 4.50 (dd, *J* = 7.9, 3.6 Hz, 1H), 3.86 (s, 3H), 3.25 (dd, *J* = 19.2, 7.9 Hz, 1H), 2.63 (dd, *J* = 19.2, 3.6 Hz, 1H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.4, 159.8, 150.1, 142.4, 138.0, 132.7, 129.0, 128.8, 127.5, 124.6, 104.5, 55.6, 47.4, 43.1; IR (KBr) ν 3357, 2989, 2922, 2853, 1709, 1658, 1612 1487, 846 cm^{-1}; HRMS (EI) for $C_{16}H_{13}O_2Cl$ [M]$^+$ calcd 272.0604, found 272.0605.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

NMR and HPLC spectra for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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