Supporting Information for

Enantioselective γ-Alkylation of α,β-Unsaturated Malonates and Ketoesters by a Sequential Ir-Catalyzed Asymmetric Allylic Alkylation/Cope Rearrangement.

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Materials and Methods

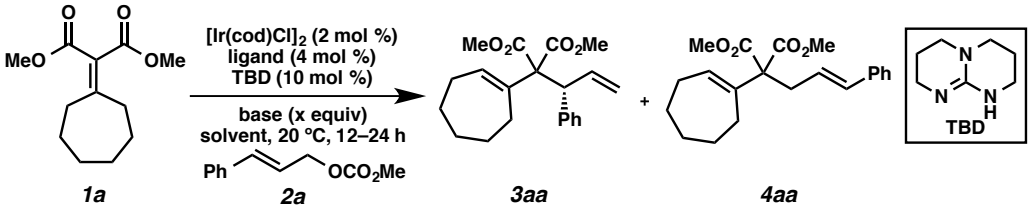
Unless otherwise stated, reactions were performed in flame-dried glassware under an argon or nitrogen atmosphere using dry, deoxygenated solvents. Solvents were dried by passage through an activated alumina column under argon.[1] Reaction progress was monitored by thin-layer chromatography (TLC) or Agilent 1290 UHPLC-MS. TLC was performed using E. Merck silica gel 60 F254 precoated glass plates (0.25 mm) and visualized by UV fluorescence quenching, *p*-anisaldehyde, or $KMnO_4$ staining. Silicycle Silia*Flash*® P60 Academic Silica gel (particle size 40–63 nm) was used for flash chromatography. ^{1}H NMR spectra were recorded on Varian Inova 500 MHz and Bruker 400 MHz spectrometers and are reported relative to residual $CHCl_3$ (δ 7.26 ppm). ^{13}C NMR spectra were recorded on a Varian Inova 500 MHz spectrometer (125 MHz) and Bruker 400 MHz spectrometers (100 MHz) and are reported relative to $CHCl_3$ (δ 77.16 ppm). Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm) (multiplicity, coupling constant (Hz), integration). Multiplicities are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, sept = septuplet, m = multiplet, br s = broad singlet, br d = broad doublet, app = apparent. Data for ^{13}C NMR are reported in terms of chemical shifts (δ ppm). IR spectra were obtained by use of a Perkin Elmer Spectrum BXII spectrometer or Nicolet 6700 FTIR spectrometer using thin films deposited on NaCl plates and reported in frequency of absorption (cm^{-1}). Optical rotations were measured with a Jasco P-2000 polarimeter operating on the sodium D-line (589 nm), using a 100 mm path-length cell and are reported as: $[\alpha]_D^T$ (concentration in 10 mg/1 mL, solvent). Analytical SFC was performed with a Mettler SFC supercritical CO_2 analytical chromatography system utilizing Chiralpak (AD-H, AS-H or IC) or Chiralcel (OD-H, OJ-H, or OB-H) columns (4.6 mm x 25 cm) obtained from Daicel Chemical Industries, Ltd. High resolution mass spectra (HRMS) were obtained from Agilent 6200 Series TOF with an Agilent G1978A Multimode source in electrospray ionization (ESI+), atmospheric pressure chemical ionization (APCI+), or mixed ionization mode (MM: ESI-APCI+), or obtained from Caltech mass spectrometry laboratory.

Reagents were purchased from Sigma-Aldrich, Acros Organics, Strem, or Alfa Aesar and used as received unless otherwise stated. Ligands **L1**, **L4–L6**,[2] and allyl carbonates,[3] were prepared by known methods.

List of Abbreviations:

ee – enantiomeric excess, dr – diastereomeric ratio, SFC – supercritical fluid chromatography, TLC – thin-layer chromatography, THF – tetrahydrofuran, IPA – isopropanol, TBD – 1,5,7-triazabicyclo[4.4.0]dec-5-ene, cod – *cis,cis*-1,5-cyclooctadiene.

Table S1. Optimization of Reaction Parameters.



1a *2a* *3aa* *4aa*

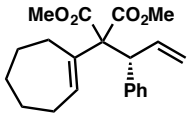
entry[a]	ligand	solvent	base (x equiv)	equiv of *1a*	equiv of *2a*	conv (%)[b,c]	*3aa*:*4aa*[b]	ee of *3aa* (%)[d]
1	*L1*	THF	LiO*t*-Bu (1)	2	1	>95 (28)	1:1	95
2	*L1*	THF	NaO*t*-Bu (2)	2	1	>95 (47)	3:1	94
3	*L1*	THF	NaH (2)	2	1	<5	–	–
4	*L1*	THF	KO*t*-Bu (2)	2	1	>95 (43)	3:1	97
5	*L1*	THF	KO*t*-Bu (1)	2	1	>95 (57)	3:1	>99
6	*L1*	THF	KO*t*-Bu (1)	1.2	1	89	3:1	>99
7	*L1*	THF	KO*t*-Bu (0.3)	1.2	1	32	3:1	–
8	*L1*	THF	Cs_2CO_3 (1)	1.2	1	14	1:1	–
9	*L1*	THF	$CsOH·H_2O$ (1)	1.2	1	74	3:1	–
10	*L1*	dioxane	KO*t*-Bu (1)	2	1	>95 (54)	3:1	>99
11	*L1*	Et_2O	KO*t*-Bu (1)	2	1	90	2:1	>99
12	*L1*	MTBE	KO*t*-Bu (1)	2	1	86	2:1	95
13	*L1*	CH_2Cl_2	KO*t*-Bu (1)	2	1	>95	2:1	97
14	*L1*	DCE	KO*t*-Bu (1)	2	1	59	2:1	98
15	*L1*	toluene	KO*t*-Bu (1)	2	1	94	2:1	97
16	*L1*	cyclohexane	KO*t*-Bu (1)	2	1	94	2:1	97
17	*L1*	MeCN	KO*t*-Bu (1)	2	1	>95	1:1	94
18	*L1*	DMF	KO*t*-Bu (1)	2	1	>95	1:1	99
19	*L2*	THF	KO*t*-Bu (1)	2	1	<10[e]	–	–
20	*L3*	THF	KO*t*-Bu (1)	2	1	>95[e]	>20:1	>99
21	*(±)-L4*	THF	KO*t*-Bu (1)	2	1	>95	1:1	–
22	*L5*	THF	KO*t*-Bu (1)	2	1	52	2:1	40
23	*L6*	THF	KO*t*-Bu (1)	2	1	>95 (69)	>20:1	>99
24	*L6*	THF	KO*t*-Bu (1)	1	1.5	89 (84)	>20:1	>99
25	*L6*	THF	LiO*t*-Bu (1.2)	1	1.5	92 (90)	>20:1	>99
26	*L6*	THF	LiO*t*-Bu (1.2)	1	2	>95 (93)	>20:1	>99

[a] Reactions performed at 0.1 mmol scale in THF (1 mL) at 20 °C for 12–24 h. [b] Determined by ^{1}H NMR analysis of the crude reaction mixture. [c] Yield of isolated product **3aa** given in parenthesis. [d] Determined by SFC analysis (Chiralpak AD-H). [e] Complex mixture.

General Procedure for Optimization Reactions (Table S1):

All experiments were performed in a nitrogen-filled glove box.

To a 2 dram vial (vial A) equipped with a magnetic stirring bar was added $[Ir(cod)Cl]_2$ (1.4 mg, 0.002 mmol, 2 mol%), ligand **L** (0.004 mmol, 4 mol%), TBD (1.4 mg, 0.01 mmol, 10 mol%), and 0.5 mL of THF. Vial A was stirred at 20 °C (~10 min) while another 2 dram vial (vial B) was charged with base, 0.5 mL of THF, alkylidene malonate **1a**, and carbonate **2a**. The pre-formed catalyst solution (vial A) was then transferred to vial B. The vial was sealed, stirred at 20 °C and monitored by TLC or UHPLC-MS. Upon completion of the reaction, the vial was removed from the glovebox and the THF removed under reduced pressure. The resulting residue was dissolved in Et_2O and filtered through a silica pad, rinsing with Et_2O. The regioselectivity (branched to linear) was determined by ^1H NMR analysis of this crude mixture. The residue was purified by silica gel flash chromatography (gradient elution, 0→5→10% Et_2O in hexanes) to afford the desired product.

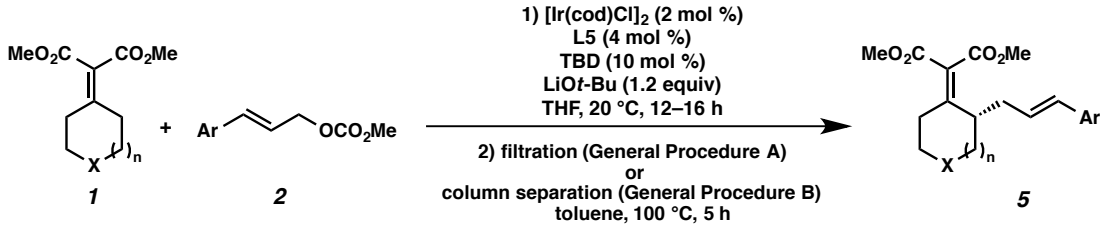


Dimethyl (R)-2-(cyclohept-1-en-1-yl)-2-(1-phenylallyl)malonate (3aa)

White solid, >99% ee, $[\alpha]_D^{25}$ –72.1 (*c* 0.76, $CHCl_3$); R_f = 0.3 (10% Et_2O in hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 2H), 7.26 – 7.21 (m, 2H), 7.20 – 7.14 (m, 1H), 6.36 (ddd, *J* = 17.0, 10.2, 8.9 Hz, 1H), 6.17 (t, *J* = 6.8 Hz, 1H), 5.06 (ddd, *J* = 10.2, 1.8, 0.8 Hz, 1H), 5.00 (ddd, *J* = 17.1, 1.8, 1.1 Hz, 1H), 4.29 (d, *J* = 8.9 Hz, 1H), 3.68 (s, 3H), 3.61 (s, 3H), 2.18–2.10 (m, 2H), 1.96–1.81 (m, 2H), 1.75–1.66 (m, 1H), 1.64–1.55 (m, 1H), 1.54–1.31 (m, 3H), 1.31–1.20 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.7, 170.3, 140.5, 139.2, 138.6, 132.2, 130.2, 127.9, 126.8, 116.9, 70.1, 53.9, 52.3, 52.2, 32.7, 32.4, 28.7, 26.3, 26.2; IR (Neat Film, NaCl) 2925, 1737, 1728, 1451, 1433, 1241, 1050 cm^{-1}; HRMS (ESI-APCI+) *m/z* calc'd for $C_{21}H_{27}O_4$ $[M+H]^+$: 343.1904, found 343.1905; SFC conditions: 2% IPA, 2.5 mL/min, Chiralpak AD-H column, λ = 210 nm, t_R (min): minor = 7.34, major = 8.12.

General Procedure for the Ir-Catalyzed Asymmetric Allylic Alkylation/Cope Rearrangement Reactions of Cyclic Alkylidene Malonates.

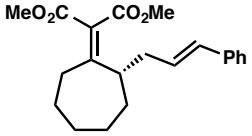
Please note that the absolute configuration was determined only for compound **5a** *via X-ray analysis of its derivative (vide infra). The absolute configuration for all other products* ***5*** *has been inferred by analogy. For respective SFC conditions, please refer to Table S2.*



General Procedure A (One-pot): In a nitrogen-filled glove box, $[Ir(cod)Cl]_2$ (2.7 mg, 0.004 mmol, 2 mol%), ligand **L6** (4.9 mg, 0.008 mmol, 4 mol%), and TBD (2.8 mg, 0.02 mmol, 10 mol%) were added to a 2 dram vial equipped with a magnetic stirring bar. The vial was then charged with THF (1 mL) and stirred at 20 °C for 10 min, generating a brown solution. To another 2 dram vial was added LiO*t*-Bu (19.2 mg, 0.24 mmol, 1.2 equiv), alkylidene malonates **1** (0.2 mmol, 1 equiv), allylic carbonates **2** (0.3–0.4 mmol, 1.5–2 equiv), and 1 mL of THF. Then, the above pre-formed catalyst solution was transferred to this vial by syringe. The vial was capped and stirred at 20 °C until the alkylidene malonate was fully consumed, as indicated by TLC or UHPLC-MS analysis. Upon completion of the reaction, the vial was removed from the glovebox and the THF removed under reduced pressure. The regioselectivity (branched to linear, b:l >20:1 for all cases) was determined by ^{1}H NMR of the crude reaction mixture. The crude sample was recovered from the NMR tube and concentrated. The resulting residue was dissolved in 2 mL of toluene, placed in a sealed vial, and stirred at 100 °C for 5 h. After removal of the solvent, the residue was purified by silica gel flash chromatography to afford the desired product.

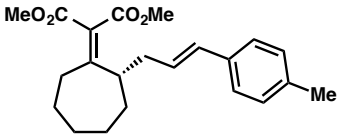
General Procedure B (Column Separation): In a nitrogen-filled glove box, $[Ir(cod)Cl]_2$ (2.7 mg, 0.004 mmol, 2 mol%), ligand **L6** (4.9 mg, 0.008 mmol, 4 mol%), and TBD (2.8 mg, 0.02 mmol, 10 mol%) were added to a 2 dram vial equipped with a

magnetic stirring bar. The vial was then charged with THF (1 mL) and stirred at 20 °C for 10 min, generating a brown solution. To another 2 dram vial was added LiO*t*-Bu (19.2 mg, 0.24 mmol, 1.2 equiv), alkylidene malonates **1** (0.2 mmol, 1 equiv), allylic carbonates **2** (0.3–0.4 mmol, 1.5–2 equiv), and 1 mL of THF. Then the above pre-formed catalyst solution was transferred to this vial by syringe. The vial was capped and stirred at 20 °C until the alkylidene malonate was fully consumed, as indicated by TLC or UHPLC-MS analysis. Upon completion of the reaction, the vial was removed from the glovebox and the THF removed under reduced pressure. The regioselectivity (branched to linear: b:l >20:1 for all cases) was determined by ^{1}H NMR of the crude reaction mixture. The residue was then purified by silica gel flash chromatography to afford the desired allylation product, which was then dissolved in 2 mL of toluene, sealed and stirred for 5 h at 100 °C. After removal of the solvent, the residue was purified by silica gel flash chromatography to afford the desired product.



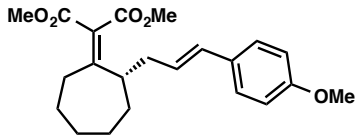
Dimethyl (*S*)-2-(2-cinnamylcyclohexylidene)malonate 5aa: The *General Procedure A* was followed. To a 2 dram scintillation vial equipped with a magnetic stirring bar was added [Ir(cod)Cl]$_2$ (2.7 mg, 0.004 mmol, 2 mol%), ligand **L6** (4.9 mg, 0.008 mmol, 4 mol%), and TBD (2.8 mg, 0.02 mmol, 10 mol%). The vial was then charged with THF (1 mL) and stirred at 20 °C for 10 min, generating a light brown solution. To another 2 dram scintillation vial equipped with a magnetic stirring bar was charged with LiO*t*-Bu (19.2 mg, 0.24 mmol, 1.2 equiv), dimethyl 2-cyclohexylidenemalonate **1a** (45.2 mg, 0.2 mmol, 1 equiv), and cinnamyl carbonate **2a** (76.8 mg, 0.4 mmol, 2.0 equiv), and 1 mL of THF. After the transformation of above prepared catalyst solution by syringe, the vial was sealed and stirred at 20 °C for 12 h, until 2-cyclohexylidenemalonate 1a was fully consumed, as indicated by TLC or UHPLC-MS analysis. Upon completion of the reaction the vial was removed from the glovebox, uncapped, and THF was evaporated under reduced pressure. Et_2O was added to the crude mixture and the resulting precipitate was filtered through a silica pad, rinsed with Et_2O and the filtrate was

concentrated under reduced pressure. The regioselectivity (branched product to linear product: b:l) was determined by ^{1}H NMR of this crude mixture as >20:1. This crude oil was then dissolved in 2 mL of toluene and stirred at 100 ºC for 5 h. After the evaporation of toluene under reduced pressure, the desired product **5aa** (62.4 mg, 91% yield) was obtained as a colorless oil after purification by silica gel flash chromatography (gradient elution, 10→20% Et_2O in hexanes). 96% ee; $[\alpha]_D^{25}$ –111.1 (*c* 0.72, $CHCl_3$); R_f = 0.2 (10% Et_2O in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 2H), 7.31 – 7.27 (m, 2H), 7.22 – 7.16 (m, 1H), 6.37 (d, *J* = 15.7 Hz, 1H), 6.17 (ddd, *J* = 15.5, 8.1, 6.8 Hz, 1H), 3.77 (s, 3H), 3.74 (s, 3H), 3.13 (ddt, *J* = 11.0, 8.4, 5.7 Hz, 1H), 2.99 – 2.90 (m, 1H), 2.45 – 2.40 (m, 1H), 2.28 – 2.22 (m, 1H), 2.11 – 1.96 (m, 3H), 1.87 – 1.69 (m, 2H), 1.51 – 1.39 (m, 1H), 1.36 – 1.24 (m, 2H), 1.17 – 1.04 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.3, 166.5, 165.8, 137.7, 131.8, 128.6, 127.9, 127.1, 126.2, 124.6, 52.2, 52.1, 44.4, 39.9, 31.7, 30.9, 29.8, 29.6, 25.9; IR (Neat Film, NaCl) 2924, 1723, 1618, 1433, 1231, 1192, 1068 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{21}H_{27}O_4$ $[M+H]^+$: 343.1909, found 343.1919; SFC conditions: 10% IPA, 2.5 mL/min, Chiralpak AD-H column, λ = 254 nm, t_R (min): major = 4.55, minor = 4.88.



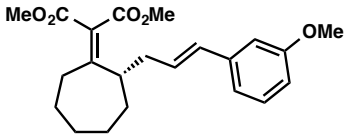
Dimethyl (*S*,*E*)-2-(2-(3-(*p*-tolyl)allyl)cycloheptylidene)malonate 5ab: The *General Procedure B* was followed. To a 2 dram scintillation vial equipped with a magnetic stirring bar was added $[Ir(cod)Cl]_2$ (2.7 mg, 0.004 mmol, 2 mol%), ligand **L6** (4.9 mg, 0.008 mmol, 4 mol%), and TBD (2.8 mg, 0.02 mmol, 10 mol%). The vial was then charged with THF (1 mL) and stirred at 20 °C for 10 min, generating a light brown solution. To another 2 dram scintillation vial equipped with a magnetic stirring bar was charged with LiO*t*-Bu (19.2 mg, 0.24 mmol, 1.2 equiv), dimethyl 2-cycloheptylidenemalonate **1a** (45.2 mg, 0.2 mmol, 1 equiv), and *p*-methylcinnamyl carbonate **2b** (82.4 mg, 0.4 mmol, 2.0 equiv), and 1 mL of THF. After the transformation of above prepared catalyst solution by syringe, the vial was sealed and stirred at 20 °C for 12 h, the vial was removed from the glovebox, uncapped, and THF was evaporated under

reduced pressure. Et_2O was added to the crude mixture and the resulting precipitate was filtered through a silica pad, rinsed with Et_2O and the filtrate was concentrated under reduced pressure. The regioselectivity (branched product to linear product: b:l) was determined by ^1H NMR of this crude mixture as >20:1. The residue was purified by silica gel flash chromatography (gradient elution, 10→20% Et_2O in hexanes) to afford a colorless oil. This oil was then dissolved in 2 mL of toluene and stirred at 100 ºC for 5 h. After the evaporation of toluene under reduced pressure, the desired product **5ab** (56.5 mg, 79% yield) was obtained as a colorless oil after purification by silica gel flash chromatography (10% Et_2O in hexanes). 96% ee, $[\alpha]_D^{25}$ –107.2 (*c* 1.67, $CHCl_3$); R_f = 0.2 (10% Et_2O in hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 7.26 – 7.21 (m, 2H), 7.14 – 7.06 (m, 2H), 6.34 (d, *J* = 15.7 Hz, 1H), 6.11 (ddd, *J* = 15.4, 8.1, 6.8 Hz, 1H), 3.76 (s, 3H), 3.74 (s, 3H), 3.14 – 3.08 (m, 1H), 3.01 – 2.89 (m, 1H), 2.44 – 2.38 (m, 1H), 2.32 (s, 3H), 2.28 – 2.17 (m, 1H), 2.11 – 1.94 (m, 3H), 1.87 – 1.70 (m, 2H), 1.50 – 1.39 (m, 1H), 1.36 – 1.23 (m, 2H), 1.15 – 1.03 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.3, 166.5, 165.7, 136.8, 134.9, 131.6, 129.3, 126.7, 126.0, 124.5, 52.1, 52.0, 44.5, 39.9, 31.6, 30.8, 29.7, 29.6, 25.9, 21.3. IR (Neat Film, NaCl) 3022, 2924, 2855, 1727, 1615, 1513, 1434, 1294, 1276, 1231, 1192, 1070, 1045, 1028, 967, 790 cm^{-1}; HRMS (MM: ESI-APCI+) calc'd for $C_{22}H_{29}O_4$ $[M+H]^+$: 357.2060, found 357.2059. SFC conditions: 5% IPA, 2.5 mL/min, Chiralpak IC column, λ = 254 nm, t_R (min): major = 7.54, minor = 10.52.



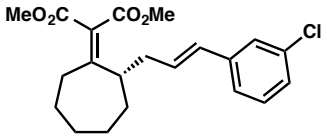
Dimethyl (*S*)-2-(2-(3-(4-methoxyphenyl)allyl)cycloheptylidene)malonate 5ac: The *General Procedure B* was followed. To a 2 dram scintillation vial equipped with a magnetic stirring bar was added $[Ir(cod)Cl]_2$ (2.7 mg, 0.004 mmol, 2 mol%), ligand **L6** (4.9 mg, 0.008 mmol, 4 mol%), and TBD (2.8 mg, 0.02 mmol, 10 mol%). The vial was then charged with THF (1 mL) and stirred at 20 °C for 10 min, generating a light brown solution. To another 2 dram scintillation vial equipped with a magnetic stirring bar was charged with LiO*t*-Bu (19.2 mg, 0.24 mmol, 1.2 equiv), dimethyl 2-cycloheptylidenemalonate **1a** (45.2 mg, 0.2 mmol, 1 equiv), and *p*-methoxylcinnamyl

carbonate **2c** (88.8 mg, 0.4 mmol, 2.0 equiv), and 1 mL of THF. After the transformation of above prepared catalyst solution by syringe, the vial was sealed and stirred at 20 °C for 12 h. Then the vial was removed from the glovebox, uncapped, and THF was evaporated under reduced pressure. Et_2O was added to the crude mixture and the resulting precipitate was filtered through a silica pad, rinsed with Et_2O and the filtrate was concentrated under reduced pressure. The regioselectivity (branched product to linear product: b:l) was determined by ^{1}H NMR of this crude mixture as >20:1. The residue was purified by silica gel flash chromatography (gradient elution, 10→20% Et_2O in hexanes) to afford a colorless oil. This oil was then dissolved in 2 mL of toluene and stirred at 100 ºC for 5 h. After the evaporation of toluene under reduced pressure, the desired product **5ac** (53.6 mg, 72% yield) was obtained as a colorless oil after purification by silica gel flash chromatography (gradient elution, 10→20% Et_2O in hexanes). 96% ee, $[\alpha]_D^{25}$ –72.7 (*c* 1.42, $CHCl_3$); R_f = 0.4 (25% Et_2O in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 – 7.17 (m, 2H), 6.79 – 6.73 (m, 2H), 6.24 (dt, *J* = 15.7, 1.3 Hz, 1H), 5.94 (ddd, *J* = 15.6, 8.1, 6.8 Hz, 1H), 3.72 (s, 3H), 3.69 (s, 3H), 3.66 (s, 3H), 3.06 – 3.00 (m, 1H), 2.91 – 2.83 (m, 1H), 2.35 – 2.30 (dddd, *J* = 13.5, 6.8, 5.3, 1.5 Hz, 1H), 2.15 (dtd, *J* = 13.5, 8.3, 1.2 Hz, 1H), 2.02 – 1.88 (m, 3H), 1.77 – 1.62 (m, 2H), 1.43 – 1.30 (m, 1H), 1.29 – 1.15 (m, 2H), 1.05 – 0.98 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.4, 166.5, 165.7, 158.9, 131.1, 130.5, 127.3, 125.6, 124.5, 114.0, 55.4, 52.2, 52.1, 44.5, 39.9, 31.6, 30.8, 29.7, 29.6, 25.9. IR (Neat Film, NaCl) 2928, 2854, 1725, 1608, 1577, 1511, 1434, 1292, 1276, 1233, 1192, 1174, 1139, 1070, 1034, 967 cm^{-1}; HRMS (MM: ESI-APCI+) calc'd for $C_{22}H_{29}O_5$ $[M+H]^+$: 373.2010, found 373.2016. SFC conditions: 10% IPA, 2.5 mL/min, Chiralpak IC column, λ = 254 nm, t_R (min): major = 7.39, minor = 9.02.



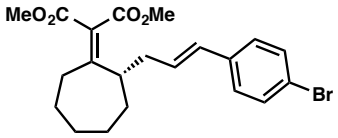
Dimethyl (*S*,*E*)-2-(2-(3-(3-methoxyphenyl)allyl)cycloheptylidene)malonate 5ad: The *General Procedure A* was followed. To a 2 dram scintillation vial equipped with a magnetic stirring bar was added $[Ir(cod)Cl]_2$ (2.7 mg, 0.004 mmol, 2 mol%), ligand **L6** (4.9 mg, 0.008 mmol, 4 mol%), and TBD (2.8 mg, 0.02 mmol, 10 mol%). The vial was

then charged with THF (1 mL) and stirred at 20 °C for 10 min, generating a light brown solution. To another 2 dram scintillation vial equipped with a magnetic stirring bar was charged with LiO*t*-Bu (19.2 mg, 0.24 mmol, 1.2 equiv), dimethyl 2-cycloheptylidenemalonate **1a** (45.2 mg, 0.2 mmol, 1 equiv), and *m*-methoxycinnamyl carbonate **2d** (88.8 mg, 0.4 mmol, 2 equiv), and 1 mL of THF. After the transformation of above prepared catalyst solution by syringe, the vial was sealed and stirred at 20 °C for 16 h, the vial was removed from the glovebox, uncapped, and THF was evaporated under reduced pressure. Et_2O was added to the crude mixture and the resulting precipitate was filtered through a silica pad, rinsed with Et_2O and the filtrate was concentrated under reduced pressure. The regioselectivity (branched product to linear product: b:l) was determined by ^{1}H NMR of this crude mixture as >20:1. The mixture was recovered from NMR tube, concentrated, and dried under vacuum. Then this crude mixture was dissolved in 2 mL of toluene and stirred at 100 ºC for 5 h. After the evaporation of toluene under reduced pressure, the desired product **5ad** (67.3 mg, 90% yield) was obtained as a colorless oil after purification by silica gel flash chromatography (gradient elution, 10→20% Et_2O in hexanes). 97% ee, $[\alpha]_D^{25}$ –98.0 (*c* 1.35, $CHCl_3$); R_f = 0.1 (10% Et_2O in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 (t, *J* = 7.9 Hz, 1H), 6.94 (dt, *J* = 7.5, 1.3 Hz, 1H), 6.88 (dd, *J* = 2.6, 1.6 Hz, 1H), 6.76 (ddd, *J* = 8.2, 2.6, 0.9 Hz, 1H), 6.35 (dt, *J* = 15.9, 1.3 Hz, 1H), 6.16 (ddd, *J* = 15.7, 8.1, 6.7 Hz, 1H), 3.81 (s, 3H), 3.76 (s, 3H), 3.74 (s, 3H), 3.19 – 3.08 (m, 1H), 3.00 – 2.86 (m, 1H), 2.45 – 2.39 (m, 1H), 2.29 – 2.18 (m, 1H), 2.12 – 1.92 (m, 3H), 1.86 – 1.68 (m, 2H), 1.51 – 1.37 (m, 1H), 1.37 – 1.19 (m, 2H), 1.16 – 1.03 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.2, 166.4, 165.7, 159.9, 139.1, 131.7, 129.5, 128.2, 124.5, 118.9, 112.8, 111.5, 55.3, 52.2, 52.1, 44.3, 39.8, 31.6, 30.8, 29.8, 29.6, 25.9. IR (Neat Film, NaCl) 2997, 2945, 2927, 2854, 1725, 1598, 1579, 1488, 1434, 1289, 1231, 1192, 1165, 1155, 1070, 1044, 968, 940, 775 cm^{-1}; HRMS (MM: ESI-APCI+) calc'd for $C_{22}H_{29}O_5$ $[M+H]^+$: 373.2010, found 373.2001. SFC conditions: 5% MeOH, 2.5 mL/min, Chiralpak IC column, λ = 254 nm, t_R (min): major = 9.50, minor = 10.16.



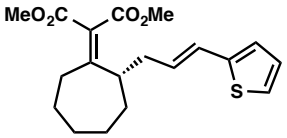
Dimethyl (*S*,*E*)-2-(2-(3-(3-chlorophenyl)allyl)cycloheptylidene)malonate 5ae: The *General Procedure A* was followed. To a 2 dram scintillation vial equipped with a magnetic stirring bar was added $[Ir(cod)Cl]_2$ (2.7 mg, 0.004 mmol, 2 mol%), ligand **L6** (4.9 mg, 0.008 mmol, 4 mol%), and TBD (2.8 mg, 0.02 mmol, 10 mol%). The vial was then charged with THF (1 mL) and stirred at 20 °C for 10 min, generating a light brown solution. To another 2 dram scintillation vial equipped with a magnetic stirring bar was charged with LiO*t*-Bu (19.2 mg, 0.24 mmol, 1.2 equiv), dimethyl 2-cycloheptylidenemalonate **1a** (45.2 mg, 0.2 mmol, 1 equiv), and *m*-chlorocinnamyl carbonate **2e** (90.4 mg, 0.4 mmol, 2.0 equiv), and 1 mL of THF. After the transformation of above prepared catalyst solution by syringe, the vial was sealed and stirred at 20 °C for 12 h, the vial was removed from the glovebox, uncapped, and THF evaporated under reduced pressure. Et_2O was added to the crude mixture and the resulting precipitate was filtered through a silica pad, rinsed with Et_2O and the filtrate was concentrated under reduced pressure. The regioselectivity (branched product to linear product: b:l) was determined by ^1H NMR of this crude mixture as >20:1. The mixture was recovered from NMR tube, concentrated, and dried under vacuum. Then this crude mixture was dissolved in 2 mL of toluene and stirred at 100 ºC for 5 h. After the evaporation of toluene under reduced pressure, the desired product **5ae** (73.3 mg, 97% yield) was obtained as a colorless oil after purification by silica gel flash chromatography (10% Et_2O in hexanes). 96% ee, $[\alpha]_D^{25}$ –88.1 (*c* 1.27, $CHCl_3$); R_f = 0.3 (10% Et_2O in hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.30 (m, 1H), 7.24 – 7.18 (m, 2H), 7.18 – 7.11 (m, 1H), 6.31 (dt, *J* = 15.6, 1.2 Hz, 1H), 6.18 (ddd, *J* = 15.7, 8.0, 6.8 Hz, 1H), 3.76 (s, 3H), 3.73 (s, 3H), 3.15 (ddt, *J* = 11.3, 8.4, 5.8 Hz, 1H), 2.95 – 2.87 (m, 1H), 2.41 (dddd, *J* = 13.5, 6.8, 5.5, 1.4 Hz, 1H), 2.24 (dtd, *J* = 13.5, 8.1, 1.0 Hz, 1H), 2.09 – 1.94 (m, 3H), 1.85 – 1.72 (m, 2H), 1.50 – 1.37 (m, 1H), 1.36 – 1.20 (m, 2H), 1.15 – 1.03 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.9, 166.4, 165.8, 139.6, 134.5, 130.5, 129.8, 129.6, 127.1, 126.1, 124.7, 124.4, 52.2, 52.1, 44.1, 39.8, 31.7, 30.8, 29.8, 29.6, 25.9. IR (Neat Film, NaCl) 2927, 2854, 1726, 1619, 1615, 1593, 1434, 1294, 1276, 1231, 1192, 1140, 1070, 1045,

1028, 964, 776 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{21}H_{26}ClO_4$ $[M+H]^+$: 377.1520, found 377.1503. SFC conditions: 3% IPA, 4 mL/min, Chiralpak IC column, λ = 254 nm, t_R (min): major = 12.00, minor = 17.72.



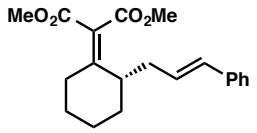
Dimethyl (*S*,*E*)-2-(2-(3-(4-bromophenyl)allyl)cycloheptylidene)malonate 5af: The *General Procedure A* was followed. To a 2 dram scintillation vial equipped with a magnetic stirring bar was added $[Ir(cod)Cl]_2$ (2.7 mg, 0.004 mmol, 2 mol%), ligand **L6** (4.9 mg, 0.008 mmol, 4 mol%), and TBD (2.8 mg, 0.02 mmol, 10 mol%). The vial was then charged with THF (1 mL) and stirred at 20 °C for 10 min, generating a light brown solution. To another 2 dram scintillation vial equipped with a magnetic stirring bar was charged with LiO*t*-Bu (19.2 mg, 0.24 mmol, 1.2 equiv), dimethyl 2-cycloheptylidenemalonate **1a** (45.2 mg, 0.2 mmol, 1 equiv), and *p*-bromocinnamyl carbonate **2f** (81.0 mg, 0.3 mmol, 1.5 equiv), and 1 mL of THF. After the transformation of above prepared catalyst solution by syringe, the vial was sealed and stirred at 20 °C for 12 h, the vial was removed from the glovebox, uncapped, and THF evaporated under reduced pressure. Et_2O was added to the crude mixture and the resulting precipitate was filtered through a silica pad, rinsed with Et_2O and the filtrate was concentrated under reduced pressure. The regioselectivity (branched product to linear product: b:l) was determined by ^1H NMR of this crude mixture as >20:1. The residue was purified by silica gel flash chromatography (10% Et_2O in hexanes) to afford a colorless oil. This oil was then dissolved in 2 mL of toluene and stirred at 100 ºC for 5 h. After the evaporation of toluene under reduced pressure, the desired product **5af** (80.2 mg, 95% yield) was obtained as a colorless oil after purification by silica gel flash chromatography (10% Et_2O in hexanes). 97% ee, $[\alpha]_D^{25}$ –69.9 (*c* 1.66, $CHCl_3$); R_f = 0.3 (10% Et_2O in hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.35 (m, 2H), 7.25 – 7.16 (m, 2H), 6.30 (d, *J* = 15.6 Hz, 1H), 6.15 (ddd, *J* = 15.6, 8.0, 6.8 Hz, 1H), 3.76 (s, 3H), 3.72 (s, 3H), 3.17 – 3.11 (m, 1H), 2.96 – 2.87 (m, 1H), 2.42 – 2.36 (m, 1H), 2.27 – 2.20 (m, 1H), 2.08 – 1.94 (m, 3H), 1.85 – 1.71 (m, 2H), 1.50 – 1.37 (m, 1H), 1.35 – 1.22 (m, 2H), 1.13 – 1.05 (m, 1H); ^{13}C

NMR (125 MHz, $CDCl_3$) δ 167.9, 166.4, 165.8, 136.6, 131.7, 130.6, 128.8, 127.7, 124.7, 120.8, 52.2, 52.1, 44.2, 39.8, 31.8, 30.8, 29.7, 29.6, 25.9. IR (Neat Film, NaCl) 2927, 2855, 1726, 1619, 1615, 1593, 1567, 1434, 1294, 1276, 1231, 1193, 1140, 1070, 1028, 964, 777 cm^{-1}; HRMS (MM: ESI-APCI+) calc'd for $C_{21}H_{24}O_4Br$ $[M–H_2+H]^+$: 419.0852, found 419.0847. SFC conditions: 9% MeOH, 2.5 mL/min, Chiralpak IC column, λ = 254 nm, t_R (min): major = 5.33, minor = 5.85.



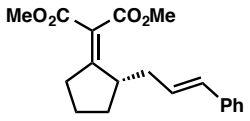
Dimethyl (*S*,*E*)-2-(2-(3-(thiophen-2-yl)allyl)cycloheptylidene)malonate 5ag: The *General Procedure A* was followed. To a 2 dram scintillation vial equipped with a magnetic stirring bar was added $[Ir(cod)Cl]_2$ (2.7 mg, 0.004 mmol, 2 mol%), ligand **L6** (4.9 mg, 0.008 mmol, 4 mol%), and TBD (2.8 mg, 0.02 mmol, 10 mol%). The vial was then charged with THF (1 mL) and stirred at 20 °C for 10 min, generating a light brown solution. To another 2 dram scintillation vial equipped with a magnetic stirring bar was charged with LiO*t*-Bu (19.2 mg, 0.24 mmol, 1.2 equiv), dimethyl 2-cycloheptylidenemalonate **1a** (45.2 mg, 0.2 mmol, 1 equiv), and (*E*)-methyl (3-(thiophen-2-yl)allyl) carbonate **2g** (79.2 mg, 0.4 mmol, 2 equiv), and 1 mL of THF. After the transformation of above prepared catalyst solution by syringe, the vial was sealed and stirred at 20 °C for 16 h. then the vial was removed from the glovebox, uncapped, and THF was evaporated under reduced pressure. Et_2O was added to the crude mixture and the resulting precipitate was filtered through a silica pad, rinsed with Et_2O and the filtrate was concentrated under reduced pressure. The regioselectivity (branched product to linear product: b:l) was determined by ^1H NMR of this crude mixture as >20:1. The residue was recovered from the NMR tube, solvents were removed, and dried under high vacuum to form a yellow oil. This oil was then dissolved in 2 mL of toluene and stirred at 100 ºC for 5 h. After the evaporation of toluene under reduced pressure, the desired product **5ag** was obtained after purification by silica gel flash chromatography (10% Et_2O in hexanes) as a inseparable mixture with **1a** (65.7 mg of mixture, contains 64.0 mg of **5ag** based on ^1H NMR, 92% yield). The analytic pure product was obtained

by preparative HPLC (ACE 5 C18, 250 x 21 2mm id column; gradient, 15–100% MeCN in H_2O in 2 min, then 100% MeCN; flow rate = 10 mL/min; λ = 254 nm) as a colorless oil. 96% ee, $[\alpha]_D^{25}$ –97.3 (*c* 1.82, $CHCl_3$); R_f = 0.2 (10% Et_2O in hexanes); ^1H NMR (400 MHz, $CDCl_3$) δ 7.09 (dt, *J* = 5.1, 0.9 Hz, 1H), 6.92 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.87 (d, *J* = 3.3 Hz, 1H), 6.50 (d, *J* = 15.5 Hz, 1H), 5.99 (ddd, *J* = 15.3, 8.1, 6.9 Hz, 1H), 3.75 (s, 3H), 3.75 (s, 3H), 3.15 – 3.08 (m, 1H), 3.00 – 2.84 (m, 1H), 2.42 – 2.36 (m, 1H), 2.28 – 2.10 (m, 1H), 2.10 – 1.90 (m, 3H), 1.90 – 1.65 (m, 2H), 1.54 – 1.37 (m, 1H), 1.34 – 1.23 (m, 2H), 1.17 – 0.94 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 166.4, 165.7, 142.8, 127.7, 127.3, 125.0, 124.7, 124.6, 123.5, 52.2, 52.1, 44.3, 39.7, 31.6, 30.8, 29.8, 29.6, 25.9. IR (Neat Film, NaCl) 2927, 2855, 1726, 1619, 1615, 1593, 1567, 1434, 1294, 1276, 1231, 1193, 1140, 1070, 1028, 964, 777 cm^{-1}; HRMS (MM: ESI-APCI+) calc'd for $C_{19}H_{25}O_4S$ $[M+H]^+$: 349.1468, found 349.1469. SFC conditions: 3% MeOH, 2.5 mL/min, Chiralpak IC column, λ = 254 nm, t_R (min): major = 11.55, minor = 12.69.



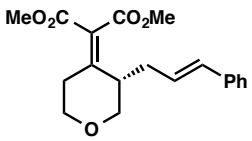
Dimethyl (*S*)-2-(2-cinnamylcyclohexylidene)malonate 5ba: The *General Procedure B* was followed. To a 2 dram scintillation vial equipped with a magnetic stirring bar was added $[Ir(cod)Cl]_2$ (2.7 mg, 0.004 mmol, 2 mol%), ligand **L6** (4.9 mg, 0.008 mmol, 4 mol%), and TBD (2.8 mg, 0.02 mmol, 10 mol%). The vial was then charged with THF (1 mL) and stirred at 20 °C for 10 min, generating a light brown solution. To another 2 dram scintillation vial equipped with a magnetic stirring bar was charged with LiO*t*-Bu (19.2 mg, 0.24 mmol, 1.2 equiv), dimethyl 2-cyclohexylidenemalonate **1b** (42.4 mg, 0.2 mmol, 1 equiv), and cinnamyl carbonate **2a** (76.8 mg, 0.4 mmol, 2.0 equiv), and 1 mL of THF. After the transformation of above prepared catalyst solution by syringe, the vial was sealed and stirred at 20 °C for 12 h, the vial was removed from the glovebox, uncapped, and THF was evaporated under reduced pressure. Et_2O was added to the crude mixture and the resulting precipitate was filtered through a silica pad, rinsed with Et_2O and the filtrate was concentrated under reduced pressure. The regioselectivity (branched product to linear product: b:l) was determined by ^1H NMR of this crude mixture as

>20:1. The residue was purified by silica gel flash chromatography (10% Et_2O in hexanes) to afford a colorless oil. This oil was then dissolved in 2 mL of toluene and stirred at 100 ºC for 5 h. After the evaporation of toluene under reduced pressure, the desired product **5ba** (54.3 mg, 83% yield) was obtained as a colorless oil after purification by silica gel flash chromatography (gradient elution, 10→20% Et_2O in hexanes). 91% ee, $[\alpha]_D^{25}$ –36.3 (*c* 0.73, $CHCl_3$); R_f = 0.2 (10% Et_2O in hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.32 (m, 2H), 7.32 – 7.27 (m, 2H), 7.23 – 7.16 (m, 1H), 6.40 (d, *J* = 15.7 Hz, 1H), 6.14 (ddd, *J* = 15.6, 7.8, 6.8 Hz, 1H), 3.76 (s, 3H), 3.72 (s, 3H), 3.29 – 3.21 (m, 1H), 3.05 – 2.96 (m, 1H), 2.55 – 2.42 (m, 2H), 2.17 (td, *J* = 13.9, 4.9 Hz, 1H), 1.98 – 1.91 (m, 1H), 1.91 – 1.84 (m, 1H), 1.74 – 1.56 (m, 3H), 1.53 – 1.39 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.3, 166.2, 164.4, 137.7, 131.7, 128.6, 128.2, 127.2, 126.2, 122.2, 52.24, 52.18, 39.7, 35.6, 30.5, 27.9, 27.8, 20.3. IR (Neat Film, NaCl) 2933, 2858, 1727, 1626, 1599, 1495, 1449, 1434, 1365, 1336, 1296, 1271, 1251, 1216, 1143, 1103, 1085, 1058, 1016, 966, 743 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{20}H_{25}O_4$ $[M+H]^+$: 329.1753, found 329.1750; SFC conditions: 15% IPA, 2.5 mL/min, Chiralcel OJ-H column, λ = 254 nm, t_R (min): minor = 2.87, major = 4.16.



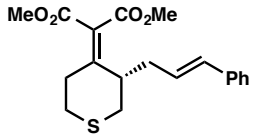
Dimethyl (*S*)-2-(2-cinnamylcyclopentylidene)malonate 5ca: The *General Procedure B* was followed. To a 2 dram scintillation vial equipped with a magnetic stirring bar was added $[Ir(cod)Cl]_2$ (2.7 mg, 0.004 mmol, 2 mol%), ligand **L6** (4.9 mg, 0.008 mmol, 4 mol%), and TBD (2.8 mg, 0.02 mmol, 10 mol%). The vial was then charged with THF (1 mL) and stirred at 20 °C for 10 min, generating a light brown solution. To another 2 dram scintillation vial equipped with a magnetic stirring bar was charged with LiO*t*-Bu (19.2 mg, 0.24 mmol, 1.2 equiv), dimethyl 2-cyclopentylidenemalonate **1c** (40.1 mg, 0.2 mmol, 1 equiv), and cinnamyl carbonate **2a** (76.8 mg, 0.4 mmol, 2.0 equiv), and 1 mL of THF. After the transformation of above prepared catalyst solution by syringe, the vial was sealed and stirred at 20 °C for 12 h. Then the vial was removed from the glovebox, uncapped, and THF was evaporated under reduced pressure. Et_2O was added to the crude mixture and the resulting precipitate was filtered through a silica pad, rinsed with Et_2O

and the filtrate was concentrated under reduced pressure. The regioselectivity (branched product to linear product: b:l) was determined by ^{1}H NMR of this crude mixture as >20:1. The residue was purified by silica gel flash chromatography (10% Et_2O in hexanes) to afford a colorless oil. This oil was then dissolved in 2 mL of toluene and stirred at 100 ºC for 5 h. After the evaporation of toluene under reduced pressure, the desired product **5ca** (47.2 mg, 75% yield) was obtained as a colorless oil after purification by silica gel flash chromatography (gradient elution, 10→20% Et_2O in hexanes). 90% ee, $[\alpha]_D^{25}$ –49.9 (*c* 1.13, $CHCl_3$); R_f = 0.2 (10% Et_2O in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.33 (m, 2H), 7.31 – 7.28 (m, 2H), 7.23 – 7.18 (m, 1H), 6.38 (dt, *J* = 15.8, 1.3 Hz, 1H), 6.16 (ddd, *J* = 15.7, 8.2, 6.3 Hz, 1H), 3.78 (s, 3H), 3.75 (s, 3H), 3.36 – 3.32 (m, 1H), 2.82 – 2.74 (m, 1H), 2.74 – 2.60 (m, 1H), 2.46 – 2.40 (m, 1H), 2.18 – 2.11 (m, 1H), 1.87 – 1.68 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.3, 165.9, 137.5, 131.9, 131.9, 128.6, 128.2, 127.2, 126.2, 120.6, 52.2, 52.1, 44.6, 36.9, 33.5, 30.3, 22.8. IR (Neat Film, NaCl) 2951, 2877, 1725, 1634, 1598, 1494, 1435, 1317, 1274, 1232, 1194, 1173, 1061, 1013, 968, 743 cm^{-1}; HRMS (MM: ESI-APCI+) calc'd for $C_{19}H_{23}O_4$ $[M+H]^+$: 315.1591, found 315.1600. SFC conditions: 10% IPA, 2.5 mL/min, Chiralpak AD-H column, λ = 254 nm, t_R (min): minor = 4.41, major = 4.79.



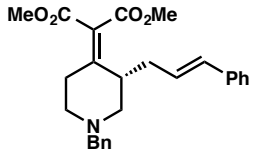
Dimethyl (*S*)-2-(3-cinnamyltetrahydro-4*H*-pyran-4-ylidene)malonate 5da: The *General Procedure B* was followed. To a 2 dram scintillation vial equipped with a magnetic stirring bar was added $[Ir(cod)Cl]_2$ (2.7 mg, 0.004 mmol, 2 mol%), ligand **L6** (4.9 mg, 0.008 mmol, 4 mol%), and TBD (2.8 mg, 0.02 mmol, 10 mol%). The vial was then charged with THF (1 mL) and stirred at 20 °C for 10 min, generating a light brown solution. To another 2 dram scintillation vial equipped with a magnetic stirring bar was charged with LiO*t*-Bu (19.2 mg, 0.24 mmol, 1.2 equiv), dimethyl 2-(tetrahydro-4*H*-pyran-4-ylidene)malonate **1d** (42.8 mg, 0.2 mmol, 1 equiv), and cinnamyl carbonate **2a** (76.8 mg, 0.4 mmol, 2.0 equiv), and 1 mL of THF. After the transformation of above prepared catalyst solution by syringe, the vial was sealed and stirred at 20 °C for 12 h,

until 2-cyclopentylidenemalonate **1d** was fully consumed, as indicated by TLC or UHPLC-MS analysis. Upon completion of the reaction the vial was removed from the glovebox, uncapped, and THF was evaporated under reduced pressure. Et_2O was added to the crude mixture and the resulting precipitate was filtered through a silica pad, rinsed with Et_2O and the filtrate was concentrated under reduced pressure. The regioselectivity (branched product to linear product: b:l) was determined by ^1H NMR of this crude mixture as >20:1. The residue was purified by silica gel flash chromatography (10% Et_2O in hexanes) to afford a colorless oil. This oil was then dissolved in 2 mL of toluene and stirred at 100 ºC for 5 h. After the evaporation of toluene under reduced pressure, the desired product **5da** (60.3 mg, 91% yield) was obtained as a colorless oil after purification by silica gel flash chromatography (gradient elution, 10→20% Et_2O in hexanes). 94% ee, $[\alpha]_D^{25}$ –52.9 (*c* 1.26, $CHCl_3$); R_f = 0.2 (10% Et_2O in hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 2H), 7.30 – 7.27 (m, 2H), 7.24 – 7.14 (m, 1H), 6.46 (dt, *J* = 15.7, 1.3 Hz, 1H), 6.16 (ddd, *J* = 15.7, 8.2, 6.6 Hz, 1H), 4.11 (dd, *J* = 11.1, 6.1 Hz, 1H), 3.99 (dt, *J* = 11.6, 1.3 Hz, 1H), 3.77 (s, 3H), 3.72 (s, 3H), 3.53 (dd, *J* = 11.6, 2.8 Hz, 1H), 3.47 (ddd, *J* = 12.5, 11.1, 2.5 Hz, 1H), 3.09 (t, *J* = 7.3 Hz, 1H), 2.94 (d, *J* = 14.8 Hz, 1H), 2.68 (dtd, *J* = 13.7, 8.4, 1.2 Hz, 1H), 2.61 – 2.52 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.7, 158.8, 137.4, 132.6, 128.6, 127.3, 127.2, 126.2, 123.3, 70.2, 68.4, 52.4, 52.3, 41.1, 35.0, 29.0. IR (Neat Film, NaCl) 2952, 2847, 1725, 1633, 1495, 1434, 1384, 1299, 1245, 1228, 1102, 1067, 1047, 1031, 967 cm^{-1}; HRMS (MM: ESI-APCI+) calc'd for $C_{19}H_{23}O_5$ $[M+H]^+$: 331.1540, found 331.1544. SFC conditions: 15% IPA, 2.5 mL/min, Chiralcel OJ-H column, λ = 254 nm, t_R (min): minor = 2.79, major = 4.44.



Dimethyl (*S*)-2-(3-cinnamyltetrahydro-4*H*-thiopyran-4-ylidene)malonate 5ea: The *General Procedure A* was followed. To a 2 dram scintillation vial equipped with a magnetic stirring bar was added $[Ir(cod)Cl]_2$ (2.7 mg, 0.004 mmol, 2 mol%), ligand **L6** (4.9 mg, 0.008 mmol, 4 mol%), and TBD (2.8 mg, 0.02 mmol, 10 mol%). The vial was then charged with THF (1 mL) and stirred at 20 °C for 10 min, generating a light brown

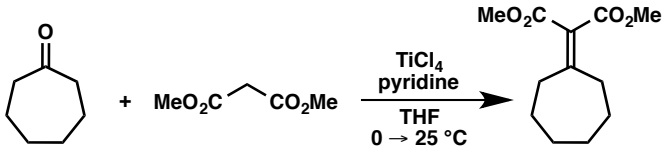
solution. To another 2 dram scintillation vial equipped with a magnetic stirring bar was charged with LiO*t*-Bu (19.2 mg, 0.24 mmol, 1.2 equiv), dimethyl 2-(tetrahydro-4*H*-thiopyran-4-ylidene)malonate **1e** (46.0 mg, 0.20 mmol, 1.0 equiv), cinnamyl carbonate **2a** (76.8 mg, 0.4 mmol, 2.0 equiv), and 1 mL of THF. After the transformation of above prepared catalyst solution by syringe, the vial was sealed and stirred at 20 °C for 12 h, the vial was removed from the glovebox, uncapped, and THF was evaporated under reduced pressure. Et_2O was added to the crude mixture and the resulting precipitate was filtered through a silica pad, rinsed with Et_2O and the filtrate was concentrated under reduced pressure. The regioselectivity (branched product to linear product: b:l) was determined by ^{1}H NMR of this crude mixture as >20:1. The mixture was recovered from NMR tube, concentrated, and dried under vacuum. Then this crude mixture was dissolved in 2 mL of toluene and stirred at 100 ºC for 5 h. After the evaporation of toluene under reduced pressure, the desired product **5ae** (38.7 mg, 56% yield) was obtained as a colorless oil after purification by silica gel flash chromatography (25% Et_2O in hexanes). 93% ee, $[\alpha]_D^{25}$ –50.9 (*c* 0.67, $CHCl_3$); R_f = 0.4 (25% Et_2O in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.29 (m, 4H), 7.26 – 7.19 (m, 1H), 6.50 (dd, *J* = 15.8, 1.3 Hz, 1H), 6.14 (ddd, *J* = 15.7, 8.1, 6.6 Hz, 1H), 3.79 (s, 3H), 3.78 (s, 3H), 3.45 (ddt, *J* = 9.3, 6.5, 3.4 Hz, 1H), 3.28 (dt, *J* = 13.8, 3.2 Hz, 1H), 3.02 (dd, *J* = 13.9, 3.5 Hz, 1H), 2.96 – 2.79 (m, 2H), 2.79 – 2.62 (m, 3H), 2.54 (ddd, *J* = 14.0, 12.4, 4.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 165.7, 160.5, 137.4, 132.7, 128.6, 127.3, 127.0, 126.2, 124.1, 52.4,4 52.43, 39.6, 34.7, 33.9, 30.4, 29.0. IR (Neat Film, NaCl) 3024, 2950, 2905, 2841, 1727, 1626, 1599, 1494, 1434, 1255, 1231, 1208, 1146, 1061, 1022, 967, 930, 745 cm^{-1}; HRMS (MM: ESI-APCI+) calc'd for $C_{19}H_{23}O_4S$ $[M+H]^+$: 347.1312, found 347.1303. SFC conditions: 10% IPA, 2.5 mL/min, Chiralpak IC column, λ = 254 nm, t_R (min): major = 2.75, minor = 2.92.



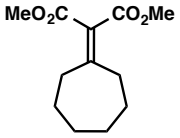
Dimethyl (*S*)-2-(1-benzyl-3-cinnamylpiperidin-4-ylidene)malonate 5fa: The *General Procedure A* was followed. To a 2 dram scintillation vial equipped with a magnetic stirring bar was added $[Ir(cod)Cl]_2$ (2.7 mg, 0.004 mmol, 2 mol%), ligand **L6** (4.9 mg, 0.008 mmol, 4 mol%), and TBD (2.8 mg, 0.02 mmol, 10 mol%). The vial was then

charged with THF (1 mL) and stirred at 20 °C for 10 min, generating a light brown solution. To another 2 dram scintillation vial equipped with a magnetic stirring bar was charged with LiO*t*-Bu (19.2 mg, 0.24 mmol, 1.2 equiv), dimethyl 2-(1-benzylpiperidin-4-ylidene)malonate **1f** (60.6 mg, 0.20 mmol, 1.0 equiv), cinnamyl carbonate **2a** (76.8 mg, 0.4 mmol, 2.0 equiv), and 1 mL of THF. After the transformation of above prepared catalyst solution by syringe, the vial was sealed and stirred at 20 °C for 12 h. Then the vial was removed from the glovebox, uncapped, and THF was evaporated under reduced pressure. EtOAc was added to the crude mixture and the resulting precipitate was filtered through a silica pad, rinsed with EtOAc and the filtrate was concentrated under reduced pressure. The regioselectivity (branched product to linear product: b:l) was determined by ^{1}H NMR of this crude mixture as >20:1. The mixture was recovered from NMR tube, concentrated, and dried under vacuum. Then this crude mixture was dissolved in 2 mL of toluene and stirred at 100 ºC for 5 h. After the evaporation of toluene under reduced pressure, the desired product **5fa** (79.2 mg, 95% yield) was obtained as a yellow oil after purification by silica gel flash chromatography (15% EtOAc in hexanes). 95% ee, $[\alpha]_D^{25}$ –26.1 (*c* 1.18, $CHCl_3$); R_f = 0.2 (25% Et_2O in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.29 (m, 4H), 7.29 – 7.22 (m, 5H), 7.21 – 7.15 (m, 1H), 6.31 (dt, *J* = 15.8, 1.3 Hz, 1H), 6.06 (ddd, *J* = 15.4, 8.1, 6.8 Hz, 1H), 3.76 (s, 3H), 3.71 (s, 3H), 3.57 (d, *J* = 13.1 Hz, 1H), 3.37 (d, *J* = 13.1 Hz, 1H), 3.14 – 2.94 (m, 3H), 2.91 (dt, *J* = 11.6, 2.2 Hz, 1H), 2.80 – 2.67 (m, 1H), 2.62 – 2.45 (m, 2H), 2.12 (ddd, *J* = 23.7, 11.2, 3.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 165.9, 161.2, 138.7, 137.6, 132.0, 129.0, 128.5, 128.4, 128.0, 127.2, 127.1, 126.2, 122.6, 62.5, 55.8, 54.4, 52.3, 52.2, 40.8, 35.8, 28.5. IR (Neat Film, NaCl) 3026, 2949, 2802, 1737, 1732, 1722, 1716, 1633, 1494, 1434, 1366, 1348, 1300, 1226, 1066, 1038, 1009, 966, 745 cm^{-1}; HRMS (MM: ESI-APCI+) calc'd for $C_{26}H_{30}NO_4$ $[M+H]^+$: 420.2169, found 420.2172. SFC conditions: 10% IPA, 2.5 mL/min, Chiralpak IC column, λ = 254 nm, t_R (min): major = 6.64, minor = 7.42.

General Procedure for the Synthesis of Cyclic Alkylidene Malonates.

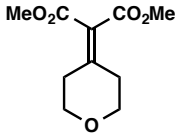


A known procedure was followed with a slight modification:[4] A flame-dried flask containing 25 mL of THF chilled with an ice bath was treated with $TiCl_4$ (13.5 mmol, 3 equiv.) slowly via syringe. To the resulting yellow solution was added dropwise a mixture of ketone (4.5 mmol), dimethyl malonate (13.5 mmol, 3 equiv), pyridine (13.5 mmol, 3 equiv) in THF (8 mL) and the reaction mixture was allowed to slowly warm to room temperature. Upon completion, as determined by TLC, the reaction was quenched by slow addition of water until a homogenous solution was obtained. THF was then removed *in vacuo* and the resulting aqueous solution was extracted with EtOAc. The combined organic layers were sequentially washed with 1 M HCl and brine, and then dried over Na_2SO_4. The crude residue was purified by silica gel flash chromatography to afford the desired product.



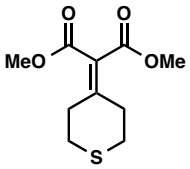
Dimethyl 2-cycloheptylidenemalonate (1a).

Colorless oil, 45% yield, R_f = 0.4 (15% EtOAc in hexanes), purified by silica gel flash chromatography (6% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.76 (s, 6H), 2.65 – 2.58 (m, 4H), 1.70 (dt, *J* = 4.3, 2.3 Hz, 4H), 1.55 – 1.51 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.1, 165.2, 123.4, 52.0, 34.1, 28.9, 26.6; IR (Neat Film, NaCl) 2926.3, 2856.8, 1729.0, 1622.0, 1435.3, 1275.5, 1234.1, 1194.3, 1169.8, 1150.3, 1103.5, 1074.1, 1037.7, 1023.5, 941.5, 749.6 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{12}H_{19}O_4$ $[M+H]^+$: 227.1283, found 227.1273.



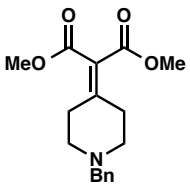
Dimethyl 2-(tetrahydro-4*H*-pyran-4-ylidene)malonate (1d).

Colorless oil, 42% yield R_f = 0.2 (15% EtOAc in hexanes), purified by silica gel flash chromatography (10% EtOAc in hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.80 – 3.76 (m, 10H), 2.68 (t, *J* = 5.5 Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.7, 156.4, 122.5, 68.3, 52.3, 33.0; IR (Neat Film, NaCl) 2955.2, 2914.9, 2849.5, 1726.3, 1639.6, 1634.0, 1435.2, 1382.8, 1357.7, 1295.0, 1259.1, 1242.4, 1205.3, 1097.7, 1061.6, 1031.0, 1005.6, 982.5, 947.1, 912.4, 838.8, 765.5 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{10}H_{14}O_5$ $[M+H]^+$: 215.0914, found 215.0907.



Dimethyl 2-(tetrahydro-4*H*-thiopyran-4-ylidene)malonate (1e).

Colorless oil, 83% yield R_f = 0.4 (25% Et_2O in hexanes), purified by silica gel flash chromatography (25% Et_2O in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.76 (d, *J* = 0.7 Hz, 6H), 2.96 – 2.83 (m, 4H), 2.83 – 2.70 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 158.5, 123.4, 52.4, 34.5, 30.8; IR (Neat Film, NaCl) 3000, 2951, 2915, 2841, 1725, 1633, 1434, 1321, 1294, 1256, 1228, 1203, 1168, 1060, 1031, 1007, 973, 942 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{10}H_{15}SO_4$ $[M+H]^+$: 231.0686, found 231.0684.



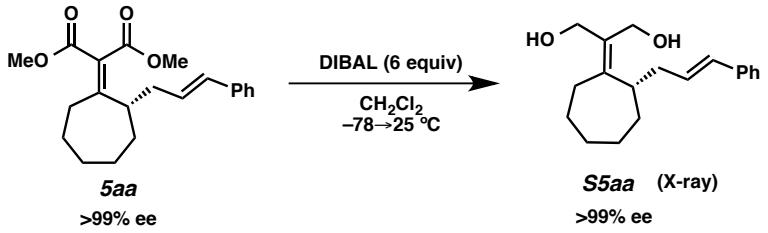
Dimethyl 2-(1-benzylpiperidin-4-ylidene)malonate (1f)

Yellow oil, 56% yield R_f = 0.2 (25% EtOAc in hexanes), purified by silica gel flash chromatography (25% EtOAc in hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.21 (m, 5H), 3.75 (s, 6H), 3.52 (s, 2H), 2.67 (d, *J* = 5.7 Hz, 4H), 2.56 (t, *J* = 5.6 Hz, 4H); ^{13}C

NMR (100 MHz, $CDCl_3$) δ 166.0, 158.9, 138.1, 129.2, 128.4, 127.3, 122.1, 62.5, 54.0, 52.3, 31.9. IR (Neat Film, NaCl) 2951, 1907, 2801, 2760, 1732, 1639, 1634, 1494, 1435, 1365, 1347, 1295, 1254, 1231, 1208, 1144, 1063, 1033, 997 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{17}H_{22}NO_4$ $[M+H]^+$: 304.1543, found 304.1545.

Determination of the Absolute Configuration of 5aa.

The absolute configuration of 5aa was assigned by the X-ray analysis of reduced product ***S5aa****.*

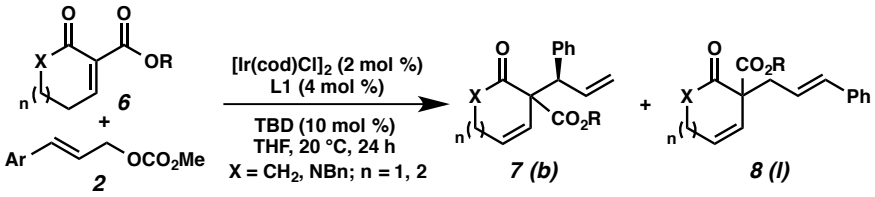


To a flame-dried flask was added malonate **5aa** (258.0 mg, 0.75 mmol) and CH_2Cl_2 (30 mL). The solution was cooled to –78 ºC and DIBAL (neat, 0.8 mL, 4.5 mmol, 6 equiv) was added slowly via syringe. The mixture was stirred at –78 ºC for 1 h and then room temperature overnight. The reaction was quenched with saturated Rochelle's salt at 0 ºC, and stirred until two clear phases were obtained. The aqueous layer was partitioned with 60 mL of EtOAc, and the combined organic phase was washed with brine, dried over Na_2SO_4, filtered and concentrated. The crude mixture was then filtered though a silica pad, and the resulting solid obtained was purified by recrystallization with Et_2O/hexanes, affording the desired product **S5aa** (163.2 mg, 76% yield) as colorless crystals. >99% ee, $[\alpha]_D^{25}$ –85.2 (*c* 1.31, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.28 (m, 4H), 7.25 – 7.14 (m, 1H), 6.36 (d, *J* = 15.9 Hz, 1H), 6.19 (dt, *J* = 15.8, 7.4 Hz, 1H), 4.51 – 4.27 (m, 4H), 2.92 – 2.85 (m, 1H), 2.53 (ddd, *J* = 12.6, 6.0, 1.9 Hz, 1H), 2.35 – 2.14 (m, 2H), 2.09 – 1.86 (m, 5H), 1.86 – 1.68 (m, 2H), 1.39 – 1.03 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.6, 137.5, 132.5, 131.4, 128.8, 128.7, 127.2, 126.1, 62.5, 61.8, 41.5, 40.0, 33.1, 31.1, 30.6, 26.8, 26.0; IR (Neat Film, NaCl) 3349, 2921, 2851, 1643, 1597, 1493, 1447, 1352, 1231, 1046, 998, 965, 745, 692 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{19}H_{25}O$ $[M–H_2O+H]^+$: 269.1900, found 269.1896;

SFC conditions: 20% IPA, 2.5 mL/min, Chiralpak IC column, λ = 254 nm, t_R (min): minor = 6.98, major = 8.97.

General Procedure for the Ir-Catalyzed Asymmetric Allylic Alkylation of Endocyclic α,β-Unsaturated β−Ketoesters

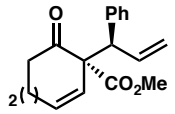
*Please note that the absolute configuration was determined only for the major isomer of compound **7ca** (vide infra). The absolute configuration for all other products 7 has been inferred by analogy. For respective SFC conditions, please refer to Table S2. Isolated yields are given in Scheme 4 (see manuscript).*



In a nitrogen-filled glove box, $[Ir(cod)Cl]_2$ (2.69 mg, 0.004 mmol, 2 mol %), ligand **L1** (3.71 mg, 0.008 mmol, 4 mol %), and TBD (2.78 mg, 0.02 mmol, 10 mol %) were added to a 2 dram scintillation vial equipped with a magnetic stirring bar. The vial was then charged with THF (1 mL) and stirred at 25 °C for 10 min. To a 20 mL scintillation vial was added α,β-unsaturated β–ketoester (0.4 mmol, 2.0 eq), cinnamyl carbonate **2a** (38.4 mg, 0.2 mmol, 1.0 equiv) and 1 mL of THF, then the above pre-formed catalyst solution was transferred to this vial. The vial was sealed and stirred at 25 °C for 1 day. The reaction mixture was filtered through a pad of silica gel, rinsed with hexane/ethyl acetate (5:1, v/v), and concentrated under reduced pressure. The residue was purified by silica gel flash chromatography and preparative HPLC.

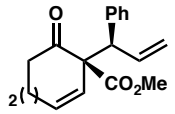
Methyl (*S*)-7-oxo-1-((*R*)-1-phenylallyl)cyclohept-2-ene-1-carboxylate (7aa) and methyl (*R*)-7-oxo-1-((*R*)-1-phenylallyl)cyclohept-2-ene-1-carboxylate (7aa').

Products **7aa** and **7aa'** were isolated by silica gel chromatography (3% EtOAc in hexanes) as a mixture of diastereomers (2:1), where were separated by preparative HPLC (3% EtOAc in hexanes).



7aa

The major diastereomer was isolated as a colorless oil, 95% ee, $[\alpha]_D^{25}$ –15.4 (*c* 1.79, $CHCl_3$); R_f = 0.2 (9% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.28 (m, 2H), 7.25 – 7.15 (m, 3H), 6.22 (ddd, *J* = 16.7, 10.3, 9.1 Hz, 1H), 6.04 – 5.91 (m, 2H), 5.15–5.04 (m, 2H), 4.39 (d, *J* = 9.1 Hz, 1H), 3.68 (s, 3H), 2.71 (dt, *J* = 12.6, 7.5 Hz, 1H), 2.28 (dt, *J* = 12.5, 6.2 Hz, 1H), 1.98 – 1.87 (m, 1H), 1.73 – 1.61 (m, 2H), 1.48 – 1.37 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.8, 170.4, 139.1, 137.0, 132.3, 130.5, 127.8, 127.0, 126.1, 117.8, 71.3, 54.3, 52.9, 40.4, 25.3, 22.9; IR (Neat Film, NaCl) 3030, 2948, 2359, 2341, 1738, 1716, 1493, 1453, 1433, 1296, 1226, 1194, 1123, 1056 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{18}H_{21}O_3$ $[M+H]^+$: 285.1491, found 285.1496; SFC conditions: 5% IPA, 2.5 mL/min, Chiralpak AD-H column, λ = 210 nm, t_R (min): minor = 4.99, major = 7.08.



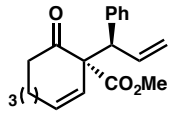
7aa'

The minor diastereomer was isolated as a colorless oil, 88% ee, $[\alpha]_D^{25}$ –75.1 (*c* 0.61, $CHCl_3$); R_f = 0.2 (9% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.16 (m, 5H), 6.20 (ddd, *J* = 17.0, 10.2, 8.4 Hz, 1H), 6.12 – 6.01 (m, 2H), 5.22 – 5.10 (m, 2H), 4.38 (d, *J* = 8.5 Hz, 1H), 3.50 (s, 3H), 2.79 (ddd, *J* = 12.7, 8.8, 7.2 Hz, 1H), 2.39 (ddd, *J* = 12.7, 6.5, 5.1 Hz, 1H), 2.16 – 1.98 (m, 2H), 1.96–1.85 (m, 1H), 1.85 – 1.71 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.7, 170.0, 139.5, 137.1, 131.7, 129.6, 128.2, 127.2, 126.2, 118.5, 70.6, 53.3, 52.7, 40.0, 25.2, 23.5; IR (Neat Film, NaCl) 3030, 2948, 1737, 1719, 1493, 1453, 1434, 1296, 1230, 1194, 1121 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{18}H_{21}O_3$

$[M+H]^+$: 285.1491, found 285.1498; SFC conditions: 5% IPA, 2.5 mL/min, Chiralpak AD-H column, λ = 210 nm, t_R (min): major = 5.62, minor = 7.98.

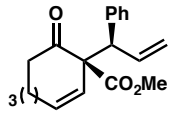
Methyl (*S*,*Z*)-8-oxo-1-((*R*)-1-phenylallyl)cyclooct-2-ene-1-carboxylate (7ba) and **methyl (*R*,*Z*)-8-oxo-1-((*R*)-1-phenylallyl)cyclooct-2-ene-1-carboxylate (7ba')**.

Products **7ba** and **7ba'** were isolated by silica gel chromatography (2% EtOAc in hexanes) as a mixture of diastereomers (3:1), where were separated by preparative HPLC (3% EtOAc in hexanes).



7ba

The major diastereomer was isolated as a colorless oil, 90% ee, $[\alpha]_D^{25}$ +59.3 (*c* 1.60, $CHCl_3$); R_f = 0.4 (9% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.38 (m, 2H), 7.24 – 7.18 (m, 2H), 7.18 – 7.11 (m, 1H), 6.15 (dt, *J* = 16.8, 10.1 Hz, 1H), 6.08 (dd, *J* = 11.4, 1.0 Hz, 1H), 5.87 – 5.76 (m, 1H), 5.14 – 5.03 (m, 2H), 4.46 (d, *J* = 10.1 Hz, 1H), 3.68 (s, 3H), 2.63 – 2.52 (m, 1H), 2.23 – 2.13 (m, 1H), 1.80 – 1.69 (m, 2H), 1.49 – 1.37 (m, 2H), 1.20 – 1.07 (m, 1H), 0.66 – 0.55 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.5, 169.8, 139.1, 137.4, 135.4, 131.0, 127.5, 126.7, 124.7, 117.2, 70.8, 53.7, 53.0, 39.0, 27.6, 25.4, 24.8; IR (Neat Film, NaCl) 3029, 2931, 2859, 1740, 1712, 1492, 1453, 1432, 1331, 1224, 1176, 1123, 1061 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{19}H_{23}O_3$ $[M+H]^+$: 299.1647, found 299.1645; SFC conditions: 5% IPA, 2.5 mL/min, Chiralpak IA column, λ = 210 nm, t_R (min): minor = 4.52, major = 6.36.



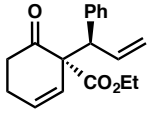
7ba'

The minor diastereomer was isolated as a colorless oil, 77% ee, $[\alpha]_D^{25}$ –114.2 (*c* 0.52, $CHCl_3$); R_f = 0.4 (9% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 – 7.15 (m, 5H), 6.17 – 6.02 (m, 2H), 6.01 – 5.91 (m, 1H), 5.29 (ddd, *J* = 17.0, 1.9, 0.9 Hz, 1H), 5.11 (ddd, *J* = 10.1, 1.8, 0.7 Hz, 1H), 4.43 (d, *J* = 8.9 Hz, 1H), 3.49 (s, 3H), 2.66 (td, *J* = 12.2, 2.5 Hz, 1H), 2.25 (ddd, *J* = 12.3, 7.0, 2.6 Hz, 1H), 2.05 – 1.81 (m, 3H), 1.74 – 1.53 (m,

2H), 1.31 – 1.21 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.2, 169.5, 140.0, 137.0, 134.0, 129.3, 128.3, 127.1, 124.9, 118.1, 69.5, 52.8, 52.7, 39.2, 27.6, 26.0, 25.3; IR (Neat Film, NaCl) 3028, 2931, 2859, 1740, 1715, 1491, 1453, 1432, 1228, 1177, 1432, 1228, 1177, 1133, 1059 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{19}H_{23}O_3$ $[M+H]^+$: 299.1647, found 299.1654; SFC conditions: 5% IPA, 2.5 mL/min, Chiralpak IA column, λ = 210 nm, t_R (min): major = 5.79, minor = 7.41.

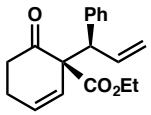
Ethyl (*S*)-6-oxo-1-((*R*)-1-phenylallyl)cyclohex-2-ene-1-carboxylate (7ca) and Ethyl (*R*)-6-oxo-1-((*R*)-1-phenylallyl)cyclohex-2-ene-1-carboxylate (7ca').

Products **7ca** and **7ca'** were isolated by silica gel chromatography (3% EtOAc in hexanes) as a mixture of diastereomers (5:1), where were separated by preparative HPLC (4% EtOAc in hexanes).



7ca

The major diastereomer was isolated as a colorless oil, 98% ee, $[\alpha]_D^{25}$ –35.8 (*c* 0.71, $CHCl_3$); R_f = 0.2 (9% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 – 7.14 (m, 5H), 6.25 – 6.16 (m, 1H), 6.17 – 6.11 (m, 1H), 6.05 (ddd, *J* = 10.1, 1.9, 1.3 Hz, 1H), 5.23 – 5.10 (m, 2H), 4.49 (dt, *J* = 8.2, 1.2 Hz, 1H), 4.16 (qd, *J* = 7.1, 2.2 Hz, 2H), 2.37 – 2.23 (m, 2H), 1.94 – 1.76 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.9, 169.3, 138.8, 136.4, 130.5, 130.3, 128.1, 127.1, 126.1, 118.5, 65.6, 62.0, 54.4, 38.3, 24.5, 14.2; IR (Neat Film, NaCl) 3033, 2980, 1743, 1719, 1493, 1454, 1416, 1391, 1365, 1342, 1299, 1213, 1165, 1130, 1096, 1044, 1016 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{18}H_{21}O_3$ $[M+H]^+$: 285.1485, found 285.1482; SFC conditions: 2% IPA, 3.0 mL/min, Chiralpak IA column, λ = 210 nm, t_R (min): minor = 6.82, major = 13.26.



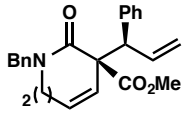
7ca'

The minor diastereomer was isolated as a colorless oil, 91% ee, $[\alpha]_D^{25}$ +28.9 (*c* 0.30, $CHCl_3$); R_f = 0.2 (9% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.16 (m,

5H), 6.29 – 6.18 (m, 1H), 6.15 – 6.07 (m, 1H), 5.94 (ddd, *J* = 10.0, 2.4, 1.0 Hz, 1H), 5.15 – 5.07 (m, 2H), 4.34 (d, *J* = 9.0 Hz, 1H), 4.03 (q, *J* = 7.1 Hz, 2H), 2.60 – 2.49 (m, 1H), 2.47 – 2.34 (m, 2H), 2.29–2.17 (m, 1H), 1.14 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.6, 169.2, 139.2, 136.8, 130.0, 129.7, 128.2, 127.4, 127.2, 118.2, 65.0, 61.9, 54.5, 39.2, 24.8, 14.0; IR (Neat Film, NaCl) 3032, 2980, 2931, 1736, 1719, 1637, 1601, 1493, 1453, 1444, 1419, 1389, 1365, 1342, 1298, 1218, 1166, 1118, 1097, 1045, 1018 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{18}H_{21}O_3$ $[M+H]^+$: 285.1485, found 285.1480; SFC conditions: 2% IPA, 3.0 mL/min, Chiralpak IA column, λ = 210 nm, t_R (min): major = 6.95, minor = 11.43.

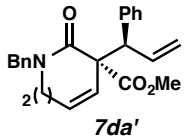
Methyl (*R*)-1-benzyl-2-oxo-3-((*R*)-1-phenylallyl)-2,3,6,7-tetrahydro-1*H*-azepine-3-carboxylate (7da) and methyl (*S*)-1-benzyl-2-oxo-3-((*R*)-1-phenylallyl)-2,3,6,7-tetrahydro-1*H*-azepine-3-carboxylate (7da').

Products **7da** and **7da'** were isolated by silica gel chromatography (3% EtOAc in hexanes) as a mixture of diastereomers (2:1), where were separated by preparative HPLC (12% EtOAc in hexanes).



7da

The major diastereomer was isolated as a colorless oil, 79% ee, $[\alpha]_D^{25}$ –14.6 (*c* 0.19, $CHCl_3$); R_f = 0.4 (25% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.19 (m, 10H), 6.27 (ddd, *J* = 17.3, 10.6, 5.4 Hz, 1H), 5.99 – 5.90 (m, 2H), 5.24 (dt, *J* = 10.6, 1.7 Hz, 1H), 5.09 (d, *J* = 14.9 Hz, 1H), 5.02 (dt, *J* = 17.3, 1.7 Hz, 1H), 4.74 (dt, *J* = 5.4, 1.9 Hz, 1H), 4.34 (d, *J* = 14.9 Hz, 1H), 3.54 – 3.44 (m, 1H), 3.39 (s, 3H), 3.09 – 3.00 (m, 1H), 2.26 – 2.07 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.7, 170.7, 139.3, 138.9, 137.7, 132.0, 130.4, 128.7, 128.3, 127.9, 127.5, 127.4, 124.7, 118.1, 62.3, 54.7, 52.4, 51.4, 44.0, 28.3; IR (Neat Film, NaCl) 3029, 2048, 1737, 1728, 1656, 1652, 1495, 1480, 1431, 1416, 1357, 1242, 1227, 1164, 1045,1001 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{24}H_{26}NO_3$ $[M+H]^+$: 376.1907, found 376.1917; SFC conditions: 10% MeCN, 2.5 mL/min, Chiralcel OD-H column, λ = 210 nm, t_R (min): minor = 13.74, major = 16.85.

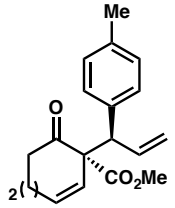


7da'

The minor diastereomer was isolated as a colorless oil, 62% ee, $[\alpha]_D^{25}$ –42.3 (*c* 0.12, $CHCl_3$); R_f = 0.4 (25% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 – 7.42 (m, 2H), 7.36 – 7.16 (m, 8H), 6.40 (ddd, *J* = 16.9, 10.1, 9.1 Hz, 1H), 5.88 (dddd, *J* = 11.8, 4.7, 3.1, 1.3 Hz, 1H), 5.73 (dt, *J* = 11.9, 2.2 Hz, 1H), 5.23 – 5.05 (m, 2H), 4.99 (d, *J* = 14.8 Hz, 1H), 4.45 (d, *J* = 9.1 Hz, 1H), 4.32 (d, *J* = 14.9 Hz, 1H), 3.63 (s, 3H), 3.51 – 3.42 (m, 1H), 3.10 – 3.02 (m, 1H), 2.22 – 2.04 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.0, 170.3, 140.2, 137.7, 137.7, 131.1, 130.3, 128.7, 128.0, 127.9, 127.5, 126.7, 126.2, 118.2, 63.1, 56.6, 52.7, 51.4, 44.2, 28.2; IR (Neat Film, NaCl) 3028, 2948, 1732, 1656, 1652, 1495, 1480, 1429, 1417, 1357, 1241, 1226, 1163, 1044, 1002 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{24}H_{26}NO_3$ $[M+H]^+$: 376.1907, found 376.1915; SFC conditions: 10% MeCN, 2.5 mL/min, Chiralcel OD-H column, λ = 210 nm, t_R (min): major = 12.34, minor = 15.02.

Methyl (*S*)-7-oxo-1-((*R*)-1-(*p*-tolyl)allyl)cyclohept-2-ene-1-carboxylate (7ab) and methyl (*R*)-7-oxo-1-((*R*)-1-(*p*-tolyl)allyl)cyclohept-2-ene-1-carboxylate (7ab').

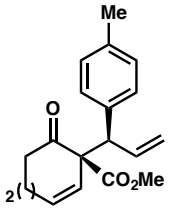
Products **7ab** and **7ab'** were isolated by silica gel chromatography (2% EtOAc in hexanes) as a mixture of diastereomers (1.2:1), where were separated by preparative HPLC (3% EtOAc in hexanes).



7ab

The major diastereomer was isolated as a colorless oil, 95% ee, $[\alpha]_D^{25}$ –17.5 (*c* 0.195, $CHCl_3$); R_f = 0.3 (9% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 (d, *J* = 8.1 Hz, 2H), 7.03 (d, *J* = 7.7 Hz, 2H), 6.21 (ddd, *J* = 16.7, 10.4, 9.1 Hz, 1H), 6.00 – 5.90 (m, 2H), 5.13 – 5.04 (m, 2H), 4.33 (d, *J* = 9.0 Hz, 1H), 3.69 (s, 3H), 2.71 (dt, *J* = 12.7, 7.3 Hz, 1H), 2.36 – 2.25 (m, 4H), 2.01 – 1.89 (m, 1H), 1.73 – 1.62 (m, 2H), 1.56 – 1.43 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.9, 170.5, 137.2, 136.6, 136.1, 132.3, 130.2,

128.6, 126.2, 117.6, 71.1, 54.0, 52.9, 40.6, 25.6, 22.9, 21.2; IR (Neat Film, NaCl) 2948, 1738, 1716, 1514, 1435, 1225, 1123 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{19}H_{23}O_3$ $[M+H]^+$: 299.1647, found 299.1655; SFC conditions: 8% IPA, 2.5 mL/min, Chiralpak AD-H column, λ = 210 nm, t_R (min): minor = 4.13, major = 4.50.

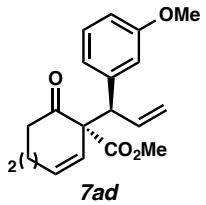


7ab'

The minor diastereomer was isolated as a colorless oil, 91% ee, $[\alpha]_D^{25}$ –76.0 (*c* 0.17, $CHCl_3$); R_f = 0.3 (9% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.13 – 7.00 (m, 4H), 6.17 (ddd, *J* = 17.0, 10.2, 8.5 Hz, 1H), 6.11 – 6.00 (m, 2H), 5.17 (ddd, *J* = 17.0, 1.8, 1.0 Hz, 1H), 5.12 (ddd, *J* = 10.2, 1.8, 0.8 Hz, 1H), 4.35 (d, *J* = 8.5 Hz, 1H), 3.52 (s, 3H), 2.79 (ddd, *J* = 12.7, 8.7, 7.1 Hz, 1H), 2.39 (ddd, *J* = 12.6, 6.4, 5.2 Hz, 1H), 2.30 (s, 3H), 2.17 – 2.00 (m, 2H), 1.96 – 1.85 (m, 1H), 1.85 – 1.73 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.8, 170.0, 137.2, 136.7, 136.4, 131.6, 129.3, 129.0, 126.3, 118.2, 70.6, 52.9, 52.7, 40.0, 25.2, 23.5, 21.2; IR (Neat Film, NaCl) 2948, 1736, 1720, 1716, 1513, 1435, 1230, 1194, 1123 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{19}H_{23}O_3$ $[M+H]^+$: 299.1647, found 299.1640; SFC conditions: 10% IPA, 2.5 mL/min, Chiralpak AD-H column, λ = 210 nm, t_R (min): minor = 3.43, major = 4.49.

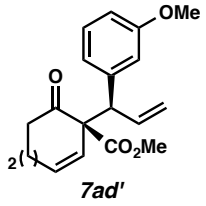
Methyl (*S*)-1-((*R*)-1-(3-methoxyphenyl)allyl)-7-oxocyclohept-2-ene-1-carboxylate (7ad) and methyl (*R*)-1-((*R*)-1-(3-methoxyphenyl)allyl)-7-oxocyclohept-2-ene-1-carboxylate (7ad')

Products **7ba** and **7ba'** were isolated by silica gel chromatography (2% EtOAc in hexanes) as a mixture of diastereomers (2:1), where were separated by preparative HPLC (7% EtOAc in hexanes).



7ad

The major diastereomer was isolated as a colorless oil, 91% ee, $[\alpha]_D^{25}$ –14.9 (*c* 0.29, $CHCl_3$); R_f = 0.3 (17% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.14 (t, *J* = 8.1 Hz, 1H), 6.93 – 6.87 (m, 2H), 6.74 (ddd, *J* = 8.2, 2.5, 1.1 Hz, 1H), 6.26 – 6.14 (m, 1H), 6.02 – 5.91 (m, 2H), 5.15 – 5.06 (m, 2H), 4.35 (d, *J* = 9.1 Hz, 1H), 3.78 (s, 3H), 3.69 (s, 3H), 2.71 (dt, *J* = 12.7, 7.3 Hz, 1H), 2.30 (dt, *J* = 12.6, 6.2 Hz, 1H), 2.04 – 1.92 (m, 1H), 1.74 – 1.63 (m, 2H), 1.56 – 1.47 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.7, 170.4, 159.0, 140.7, 136.9, 132.3, 128.8, 126.2, 122.8, 117.9, 116.2, 112.4, 71.1, 55.3, 54.4, 52.9, 40.5, 25.6, 22.8; IR (Neat Film, NaCl) 2949, 1738, 1716, 1599, 1583, 1489, 1455, 1435, 1225, 1050 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{19}H_{23}O_4$ $[M+H]^+$: 315.1596, found 315.1592; SFC conditions: 8% IPA, 2.5 mL/min, Chiralpak AD-H column, λ = 210 nm, t_R (min): minor = 4.28, major = 4.75.

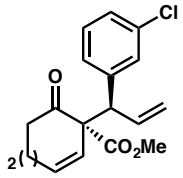


7ad'

The minor diastereomer was isolated as a colorless oil, 81% ee, $[\alpha]_D^{25}$ –64.5 (*c* 0.135, $CHCl_3$); R_f = 0.3 (17% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17 (t, *J* = 7.9 Hz, 1H), 6.84 – 6.71 (m, 3H), 6.15 (ddd, *J* = 17.0, 10.2, 8.6 Hz, 1H), 6.11 – 6.02 (m, 2H), 5.21 (ddd, *J* = 17.1, 1.8, 1.0 Hz, 1H), 5.13 (ddd, *J* = 10.2, 1.7, 0.8 Hz, 1H), 4.37 (d, *J* = 8.6 Hz, 1H), 3.78 (s, 3H), 3.53 (s, 3H), 2.79 (ddd, *J* = 12.5, 8.8, 7.3 Hz, 1H), 2.39 (ddd, *J* = 12.4, 6.6, 4.9 Hz, 1H), 2.17 – 2.01 (m, 2H), 1.98 – 1.86 (m, 1H), 1.86 – 1.72 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.7, 169.9, 159.3, 141.1, 136.8, 131.5, 129.2, 126.3, 121.8, 118.5, 115.6, 112.3, 70.7, 55.3, 53.2, 52.7, 39.8, 25.1, 23.6; IR (Neat Film, NaCl) 2949, 1735, 1719, 1599, 1583, 1491, 1453, 1434, 1230, 1049 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{19}H_{23}O_4$ $[M+H]^+$: 315.1596, found 315.1603; SFC conditions: 10% IPA, 2.5 mL/min, Chiralpak IC column, λ = 210 nm, t_R (min): minor = 5.40, major = 5.99.

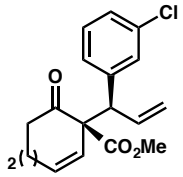
Methyl (*S*)-1-((*R*)-1-(3-chlorophenyl)allyl)-7-oxocyclohept-2-ene-1-carboxylate (7ae) and methyl (*R*)-1-((*R*)-1-(3-chlorophenyl)allyl)-7-oxocyclohept-2-ene-1-carboxylate (7ae')

Products **7ae** and **7ae'** were isolated by silica gel chromatography (2% EtOAc in hexanes) as a mixture of diastereomers (3:1), where were separated by preparative HPLC (3.5% EtOAc in hexanes).



7ae

The major diastereomer was isolated as a colorless oil, 91% ee, $[\alpha]_D^{25}$ –4.9 (*c* 0.325, $CHCl_3$); R_f = 0.4 (17% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.28 (m, 1H), 7.25 – 7.20 (m, 1H), 7.18 – 7.14 (m, 2H), 6.15 (ddd, *J* = 16.8, 10.2, 9.2 Hz, 1H), 6.05–5.93 (m, 2H), 5.16 – 5.06 (m, 2H), 4.35 (d, *J* = 9.2 Hz, 1H), 3.69 (s, 3H), 2.74 (ddd, *J* = 12.6, 8.0, 7.4 Hz, 1H), 2.31 (dt, *J* = 12.5, 6.0 Hz, 1H), 2.01 – 1.87 (m, 1H), 1.75 – 1.63 (m, 2H), 1.48 – 1.35 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.5, 170.1, 141.3, 136.3, 133.5, 132.6, 130.4, 129.0, 128.8, 127.1, 125.8, 118.4, 71.2, 53.8, 53.0, 40.2, 25.2, 22.9; IR (Neat Film, NaCl) 2949, 1738, 1716, 1594, 1571, 1432, 1228, 1195, 1123, 1094 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{18}H_{20}O_3Cl$ $[M+H]^+$: 319.1101, found 319.1112; SFC conditions: 7% IPA, 2.5 mL/min, Chiralpak AD-H column, λ = 210 nm, t_R (min): minor = 4.14, major = 4.85.



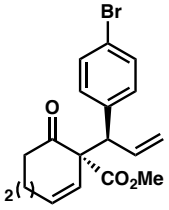
7ae'

The minor diastereomer was isolated as a colorless oil, 75% ee, $[\alpha]_D^{25}$ –56.2 (*c* 0.105, $CHCl_3$); R_f = 0.4 (17% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 – 7.15 (m, 3H), 7.15 – 7.08 (m, 1H), 6.15 (ddd, *J* = 17.0, 10.2, 8.6 Hz, 1H), 6.09 (ddd, *J* = 11.4, 7.2, 5.5 Hz, 1H), 5.99 (dd, *J* = 11.5, 2.1 Hz, 1H), 5.23 – 5.13 (m, 2H), 4.34 (d, *J* = 8.6 Hz, 1H), 3.55 (s, 3H), 2.80 (ddd, *J* = 12.6, 8.8, 7.2 Hz, 1H), 2.40 (ddd, *J* = 12.7, 6.5, 5.0 Hz,

1H), 2.17 – 2.08 (m, 1H), 2.08 – 1.97 (m, 1H), 1.97 – 1.86 (m, 1H), 1.86 – 1.73 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.3, 169.9, 141.7, 136.4, 133.9, 132.1, 129.7, 129.4, 127.7, 127.4, 125.8, 119.0, 70.4, 53.0, 52.8, 39.9, 25.2, 23.4; IR (Neat Film, NaCl) 2949, 1738, 1720, 1594, 1571, 1476, 1455, 1432, 1231, 1194, 1121, 1095 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{18}H_{20}O_3Cl$ $[M+H]^+$: 319.1101, found 319.1089; SFC conditions: 7% IPA, 2.5 mL/min, Chiralpak AD-H column, λ = 210 nm, t_R (min): major = 4.67, minor = 5.28.

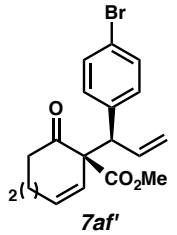
Methyl (*S*)-1-((*R*)-1-(4-bromophenyl)allyl)-7-oxocyclohept-2-ene-1-carboxylate (7af) and methyl (*R*)-1-((*R*)-1-(4-bromophenyl)allyl)-7-oxocyclohept-2-ene-1-carboxylate (7af')

Products **7af** and **7af'** were isolated by silica gel chromatography (2% EtOAc in hexanes) as a mixture of diastereomers (2:1), where were separated by preparative HPLC (4% EtOAc in hexanes).



7af

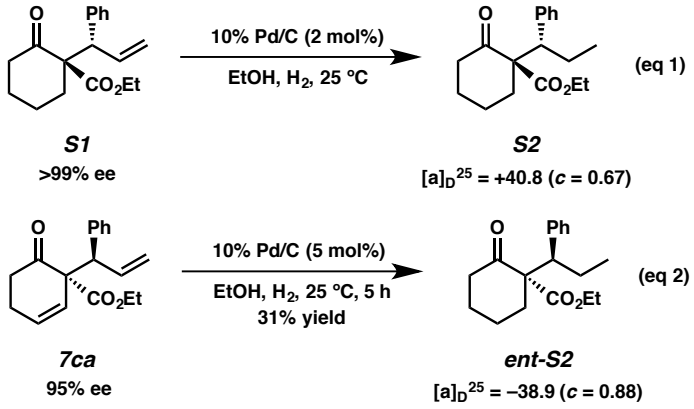
The major diastereomer was isolated as a colorless oil, 88% ee, $[\alpha]_D^{25}$ –20.4 (*c* 0.31, $CHCl_3$); R_f = 0.3 (9% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.5 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 6.14 (ddd, *J* = 16.8, 10.2, 9.2 Hz, 1H), 6.03 – 5.93 (m, 2H), 5.15 – 5.04 (m, 2H), 4.36 (d, *J* = 9.2 Hz, 1H), 3.68 (s, 3H), 2.73 (ddd, *J* = 12.5, 8.1, 7.4 Hz, 1H), 2.29 (dt, *J* = 12.5, 5.9 Hz, 1H), 1.98 – 1.86 (m, 1H), 1.76 – 1.63 (m, 2H), 1.47 – 1.33 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.7, 170.1, 138.3, 136.4, 132.5, 132.2, 130.9, 125.9, 121.0, 118.2, 71.3, 53.5, 53.0, 40.06, 25.2, 23.1; IR (Neat Film, NaCl) 2948, 1738, 1720, 1716, 1487, 1432, 1227, 1194, 1010 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{18}H_{20}BrO_3$ $[M+H]^+$: 363.0596, found 363.0588; SFC conditions: 10% IPA, 2.5 mL/min, Chiralpak AD-H column, λ = 210 nm, t_R (min): minor = 4.68, major = 5.17.



The minor diastereomer was isolated as a colorless oil, 79% ee, $[\alpha]_D^{25}$ –76.3 (*c* 0.16, $CHCl_3$); R_f = 0.3 (9% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.5 Hz, 2H), 7.11 (d, *J* = 8.4 Hz, 2H), 6.22 – 6.11 (m, 1H), 6.06 (ddd, *J* = 11.4, 7.2, 5.4 Hz, 1H), 5.97 (dd, *J* = 11.5, 2.1 Hz, 1H), 5.19 – 5.10 (m, 2H), 4.30 (d, *J* = 8.5 Hz, 1H), 3.54 (s, 3H), 2.80 (ddd, *J* = 12.7, 8.7, 7.1 Hz, 1H), 2.40 (ddd, *J* = 12.7, 6.4, 5.2 Hz, 1H), 2.17 – 2.07 (m, 1H), 2.04 – 1.94 (m, 1H), 1.94 – 1.85 (m, 1H), 1.84 – 1.73 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.5, 170.0, 138.6, 136.6, 132.1, 131.4, 131.3, 125.9, 121.2, 118.8, 70.4, 52.9, 52.8, 40.0, 25.3, 23.3; IR (Neat Film, NaCl) 2948, 1737, 1716, 1488, 1230, 1194, 1075, 1010 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{18}H_{20}BrO_3$ $[M+H]^+$: 363.0596, found 363.0604; SFC conditions: 10% IPA, 2.5 mL/min, Chiralpak IC column, λ = 210 nm, t_R (min): minor = 4.43, major = 5.01.

Determination of the Absolute Configuration of 7ca.

*The absolute configuration of **7ca** was determined by comparing the optical rotation of its derivative with compound **S2** obtained from the previously known compound **S1**.*[5]



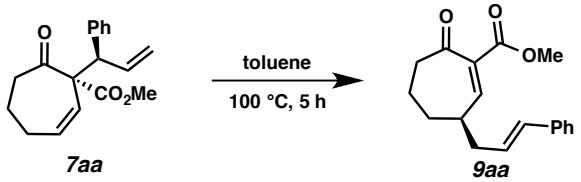
General procedure for the Pd/C-catalyzed hydrogenation (for eq 1): To a round bottom flask was added ethyl (*R*)-2-oxo-1-((*S*)-1-phenylallyl)cyclohexane-1-carboxylate **S1** (42.0 mg, >99% ee, 0.15 mmol), 10% Pd/C (2.9 mg, 2 mol%) and EtOH (4 mL). A hydrogen

balloon was then connected via a three-way stopcock. The flask was vacuumed/purged with H_2 quickly three times, then stirred for 2 h at room temperature. The mixture was filtered through a silica pad and the desired product **S2** (25.0 mg, 59% yield) was obtained as a colorless oil after purification by silica gel flash chromatography (1→5% EtOAc in hexanes). R_f = 0.4 (5% EtOAc in hexanes); $[a]_D^{25}$ +40.84 (*c* 0.67, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.23 (m, 2H), 7.23 – 7.18 (m, 1H), 7.18 – 7.12 (m, 2H), 4.21 (qd, *J* = 7.1, 2.2 Hz, 2H), 3.12 (dd, *J* = 12.1, 2.8 Hz, 1H), 2.54 – 2.39 (m, 2H), 1.95 (ddq, *J* = 19.7, 9.0, 3.1 Hz, 2H), 1.91 – 1.82 (m, 1H), 1.70 – 1.61 (m, 1H), 1.61 – 1.47 (m, 3H), 1.36 – 1.30 (m, 1H), 1.27 (t, *J* = 7.1 Hz, 3H), 0.69 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.9, 171.4, 139.9, 130.4, 127.9, 126.8, 64.6, 61.2, 51.3, 41.9, 36.9, 28.0, 24.7, 22.9, 14.2, 13.0. IR (Neat Film NaCl) 3026, 2961, 2935, 2870, 1712, 1495, 1451, 1368, 1308, 1269, 1233, 1194, 1138, 1090, 1025, 908, 865, 812, 759 cm^{-1}; HRMS (ESI) calc'd for $C_{18}H_{25}O_3$ $[M+H]^+$: 289.1798, found 289.1798.

For eq 2: Followed the same procedure as eq 1. The reaction was conducted with **7ba** (76.4 mg, 0.27 mmol), 10% Pd/C (14.3 mg, 5 mol%) and EtOH (5 mL). The desired hydrogenation product was obtained in 31% yield (24.0 mg) with the same ^1H NMR spectrum and opposite optical rotation when compared to **S2**.

General Procedure for the Cope Rearrangment of β−Ketoesters 7.

A solution of compound **7** in toluene (0.1 M) was heated at 100 °C for five hours. After cooling to room temperature, the reaction mixture was concentrated *in vacuo*. The residue was purified by silica gel flash chromatography to afford the desired product **9**.



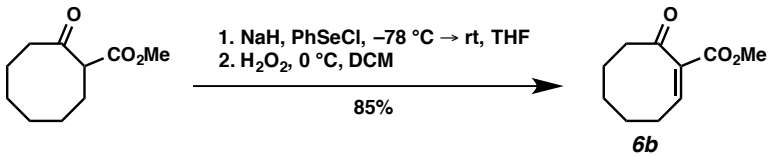
7aa *9aa*

Methyl (*R*)-3-cinnamyl-7-oxocyclohept-1-ene-1-carboxylate (9aa)

9aa was isolated by silica gel chromatography (3→9→17% EtOAc in hexanes, 72% yield) as a colorless oil. $[\alpha]_D^{25}$ –23.6 (*c* 0.49, $CHCl_3$); 95% ee; R_f = 0.4 (25% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.28 (m, 4H), 7.27 – 7.18 (m, 2H), 6.46 (d, *J* = 15.8 Hz, 1H), 6.15 (dt, *J* = 15.7, 7.2 Hz, 1H), 3.77 (s, 3H), 2.74 – 2.57 (m, 3H), 2.54 – 2.34 (m, 2H), 2.00 – 1.80 (m, 3H), 1.56 – 1.48 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.0, 165.5, 151.9, 137.2, 135.4, 133.1, 128.7, 127.6, 126.8, 126.3, 52.5, 43.3, 39.6, 39.1, 30.2, 21.5; IR (Neat Film, NaCl) 3024, 2929, 2858, 1722, 1716, 1495, 1435, 1377, 1256, 1202, 1027 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{18}H_{21}O_3$ $[M+H]^+$: 285.1491, found 285.1491; SFC conditions: 10% IPA, 2.5 mL/min, Chiralcel OB-H column, λ = 210 nm, t_R (min): major = 13.72, minor = 15.18.

Synthesis of Endocyclic α,β-Unsaturated β–Ketoesters.

The α,β-unsaturated β–ketoesters **6a**[6] and **6c**[7] were prepared following literature procedures.

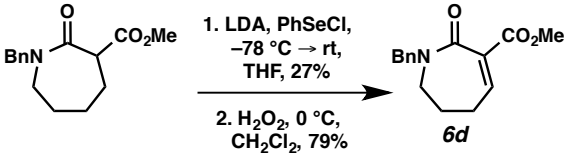


6b

Methyl (*E*)-8-oxocyclooct-1-ene-1-carboxylate (6b)

Following a modified literature procedure,[8] NaH (60% in mineral oil, 440 mg, 1.1 equiv) was added to a 250 mL round bottom flask and flushed with N_2. THF (27 mL) was then added, and the resulting suspension cooled to 0 °C. A solution of methyl 2-oxocyclooctane-1-carboxylate[9] (1.84 g, 10 mmol) in THF (5 mL) was added slowly at 0 °C, and then the reaction mixture was warmed to room temperature. After stirring for 1 h, the enolate solution was cooled to –78 °C and a solution of PhSeCl (2.01 g, 1.05 equiv) in THF (8 mL) was added. After stirring for 1 h at –78 °C, the reaction mixture was warmed to room temperature and stirred for an additional 1 h. Upon completion, the solution was diluted with Et_2O and washed twice with 1 M HCl, followed by brine. The organic layer was dried over Na_2SO_4 and concentrated. The crude product was dissolved in CH_2Cl_2 (100 mL), cooled to 0 °C, and treated with a solution of H_2O_2 (35% in water, 1.84 mL, 2.1 equiv) dropwise over 30 min. After stirring for an additional 1 h, water was added and the aqueous layer extracted with CH_2Cl_2. The combined organic layers were

washed with saturated $NaHCO_3$, water, brine and dried with Na_2SO_4. The crude product was purified by silica gel flash chromatography (5→9% EtOAc in hexanes) to provide **6b** as a colorless oil (1.54 g, 85%). R_f = 0.3 (17% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (t, *J* = 4.7 Hz, 1H), 3.73 (s, 3H), 2.60 – 2.53 (m, 2H), 2.43 – 2.36 (m, 2H), 1.94 – 1.85 (m, 2H), 1.73 – 1.61 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 209.2, 165.0, 147.3, 131.3, 52.4, 44.6, 30.4, 29.3, 22.2, 21.8; IR (Neat Film, NaCl) 2946, 1719, 1696, 1638, 1434, 1411, 1376, 1266, 1237, 1219, 1157, 1068 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{10}H_{14}O_3$ $[M+H]^+$: 183.1021, found 183.1029.

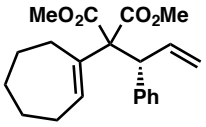
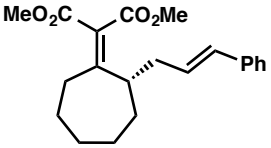
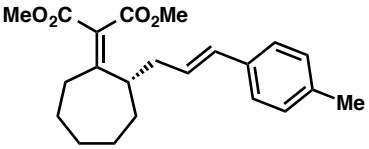
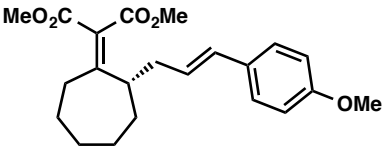
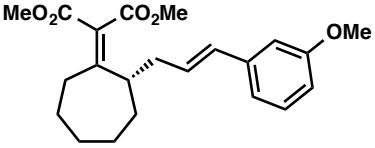
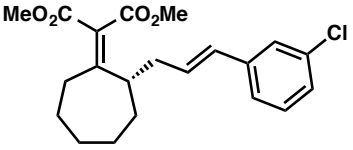


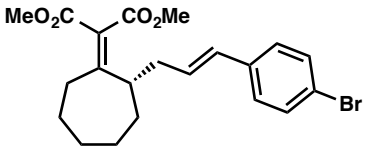
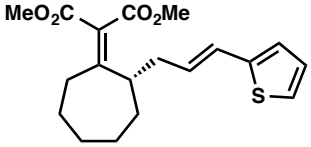
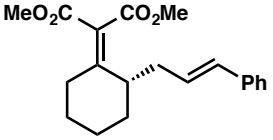
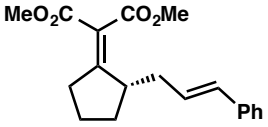
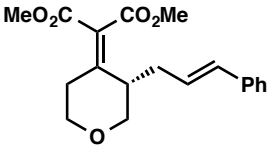
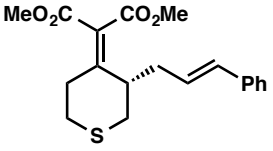
Methyl 1-benzyl-2-oxo-2,5,6,7-tetrahydro-1*H*-azepine-3-carboxylate (6d)

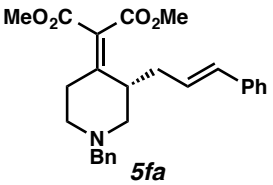
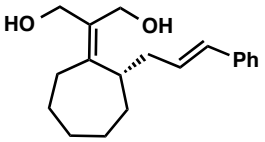
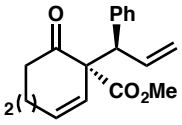
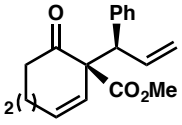
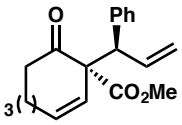
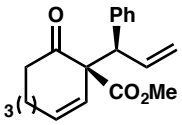
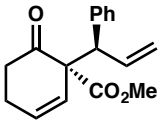
To a solution of LDA [1.2 equiv, prepared fresh from diisopropylamine (513 μL) and *n*-BuLi, (2.5 M in hexanes, 1.46 mL) in THF (10 mL) at 0 °C for 15 min] was added dropwise a solution of methyl 1-benzyl-2-oxoazepane-3-carboxylate (798 mg, 3.05 mmol) in THF (3 mL) at –78 °C and the resulting mixture was stirred for 1 h at –78 °C. A solution of PhSeCl (615 mg, 1.05 equiv) in THF (3 mL) was then added, and the mixture was slowly warmed to room temperature. The mixture was diluted with ethyl acetate, washed twice with 1 M HCl, followed by brine, and dried over Na_2SO_4. The crude mixture was purified by silica gel flash chromatography (9→17→20% EtOAc in hexanes) to provide methyl 1-benzyl-2-oxo-3-(phenylselanyl)azepane-3-carboxylate as a yellow oil (343 mg, 27%). The isolated compound was carried forward without complete characterization by dissolving in CH_2Cl_2 (8 mL) and cooling to 0 °C. A solution of H_2O_2 (35% in water, 145 μL, 2.1 equiv) was added dropwise over 30 min. After stirring for an additional 1 h, water was added and the aqueous later extracted with CH_2Cl_2. The combined organic layers were washed with saturated $NaHCO_3$, water, brine and dried with Na_2SO_4. The crude product was purified by silica gel flash chromatography (25→50% EtOAc in hexanes) to provide **9** as a pale yellow oil (170 mg, 79%). R_f = 0.3 (50% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.27 (m, 6H), 4.72 (s, 2H), 3.83 (s, 3H), 3.30 (t, *J* = 6.3 Hz, 2H), 2.26 (q, *J* = 7.4 Hz, 2H), 1.74 – 1.64 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.5, 165.1, 143.8, 138.0, 132.4, 128.9, 128.5, 127.8, 52.5,

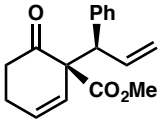
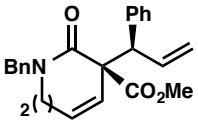
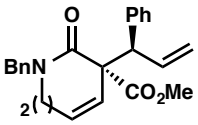
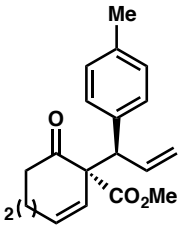
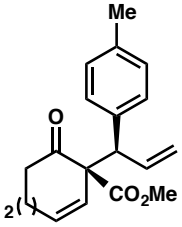
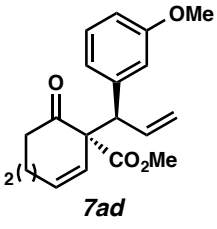
49.8, 45.4, 27.9, 23.7; IR (Neat Film, NaCl) 3493, 3029, 2952, 1721, 1650, 1621, 1471, 1435, 1359, 1274, 1251, 1193, 1159, 1103, 1067, 1053 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{15}H_{18}NO_3$ $[M+H]^+$: 260.1281, found 260.1285.

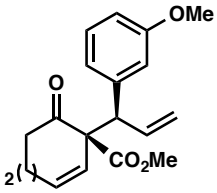
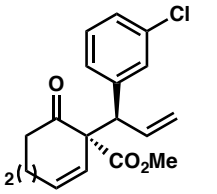
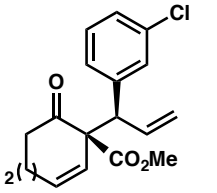
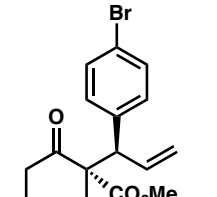
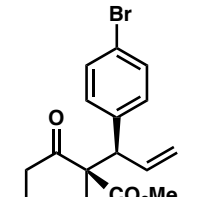
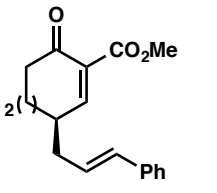
Table S2. Determination of Enantiomeric Excess

entry	compound	SFC analytic conditions	ee (%)
1	 ***3aa***	Chiralpak AD-H, λ = 210 nm 2% IPA/CO_2, 2.5 mL/min t_R (min) minor 7.34, major 8.12	>99
2	 ***5aa***	Chiralpak AD-H, λ = 254 nm 10% IPA/CO_2, 2.5 mL/min t_R (min) major 4.55, minor 4.88	96
3	 ***5ab***	Chiralpak IC, λ = 254 nm 5% IPA/CO_2, 2.5 mL/min t_R (min) major 7.54, minor 10.52	96
4	 ***5ac***	Chiralpak IC, λ = 254 nm 10% IPA/CO_2, 2.5 mL/min t_R (min) major 7.39, minor 9.02	96
5	 ***5ad***	Chiralpak IC, λ = 254 nm 5% MeOH/CO_2, 2.5 mL/min t_R (min) major 9.50, minor 10.16	97
6	 ***5ae***	Chiralpak IC, λ = 254 nm 3% IPA/CO_2, 4.0 mL/min t_R (min) major 12.00, minor 17.72	96

entry	compound	SFC analytic conditions	ee (%)
7	 ***5af***	**Chiralpak IC, λ = 254 nm 9% MeOH/CO_2, 2.5 mL/min t_R (min) major 5.33, minor 5.85**	**97**
8	 ***5ag***	**Chiralpak IC, λ = 254 nm 3% MeOH/CO_2, 2.5 mL/min t_R (min) major 11.55, minor 12.69**	**96**
9	 ***5ba***	**Chiralcel OJ-H, λ = 254 nm 15% IPA/CO_2, 2.5 mL/min t_R (min) minor 2.87, major 4.16**	**91**
10	 ***5ca***	**Chiralpak AD-H, λ = 254 nm 10% IPA/CO_2, 2.5 mL/min t_R (min) minor 4.41, major 4.79**	**90**
11	 ***5da***	**Chiralcel OJ-H, λ = 254 nm 15% IPA/CO_2, 2.5 mL/min t_R (min) minor 2.79, major 4.44**	**94**
12	 ***5ea***	**Chiralpak IC, λ = 254 nm 10% IPA/CO_2, 2.5 mL/min t_R (min) major 2.75, minor 2.92**	**93**

entry	compound	SFC analytic conditions	ee (%)
13	 ***5fa***	**Chiralpak IC, λ = 254 nm** **10% IPA/CO_2, 2.5 mL/min** **t_R (min) major 6.64, minor 7.42**	**95**
14	 ***S5aa***	**Chiralpak IC, λ = 254 nm** **20% IPA/CO_2, 2.5 mL/min** **t_R (min) minor 6.98, major 8.97**	**>99**
15	 ***7aa***	**Chiralpak AD-H, λ = 210 nm** **5% IPA/CO_2, 2.5 mL/min** **t_R (min) minor 4.99, major 7.08**	**95**
16	 ***7aa'***	**Chiralpak AD-H, λ = 210 nm** **5% IPA/CO_2, 2.5 mL/min** **t_R (min) major 5.62, minor 7.98**	**88**
17	 ***7ba***	**Chiralpak IA, λ = 210 nm** **5% IPA/CO_2, 2.5 mL/min** **t_R (min) minor 4.52, major 6.36**	**90**
18	 ***7ba'***	**Chiralpak IA, λ = 210 nm** **5% IPA/CO_2, 2.5 mL/min** **t_R (min) major 5.79, minor 7.41**	**77**
19	 ***7ca***	**Chiralpak IA, λ = 210 nm** **2% IPA/CO_2, 3.0 mL/min** **t_R (min) minor 6.82, major 13.26**	**98**

entry	compound	SFC analytic conditions	ee (%)
20	 ***7ca'***	**Chiralpak IA, λ = 210 nm 2% IPA/CO_2, 3.0 mL/min t_R (min) major 6.95, minor 11.43**	**91**
21	 ***7da***	**Chiralcel OD-H, λ = 210 nm 10% MeCN/CO_2, 2.5 mL/min t_R (min) minor 13.74, major 16.85**	**79**
22	 ***7da'***	**Chiralcel OD-H, λ = 210 nm 10% MeCN/CO_2, 2.5 mL/min t_R (min) major 12.34, minor 15.02**	**62**
23	 ***7ab***	**Chiralpak AD-H, λ = 210 nm 8% IPA/CO_2, 2.5 mL/min t_R (min) minor 4.13, major 4.50**	**95**
24	 ***7ab'***	**Chiralpak AD-H, λ = 210 nm 10% IPA/CO_2, 2.5 mL/min t_R (min) minor 3.43, major 4.49**	**91**
25	 ***7ad***	**Chiralpak AD-H, λ = 210 nm 8% IPA/CO_2, 2.5 mL/min t_R (min) minor 4.28, major 4.75**	**91**

entry	compound	SFC analytic conditions	ee (%)
26	 ***7ad'***	**Chiralpak IC, λ = 210 nm 10% IPA/CO_2, 2.5 mL/min t_R (min) minor 5.40, major 5.99**	**81**
27	 ***7ae***	**Chiralpak AD-H, λ = 210 nm 7% IPA/CO_2, 2.5 mL/min t_R (min) minor 4.14, major 4.85**	**91**
28	 ***7ae'***	**Chiralpak AD-H, λ = 210 nm 7% IPA/CO_2, 2.5 mL/min t_R (min) major 4.67, minor 5.28**	**75**
29	 ***7af***	**Chiralpak AD-H, λ = 210 nm 10% IPA/CO_2, 2.5 mL/min t_R (min) minor 4.68, major 5.17**	**88**
30	 ***7af'***	**Chiralpak IC, λ = 210 nm 10% IPA/CO_2, 2.5 mL/min t_R (min) minor 4.43, major 5.01**	**79**
31	 ***9aa***	**Chiralcel OB-H, λ = 210 nm 10% IPA/CO_2, 2.5 mL/min t_R (min) major 13.72, minor 15.18**	**95**

Crystal Structure Analysis of Alkylation Product 3aa (smaple No.: p15559):

The α-alkylated Malonate 3aa (>99% ee) was recrystallized from Et_2O/hexanes (liquid/liquid diffusion) at 0 ºC to provide suitable crystals for X-ray analysis, m.p. = 53 – 55 ºC (hexanes/Et_2O).

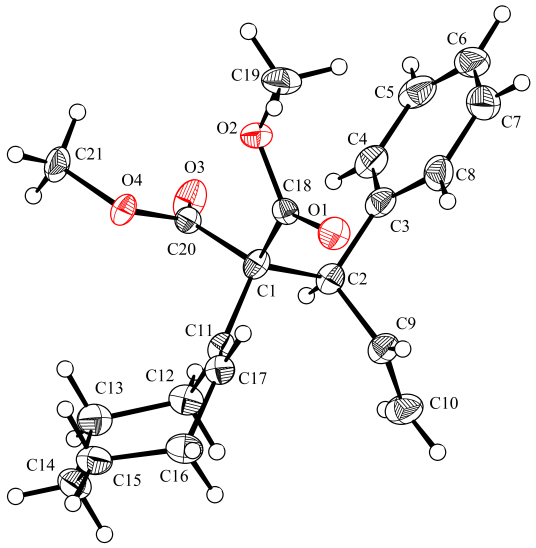


Table 1. Crystal data and structure refinement for p15559.

Identification code	p15559	
Empirical formula	C21 H26 O4	
Formula weight	342.42	
Temperature	100 K	
Wavelength	1.54178 ≈	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 7.7585(6) ≈	α= 90∞
	b = 9.1039(7) ≈	β= 90∞
	c = 26.2256(17) ≈	γ = 90∞
Volume	1852.4(2) ≈^{3}	
Z	4	
Density (calculated)	1.228 Mg/m^3	
Absorption coefficient	0.674 mm^{-1}	

F(000)	736
Crystal size	0.21 x 0.19 x 0.17 mm^3
Theta range for data collection	3.370 to 78.511∞.
Index ranges	-9<=h<=9, -11<=k<=11, -32<=l<=33
Reflections collected	39232
Independent reflections	3967 [R(int) = 0.0517]
Completeness to theta = 67.000∞	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9612 and 0.9073
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3967 / 0 / 228
Goodness-of-fit on F^2	1.078
Final R indices [I>2sigma(I)]	R1 = 0.0402, wR2 = 0.1023
R indices (all data)	R1 = 0.0418, wR2 = 0.1032
Absolute structure parameter	0.12(7)
Extinction coefficient	n/a
Largest diff. peak and hole	0.476 and -0.182 e.≈$^{-3}$

Table 2. Atomic coordinates (x 10^5) and equivalent isotropic displacement parameters (≈^{2}x 10^4) for p15559. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	47530(20)	48207(19)	71564(6)	265(4)
O(2)	59320(20)	31380(18)	66418(6)	230(3)
O(3)	40030(20)	33780(20)	54882(7)	328(4)
O(4)	64670(20)	44547(18)	57227(6)	219(3)
C(1)	40600(30)	48920(30)	62552(8)	203(4)
C(2)	20770(30)	45310(30)	62993(9)	228(5)
C(3)	17000(30)	29830(30)	64929(10)	254(5)
C(4)	11800(30)	19040(30)	61504(11)	301(5)
C(5)	8120(30)	4840(30)	63209(13)	365(6)
C(6)	9650(40)	1220(30)	68287(12)	378(6)
C(7)	14440(40)	11840(30)	71745(12)	363(6)
C(8)	17930(30)	26150(30)	70102(10)	305(5)

C(9)	11240(30)	56730(30)	66066(10)	263(5)
C(10)	-2930(30)	63250(30)	64348(12)	344(6)
C(11)	43340(30)	65720(30)	61761(9)	216(4)
C(12)	35600(30)	71790(30)	56886(9)	270(5)
C(13)	48620(40)	78740(30)	53139(9)	297(5)
C(14)	55050(40)	93870(30)	54684(10)	308(5)
C(15)	65400(30)	94390(30)	59605(10)	292(5)
C(16)	55380(30)	90340(30)	64394(10)	289(5)
C(17)	52000(30)	74110(30)	65029(9)	237(5)
C(18)	49700(30)	43240(20)	67335(8)	184(4)
C(19)	68200(40)	25170(30)	70738(10)	337(6)
C(20)	48010(30)	41220(20)	57798(8)	191(4)
C(21)	73250(30)	37220(30)	53078(9)	288(5)

Table 3. Bond lengths [≈] and angles [∞] for p15559.

O(1)-C(18)	1.210(3)
O(2)-C(18)	1.334(3)
O(2)-C(19)	1.441(3)
O(3)-C(20)	1.194(3)
O(4)-C(20)	1.336(3)
O(4)-C(21)	1.440(3)
C(1)-C(2)	1.577(3)
C(1)-C(11)	1.558(3)
C(1)-C(18)	1.530(3)
C(1)-C(20)	1.541(3)
C(2)-H(2)	1.0000
C(2)-C(3)	1.526(3)
C(2)-C(9)	1.509(3)
C(3)-C(4)	1.391(3)
C(3)-C(8)	1.400(4)
C(4)-H(4)	0.9500
C(4)-C(5)	1.397(4)
C(5)-H(5)	0.9500
C(5)-C(6)	1.377(5)

C(6)-H(6)	0.9500
C(6)-C(7)	1.377(4)
C(7)-H(7)	0.9500
C(7)-C(8)	1.398(4)
C(8)-H(8)	0.9500
C(9)-H(9)	0.9500
C(9)-C(10)	1.328(4)
C(10)-H(10A)	0.9500
C(10)-H(10B)	0.9500
C(11)-C(12)	1.517(3)
C(11)-C(17)	1.330(3)
C(12)-H(12A)	0.9900
C(12)-H(12B)	0.9900
C(12)-C(13)	1.545(4)
C(13)-H(13A)	0.9900
C(13)-H(13B)	0.9900
C(13)-C(14)	1.520(4)
C(14)-H(14A)	0.9900
C(14)-H(14B)	0.9900
C(14)-C(15)	1.521(4)
C(15)-H(15A)	0.9900
C(15)-H(15B)	0.9900
C(15)-C(16)	1.522(4)
C(16)-H(16A)	0.9900
C(16)-H(16B)	0.9900
C(16)-C(17)	1.510(3)
C(17)-H(17)	0.9500
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800

C(18)-O(2)-C(19)	116.30(18)
C(20)-O(4)-C(21)	115.29(18)

C(11)-C(1)-C(2)	110.31(18)
C(18)-C(1)-C(2)	108.65(18)
C(18)-C(1)-C(11)	112.22(18)
C(18)-C(1)-C(20)	109.73(18)
C(20)-C(1)-C(2)	109.16(18)
C(20)-C(1)-C(11)	106.72(18)
C(1)-C(2)-H(2)	106.4
C(3)-C(2)-C(1)	113.83(19)
C(3)-C(2)-H(2)	106.4
C(9)-C(2)-C(1)	111.94(19)
C(9)-C(2)-H(2)	106.4
C(9)-C(2)-C(3)	111.37(19)
C(4)-C(3)-C(2)	119.5(2)
C(4)-C(3)-C(8)	118.1(2)
C(8)-C(3)-C(2)	122.3(2)
C(3)-C(4)-H(4)	119.8
C(3)-C(4)-C(5)	120.4(3)
C(5)-C(4)-H(4)	119.8
C(4)-C(5)-H(5)	119.6
C(6)-C(5)-C(4)	120.9(3)
C(6)-C(5)-H(5)	119.6
C(5)-C(6)-H(6)	120.3
C(7)-C(6)-C(5)	119.5(3)
C(7)-C(6)-H(6)	120.3
C(6)-C(7)-H(7)	119.9
C(6)-C(7)-C(8)	120.2(3)
C(8)-C(7)-H(7)	119.9
C(3)-C(8)-H(8)	119.6
C(7)-C(8)-C(3)	120.8(3)
C(7)-C(8)-H(8)	119.6
C(2)-C(9)-H(9)	118.9
C(10)-C(9)-C(2)	122.2(2)
C(10)-C(9)-H(9)	118.9
C(9)-C(10)-H(10A)	120.0
C(9)-C(10)-H(10B)	120.0
H(10A)-C(10)-H(10B)	120.0

C(12)-C(11)-C(1)	114.59(19)
C(17)-C(11)-C(1)	123.1(2)
C(17)-C(11)-C(12)	122.3(2)
C(11)-C(12)-H(12A)	108.5
C(11)-C(12)-H(12B)	108.5
C(11)-C(12)-C(13)	115.3(2)
H(12A)-C(12)-H(12B)	107.5
C(13)-C(12)-H(12A)	108.5
C(13)-C(12)-H(12B)	108.5
C(12)-C(13)-H(13A)	108.6
C(12)-C(13)-H(13B)	108.6
H(13A)-C(13)-H(13B)	107.6
C(14)-C(13)-C(12)	114.6(2)
C(14)-C(13)-H(13A)	108.6
C(14)-C(13)-H(13B)	108.6
C(13)-C(14)-H(14A)	108.4
C(13)-C(14)-H(14B)	108.4
C(13)-C(14)-C(15)	115.3(2)
H(14A)-C(14)-H(14B)	107.5
C(15)-C(14)-H(14A)	108.4
C(15)-C(14)-H(14B)	108.4
C(14)-C(15)-H(15A)	108.5
C(14)-C(15)-H(15B)	108.5
C(14)-C(15)-C(16)	115.0(2)
H(15A)-C(15)-H(15B)	107.5
C(16)-C(15)-H(15A)	108.5
C(16)-C(15)-H(15B)	108.5
C(15)-C(16)-H(16A)	108.6
C(15)-C(16)-H(16B)	108.6
H(16A)-C(16)-H(16B)	107.6
C(17)-C(16)-C(15)	114.6(2)
C(17)-C(16)-H(16A)	108.6
C(17)-C(16)-H(16B)	108.6
C(11)-C(17)-C(16)	125.4(2)
C(11)-C(17)-H(17)	117.3
C(16)-C(17)-H(17)	117.3

O(1)-C(18)-O(2)	123.1(2)
O(1)-C(18)-C(1)	124.1(2)
O(2)-C(18)-C(1)	112.58(18)
O(2)-C(19)-H(19A)	109.5
O(2)-C(19)-H(19B)	109.5
O(2)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
O(3)-C(20)-O(4)	123.9(2)
O(3)-C(20)-C(1)	125.6(2)
O(4)-C(20)-C(1)	110.38(18)
O(4)-C(21)-H(21A)	109.5
O(4)-C(21)-H(21B)	109.5
O(4)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\approx^2$x 10^4) for p15559. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	333(9)	280(8)	183(7)	-48(7)	-16(7)	-5(7)
O(2)	272(8)	184(7)	234(8)	-17(6)	-28(7)	29(7)
O(3)	275(9)	437(10)	271(9)	-183(8)	0(7)	-67(8)
O(4)	200(8)	270(8)	189(7)	-67(6)	31(6)	6(7)
C(1)	184(10)	259(11)	166(9)	-48(8)	-11(8)	10(9)
C(2)	192(10)	258(11)	234(11)	-40(9)	-7(8)	-12(9)
C(3)	190(10)	242(11)	330(12)	-54(10)	10(9)	2(9)
C(4)	232(11)	291(12)	382(13)	-85(11)	19(10)	2(10)
C(5)	244(12)	264(12)	587(18)	-120(12)	35(12)	-9(10)
C(6)	279(13)	229(12)	625(18)	26(12)	73(12)	-13(11)

C(7)	288(13)	336(13)	466(16)	53(12)	30(12)	-15(11)
C(8)	250(12)	326(13)	339(13)	-26(11)	54(10)	-43(10)
C(9)	224(11)	237(11)	329(12)	-54(10)	16(10)	-12(9)
C(10)	238(12)	258(12)	536(16)	-36(12)	-13(12)	9(10)
C(11)	175(10)	247(11)	227(10)	-37(9)	15(9)	7(8)
C(12)	261(12)	250(12)	298(12)	3(10)	-70(10)	-14(10)
C(13)	365(13)	291(12)	237(11)	-11(10)	-38(10)	32(11)
C(14)	373(14)	258(11)	294(12)	53(10)	1(11)	2(10)
C(15)	274(12)	220(11)	383(14)	14(10)	-49(10)	-2(10)
C(16)	335(13)	211(11)	320(12)	-46(10)	-59(11)	-18(10)
C(17)	229(11)	236(11)	247(11)	-5(9)	-12(9)	-2(9)
C(18)	209(10)	154(9)	189(10)	-23(8)	-5(8)	-42(8)
C(19)	455(15)	255(12)	301(13)	35(11)	-67(12)	103(12)
C(20)	218(10)	189(10)	165(10)	-10(8)	-2(8)	-3(9)
C(21)	313(13)	338(13)	213(11)	-62(10)	103(10)	6(10)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (≈^{2}x 10^3) for p15559.

	x	y	z	U(eq)
H(2)	1602	4583	5945	27
H(4)	1074	2134	5798	36
H(5)	452	-242	6083	44
H(6)	741	-853	6940	45
H(7)	1538	944	7526	44
H(8)	2097	3345	7253	37
H(9)	1551	5935	6934	32
H(10A)	-738	6077	6108	41
H(10B)	-862	7040	6638	41
H(12A)	2691	7930	5780	32
H(12B)	2950	6373	5511	32
H(13A)	5865	7209	5281	36
H(13B)	4312	7949	4974	36

H(14A)	4498	10046	5505	37
H(14B)	6230	9779	5189	37
H(15A)	7007	10443	6003	35
H(15B)	7532	8761	5928	35
H(16A)	6187	9387	6740	35
H(16B)	4419	9556	6434	35
H(17)	5641	6951	6801	28
H(19A)	7662	1791	6955	51
H(19B)	5985	2039	7300	51
H(19C)	7417	3299	7260	51
H(21A)	6846	4065	4983	43
H(21B)	7153	2659	5338	43
H(21C)	8561	3943	5320	43

Table 6. Torsion angles [∞] for p15559.

C(1)-C(2)-C(3)-C(4)	-103.3(3)
C(1)-C(2)-C(3)-C(8)	79.2(3)
C(1)-C(2)-C(9)-C(10)	128.7(3)
C(1)-C(11)-C(12)-C(13)	-119.0(2)
C(1)-C(11)-C(17)-C(16)	178.5(2)
C(2)-C(1)-C(11)-C(12)	-62.6(2)
C(2)-C(1)-C(11)-C(17)	118.5(2)
C(2)-C(1)-C(18)-O(1)	-67.1(3)
C(2)-C(1)-C(18)-O(2)	107.8(2)
C(2)-C(1)-C(20)-O(3)	0.4(3)
C(2)-C(1)-C(20)-O(4)	177.69(18)
C(2)-C(3)-C(4)-C(5)	-179.4(2)
C(2)-C(3)-C(8)-C(7)	-179.8(2)
C(3)-C(2)-C(9)-C(10)	-102.6(3)
C(3)-C(4)-C(5)-C(6)	-0.3(4)
C(4)-C(3)-C(8)-C(7)	2.7(4)
C(4)-C(5)-C(6)-C(7)	1.6(4)
C(5)-C(6)-C(7)-C(8)	-0.8(4)
C(6)-C(7)-C(8)-C(3)	-1.4(4)
C(8)-C(3)-C(4)-C(5)	-1.8(4)

C(9)-C(2)-C(3)-C(4)	129.0(2)
C(9)-C(2)-C(3)-C(8)	-48.5(3)
C(11)-C(1)-C(2)-C(3)	-167.21(18)
C(11)-C(1)-C(2)-C(9)	-39.8(3)
C(11)-C(1)-C(18)-O(1)	55.1(3)
C(11)-C(1)-C(18)-O(2)	-129.96(19)
C(11)-C(1)-C(20)-O(3)	-118.8(3)
C(11)-C(1)-C(20)-O(4)	58.5(2)
C(11)-C(12)-C(13)-C(14)	-75.8(3)
C(12)-C(11)-C(17)-C(16)	-0.3(4)
C(12)-C(13)-C(14)-C(15)	64.0(3)
C(13)-C(14)-C(15)-C(16)	-64.8(3)
C(14)-C(15)-C(16)-C(17)	75.6(3)
C(15)-C(16)-C(17)-C(11)	-59.5(3)
C(17)-C(11)-C(12)-C(13)	59.9(3)
C(18)-C(1)-C(2)-C(3)	-43.8(2)
C(18)-C(1)-C(2)-C(9)	83.6(2)
C(18)-C(1)-C(11)-C(12)	176.12(19)
C(18)-C(1)-C(11)-C(17)	-2.8(3)
C(18)-C(1)-C(20)-O(3)	119.4(3)
C(18)-C(1)-C(20)-O(4)	-63.3(2)
C(19)-O(2)-C(18)-O(1)	-4.3(3)
C(19)-O(2)-C(18)-C(1)	-179.2(2)
C(20)-C(1)-C(2)-C(3)	75.8(2)
C(20)-C(1)-C(2)-C(9)	-156.8(2)
C(20)-C(1)-C(11)-C(12)	55.9(2)
C(20)-C(1)-C(11)-C(17)	-123.0(2)
C(20)-C(1)-C(18)-O(1)	173.6(2)
C(20)-C(1)-C(18)-O(2)	-11.5(3)
C(21)-O(4)-C(20)-O(3)	-6.4(3)
C(21)-O(4)-C(20)-C(1)	176.25(19)

Symmetry transformations used to generate equivalent atoms:

Crystal Structure Analysis of Diol S5aa (smaple No.: p15573):

The diol S5aa (>99% ee) was recrystallized from Et_2O/hexanes (liquid/liquid diffusion) at 0 ºC to provide suitable crystals for X-ray analysis, m.p. = 91 – 92 ºC (hexanes/Et_2O).

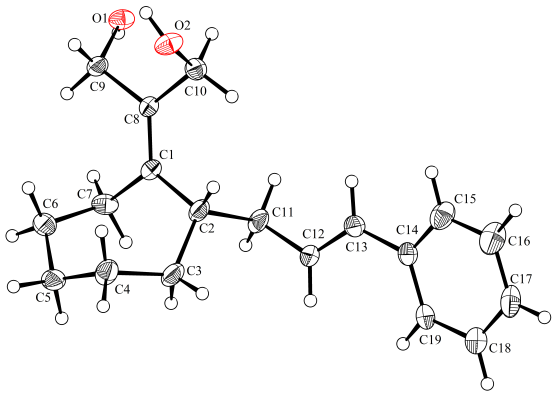


Table 1. Crystal data and structure refinement for p15573.

Identification code	p15573	
Empirical formula	C19 H26 O2	
Formula weight	286.40	
Temperature	100 K	
Wavelength	1.54178 ≈	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 6.1787(8) ≈	α= 90∞
	b = 9.0018(11) ≈	β= 90∞
	c = 29.470(3) ≈	γ = 90∞
Volume	1639.1(3) ≈^{3}	
Z	4	
Density (calculated)	1.161 Mg/m^3	
Absorption coefficient	0.569 mm^{-1}	
F(000)	624	
Crystal size	0.17 x 0.15 x 0.10 mm^3	
Theta range for data collection	2.999 to 79.168∞.	
Index ranges	-7<=h<=6, -11<=k<=11, -37<=l<=37	

Reflections collected	42476
Independent reflections	3528 [R(int) = 0.0365]
Completeness to theta = 67.000∞	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.9358
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3528 / 0 / 274
Goodness-of-fit on F^2	1.065
Final R indices [I>2sigma(I)]	R1 = 0.0269, wR2 = 0.0674
R indices (all data)	R1 = 0.0276, wR2 = 0.0680
Absolute structure parameter	0.06(3)
Extinction coefficient	n/a
Largest diff. peak and hole	0.151 and -0.151 e.≈$^{-3}$

Table 2. Atomic coordinates (x 10^5) and equivalent isotropic displacement parameters (≈^{2}x 10^4) for p15573. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	98299(14)	29698(10)	46715(3)	231(2)
O(2)	39847(15)	37085(11)	45850(3)	264(2)
C(1)	77350(20)	60425(14)	40871(4)	185(2)
C(2)	62050(20)	65375(14)	37135(4)	240(3)
C(3)	58950(30)	82309(16)	36918(4)	332(4)
C(4)	55850(20)	89964(16)	41547(5)	297(3)
C(5)	77130(20)	94951(15)	43706(4)	263(3)
C(6)	91700(20)	82470(15)	45366(5)	257(3)
C(7)	96570(20)	70494(14)	41772(5)	241(3)
C(8)	73960(20)	47967(13)	43291(4)	179(2)
C(9)	87550(20)	43732(14)	47335(4)	211(3)
C(10)	56100(20)	36983(14)	42365(4)	218(3)
C(11)	70390(70)	59480(50)	32407(13)	248(7)
C(12)	54900(30)	62780(20)	28662(5)	255(5)
C(13)	39140(40)	53410(20)	27498(8)	242(5)

C(14)	23070(60)	55120(40)	23888(11)	233(5)
C(15)	5980(50)	45320(40)	23756(10)	316(6)
C(16)	-10090(70)	46330(50)	20517(16)	387(9)
C(17)	-9830(90)	57330(60)	17220(20)	343(11)
C(18)	8040(100)	67220(60)	17270(13)	372(9)
C(19)	24250(60)	66010(40)	20567(14)	323(7)
C(11A)	64700(300)	57900(200)	32940(70)	420(50)
C(12A)	44830(140)	55960(90)	29580(30)	261(19)
C(13A)	43160(110)	60900(80)	25420(20)	240(20)
C(14A)	23680(160)	59780(130)	22540(40)	143(19)
C(15A)	5200(300)	51020(120)	23290(40)	340(30)
C(16A)	-12300(300)	52140(130)	20330(60)	290(30)
C(17A)	-9100(500)	61600(200)	16800(90)	470(60)
C(18A)	6600(400)	69300(200)	15880(50)	340(40)
C(19A)	23080(170)	68610(120)	18680(40)	210(20)

Table 3. Bond lengths [≈] and angles [∞] for p15573.

O(1)-H(1)	0.8400
O(1)-C(9)	1.4389(16)
O(2)-H(2)	0.8400
O(2)-C(10)	1.4365(16)
C(1)-C(2)	1.5181(17)
C(1)-C(7)	1.5171(18)
C(1)-C(8)	1.3455(17)
C(2)-H(2A)	1.0000
C(2)-H(2B)	1.0000
C(2)-C(3)	1.5376(19)
C(2)-C(11)	1.577(4)
C(2)-C(11A)	1.42(2)
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(3)-C(4)	1.5403(18)
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900

C(4)-C(5)	1.528(2)
C(5)-H(5A)	0.9900
C(5)-H(5B)	0.9900
C(5)-C(6)	1.5205(19)
C(6)-H(6A)	0.9900
C(6)-H(6B)	0.9900
C(6)-C(7)	1.5410(19)
C(7)-H(7A)	0.9900
C(7)-H(7B)	0.9900
C(8)-C(9)	1.5067(16)
C(8)-C(10)	1.5066(17)
C(9)-H(9A)	0.9900
C(9)-H(9B)	0.9900
C(10)-H(10A)	0.9900
C(10)-H(10B)	0.9900
C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900
C(11)-C(12)	1.491(5)
C(12)-H(12)	0.9500
C(12)-C(13)	1.333(3)
C(13)-H(13)	0.9500
C(13)-C(14)	1.463(4)
C(14)-C(15)	1.376(5)
C(14)-C(19)	1.387(4)
C(15)-H(15)	0.9500
C(15)-C(16)	1.380(6)
C(16)-H(16)	0.9500
C(16)-C(17)	1.389(6)
C(17)-H(17)	0.9500
C(17)-C(18)	1.418(9)
C(18)-H(18)	0.9500
C(18)-C(19)	1.400(5)
C(19)-H(19)	0.9500
C(11A)-H(11C)	0.9900
C(11A)-H(11D)	0.9900
C(11A)-C(12A)	1.59(2)

C(12A)-H(12A)	0.9500
C(12A)-C(13A)	1.307(12)
C(13A)-H(13A)	0.9500
C(13A)-C(14A)	1.477(12)
C(14A)-C(15A)	1.405(19)
C(14A)-C(19A)	1.387(13)
C(15A)-H(15A)	0.9500
C(15A)-C(16A)	1.39(2)
C(16A)-H(16A)	0.9500
C(16A)-C(17A)	1.36(3)
C(17A)-H(17A)	0.9500
C(17A)-C(18A)	1.22(4)
C(18A)-H(18A)	0.9500
C(18A)-C(19A)	1.31(2)
C(19A)-H(19A)	0.9500

C(9)-O(1)-H(1)	109.5
C(10)-O(2)-H(2)	109.5
C(7)-C(1)-C(2)	116.03(11)
C(8)-C(1)-C(2)	122.15(12)
C(8)-C(1)-C(7)	121.82(11)
C(1)-C(2)-H(2A)	107.9
C(1)-C(2)-H(2B)	103.1
C(1)-C(2)-C(3)	113.50(11)
C(1)-C(2)-C(11)	109.8(2)
C(3)-C(2)-H(2A)	107.9
C(3)-C(2)-H(2B)	103.1
C(3)-C(2)-C(11)	109.72(19)
C(11)-C(2)-H(2A)	107.9
C(11A)-C(2)-C(1)	114.9(8)
C(11A)-C(2)-H(2B)	103.1
C(11A)-C(2)-C(3)	116.7(9)
C(2)-C(3)-H(3A)	108.5
C(2)-C(3)-H(3B)	108.5
C(2)-C(3)-C(4)	114.97(11)
H(3A)-C(3)-H(3B)	107.5

C(4)-C(3)-H(3A)	108.5
C(4)-C(3)-H(3B)	108.5
C(3)-C(4)-H(4A)	108.9
C(3)-C(4)-H(4B)	108.9
H(4A)-C(4)-H(4B)	107.8
C(5)-C(4)-C(3)	113.15(13)
C(5)-C(4)-H(4A)	108.9
C(5)-C(4)-H(4B)	108.9
C(4)-C(5)-H(5A)	108.5
C(4)-C(5)-H(5B)	108.5
H(5A)-C(5)-H(5B)	107.5
C(6)-C(5)-C(4)	115.23(11)
C(6)-C(5)-H(5A)	108.5
C(6)-C(5)-H(5B)	108.5
C(5)-C(6)-H(6A)	108.7
C(5)-C(6)-H(6B)	108.7
C(5)-C(6)-C(7)	114.29(11)
H(6A)-C(6)-H(6B)	107.6
C(7)-C(6)-H(6A)	108.7
C(7)-C(6)-H(6B)	108.7
C(1)-C(7)-C(6)	112.66(10)
C(1)-C(7)-H(7A)	109.1
C(1)-C(7)-H(7B)	109.1
C(6)-C(7)-H(7A)	109.1
C(6)-C(7)-H(7B)	109.1
H(7A)-C(7)-H(7B)	107.8
C(1)-C(8)-C(9)	122.91(11)
C(1)-C(8)-C(10)	124.41(11)
C(10)-C(8)-C(9)	112.66(10)
O(1)-C(9)-C(8)	112.27(10)
O(1)-C(9)-H(9A)	109.1
O(1)-C(9)-H(9B)	109.1
C(8)-C(9)-H(9A)	109.1
C(8)-C(9)-H(9B)	109.1
H(9A)-C(9)-H(9B)	107.9
O(2)-C(10)-C(8)	112.23(10)

O(2)-C(10)-H(10A)	109.2
O(2)-C(10)-H(10B)	109.2
C(8)-C(10)-H(10A)	109.2
C(8)-C(10)-H(10B)	109.2
H(10A)-C(10)-H(10B)	107.9
C(2)-C(11)-H(11A)	109.2
C(2)-C(11)-H(11B)	109.2
H(11A)-C(11)-H(11B)	107.9
C(12)-C(11)-C(2)	112.2(3)
C(12)-C(11)-H(11A)	109.2
C(12)-C(11)-H(11B)	109.2
C(11)-C(12)-H(12)	118.9
C(13)-C(12)-C(11)	122.2(2)
C(13)-C(12)-H(12)	118.9
C(12)-C(13)-H(13)	116.0
C(12)-C(13)-C(14)	128.0(2)
C(14)-C(13)-H(13)	116.0
C(15)-C(14)-C(13)	118.3(3)
C(15)-C(14)-C(19)	118.3(3)
C(19)-C(14)-C(13)	123.5(3)
C(14)-C(15)-H(15)	119.0
C(14)-C(15)-C(16)	121.9(3)
C(16)-C(15)-H(15)	119.0
C(15)-C(16)-H(16)	119.2
C(15)-C(16)-C(17)	121.5(4)
C(17)-C(16)-H(16)	119.2
C(16)-C(17)-H(17)	121.6
C(16)-C(17)-C(18)	116.7(4)
C(18)-C(17)-H(17)	121.6
C(17)-C(18)-H(18)	119.5
C(19)-C(18)-C(17)	121.0(4)
C(19)-C(18)-H(18)	119.5
C(14)-C(19)-C(18)	120.5(3)
C(14)-C(19)-H(19)	119.8
C(18)-C(19)-H(19)	119.8
C(2)-C(11A)-H(11C)	107.2

C(2)-C(11A)-H(11D)	107.2
C(2)-C(11A)-C(12A)	120.5(11)
H(11C)-C(11A)-H(11D)	106.8
C(12A)-C(11A)-H(11C)	107.2
C(12A)-C(11A)-H(11D)	107.2
C(11A)-C(12A)-H(12A)	116.2
C(13A)-C(12A)-C(11A)	127.6(9)
C(13A)-C(12A)-H(12A)	116.2
C(12A)-C(13A)-H(13A)	117.3
C(12A)-C(13A)-C(14A)	125.5(9)
C(14A)-C(13A)-H(13A)	117.3
C(15A)-C(14A)-C(13A)	127.6(11)
C(19A)-C(14A)-C(13A)	117.0(9)
C(19A)-C(14A)-C(15A)	115.4(9)
C(14A)-C(15A)-H(15A)	120.3
C(16A)-C(15A)-C(14A)	119.4(10)
C(16A)-C(15A)-H(15A)	120.3
C(15A)-C(16A)-H(16A)	122.8
C(17A)-C(16A)-C(15A)	114.4(18)
C(17A)-C(16A)-H(16A)	122.8
C(16A)-C(17A)-H(17A)	115.1
C(18A)-C(17A)-C(16A)	130(3)
C(18A)-C(17A)-H(17A)	115.1
C(17A)-C(18A)-H(18A)	121.7
C(17A)-C(18A)-C(19A)	116.5(17)
C(19A)-C(18A)-H(18A)	121.7
C(14A)-C(19A)-H(19A)	117.8
C(18A)-C(19A)-C(14A)	124.4(11)
C(18A)-C(19A)-H(19A)	117.8

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\approx^2$x 10^4) for p15573. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}

O(1)	172(4)	230(4)	292(4)	75(4)	-21(4)	6(3)
O(2)	173(4)	331(5)	289(5)	115(4)	15(4)	-10(4)
C(1)	175(5)	219(6)	162(5)	19(4)	8(4)	23(5)
C(2)	308(7)	249(6)	164(5)	9(5)	-43(5)	76(5)
C(3)	542(10)	269(7)	186(6)	19(5)	-72(6)	135(7)
C(4)	369(8)	290(7)	232(6)	-21(5)	-40(6)	122(6)
C(5)	343(7)	220(6)	227(6)	15(5)	68(6)	-12(6)
C(6)	238(6)	254(6)	279(6)	15(5)	-9(5)	-67(5)
C(7)	189(6)	230(6)	305(6)	53(5)	47(5)	-20(5)
C(8)	166(6)	211(6)	161(5)	10(4)	-4(5)	3(5)
C(9)	220(6)	216(6)	198(6)	37(4)	-40(5)	-3(5)
C(10)	190(6)	225(6)	238(6)	3(5)	-7(5)	-27(5)
C(11)	340(20)	275(11)	130(13)	-19(10)	32(13)	83(12)
C(12)	381(11)	220(9)	163(8)	-7(6)	-23(7)	-7(9)
C(13)	335(11)	196(10)	196(10)	-24(8)	23(9)	16(8)
C(14)	301(12)	217(14)	179(13)	-48(10)	27(11)	12(12)
C(15)	287(11)	446(19)	215(11)	25(13)	44(8)	-46(15)
C(16)	284(14)	590(20)	284(12)	10(20)	20(10)	-146(19)
C(17)	314(15)	490(30)	228(16)	-88(19)	-10(10)	-106(17)
C(18)	550(20)	312(17)	250(20)	-34(15)	-60(20)	-42(15)
C(19)	457(14)	261(16)	252(18)	-39(14)	-111(17)	-76(13)
C(11A)	310(80)	680(90)	270(50)	240(50)	220(50)	280(60)
C(12A)	310(40)	210(40)	260(40)	-60(30)	60(30)	-70(30)
C(13A)	220(30)	260(40)	230(40)	-60(30)	20(30)	-20(30)
C(14A)	230(30)	110(50)	100(50)	20(30)	-30(40)	-50(40)
C(15A)	670(80)	170(50)	170(40)	70(40)	100(40)	80(50)
C(16A)	260(50)	320(60)	300(60)	-130(60)	80(40)	-110(50)
C(17A)	770(110)	430(110)	220(70)	-200(80)	120(60)	-150(80)
C(18A)	560(90)	260(60)	190(60)	-60(50)	220(70)	-10(50)
C(19A)	230(50)	160(40)	250(50)	-110(40)	30(50)	-70(30)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (≈^{2}x 10^3) for p15573.

	x	y	z	U(eq)
H(1)	11102	3117	4581	35
H(2)	4453	3262	4815	40
H(2A)	4760	6077	3773	29
H(2B)	4766	6175	3822	29
H(3A)	4617	8447	3500	40
H(3B)	7174	8673	3541	40
H(4A)	4637	9873	4115	36
H(4B)	4844	8300	4363	36
H(5A)	8525	10093	4146	32
H(5B)	7375	10152	4631	32
H(6A)	8476	7766	4801	31
H(6B)	10556	8681	4641	31
H(7A)	10085	7541	3890	29
H(7B)	10894	6439	4281	29
H(9A)	9852	5155	4787	25
H(9B)	7819	4318	5006	25
H(10A)	4927	3938	3942	26
H(10B)	6237	2689	4214	26
H(11A)	8452	6413	3171	30
H(11B)	7262	4860	3260	30
H(12)	5630	7187	2705	31
H(13)	3823	4452	2923	29
H(15)	522	3763	2596	38
H(16)	-2160	3933	2055	46
H(17)	-2106	5820	1503	41
H(18)	901	7479	1503	45
H(19)	3615	7269	2053	39
H(11C)	7024	4783	3363	50
H(11D)	7625	6313	3125	50
H(12A)	3276	5059	3071	31
H(13A)	5551	6561	2415	29
H(15A)	465	4438	2579	41
H(16A)	-2533	4673	2075	35

H(17A)	-2083	6235	1473	56
H(18A)	686	7555	1327	41
H(19A)	3543	7451	1802	26

Table 6. Torsion angles [∞] for p15573.

C(1)-C(2)-C(3)-C(4)	-43.6(2)
C(1)-C(2)-C(11)-C(12)	174.6(2)
C(1)-C(2)-C(11A)-C(12A)	151.8(11)
C(1)-C(8)-C(9)-O(1)	-119.85(13)
C(1)-C(8)-C(10)-O(2)	-110.60(13)
C(2)-C(1)-C(7)-C(6)	90.17(13)
C(2)-C(1)-C(8)-C(9)	-173.18(11)
C(2)-C(1)-C(8)-C(10)	5.28(19)
C(2)-C(3)-C(4)-C(5)	90.06(17)
C(2)-C(11)-C(12)-C(13)	-90.1(3)
C(2)-C(11A)-C(12A)-C(13A)	119.6(12)
C(3)-C(2)-C(11)-C(12)	-60.0(3)
C(3)-C(2)-C(11A)-C(12A)	-71.7(15)
C(3)-C(4)-C(5)-C(6)	-69.81(15)
C(4)-C(5)-C(6)-C(7)	52.74(15)
C(5)-C(6)-C(7)-C(1)	-73.65(14)
C(7)-C(1)-C(2)-C(3)	-36.48(17)
C(7)-C(1)-C(2)-C(11)	86.7(2)
C(7)-C(1)-C(2)-C(11A)	101.4(8)
C(7)-C(1)-C(8)-C(9)	5.86(18)
C(7)-C(1)-C(8)-C(10)	-175.69(11)
C(8)-C(1)-C(2)-C(3)	142.60(14)
C(8)-C(1)-C(2)-C(11)	-94.2(2)
C(8)-C(1)-C(2)-C(11A)	-79.5(8)
C(8)-C(1)-C(7)-C(6)	-88.92(15)
C(9)-C(8)-C(10)-O(2)	67.99(13)
C(10)-C(8)-C(9)-O(1)	61.53(13)
C(11)-C(2)-C(3)-C(4)	-166.9(2)
C(11)-C(12)-C(13)-C(14)	-179.2(2)

C(12)-C(13)-C(14)-C(15)	-169.1(2)
C(12)-C(13)-C(14)-C(19)	11.5(4)
C(13)-C(14)-C(15)-C(16)	178.8(3)
C(13)-C(14)-C(19)-C(18)	-178.5(3)
C(14)-C(15)-C(16)-C(17)	0.0(6)
C(15)-C(14)-C(19)-C(18)	2.1(5)
C(15)-C(16)-C(17)-C(18)	1.6(7)
C(16)-C(17)-C(18)-C(19)	-1.3(8)
C(17)-C(18)-C(19)-C(14)	-0.5(7)
C(19)-C(14)-C(15)-C(16)	-1.8(5)
C(11A)-C(2)-C(3)-C(4)	179.2(8)
C(11A)-C(12A)-C(13A)-C(14A)	-175.2(11)
C(12A)-C(13A)-C(14A)-C(15A)	-13.2(14)
C(12A)-C(13A)-C(14A)-C(19A)	165.1(8)
C(13A)-C(14A)-C(15A)-C(16A)	175.8(10)
C(13A)-C(14A)-C(19A)-C(18A)	-177.1(11)
C(14A)-C(15A)-C(16A)-C(17A)	2.3(19)
C(15A)-C(14A)-C(19A)-C(18A)	1.4(15)
C(15A)-C(16A)-C(17A)-C(18A)	-1(3)
C(16A)-C(17A)-C(18A)-C(19A)	0(3)
C(17A)-C(18A)-C(19A)-C(14A)	0(2)
C(19A)-C(14A)-C(15A)-C(16A)	-2.5(15)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for p15573 [≈ and ∞].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1)...O(2)#1	0.84	1.86	2.6640(13)	160.0
O(2)-H(2)...O(1)#2	0.84	1.89	2.7121(13)	165.9

Symmetry transformations used to generate equivalent atoms:

#1 x+1,y,z #2 x-1/2,-y+1/2,-z+1

^{1}H NMR and ^{13}C NMR Spectra

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