Supporting Information

Asymmetric Allylic C–H Alkylation via Palladium(II)/Chiral Sulfoxide-Oxazoline Catalysis

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Table of Contents

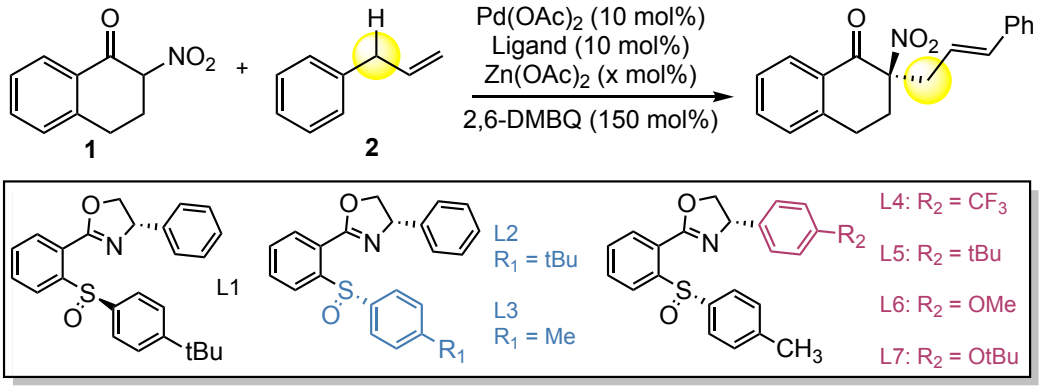
General Information

All commercially obtained reagents were used as received; $Pd(OAc)_2$ (Johnson-Matthey Chemicals) was stored in a glove box, and weighed out in the air at room temperature prior to use. Benzene and dioxane was purified prior to use by passage through a bed of activated alumina (Glass Contour, Laguna Beach, California). 2,6-Dimethylbenzoquinone and zinc acetate dihydrdate (reagent grade) were purchased from Sigma-Aldrich and used as received. All allylic C–H alkylation reactions were set up and run under ambient air with no precautions taken to exclude moisture. Reactions at 5°C were carried out in a cold room, where the temperature is monitored and maintain between 4°C–6 °C. Thin-layer chromatography (TLC) was conducted with E. Merck silica gel 60 F254 precoated plates (0.25 mm) and visualized with UV, Cerium-ammonium-molybdate and potassium permanganate stain. Flash chromatography was performed using ZEOprep 60 ECO 43-60 micron silica gel (American International Chemical, Inc.).

^{1}H NMR spectra were recorded on a Varian Unity-u400nb (500 MHz), Varian Inova-500 (500 MHz), or Varian Unity-500 (500 MHz) spectrometer and are reported in ppm using solvent as an internal standard ($CDCl_3$ at 7.26 ppm). Data reported as: s = singlet, d = doublet, t = triplet, q = quartet, quin. = quintet, sext. = sextet, sept. = septet, o = octet, m = multiplet, b = broad, ap = apparent; coupling constant(s) in Hz; integration. Proton-decoupled ^{13}C NMR spectra were recorded on a Carver-Bruker 500 (125MHz) or Varian Unity-500 (125MHz) spectrometer and are reported in ppm using solvent as an internal standard ($CDCl_3$). ^{19}F NMR spectra were recorded on a Varian Unity-500 (470 MHz) spectrometer and are reported in ppm using solvent as an internal standard ($CDCl_3$). Chiral high pressure liquid chromatography (HPLC) analysis was performed on an Agilent 1100 Series instrument equipped with a UV detector, using a CHIRALPAK AD-RH, OJ-H, IA-3, IB-3, IC-3 column. Optical rotations were measured with a sodium lamp using a 1 mL cell with a 50 mm path length on a Jasco P-1020 polarimeter. Optical rotations were obtained with a sodium lamp and are reported as follows: $[\alpha]_\lambda T^oC$ (*c* = g/100 mL solvent). High-resolution mass spectra were obtained at the University of Illinois Mass Spectrometry Laboratory. Electrospray ionization (ESI) spectra were performed on a Waters Q-Tof μLtima spectrometer, and electron ionization (EI) and field desorption (FD) spectra were performed on a Micromass 70-VSE spectrometer.

Minor impurities (i.e. solvent/quinone/grease) are labeled in the 1H NMR spectra. The 13C NMR spectra will contain the same impurities as the 1H NMR spectra as they were generally obtained from the same sample. Impurities were calculated out when reporting isolated yields.

Table S1. Reaction Development of 2-Nitrotetralone.



Entry	Ligand	$Zn(OAc)_2$ $2H_2O$ (x mol%)	T (^oC)	Yield (%)	ee (%)
1	L1	0%	45	65	-20
2	L2	0%	45	78	64
3	L3	0%	45	80	66
4	L3	100%	45	82	79
5	L3	100%	5	70	88
6	L4	100%	5	78	87
7	L5	100%	5	77	90
8	L6	100%	5	74	89
9	L7	100%	5	81	92
10	L7	50%	5	83	92
11	L7	25%	5	79	92
12	L7	25%	5	60	91

Entry 1:
To a ½ dram borosilicate vial with stir bar was added ligand **L1** (4.1 mg, 0.01 mmol, 0.1 equiv) and $Pd(OAc)_2$ (2.2 mg, 0.01 mmol, 0.1 equiv). Toluene (0.2 mL) was added, and the vial was capped and stirred at 45˚C for 10 mins. Separately, to a ½ dram borosilicate vial with stir bar was added **1** (38.2 mg, 0.20 mmol, 2 equiv), 2,6-dimethylbenzoquinone (20 mg, 0.15 mmol, 1.5 equiv). The catalyst solution was subsequently added to the reaction flask, and toluene (0.4 mL) was used to rinse the catalyst vial, also transferred and added to the reaction flask. Allylbenzene **2** (13.0 µL, 0.10 mmol, 1 equiv) was added. The ½ dram vial was sealed with a Teflon cap, and allowed to stir **for 24 hours** at 45˚C. Afterward, the vial was allowed to cool to RT, followed by the addition of saturated $NaHSO_3$ (aq.) solution (0.2 mL). The mixture was stirred at RT for 15 mins, followed by the addition of anhydrous $MgSO_4$ and filtration with dichloromethane. The majority of the solvent was removed under reduced pressure, and the remaining mixture was directly subjected to flash column chromatography (2%→5% EtOAc/hexanes) to provide **3** as a light yellow film. Run 1 (20.7 mg, 67% yield, -20% ee); Run 2 (19.4 mg, 63% yield, -20% ee) **Average: 65% Yield, -20% ee.**

Entry 2:
Reaction proceeded according to procedure in Entry 1 using ligand **L2** (4.1 mg, 0.01 mmol, 0.1 equiv). Run 1 (22.7 mg, 74% yield, 64% ee); Run 2 (25.1 mg, 82% yield, 64% ee); **Average: 78% Yield, 64% ee.**

Entry 3:
Reaction proceeded according to procedure in Entry 1 using ligand **L3** (3.7 mg, 0.01 mmol, 0.1 equiv). Run 1 (24.8 mg, 81% yield, 66% ee); Run 2 (24.1 mg, 78% yield, 66% ee); **Average: 80% Yield, 66% ee.**

Entry 4:
To a ½ dram borosilicate vial with stir bar was added ligand **L3** (3.7 mg, 0.01 mmol, 0.1 equiv) and $Pd(OAc)_2$ (2.2 mg, 0.01 mmol, 0.1 equiv). Benzene (0.2 mL) was added, and the vial was capped and stirred at 45˚C for 10 mins. Separately, to a ½ dram borosilicate vial with stir bar was added **1** (38.2 mg, 0.20 mmol, 2 equiv), 2,6-dimethylbenzoquinone (20 mg, 0.15 mmol, 1.5 equiv) and $Zn(OAc)_2$ dihydrate (22 mg, 0.1 mmol, 1.0 equiv). The catalyst solution was subsequently added to the reaction flask, and benzene (0.1 mL) and dioxane (0.3 mL) was used to rinse the catalyst vial, also transferred and added to the reaction flask. Allylbenzene **2** (13.0 µL, 0.10 mmol, 1 equiv) was added. The ½ dram vial was sealed with a Teflon cap, and allowed to stir **for 24 hours at 45˚C**. Afterward, the reaction was quenched by the addition of saturated $NaHSO_3$ (aq.) solution (0.2 mL). The mixture was stirred at RT for 15 mins, followed by the addition of anhydrous $MgSO_4$ and filtration

with dichloromethane. The majority of the solvent was removed under reduced pressure, and the remaining mixture was directly subjected to flash column chromatography (2%→5% EtOAc/hexanes) to provide **3** as a light yellow film. Run 1 (25.5 mg, 83% yield, 79% ee); Run 2 (24.5 mg, 80% yield, 79% ee); **Average: 82% Yield, 79% ee.**

Entry 5:
General procedure: To a ½ dram borosilicate vial with stir bar was added ligand **L3** (3.7 mg, 0.01 mmol, 0.1 equiv) and $Pd(OAc)_2$ (2.2 mg, 0.01 mmol, 0.1 equiv). Benzene (0.2 mL) was added, and the vial was capped and stirred at 45˚C for 10 mins. Separately, to a ½ dram borosilicate vial with stir bar was added **1** (38.2 mg, 0.20 mmol, 2 equiv), 2,6-dimethylbenzoquinone (20 mg, 0.15 mmol, 1.5 equiv) and $Zn(OAc)_2$ dihydrate (22 mg, 0.1 mmol, 1.0 equiv). The catalyst solution was subsequently added to the reaction flask, and benzene (0.1 mL) and dioxane (0.3 mL) was used to rinse the catalyst vial, also transferred and added to the reaction flask. Allylbenzene **2** (13.0 μL, 0.10 mmol, 1 equiv) was added. The ½ dram vial was sealed with a Teflon cap, and allowed to stir **for 72 hours at 5˚C**. Afterward, the reaction was quenched by the addition of saturated $NaHSO_3$ (aq.) solution (0.2 mL). The mixture was stirred at RT for 15 mins, followed by the addition of anhydrous $MgSO_4$ and filtration with dichloromethane. The majority of the solvent was removed under reduced pressure, and the remaining mixture was directly subjected to flash column chromatography (2%→5% EtOAc/hexanes) to provide **3** as a light yellow film. Run 1 (21.8 mg, 71% yield, 88% ee); Run 2 (20.8 mg, 68% yield, 88% ee); **Average: 70% Yield, 88% ee.**

Entry 6:
Reaction proceeded according to the General procedure in Entry 5 using ligand **L4** (4.3 mg, 0.01 mmol, 0.1 equiv). Run 1 (23.3 mg, 76% yield, 87% ee); Run 2 (24.5 mg, 80% yield, 87% ee); **Average: 78% Yield, 87% ee.**

Entry 7:
Reaction proceeded according to the General procedure in Entry 5 using ligand **L5** (4.2 mg, 0.01 mmol, 0.1 equiv). Run 1 (22.7 mg, 74% yield, 90% ee); Run 2 (24.3 mg, 79% yield, 90% ee); **Average: 77% Yield, 90% ee.**

Entry 8:
Reaction proceeded according to the General procedure in Entry 5 using ligand **L6** (3.9 mg, 0.01 mmol, 0.1 equiv). Run 1 (23.8 mg, 77% yield, 89% ee); Run 2 (21.5 mg, 70% yield, 89% ee); **Average: 74% Yield, 89% ee.**

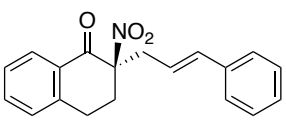
Entry 9:
Reaction proceeded according to the General procedure in Entry 5 using ligand **L7** (4.4 mg, 0.01 mmol, 0.1 equiv). Run 1 (24.0 mg, 78% yield, 92% ee); Run 2 (25.5 mg, 83% yield, 92% ee); **Average: 81% Yield, 92% ee.**

Entry 10:
Reaction proceeded according to the General procedure in Entry 5 using ligand **L7** (4.4 mg, 0.01 mmol, 0.1 equiv) and $Zn(OAc)_2$ dihydrate (**11 mg, 0.05 mmol, 0.5 equiv**). Run 1 (26.2 mg, 85% yield, 92% ee); Run 2 (25.0 mg, 81% yield, 92% ee); **Average: 83% Yield, 92% ee.** (HPLC trace and optical rotation was included for this entry)

Entry 11:
Reaction proceeded according to the General procedure in Entry 5 using ligand **L7** (4.4 mg, 0.01 mmol, 0.1 equiv) and $Zn(OAc)_2$ dihydrate (**5.5 mg, 0.025 mmol, 0.25 equiv**). Run 1 (25.2 mg, 82% yield, 92% ee); Run 2 (22.9 mg, 75% yield, 92% ee); **Average: 79% Yield, 92% ee.**

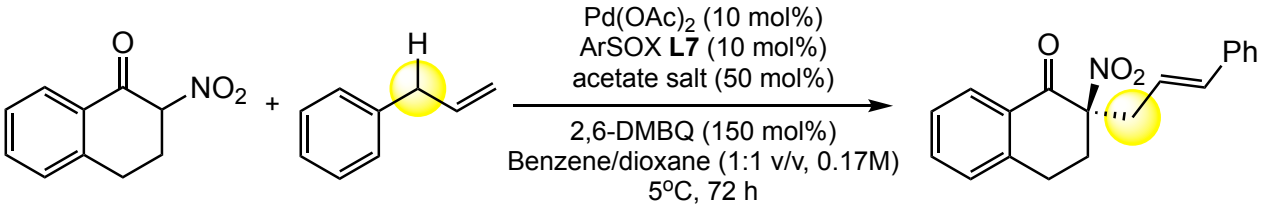
Entry 12:
Reaction proceeded according to the General procedure in Entry 5 using ligand **L7** (4.4 mg, 0.01 mmol, 0.1 equiv), nucleophile **1** (19.0 mg, 0.10 mmol, 1 equiv) and $Zn(OAc)_2$ dihydrate (**5.5 mg, 0.025 mmol, 0.25 equiv**). Run 1 (17.1 mg, 56% yield, 91% ee); Run 2 (19.5 mg, 64% yield, 91% ee); **Average: 60% Yield, 91% ee.**

The absolute stereochemistry of alkylated product with nitroketones was assigned based on crystal structure of **3p** (vide infra).

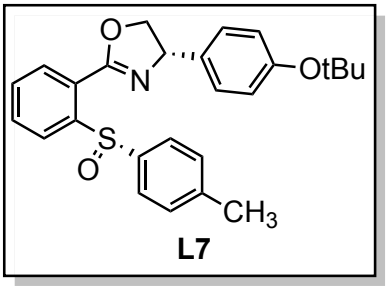


(*R*)-2-cinnamyl-2-nitro-3,4-dihydronaphthalen-1(2*H*)-one (**3**): Spectral data matches with previously reported.[1] The enantiomeric excess was determined to be 92% by chiral HPLC analysis (CHIRALPAK AD-RH column, 0.5 mL/min, 55% MeCN in H_2O, λ = 254 nm): t_R(major) = 28.309 min, t_R(minor) = 31.991 min. $[\alpha]^{23}_D$ = +16.2 (c = 1.1, $CHCl_3$).

Table S2. The Effect of Acetate Salt Additive on the Asymmetric Alkylation of 2-Nitrotetralone.



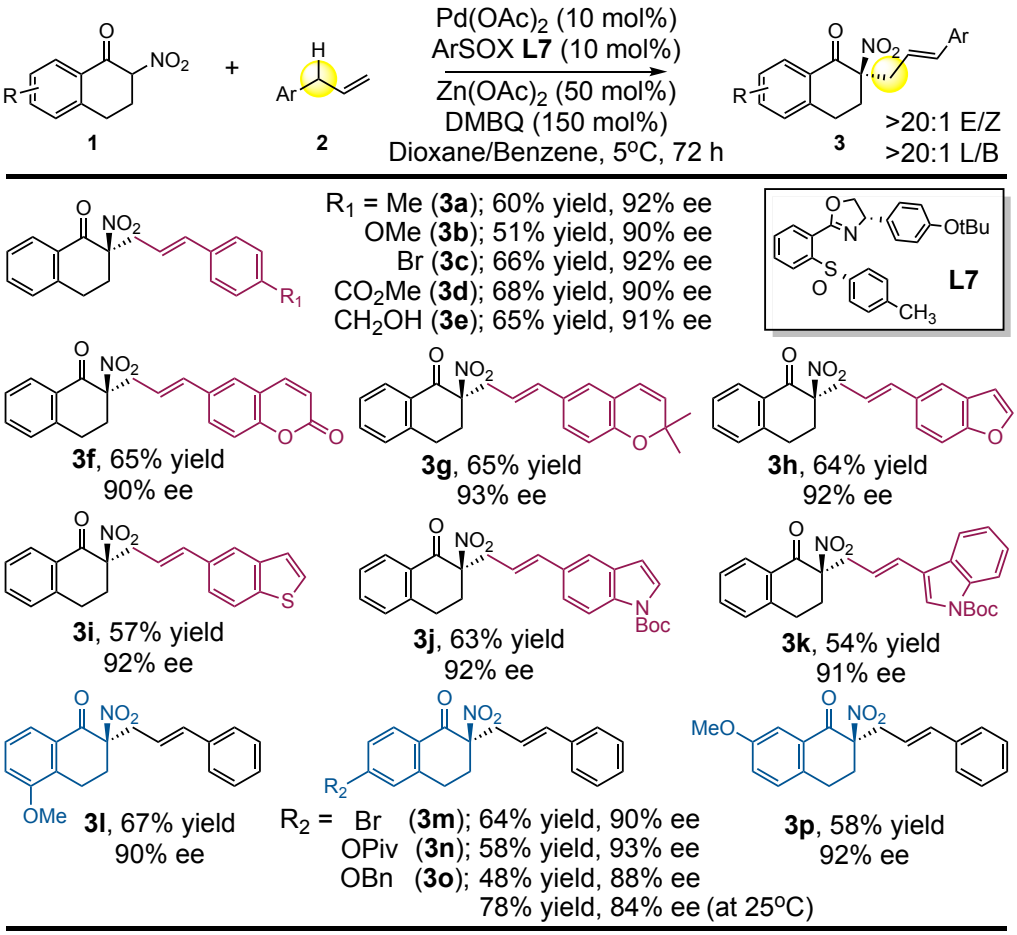
Entry	Acetate Salt	Yield (%)	ee (%)
1	none	71	77
2	$Zn(OAc)_2$	83	92
3	NH_4OAc	32	75
4	NaOAc	63	78
5	LiOAc	80	90
6	CsOAc	34	75
7	$Mn(OAc)_2$	58	90
8	$Fe(OAc)_2$	52	81



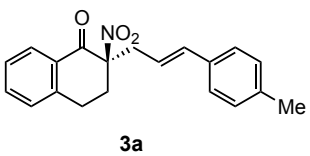
L7

Reaction proceeded according to the General procedure in Entry 5 for Table S1. The same isolation and analytical method was used.

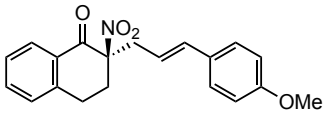
Table S3. Substrate Scope for 2-Nitrotetralone Nucleophiles



General procedure for Table S3: To a ½ dram borosilicate vial with stir bar was added ligand **L5** (8.4 mg, 0.02 mmol, 0.1 equiv) or **L7** (8.7 mg, 0.02 mmol, 0.1 equiv) and $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 0.1 equiv). Benzene (0.4 mL) was added, and the vial was capped and stirred at 45˚C for 10 mins. Separately, to a 1 dram borosilicate vial with stir bar was added **1** (76.5 mg, 0.40 mmol, 2 equiv), 2,6-dimethylbenzoquinone (40 mg, 0.3 mmol, 1.5 equiv) and $Zn(OAc)_2$ dihydrate (22 mg, 0.1 mmol, 0.5 equiv). The catalyst solution was subsequently added to the reaction flask, and benzene (0.2 mL) and dioxane (0.6 mL) was used to rinse the catalyst vial, also transferred and added to the reaction flask. Allylarene **2** (0.20 mmol, 1 equiv) was added. The 1 dram vial was sealed with a Teflon cap, and allowed to stir for 72 hours at 5˚C. Afterward, the reaction was diluted with 20 mL EtOAc, which was washed by saturated $NaHSO_3$ (aq.) solution (10 mL) or 5% K_2CO_3 (aq.) solution (10 mL) (*NOTE: The purpose of aqueous wash is for the ease of purification. $NaHSO_3$ was used to remove remaining DMBQ oxidant, whereas K_2CO_3 was used to remove remaining nitroketone nucleophile*). The organic layer was separated, dried over anhydrous $MgSO_4$ and filtered. The solvent was removed under reduced pressure, and the remaining mixture was purified by flash column chromatography to provide product.

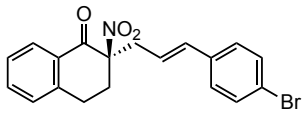


(*R*,*E*)-2-nitro-2-(3-(*p*-tolyl)allyl)-3,4-dihydronaphthalen-1(2*H*)-one (3a): 4-allyltoluene (26.4 mg, 0.20 mmol, 1 equiv) was reacted according to the general procedure using **L7** with **$NaHSO_3$ work up**. Purification by flash column chromatography (2%→5% EtOAc/hexanes) provided the product as a yellow oil. Run 1 (38.6 mg, 60% yield, 92% ee); Run 2 (36.0 mg, 56% yield, 92% ee); Run 3 (41.4 mg, 64% yield, 92% ee). **Average: 60% (±4.2%) yield, 92% ee.** The enantiomeric excess was determined by chiral HPLC analysis (CHIRALPAK AD-RH column, 0.5 mL/min, 55% MeCN in H_2O, λ = 254 nm): t_R(major) = 43.343 min, t_R(minor) = 46.711 min. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.15 (d, *J* = 8.0 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.30 – 7.27 (m, 3H), 7.14 (d, *J* = 7.7 Hz, 2H), 6.57 (d, *J* = 15.8 Hz, 1H), 6.12 (dt, *J* = 15.3, 7.4 Hz, 1H), 3.25 (ddd, *J* = 14.5, 7.3, 1.4 Hz, 1H), 3.17 – 3.10 (m, 2H), 3.08 – 2.96 (m, 2H), 2.53 (ddd, *J* = 14.1, 8.9, 4.8 Hz, 1H), 2.36 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.97, 142.35, 137.84, 135.89, 134.54, 133.64, 130.72, 129.29, 128.91, 128.83, 127.45, 126.30, 120.50, 93.93, 38.06, 31.66, 25.25, 21.20. HRMS (ESI) m/z calc'd for $C_{20}H_{19}NO_3$ [M+Na]+: 344.1263; found 344.1269. $[\alpha]^{23}_D$ = +6.4° (c = 1.1, $CHCl_3$).



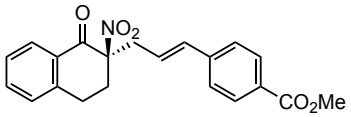
3b

(*R*,*E*)-2-(3-(4-methoxyphenyl)allyl)-2-nitro-3,4-dihydronaphthalen-1(2*H*)-one (3b): 4-allylanisole (30.0 mg, 0.20 mmol, 1 equiv) was reacted according to the general procedure using **L5** with **K_2CO_3 work up**. Purification by flash column chromatography (20%→30%→50% DCM/hexanes) provided the product as a colorless oil. Run 1 (35.4 mg, 53% yield, 90% ee); Run 2 (36.4 mg, 54% yield, 90% ee); Run 3 (31.7 mg, 47% yield, 90% ee). **Average: 51% (±3.7%) yield, 90% ee.** The enantiomeric excess was determined by chiral HPLC analysis (CHIRALPAK AD-RH column, 0.5 mL/min, 55% MeCN in H_2O, λ = 254 nm): t_R(major) = 36.912 min, t_R(minor) = 40.779 min. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.11 (d, *J* = 7.7 Hz, 1H), 7.54 (t, *J* = 7.5 Hz 1H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.29 – 7.23 (m, 3H), 6.83 (d, *J* = 8.6 Hz, 2H), 6.51 (d, *J* = 15.7 Hz, 1H), 6.00 (dt, *J* = 15.3, 7.4 Hz, 1H), 3.80 (s, 3H), 3.20 (ddd, *J* = 14.4, 7.2, 1.3 Hz, 1H), 3.14 – 3.06 (m, 2H), 3.05 – 2.92 (m, 2H), 2.50 (ddd, *J* = 14.1, 8.8, 4.8 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 188.00, 159.45, 142.35, 135.42, 134.53, 130.73, 129.24, 128.91, 128.82, 127.60, 127.45, 119.24, 114.00, 93.98, 55.30, 38.09, 31.64, 25.26. HRMS (ESI) m/z calc'd for $C_{20}H_{19}NO_4$ [M+Na]+: 360.1212; found 360.1218. $[\alpha]^{22}_D$ = +7.1° (c = 1, $CHCl_3$).



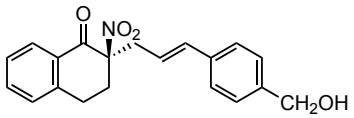
3c

(*R*,*E*)-2-(3-(4-bromophenyl)allyl)-2-nitro-3,4-dihydronaphthalen-1(2*H*)-one (3c): 4-bromoallylbenzene (39.4 mg, 0.20 mmol, 1 equiv) was reacted according to the general procedure using **L7** with **$NaHSO_3$ work up**. Purification by flash column chromatography (5%→8% EtOAc/hexanes) provided the product as a white solid. Run 1 (49.5 mg, 64% yield, 92% ee); Run 2 (51.3 mg, 66% yield, 92% ee); Run 3 (52.5 mg, 68% yield, 92% ee). **Average: 66% (±2.0%) yield, 92% ee.** The enantiomeric excess was determined by chiral HPLC analysis (CHIRALPAK AD-RH column, 0.5 mL/min, 60% MeCN in H_2O, λ = 280 nm): t_R(major) = 37.178 min, t_R(minor) = 43.913 min. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.11 (d, *J* = 7.9 Hz, 1H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.41 (d, *J* = 8.5 Hz, 2H), 7.38 (t, *J* = 8.2 Hz, 1H), 7.26 (d, *J* = 7.7 Hz, 1H), 7.20 (d, *J* = 8.5 Hz, 2H), 6.50 (d, *J* = 15.8 Hz, 1H), 6.17 (dt, *J* = 15.7, 7.4 Hz, 1H), 3.20 (ddd, *J* = 14.4, 7.2, 1.4 Hz, 1H), 3.15 – 3.06 (m, 2H), 3.05 – 2.91 (m, 2H), 2.47 (ddd, *J* = 14.2, 9.1, 4.7 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.82, 142.25, 135.34, 134.79, 134.61, 131.70, 130.71, 128.93, 128.83, 127.93, 127.51, 122.56, 121.74, 93.72, 38.12, 31.91, 25.24; HRMS (ESI) m/z calc'd for $C_{19}H_{16}BrNO_3$ [M+Na]+: 408.0211; found 408.0222. $[\alpha]^{23}_D$ = +20.8° (c = 1.43, $CHCl_3$).



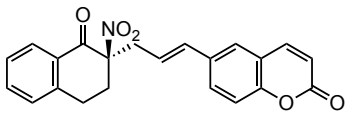
3d

Methyl (*R*,*E*)-4-(3-(2-nitro-1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)prop-1-en-1-yl)benzoate (3d): Methyl 4-allylbenzoate (35.2 mg, 0.20 mmol, 1 equiv) was reacted according to the general procedure using **L5** with **K_2CO_3 work up**. Purification by flash column chromatography (8%→10%→15% EtOAc/hexanes) provided the product as a colorless oil. Run 1 (49.2 mg, 67% yield, 90% ee); Run 2 (47.5 mg, 65% yield, 90% ee); Run 3 (52.5 mg, 72% yield, 90% ee). **Average: 68% (±3.5%) yield, 90% ee.** The enantiomeric excess was determined by chiral HPLC analysis (CHIRALCEL OJ-H column, 1 mL/min, 40% isopropanol in hexane, λ = 280 nm): t_R(major) = 22.985 min, t_R(minor) = 34.484 min. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.11 (d, *J* = 7.4 Hz, 1H), 7.96 (d, *J* = 8.3 Hz, 2H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.42 – 7.35 (m, 3H), 7.26 (d, *J* = 7.5 Hz, 1H), 6.60 (d, *J* = 15.6 Hz, 1H), 6.30 (dt, *J* = 15.4, 7.4 Hz, 1H), 3.90 (s, 3H), 3.24 (dd, *J* = 14.1, 7.1 Hz, 1H), 3.16 – 3.07 (m, 2H), 3.05 – 2.93 (m, 2H), 2.48 (ddd, *J* = 14.3, 9.1, 4.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.76, 166.75, 142.24, 140.77, 135.07, 134.64, 130.68, 129.94, 129.34, 128.94, 128.83, 127.52, 126.30, 124.56, 93.70, 52.11, 38.18, 31.97, 25.24. HRMS (ESI) m/z calc'd for $C_{21}H_{19}NO_5$ [M+H]+: 366.1341; found 366.1331. $[\alpha]^{23}_D$ = +24.8° (c = 0.72, $CHCl_3$).



3e

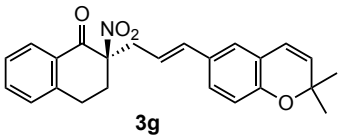
(*R*,*E*)-2-(3-(4-(hydroxymethyl)phenyl)allyl)-2-nitro-3,4-dihydronaphthalen-1(2*H*)-one (3e): (4-allylphenyl)methanol (30.0 mg, 0.20 mmol, 1 equiv) was reacted according to the general procedure using **L7** with **K_2CO_3 work up**. Purification by flash column chromatography (15%→20%→30% Acetone/hexanes) provided the product as a colorless oil. Run 1 (41.9 mg, 62% yield, 91% ee); Run 2 (44.3 mg, 66% yield, 91% ee); Run 3 (45.0 mg, 67% yield, 91% ee). **Average: 65% (±2.4%) yield, 91% ee.** The enantiomeric excess was determined by chiral HPLC analysis (CHIRALCEL OJ-H column, 1 mL/min, 40% isopropanol in hexane, λ = 260 nm): t_R(major) = 11.964 min, t_R(minor) = 18.490 min. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.11 (d, *J* = 7.2 Hz, 1H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.33 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.26 (d, *J* = 7.7 Hz, 1H), 6.56 (d, *J* = 15.7 Hz, 1H), 6.16 (dt, *J* = 15.4, 7.4 Hz, 1H), 4.66 (s, 2H), 3.22 (ddd, *J* = 14.5, 7.2, 1.4 Hz, 1H), 3.15 – 3.07 (m, 2H), 3.06 – 2.93 (m, 2H), 2.49 (ddd, *J* = 14.1, 8.9, 4.7 Hz, 1H), 1.74 (br, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.94, 142.32, 140.62, 135.85, 135.61, 134.59, 130.70, 128.93, 128.83, 127.48, 127.22, 126.59, 121.70, 93.88, 65.02, 38.09, 31.77, 25.25. HRMS (ESI) m/z calc'd for $C_{20}H_{19}NO_4$ [M+Na]+: 360.1212; found 360.1213. $[\alpha]^{23}_D$ = +14.7° (c = 1.6, $CHCl_3$).



3f

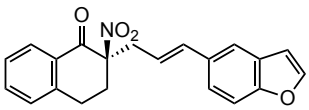
(*R*,*E*)-6-(3-(2-nitro-1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)prop-1-en-1-yl)-2*H*-chromen-2-one (3f): 6-allyl-2H-chromen-2-one (37.2 mg, 0.20 mmol, 1 equiv) was reacted according to the general procedure using **L7** with **K_2CO_3 work up**. Purification by

flash column chromatography (15%→35% EtOAc/hexanes) provided the product as a white solid. Run 1 (47.8 mg, 64% yield, 90% ee); Run 2 (50.5 mg, 67% yield, 90% ee); Run 3 (47.2 mg, 63% yield, 90% ee). **Average: 65% (±2.3%) yield, 90% ee.** The enantiomeric excess was determined by chiral HPLC analysis (CHIRALPAK OJ-H column, 1 mL/min, 50% isopropanol in hexanes, λ = 254 nm): t_R(major) = 21.454 min, t_R(minor) = 32.135 min. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.12 (d, *J* = 7.9 Hz, 1H), 7.67 (d, *J* = 9.6 Hz, 1H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.50 (dd, *J* = 8.6, 2.1 Hz, 1H), 7.42 (d, *J* = 2.1 Hz, 1H), 7.39 (t, *J* = 7.7 Hz, 1H), 7.29 – 7.23 (m, 2H), 6.61 – 6.53 (d, *J* = 15.8 Hz, 1H), 6.42 (d, *J* = 9.5 Hz, 1H), 6.21 (dt, *J* = 15.8, 7.4 Hz, 1H), 3.23 (ddd, *J* = 14.3, 7.2, 1.4 Hz, 1H), 3.17 – 3.08 (m, 2H), 3.07 – 2.95 (m, 2H), 2.48 (ddd, *J* = 14.3, 9.3, 4.5 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.80, 160.52, 153.55, 143.21, 142.20, 134.66, 134.01, 133.07, 130.73, 129.76, 128.94, 128.82, 127.54, 125.40, 122.95, 118.87, 117.14, 117.11, 93.73, 38.20, 32.12, 25.25; HRMS (ESI) *m/z* calculated for $C_{22}H_{17}NO_5$ $[M+H]^+$: 376.1185, found 376.1176. $[\alpha]^{22}_D$ = +30.6° (c = 0.81, $CHCl_3$).



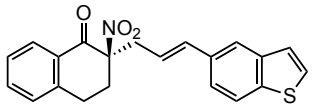
3g

(*R*,*E*)-2-(3-(2,2-dimethyl-2*H*-chromen-6-yl)allyl)-2-nitro-3,4-dihydronaphthalen-1(2*H*)-one (3g): 6-allyl-2,2-dimethyl-2H-chromene (40.0 mg, 0.20 mmol, 1 equiv) was reacted according to the general procedure using **L7** with **K_2CO_3 work up**. Purification by flash column chromatography (2%→5% EtOAc/hexanes) provided the product as a yellow oil. Run 1 (49.8 mg, 64% yield, 93% ee); Run 2 (52.7 mg, 68% yield, 93% ee); Run 3 (49.1 mg, 63% yield, 93% ee). **Average: 65% (±2.5%) yield, 93% ee.** The enantiomeric excess was determined by chiral HPLC analysis (CHIRALPAK AD-RH column, 0.5 mL/min, 65% MeCN in H_2O, λ = 254 nm): t_R(major) = 23.538 min, t_R(minor) = 29.110 min. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.11 (d, *J* = 7.9 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 1H), 7.25 (d, *J* = 6.9 Hz, 1H), 7.08 (dd, *J* = 8.3, 2.2 Hz, 1H), 6.97 (d, *J* = 2.2 Hz, 1H), 6.70 (d, *J* = 8.3 Hz, 1H), 6.46 (d, *J* = 15.8 Hz, 1H), 6.29 (d, *J* = 9.9 Hz, 1H), 5.97 (dt, *J* = 15.7, 7.5 Hz, 1H), 5.62 (d, *J* = 9.8 Hz, 1H), 3.19 (ddd, *J* = 14.3, 7.3, 1.3 Hz, 1H), 3.15 – 2.92 (m, 4H), 2.49 (ddd, *J* = 14.1, 8.9, 4.8 Hz, 1H), 1.41 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 188.00, 152.94, 142.35, 135.47, 134.52, 131.19, 130.73, 129.26, 128.90, 128.82, 127.44, 127.35, 124.07, 122.05, 121.23, 119.06, 116.40, 93.98, 76.50, 38.08, 31.65, 28.01, 25.26 ; HRMS (EI) *m/z* calculated for $C_{24}H_{23}NO_4$ $[M]^+$: 389.16271, found 389.16269. $[\alpha]^{22}_D$ = +2.8° (c = 1.26, $CHCl_3$).



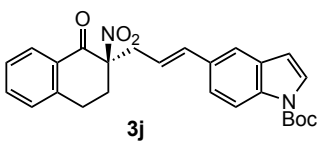
3h

(*R*,*E*)-2-(3-(benzofuran-5-yl)allyl)-2-nitro-3,4-dihydronaphthalen-1(2*H*)-one (3h): 5-allylbenzofuran (32.0 mg, 0.20 mmol, 1 equiv) was reacted according to the general procedure using **L7** with **K_2CO_3 work up**. Purification by flash column chromatography (2%→8% EtOAc/hexanes) provided the product as a yellow oil. Run 1 (38.2 mg, 55% yield, 92% ee); Run 2 (48.8 mg, 70% yield, 92% ee); Run 3 (46.1 mg, 66% yield, 92% ee). **Average: 64% (±7.9%) yield, 92% ee.** The enantiomeric excess was determined by chiral HPLC analysis (CHIRALPAK OJ-H column, 1 mL/min, 40% isopropanol in hexanes, λ = 254 nm): t_R(major) = 17.595 min, t_R(minor) = 28.628 min. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.13 (d, *J* = 7.9 Hz, 1H), 7.60 (d, *J* = 2.2 Hz, 1H), 7.57 – 7.52 (m, 2H), 7.42 (d, *J* = 8.5 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 1H), 7.31 (d, *J* = 8.6 Hz, 1H), 7.26 (d, *J* = 7.5 Hz, 1H), 6.73 (d, *J* = 2.2 Hz, 1H), 6.66 (d, *J* = 15.8 Hz, 1H), 6.13 (dt, *J* = 15.8, 7.4 Hz, 1H), 3.24 (ddd, *J* = 14.3, 7.2, 1.4 Hz, 1H), 3.16 – 3.07 (m, 2H), 3.06 – 2.95 (m, 2H), 2.55 – 2.47 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 188.00, 154.75, 145.61, 142.35, 136.13, 134.56, 131.58, 130.73, 128.93, 128.82, 127.78, 127.46, 122.89, 120.43, 119.16, 111.44, 106.64, 93.98, 38.11, 31.73, 25.27; HRMS (ESI) *m/z* calculated for $C_{21}H_{17}NO_4$ $[M+Na]^+$: 370.1055, found 370.1065. $[\alpha]^{22}_D$ = +26.8° (c = 1.33, $CHCl_3$).



3i

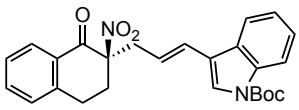
(*R*,*E*)-2-(3-(benzo[*b*]thiophen-5-yl)allyl)-2-nitro-3,4-dihydronaphthalen-1(2*H*)-one (3i): 5-allylbenzothiophene (35.0 mg, 0.20 mmol, 1 equiv) was reacted according to the general procedure using **L7** with **K_2CO_3 work up**. Purification by flash column chromatography (2%→8% EtOAc/hexanes) provided the product as a white solid. Run 1 (41.3 mg, 57% yield, 92% ee); Run 2 (42.8 mg, 59% yield, 92% ee); Run 3 (41.2 mg, 57% yield, 92% ee). **Average: 57% yield, 92% ee.** The enantiomeric excess was determined by chiral HPLC analysis (CHIRALPAK AD-RH column, 0.5 mL/min, 65% MeCN in H_2O, λ = 254 nm): t_R(major) = 31.236 min, t_R(minor) = 38.111 min. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.13 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.75 (s, 1H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.43 (d, *J* = 5.5 Hz, 1H), 7.41 – 7.35 (m, 2H), 7.30 (d, *J* = 5.5 Hz, 1H), 7.26 (d, *J* = 7.6 Hz, 1H), 6.68 (d, *J* = 15.7 Hz, 1H), 6.22 (dt, *J* = 15.7, 7.4 Hz, 1H), 3.26 (ddd, *J* = 14.2, 7.2, 1.3 Hz, 1H), 3.15 (ddd, *J* = 14.3, 7.6, 1.3 Hz, 1H), 3.12 – 3.08 (m, 1H), 3.05 – 2.96 (m, 2H), 2.57 – 2.47 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.95, 142.32, 139.96, 139.23, 136.07, 134.56, 132.85, 130.74, 128.92, 128.85, 127.48, 127.09, 123.87, 122.54, 122.43, 121.73, 121.24, 93.91, 38.18, 31.79, 25.27; HRMS (ESI) *m/z* calculated for $C_{21}H_{17}NO_3S$ $[M+H]^+$: 364.0983, found 364.0997. $[\alpha]^{22}_D$: +9.4° (c = 1.04, $CHCl_3$).



3j

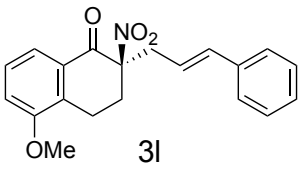
***Tert*-butyl (*R*,*E*)-5-(3-(2-nitro-1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)prop-1-en-1-yl)-1*H*-indole-1-carboxylate (3j):** Tert-butyl 5-allyl-1H-indole-1-carboxylate 5-allylbenzofuran (51.4 mg, 0.20 mmol, 1 equiv) was reacted according to the general procedure using **L7** with **K_2CO_3 work up**. Purification by flash column chromatography (2%→5% EtOAc/hexanes)

provided the product as a yellow oil. Run 1 (56.2 mg, 63% yield, 92% ee); Run 2 (56.2 mg, 63% yield, 92% ee); Run 3 (56.3 mg, 63% yield, 92% ee). **Average: 63% (±0.1%) yield, 92% ee.** The enantiomeric excess was determined by chiral HPLC analysis (CHIRALPAK OJ-H column, 1 mL/min, 20% isopropanol in hexanes, λ = 254 nm): t_R(major) = 16.544 min, t_R(minor) = 25.050 min. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.13 (d, *J* = 8.0 Hz, 1H), 8.05 (d, *J* = 8.6 Hz, 1H), 7.60 – 7.52 (m, 2H), 7.51 (d, *J* = 1.7 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.32 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.26 (d, *J* = 7.5 Hz, 1H), 6.66 (d, *J* = 15.8 Hz, 1H), 6.52 (d, *J* = 3.7 Hz, 1H), 6.14 (dt, *J* = 15.7, 7.4 Hz, 1H), 3.24 (ddd, *J* = 14.4, 7.3, 1.3 Hz, 1H), 3.17 – 3.08 (m, 2H), 3.07 – 2.94 (m, 2H), 2.53 (ddd, *J* = 14.1, 8.8, 4.5 Hz, 1H), 1.66 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 188.00, 149.59, 142.36, 136.33, 134.88, 134.53, 131.20, 130.84, 130.74, 128.91, 128.84, 127.45, 126.53, 122.69, 120.20, 118.96, 115.19, 107.31, 93.99, 83.82, 38.14, 31.69, 28.20, 25.28; HRMS (ESI): *m/z* calculated for $C_{26}H_{26}N_2O_5$ $[M+H]^+$: 447.1920, found 447.1923. $[\alpha]^{22}_D$ = +2.5° (c = 1.57, $CHCl_3$).



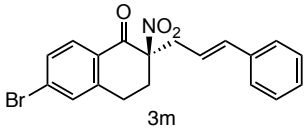
3k

***Tert*-butyl (*R*,*E*)-3-(3-(2-nitro-1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)prop-1-en-1-yl)-1*H*-indole-1-carboxylate (3k):** Tert-butyl 3-allyl-1H-indole-1-carboxylate (51.4 mg, 0.2 mmol, 1 equiv) was reacted according to the general procedure using **L7** with **K_2CO_3 work up**. Purification by flash column chromatography (2%→5% EtOAc/hexanes) provided the product as a clear oil. Run 1 (49.2 mg, 55% yield, 91% ee); Run 2 (48.7 mg, 55% yield, 91% ee); Run 3 (47.7 mg, 53% yield, 91% ee). **Average: 54% (±0.9%) yield, 91% ee.** The enantiomeric excess was determined by chiral HPLC analysis (CHIRALPAK AD-RH column, 0.5 mL/min, 65% MeCN in H_2O, λ = 254 nm): t_R(major) = 23.775 min, t_R(minor) = 29.914 min. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.16 (d, *J* = 8.2 Hz, 1H), 8.13 (d, *J* = 8.0 Hz, 1H), 7.69 (d, *J* = 7.8 Hz, 1H), 7.59 (s, 1H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.33 (dd, *J* = 8.4, 7.2 Hz, 1H), 7.29 – 7.24 (m, 2H), 6.67 (d, *J* = 15.9 Hz, 1H), 6.23 (dt, *J* = 15.9, 7.4 Hz, 1H), 3.27 (ddd, *J* = 14.3, 7.2, 1.3 Hz, 1H), 3.17 – 3.08 (m, 2H), 3.08 – 2.96 (m, 2H), 2.57 – 2.48 (m, 1H), 1.67 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 188.00, 149.48, 142.32, 135.87, 134.57, 130.75, 128.93, 128.84, 128.42, 127.47, 127.28, 124.77, 124.07, 123.02, 121.85, 119.82, 117.99, 115.39, 93.98, 83.99, 38.72, 31.78, 28.20, 25.28; HRMS (ESI) *m/z* calculated for $C_{26}H_{26}N_2O_5$ $[M+H]^+$: 447.1920, found 447.1916. $[\alpha]^{22}_D$ = +13.2° (c = 1.59, $CHCl_3$).



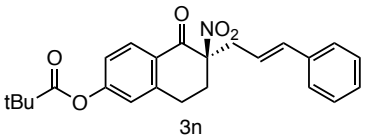
3l

(*R*)-2-cinnamyl-5-methoxy-2-nitro-3,4-dihydronaphthalen-1(2*H*)-one (3l): 5-methoxy-2-nitro-3,4-dihydronaphthalen-1(2*H*)-one (88.5 mg, 0.4 mmol, 2 equiv) was reacted with allylbenzene (26.0 µL, 0.20 mmol, 1 equiv) according to the general procedure using **L7** with **$NaHSO_3$ work up**. Purification by flash column chromatography (2%→5%→10% EtOAc/hexanes) provided the product as a clear oil. Run 1 (43.7 mg, 65% yield, 89% ee); Run 2 (44.8 mg, 66% yield, 90% ee); Run 3 (46.9 mg, 70% yield, 90% ee). **Average: 67% (±2.4%) yield, 90% ee.** The enantiomeric excess was determined by chiral HPLC analysis (CHIRALPAK AD-RH column, 0.5 mL/min, 55% MeCN in H_2O, λ = 254 nm): t_R(major) = 37.080 min, t_R(minor) = 57.154 min. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.71 (d, *J* = 7.9 Hz, 1H), 7.35 (m, 3H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.24 (t, *J* = 7.1 Hz, 1H), 7.07 (d, *J* = 8.1 Hz, 1H), 6.57 (d, *J* = 15.6 Hz, 1H), 6.17 (dt, *J* = 15.4, 7.4 Hz, 1H), 3.87 (s, 3H), 3.22 (ddd, *J* = 14.6, 7.3, 1.4 Hz, 1H), 3.05 (ddd, *J* = 14.6, 7.8, 1.3 Hz, 1H), 3.01 – 2.90 (m, 3H), 2.49 – 2.39 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 188.32, 156.68, 136.46, 135.92, 131.54, 131.35, 128.59, 127.89, 127.83, 126.41, 121.69, 120.12, 115.14, 93.86, 55.75, 37.77, 30.79, 19.42. HRMS (ESI) *m/z* calculated for $C_{20}H_{19}NO_4$ $[M+Na]^+$: 360.1212, found 360.1216. $[\alpha]^{22}_D$ = +19.3° (c = 1, $CHCl_3$).



3m

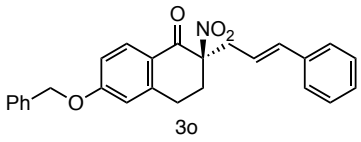
(*R*)-6-bromo-2-cinnamyl-2-nitro-3,4-dihydronaphthalen-1(2*H*)-one (3m): 6-bromo-2-nitro-3,4-dihydronaphthalen-1(2*H*)-one (108 mg, 0.4 mmol, 2 equiv) was reacted with allylbenzene (26.0 µL, 0.20 mmol, 1 equiv) according to the general procedure in **benzene (0.8 mL)/dioxane (0.8 mL)*** using **L7** with **$NaHSO_3$ work up**. Purification by flash column chromatography (0%→20%→30% DCM/hexanes) provided the product as a clear oil. Run 1 (49.2 mg, 64% yield, 90% ee); Run 2 (47.8 mg, 62% yield, 90% ee); Run 3 (51.3 mg, 66% yield, 90% ee). **Average: 64% (±2.3%) yield, 90% ee.** The enantiomeric excess was determined by chiral HPLC analysis (CHIRALPAK AD-RH column, 0.5 mL/min, 70% MeCN in H_2O, λ = 280 nm): t_R(major) = 18.295 min, t_R(minor) = 21.638 min. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 8.5 Hz, 1H), 7.52 (d, *J* = 8.5 Hz, 1H), 7.45 (s, 1H), 7.36 – 7.28 (m, 4H), 7.24 (t, *J* = 7.1 Hz, 1H), 6.57 (d, *J* = 15.7 Hz, 1H), 6.13 (dt, *J* = 15.4, 7.4 Hz, 1H), 3.20 (ddd, *J* = 14.3, 7.3, 1.4 Hz, 1H), 3.11 (ddd, *J* = 14.3, 7.6, 1.3 Hz, 1H), 3.06 (m, 1H), 3.02 – 2.89 (m, 2H), 2.47 (ddd, *J* = 14.3, 9.4, 5.8 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.08, 143.87, 136.31, 136.23, 131.86, 131.05, 130.37, 130.08, 129.61, 128.62, 128.01, 126.41, 121.30, 93.50, 38.14, 31.61, 24.99. HRMS (ESI) *m/z* calculated for $C_{19}H_{16}BrNO_3$ $[M+H]^+$: 386.0392, found 386.0381. $[\alpha]^{22}_D$ = +43.6° (c = 0.52, $CHCl_3$); **NOTE: while running at standard molarity (0.17 M) gave inconsistent enantioselectivities (88%-90%), running at slightly diluted molarity (0.12 M) resolved the issue, possibly due to improved homogeneity.*



3n

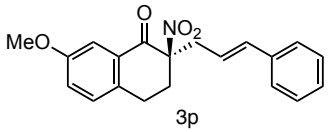
(*R*)-6-cinnamyl-6-nitro-5-oxo-5,6,7,8-tetrahydronaphthalen-2-yl pivalate (3n): 6-nitro-5-oxo-5,6,7,8-tetrahydronaphthalen-2-yl pivalate (116.5 mg, 0.4 mmol, 2 equiv) was reacted with allylbenzene (26.0 µL, 0.20 mmol, 1 equiv) according to the general

procedure using **L7** with **$NaHSO_3$ work up**. Purification by flash column chromatography (2%→5%→10% EtOAc/hexanes) provided the product as a clear oil. Run 1 (47.2 mg, 58% yield, 93% ee); Run 2 (45.2 mg, 55% yield, 93% ee); Run 3 (49.7 mg, 61% yield, 92% ee). **Average: 58% (±2.8%) yield, 93% ee.** The enantiomeric excess was determined by chiral HPLC analysis (CHIRALPAK AD-RH column, 0.5 mL/min, 60% MeCN in H_2O, λ = 260 nm): t_R(major) = 33.431 min, t_R(minor) = 44.185 min. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.15 (d, *J* = 8.6 Hz, 1H), 7.33 (d, *J* = 7.2 Hz, 2H), 7.29 (t, *J* = 7.4 Hz, 2H), 7.24 (t, *J* = 7.1 Hz, 1H), 7.08 (dd, *J* = 8.6, 2.3 Hz, 1H), 7.01 (d, *J* = 2.2 Hz, 1H), 6.57 (d, *J* = 15.8 Hz, 1H), 6.14 (dt, *J* = 15.5, 7.4 Hz, 1H), 3.23 (dd, *J* = 14.5, 7.0 Hz, 1H), 3.14 – 3.06 (m, 2H), 3.03 - 2.92 (m, 2H), 2.50 (m, 1H), 1.37 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 186.86, 176.37, 155.89, 144.21, 136.36, 136.11, 130.81, 128.61, 128.20, 127.95, 126.42, 121.56, 121.48, 121.14, 93.72, 39.29, 38.04, 31.64, 27.05, 25.33. HRMS (ESI) *m/z* calculated for $C_{24}H_{25}NO_5$ $[M+H]^+$: 408.1811, found 408.1805. $[\alpha]^{23}_D$ = +16.1° (c = 0.64, $CHCl_3$).



3o

(*R*)-6-(benzyloxy)-2-cinnamyl-2-nitro-3,4-dihydronaphthalen-1(2*H*)-one (3o): 6-(benzyloxy)-2-nitro-3,4-dihydronaphthalen-1(2*H*)-one (60 mg, 0.2 mmol, 2 equiv) was reacted with allylbenzene (13.0 µL, 0.10 mmol, 1 equiv) according to the general procedure using **L7 without work up** (directly dry-loaded onto column). Purification by flash column chromatography (5%→10% EtOAc/hexanes) provided the product as a clear oil. Run 1 (19.5 mg, 47% yield, 88% ee); Run 2 (20.2 mg, 49% yield, 88% ee); Run 3 (20.0 mg, 48% yield, 88% ee). **Average: 48% (±0.9%) yield, 88% ee**. **Reaction at 25°C: Run 4 (32.4 mg, 78% yield, 84% ee)**. The enantiomeric excess was determined by chiral HPLC analysis (CHIRALPAK AD-RH column, 0.5 mL/min, 70% MeCN in H_2O, λ = 254 nm): t_R(major) = 28.220 min, t_R(minor) = 33.725 min. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.09 (d, *J* = 8.8 Hz, 1H), 7.44 – 7.28 (m, 9H), 7.24 (t, *J* = 7.3 Hz, 1H), 6.97 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.77 (d, *J* = 2.5 Hz, 1H), 6.57 (d, *J* = 15.6 Hz, 1H), 6.15 (dt, *J* = 15.3, 7.4 Hz, 1H), 5.13 (s, 2H), 3.22 (dd, *J* = 14.4, 7.2 Hz, 1H), 3.10 (dd, *J* = 14.5, 7.4 Hz, 1H), 3.05 (dt, *J* = 11.0, 5.0 Hz, 1H), 3.00 – 2.90 (m, 2H), 2.51 – 2.43 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 186.48, 163.69, 144.98, 136.46, 135.87, 135.81, 131.47, 128.76, 128.59, 128.38, 127.88, 127.45, 126.39, 124.26, 121.89, 114.90, 113.61, 93.78, 70.28, 38.17, 31.72, 25.60. HRMS (ESI) *m/z* calculated for $C_{26}H_{23}NO_4$ $[M+H]^+$: 414.1705, found 414.1720. $[\alpha]^{22}_D$ = +65.7° (c = 1, $CHCl_3$).

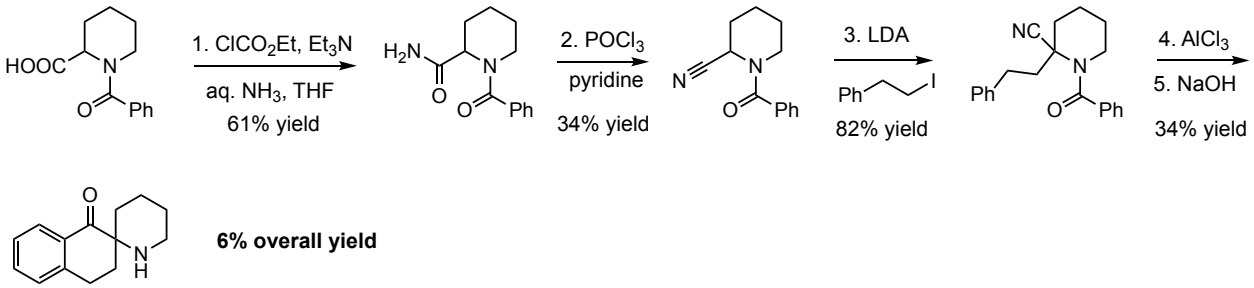


3p

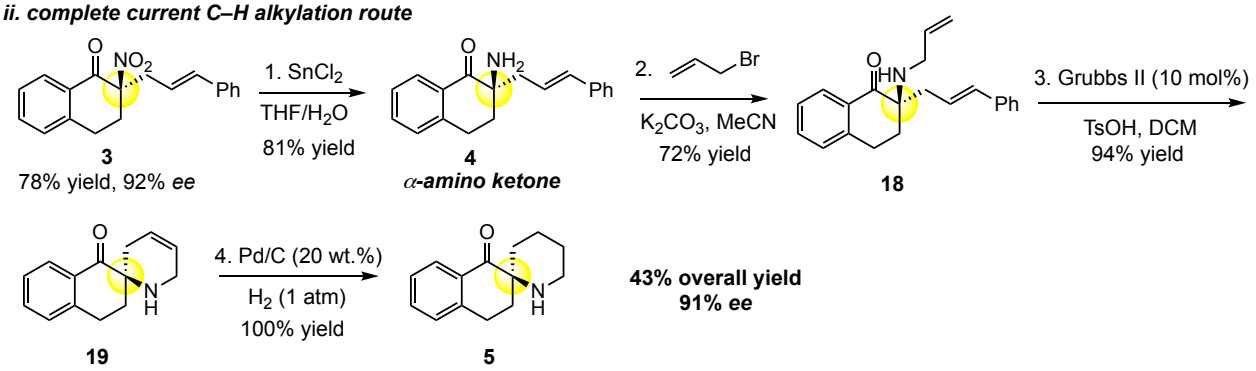
(*R*)-2-cinnamyl-7-methoxy-2-nitro-3,4-dihydronaphthalen-1(2*H*)-one (3p): 7-methoxy-2-nitro-3,4-dihydronaphthalen-1(2*H*)-one (88.5 mg, 0.4 mmol, 2 equiv) was reacted with allylbenzene (26.0 µL, 0.20 mmol, 1 equiv) according to the general procedure using **L7 without work up** (directly dry-loaded onto column). Purification by flash column chromatography (2%→8% EtOAc/hexanes) provided the product as a white powder. Run 1 (38.0 mg, 56% yield, 92% ee); Run 2 (38.7 mg, 57% yield, 92% ee); Run 3 (41.1 mg, 61% yield, 92% ee). **Average: 58% (±2.4%) yield, 92% ee.** The enantiomeric excess was determined by chiral HPLC analysis (CHIRALPAK OJ-H column, 1 mL/min, 30% isopropanol in hexanes, λ = 254 nm): t_R(major) = 12.481 min, t_R(minor) = 19.875 min. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.56 (d, *J* = 2.7 Hz, 1H), 7.36 – 7.32 (m, 2H), 7.32 – 7.27 (m, 2H), 7.26 – 7.21 (m, 1H), 7.17 (d, *J* = 8.5 Hz, 1H), 7.12 (dd, *J* = 8.5, 2.7 Hz, 1H), 6.57 (d, *J* = 15.9 Hz, 1H), 6.16 (dt, *J* = 15.8, 7.4 Hz, 1H), 3.86 (s, 3H), 3.21 (ddd, *J* = 14.4, 7.2, 1.4 Hz, 1H), 3.12 (ddd, *J* = 14.3, 7.6, 1.3 Hz, 1H), 3.07 – 2.91 (m, 3H), 2.51 – 2.44 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.94, 158.84, 136.42, 136.00, 134.95, 131.48, 130.15, 128.60, 127.92, 126.40, 123.30, 121.67, 110.28, 93.81, 55.59, 38.11, 32.05, 24.52; HRMS (ESI) *m/z* calculated for $C_{20}H_{19}NO_4$ $[M+H]^+$: 338.1392, found 338.1381. $[\alpha]^{23}_D$: +2.9° (c = 0.59, $CHCl_3$). ***Single crystals were grown by recrystallization from warm diethyl ether. The absolute stereochemistry is determined by X-ray crystallography shown on page S31.***

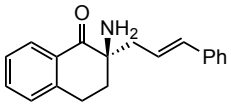
Scheme S1: Comparison of Synthetic Routes for Compound 5

i. complete previous route (Imaeda T. et al., *Bioorganic Med. Chem.* **2017**, *25*, 3719.)



ii. complete current C–H alkylation route

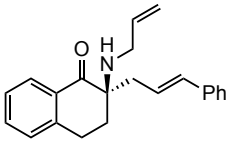




4

(*R*)-2-amino-2-cinnamyl-3,4-dihydronaphthalen-1(2*H*)-one (4)

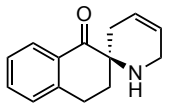
To a 20 mL vial fitted with a magnetic stir bar was added 2-nitrotetralone **3a** (277 mg, 0.9 mmol, 1 equiv, 92% ee), THF (4 mL), and H_2O (0.5 mL), followed by the addition of $SnCl_2$ dihydrate (2 g, 9 mmol, 10 equiv). The reaction was capped and stirred at 45°C for 24 h. After cooled down to room temperature, the reaction was quenched with 50 mL saturated $NaHCO_3$ (aq.) (CAUTION: gas evolved). The aqueous layer was extracted with EtOAc (4 x 40 mL). The organic layers were combined and dried over anhydrous Na_2SO_4. The solid was filtered off and the solvent was removed under reduced pressure. The crude was purified by silica column chromatography (0%→1%→2%→5% MeOH/DCM) to afford pure product **4** as a yellowish thick oil (**202 mg, 0.73 mmol, 81% yield**). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.08 (d, *J* = 7.9 Hz, 1H), 7.50 (td, *J* = 7.5 Hz, 1H), 7.38 – 7.33 (m, 3H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.27 – 7.25 (m, 1H), 7.22 (t, *J* = 7.3 Hz, 1H), 6.48 (d, *J* = 16.0 Hz, 1H), 6.24 (ddd, *J* = 15.7, 8.3, 6.5 Hz, 1H), 3.15 (ddd, *J* = 16.8, 11.3, 5.0 Hz, 1H), 2.99 (dt, *J* = 17.6, 4.5 Hz, 1H), 2.55 (ddd, *J* = 14.1, 8.4, 1.1 Hz, 1H), 2.48 (ddd, *J* = 14.1, 6.6, 1.5 Hz, 1H), 2.25 (ddd, *J* = 13.6, 5.0, 3.8 Hz, 1H), 2.08 (ddd, *J* = 13.6, 11.3, 5.2 Hz, 1H), 1.99 (br, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 201.29, 143.19, 137.09, 134.23, 133.55, 130.87, 128.86, 128.52, 128.18, 127.38, 126.88, 126.25, 124.15, 59.22, 40.05, 34.43, 25.81. HRMS (ESI) m/z calc'd for $C_{19}H_{19}NO$ [M+H]+: 278.1545; found 278.1545. $[\alpha]^{22}_D$ = -6.7° (c = 1.06, $CHCl_3$).



18

(*R*)-2-(allylamino)-2-cinnamyl-3,4-dihydronaphthalen-1(2*H*)-one (18)

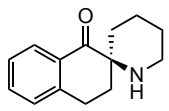
To an oven-dried 1 dram vial was added 2-aminotetralone **4** (111 mg, 0.4 mmol, 1 equiv), anhydrous K_2CO_3 (61 mg, 0.44 mmol, 1.1 equiv) and acetonitrile (1 mL, 0.4 M) under N_2. Allyl bromide (0.04 mL, 0.44 mmol, 1.1 equiv) was then added. The reaction was stirred under N_2 at 50°C for 24 h. After cooled down to room temperature, the volatiles were removed under reduced pressure. The crude was purified by silica column chromatography (5%→8%→10%→15% EtOAc/Hexanes) to afford pure product **18** as a colorless oil (**92 mg, 0.29 mmol, 72% yield**). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.10 (d, *J* = 7.9 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.35 (m, 3H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.22 (m, 2H), 6.47 (d, *J* = 15.8 Hz, 1H), 6.21 (dt, *J* = 15.4, 7.4 Hz, 1H), 5.91 (ddt, *J* = 16.4, 11.1, 6.0 Hz, 1H), 5.20 (d, *J* = 17.2 Hz, 1H), 5.06 (d, *J* = 10.1 Hz, 1H), 3.24 – 3.15 (m, 2H), 3.15 – 2.98 (m, 2H), 2.60 (d, *J* = 7.4 Hz, 2H), 2.35 (ddd, *J* = 14.6, 9.7, 5.4 Hz, 1H), 2.16 (dt, *J* = 13.7, 5.1 Hz, 1H), 2.02 (br, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.39, 143.13, 137.26, 137.08, 133.78, 133.43, 131.62, 128.77, 128.49, 128.08, 127.27, 126.81, 126.24, 124.61, 115.81, 62.83, 45.82, 38.37, 31.49, 25.57. HRMS (ESI) m/z calc'd for $C_{22}H_{23}NO$ [M+H]+: 318.1858; found 318.1867. $[\alpha]^{22}_D$ = +35.0° (c = 1.34, $CHCl_3$). **The major side product was found to be the double allylation product of the amino group, accounting for ~20% yield.*



19

(*R*)-3,3',4,6'-tetrahydro-1*H*,1'*H*-spiro[naphthalene-2,2'-pyridin]-1-one (19)

(**NOTE**: commercial *p*-Toluenesulfonic acid monohydrate was azeotroped with benzene 5 times to afford anhydrous TsOH) To a 100 mL flamed-dried RBF fitted with a magnetic stir bar was added **18** (85 mg, 0.27 mmol, 1 equiv), anhydrous TsOH (46 mg, 0.27 mmol, 1 equiv) and dry DCM (27 mL, 0.01M) under N_2. The solution was stirred at room temperature for 30 mins. Grubbs catalyst (2nd generation) (23 mg, 0.027 mmol, 0.1 equiv) was then added. The reaction was fitted with an oven-dried condenser and refluxed at 55°C under N_2 for 24 h. After cooled down to room temperature, the reaction was quenched with 40 mL saturated $NaHCO_3$ (aq.). The layers were separated and the aqueous layer was extracted with DCM (4 x 30 mL). The organic layers were combined and dried over anhydrous Na_2SO_4. The solid was filtered off and the solvent was removed under reduced pressure. The crude was purified by silica column chromatography (0%→1%→2%→5% MeOH/DCM) to afford pure product **19** as a yellowish oil (**54.3 mg, 0.25 mmol, 94% yield**). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.04 (d, *J* = 7.9 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.31 (t, *J* = 7.8 Hz, 1H), 7.23 (d, *J* = 7.7 Hz, 1H), 5.85 – 5.80 (m, 1H), 5.79 – 5.73 (m, 1H), 3.50 – 3.42 (m, 1H), 3.42 – 3.36 (m, 1H), 3.10 (ddd, *J* = 17.5, 6.6, 5.1 Hz, 1H), 2.94 (ddd, *J* = 17.5, 8.5, 5.1 Hz, 1H), 2.35 (ap. dp, *J* = 17.6, 2.9 Hz, 1H), 2.26 (ddd, *J* = 13.7, 6.7, 5.1 Hz, 1H), 2.19 – 2.11 (m, 1H), 2.06 (ddd, *J* = 17.7, 4.8, 3.2, 1H), 2.02 – 1.99 (br, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.24, 142.99, 133.33, 131.18, 128.68, 128.20, 126.73, 126.08, 123.18, 56.94, 41.53, 31.08, 29.63, 25.28. HRMS (ESI) m/z calc'd for $C_{14}H_{15}NO$ [M+H]+: 214.1232; found 214.1238. $[\alpha]^{22}_D$ = +23.9^o (c = 0.71, $CHCl_3$).



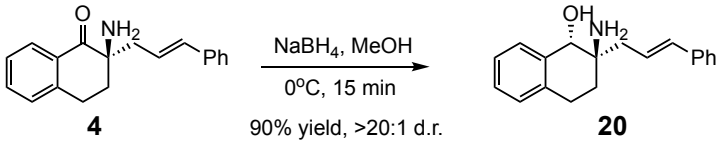
5

(*S*)-3,4-dihydro-1*H*-spiro[naphthalene-2,2'-piperidin]-1-one (5)

To a 10 mL RBF was added **19** (42.5 mg, 0.2 mmol, 1 equiv) and methanol (2 mL, 0.1M). The flask was flushed with nitrogen. Palladium on carbon (5 wt. % loading) (11 mg) was added and the flask was then flushed with hydrogen for 5 mins. The reaction was stirred under H_2 at room temperature for **2 hours**. (IMPORTANT: prolonged reaction time could lead to over-reduction of the ketone). The reaction was filtered through a Celite plug to remove Pd/C. The solvent was removed under reduced pressure to afford the product **5** as a colorless oil (**43.2 mg, *quantitative*, 91% ee**). *Proton NMR matches with the previously reported data.*[2] ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 7.9 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.21 (d, *J* = 7.7 Hz, 1H), 3.10 – 3.02 (m, 1H), 3.02 – 2.92 (m, 2H), 2.85 (ddd, *J* = 13.1, 9.1, 3.7 Hz, 1H), 2.41 (dt, *J* = 13.8, 5.0 Hz, 1H), 2.11 (br, 1H), 2.03 (ddd, *J* = 13.7, 9.8, 5.8 Hz, 1H), 1.81 – 1.61 (m, 3H), 1.58 – 1.51 (m, 2H), 1.49 – 1.40 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.91, 142.40, 133.34, 131.17, 128.66, 128.11, 126.74, 59.20, 41.32, 31.37, 30.37, 26.01, 25.34, 20.23; HRMS (ESI) m/z calc'd for $C_{14}H_{17}NO$ [M+H]+: 216.1388; found 216.1385. $[\alpha]^{22}_D$ = +36.7^o (c = 0.5, $CHCl_3$). Product **5** was converted to *N*-acetylated product for the determination of enantiomeric excess. **The enantiomeric excess was determined to be 91%** by chiral HPLC analysis (CHIRALPAK OJ-H column, 1 mL/min, 5% isopropanol in hexanes, λ = 254 nm): t_R(major) = 14.549 min, t_R(major) = 30.668 min.

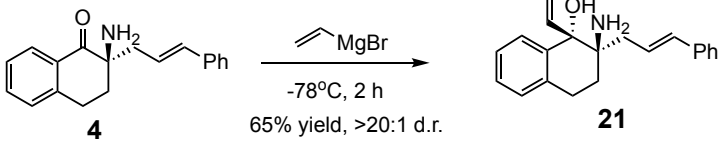
Scheme S2: Synthetic Diversification of Aminoketone 4 to generate 1,2-Amino Alcohols.

i. reduction:

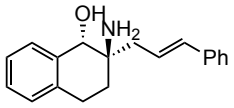


4 90% yield, >20:1 d.r. **20**

ii. Grignard addition:



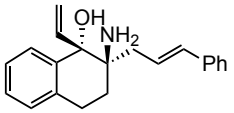
4 65% yield, >20:1 d.r. **21**



20

(1*S*,2*R*)-2-amino-2-cinnamyl-1,2,3,4-tetrahydronaphthalen-1-ol (20)

To a 20 mL vial was added **4** (57 mg, 0.2 mmol, 1 equiv) and methanol (4 mL, 0.05 M). The vial was cooled to 0°C in an ice bath. $NaBH_4$ (8.5 mg, 0.22 mmol, 1.1 equiv.) was added at 0°C (CAUTION: gas evolved). Then the reaction was stirred at 0°C for 10 min, before removal of all the volatiles under reduced pressure. The crude was purified via silica column chromatography (1%→2%→5%→10% MeOH/DCM) to afford pure product **20** as a white paste (**51.7 mg, 90% yield**). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.47 (dd, *J* = 5.5, 3.5 Hz, 1H), 7.40 (d, *J* = 7.1 Hz, 2H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.24 – 7.20 (m, 3H), 7.14 (dd, *J* = 5.4, 3.4 Hz, 1H), 6.53 (d, *J* = 15.8 Hz, 1H), 6.40 (dt, *J* = 15.5, 7.5 Hz, 1H), 4.48 (s, 1H), 2.90 (t, *J* = 6.8 Hz, 2H), 2.55 (dd, *J* = 14.0, 7.5 Hz, 1H), 2.30 (dd, *J* = 14.0, 7.6 Hz, 1H), 2.15 (br, 3H), 2.05 (dt, *J* = 13.4, 6.6 Hz, 1H), 1.72 (dt, *J* = 13.7, 6.9 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.28, 137.16, 135.32, 134.16, 128.72, 128.56, 128.54, 127.60, 127.30, 126.47, 126.19, 125.10, 75.78, 54.66, 38.19, 31.06, 25.87. HRMS (ESI) m/z calc'd for $C_{19}H_{21}NO$ [M+H]+: 280.1701; found 280.1708. $[\alpha]^{23}_D$ = -34.4° (c = 0.89, $CHCl_3$). *The amino alcohol was derivatized into oxazolidinone for the determination of relative stereochemistry via 2D-NMR analysis, shown in* ***Scheme S3****.*[3]



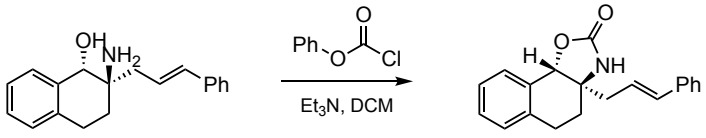
21

(1*S*,2*R*)-2-amino-2-cinnamyl-1-vinyl-1,2,3,4-tetrahydronaphthalen-1-ol (21)

To a flamed-dried 25 mL RBF was added **4** (55.5 mg, 0.18 mmol, 1 equiv) and THF (2 mL, 0.1 M) under N_2. The solution was cooled to -78°C, followed by the addition of vinylmagnesium bromide solution (1 M in THF) (0.6 mL, 0.6 mmol, 3 equiv.). The reaction was stirred at -78°C for 2 h and then quenched with sat. NH_4Cl solution. The aqueous layer was extracted with DCM (10 mL x 3). The organic layers were combined and dried over anhydrous $NaSO_4$. After filtration, all the volatiles were removed under reduced pressure. The crude was purified via silica column chromatography (1%→2%→5%→10% MeOH/DCM) to afford pure product **21** as a white paste (**36.0 mg, 65% yield**). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.53 – 7.44 (m, 1H), 7.39 – 7.36 (m, 2H), 7.30 (dd, *J* = 8.5, 6.9 Hz, 2H), 7.24 – 7.19 (m, 3H), 7.15 – 7.08 (m, 1H), 6.47 (d, *J* = 15.8 Hz, 1H), 6.35 (dt, *J* = 15.4, 7.4 Hz, 1H), 6.20 (dd, *J* = 17.1, 10.7 Hz, 1H), 5.30 – 5.20 (m, 2H), 3.04 – 2.86 (m, 2H), 2.49 (dd, *J* = 14.2, 7.7 Hz, 1H), 2.37 (dd, *J* = 14.2, 7.2 Hz, 1H), 1.98 (ddd, *J* = 13.8, 6.7, 4.2 Hz, 1H), 1.89 (ddd, *J* = 13.9, 9.1, 7.3 Hz, 1H), 2.08 – 1.45 (br, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.90, 139.59, 137.37, 134.91, 133.76, 128.55, 128.53, 127.23, 127.16, 127.13, 126.37, 126.12, 126.06, 115.41, 78.75, 56.57, 37.46, 31.14, 26.15. HRMS (ESI) m/z calc'd for $C_{21}H_{23}NO$ [M+H]+: 306.1858; found 306.1862. $[\alpha]^{24}_D$ = -89.93° (c = 1.54, $CHCl_3$). *The relative stereochemistry was determined via 2D-NMR analysis, shown in* ***Scheme S3****.*

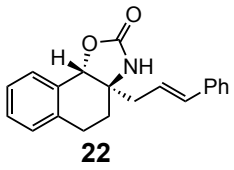
Scheme S3: Determination of Relative Stereochemistry of the Amino Alcohols.

Oxazolidinone formation:



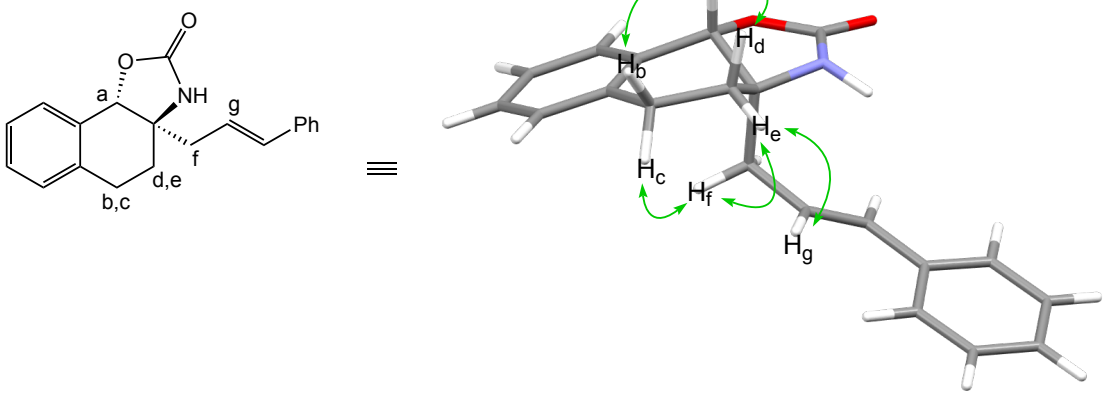
To an oven-dried 1-dram vial was added **20** (50 mg, 0.18 mmol, 1 equiv), dry DCM (0.9 mL) and triethylamine (0.05 mL, 0.36 mmol, 2 equiv) under N_2. Phenyl chloroformate (28 mg, 0.18 mmol, 1 equiv.) was added at room temperature. The reaction was stirred for 90 mins. Then, the volatiles were removed under reduced pressure. The crude was purified via silica column chromatography (10%→20%→30% EtOAc/Hexanes) to afford pure product **22** as a thick paste (15.9 mg, 30% yield). The un-cyclized carbamate was also isolated as the major side product (30.5 mg, 42% yield).

Compound **21** was also exposed to the same condition. However, only un-cyclized carbamate was isolated without the formation of oxazolidinone, presumably due to the congested tertiary alcohol in **21**.



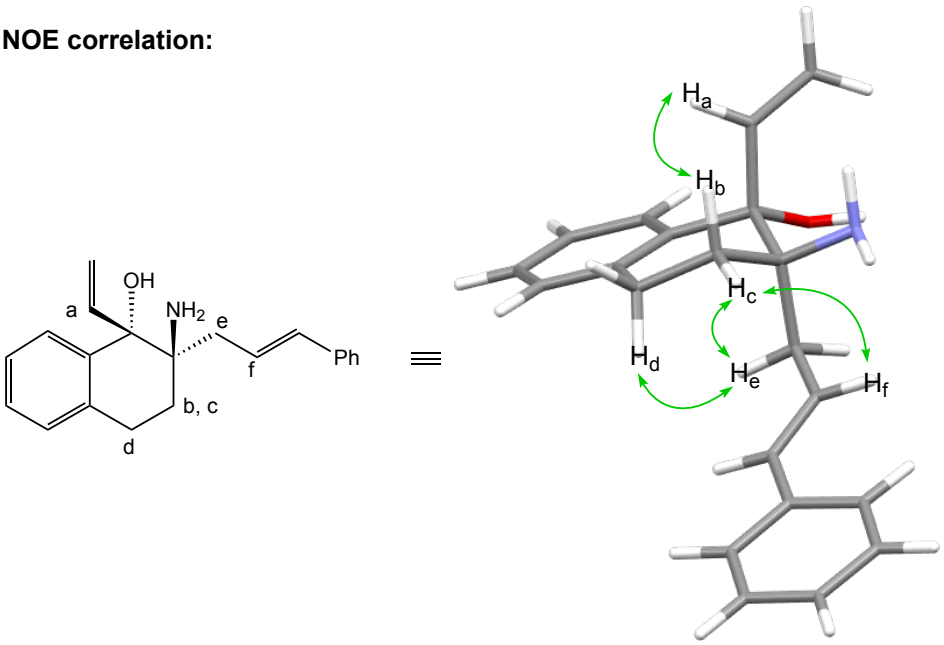
(3a*R*,9b*S*)-3a-cinnamyl-3a,4,5,9b-tetrahydronaphtho[2,1-*d*]oxazol-2(3*H*)-one (22): ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.42 – 7.38 (m, 1H), 7.34 – 7.26 (m, 6H), 7.25 – 7.18 (m, 2H), 6.39 (d, *J* = 15.7 Hz, 1H), 6.08 (ddd, *J* = 15.6, 8.3, 7.1 Hz, 1H), 5.59 (s, 1H), 5.33 (s, 1H), 3.12 (ddd, *J* = 18.1, 10.4, 2.6 Hz, 1H), 2.98 (ddd, *J* = 17.6, 9.5, 7.2 Hz, 1H), 2.26 (ddd, *J* = 13.1, 9.4, 2.5 Hz, 1H), 2.11 – 1.99 (m, 2H), 1.91 (ddd, *J* = 14.0, 7.1 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.02, 136.58, 135.84, 134.17, 132.24, 128.62, 128.40, 127.78, 127.73, 126.40, 126.24, 122.58, 122.18, 83.19, 61.75, 35.42, 28.17, 25.16.

NOE correlation:



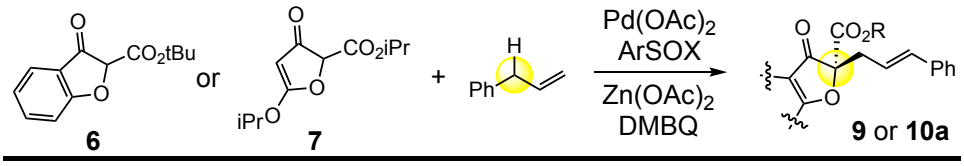
The ^{1}H signals of compound **22** were unambiguously assigned by ^{1}H, ^{13}C, COSY and HSQC NMR analysis. NOESY NMR revealed the following NOE correlation: H_a (δ 5.33) → H_b (δ 3.11), H_a (δ 5.33) → H_d (δ 2.02), H_c (δ 2.98) → H_f (δ 1.90), H_e (δ 2.25) → H_f (δ 1.90), H_e (δ 2.25) → H_g (δ 6.08). These NOE strongly agree with the conformation shown above, which establishes the ***trans-*** relationship[3] between the hydroxyl and the amino group.

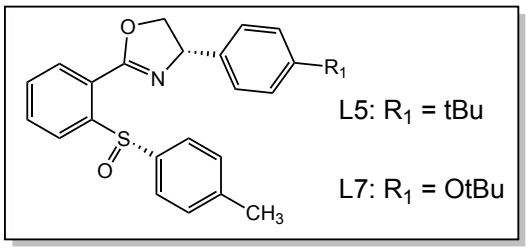
NOE correlation:

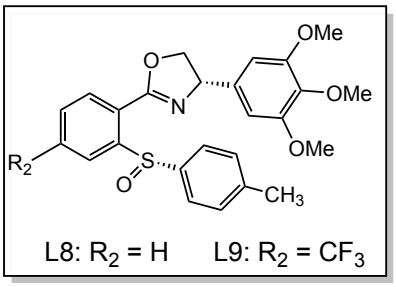


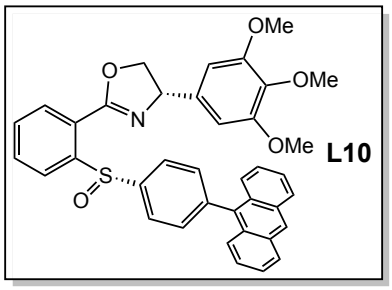
The ^{1}H signals of compound **21** were unambiguously assigned by ^{1}H, ^{13}C, COSY and HSQC NMR analysis. NOESY NMR revealed the NOE correlation between H_a (δ 6.20) → H_b (δ 1.89), which dictates the vinyl group at the (pseudo)axial position; H_d (δ 2.94) → H_e (δ 2.37), which dictates the phenylpropenyl group also at the (pseudo)axial position. These two results establish the ***trans-*** relationship between the hydroxyl and the amino group. Additional NOE signals also agree with the conformation shown above: H_c (δ 1.98) → H_e (δ 2.37), H_c (δ 1.98) → H_f (δ 6.35).

Table S4. Optimization for the Asymmetric C–H Alkylation with β-ketoester Nucleophiles.









Entry	Nuc.	Ligand	Yield (%)	ee (%)
1	**6**	L5	85	74
2	**6**	L7	91	70
3	**6**	L8	88	89
4	**6**	L9	94	91
5	**7**	L9	81	87
6	**7**	L10	66	90

Entry 1:
General procedure for **β-ketoester 6**: To a ½ dram borosilicate vial with stir bar was added ligand **L5** (4.2 mg, 0.01 mmol, 0.1 equiv) and $Pd(OAc)_2$ (2.2 mg, 0.01 mmol, 0.1 equiv). Benzene (0.2 mL) was added, and the vial was capped and stirred at 45˚C for 10 mins. Separately, to a ½ dram borosilicate vial with stir bar was added $Zn(OAc)_2$ dihydrate (11 mg, 0.05 mmol, 0.5 equiv), 2,6-dimethylbenzoquinone (20 mg, 0.15 mmol, 1.5 equiv) and **6** (47 mg, 0.20 mmol, 2 equiv). The catalyst solution was subsequently added to the reaction flask, and benzene (0.4 mL) was used to rinse the catalyst vial, also transferred and added to the reaction flask. Allylbenzene (13.0 µL, 0.10 mmol, 1 equiv) was added. The ½ dram vial was sealed with a Teflon cap, and allowed to stir **for 72 hours** at 5˚C. Afterward, the reaction mixture was directly subjected to flash column chromatography (1%→2% EtOAc/hexanes) to provide product **9** as a white film. Run 1 (29.8 mg, 85% yield, 74% ee); Run 2 (29.4 mg, 84% yield, 74% ee) **Average: 85% Yield, 74% ee.**

Entry 2:
Reaction proceeded according to the General procedure for Entry 1 using ligand **L7** (4.4 mg, 0.01 mmol, 0.1 equiv). Run 1 (31.3 mg, 89% yield, 70% ee); Run 2 (32.2 mg, 92% yield, 70% ee); **Average: 91% Yield, 70% ee.**

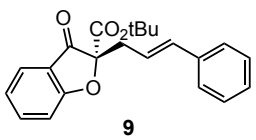
Entry 3:
Reaction proceeded according to the General procedure for Entry 1 using ligand **L8** (4.5 mg, 0.01 mmol, 0.1 equiv). Run 1 (31.6 mg, 90% yield, 89% ee); Run 2 (30.1 mg, 86% yield, 89% ee); **Average: 88% Yield, 89% ee.**

Entry 4:
Reaction proceeded according to the General procedure for Entry 1 using ligand **L9** (5.2 mg, 0.01 mmol, 0.1 equiv). Run 1 (33.2 mg, 95% yield, 92% ee); Run 2 (32.6 mg, 93% yield, 92% ee); **Average: 94% Yield, 91% ee.**

Entry 5:
General procedure for **β-ketoester 7**: To a ½ dram borosilicate vial with stir bar was added ligand **L9** (5.2 mg, 0.01 mmol, 0.1 equiv) and $Pd(OAc)_2$ (2.2 mg, 0.01 mmol, 0.1 equiv). Dioxane (0.3 mL) was added, and the vial was capped and stirred at 45˚C for 10 mins. Separately, to a ½ dram borosilicate vial with stir bar was added $Zn(OAc)_2$ dihydrate (11 mg, 0.05 mmol, 0.5 equiv), 2,6-dimethylbenzoquinone (20 mg, 0.15 mmol, 1.5 equiv) and **7** (45 mg, 0.20 mmol, 2 equiv). The catalyst solution was subsequently added to the reaction flask, and dioxane (0.3 mL) was used to rinse the catalyst vial, also transferred and added to the reaction flask. The vial was sealed with a Teflon cap, cooled to 5˚C in a cold room for 10 min. Allylbenzene (13 µL, 0.1 mmol) was added via syringe, and the reaction vial was again capped and stirred for 72 hours at 5˚C. Subsequently, the reaction mixture was directly subjected to flash column chromatography (10%→20%→30%→50% EtOAc/hexanes) to provide the alkylated product **10** as a clear oil: **27.9 mg, 81% yield, 87% ee.**

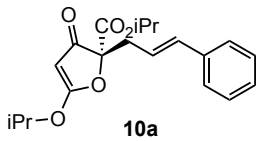
Entry 6:
Reaction proceeded according to the General procedure for Entry 5 using ligand **L10** (6.1 mg, 0.01 mmol, 0.1 equiv). Run 1 (19.9 mg, 58% yield, 90% ee); Run 2 (24.4 mg, 71% yield, 90% ee); Run 3 (23.8 mg, 69% yield, 90% ee). **Average: 66% yield, 90% ee.**

The absolute stereochemistry of alkylated product with β-ketoesters **6** was assigned based on crystal structure of **9e** (vide infra). For alkylation with β-ketoesters **7**, the absolute stereochemistry was inferred from **9e**.



9

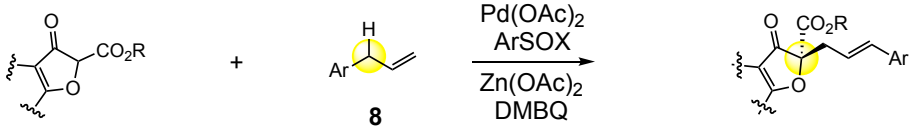
***Tert*-butyl 2-cinnamyl-3-oxo-2,3-dihydrobenzofuran-2-carboxylate** (**9**): ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.72 – 7.59 (m, 2H), 7.28 – 7.25 (m, 5H), 7.20 (m, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 6.57 (d, *J* = 15.8 Hz, 1H), 6.10 (dt, *J* = 15.8, 7.3 Hz, 1H), 3.20 (dd, *J* = 14.6, 7.6 Hz, 1H), 2.91 (dd, *J* = 14.5, 7.0 Hz, 1H), 1.46 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.97, 172.30, 164.21, 138.44, 136.86, 135.16, 128.45, 127.50, 126.27, 124.87, 122.47, 121.37, 119.66, 113.47, 91.48, 83.80, 37.54, 27.83. The enantiomeric excess was determined to be **91%** by chiral HPLC analysis (CHIRALPAK AD-RH column, 0.5 mL/min, 50% MeCN in H_2O, λ = 280 nm): t_R(minor) = 26.470 min, t_R(major) = 29.699 min. $[\alpha]^{22}_D$ = +104.5 (c = 0.59, $CHCl_3$). HRMS (ESI) m/z calc'd for $C_{22}H_{22}O_4$ [M+Na]+: 373.1416; found 373.1416.

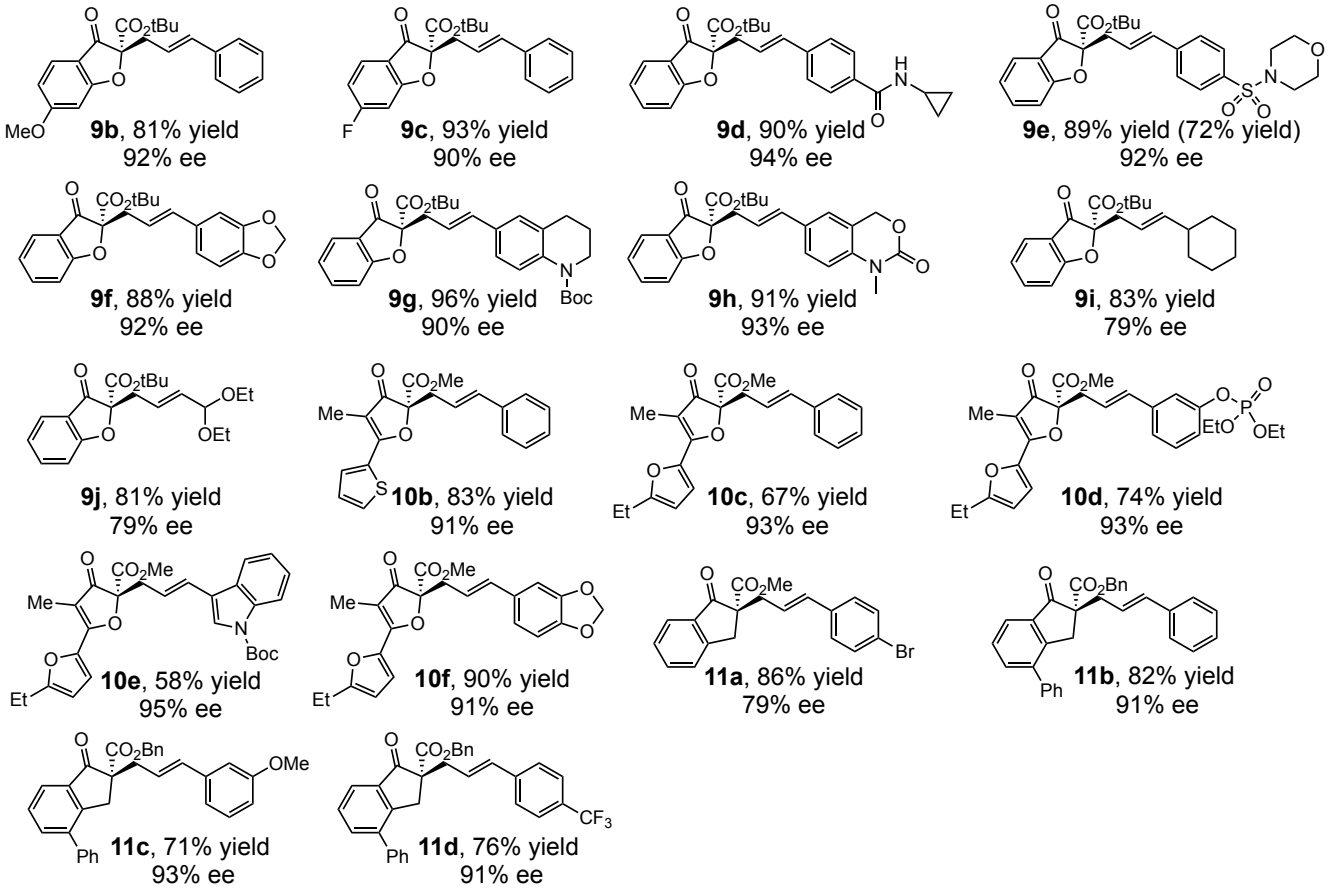


10a

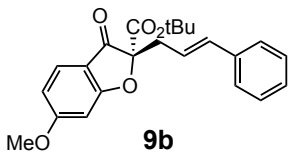
Isopropyl 2-cinnamyl-5-isopropoxy-3-oxo-2,3-dihydrofuran-2-carboxylate (10a): ^{1}H NMR (500MHz, $CDCl_3$) δ 7.37 – 7.17 (m, 5H), 6.55 (d, *J* = 15.8 Hz, 1H), 6.07 (td, *J* = 14.9, 6.3 Hz, 1H), 5.08 (hept, *J* = 6.6 Hz, 1H), 4.79 (hept, *J* = 6.3 Hz, 1H), 4.71 (s, 1H), 3.10 (dd, *J* = 14.7, 8.1 Hz, 1H), 2.95 (dd, *J* = 14.8, 6.7 Hz, 1H), 1.41 (m, 6H), 1.28 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.3, 184.2, 164.7, 137.0, 135.4, 128.6, 127.7, 126.4, 121.1, 92.1, 79.6, 70.7, 36.9, 21.9, 21.8, 21.75. The enantiomeric excess was determined to be 90% by chiral HPLC analysis (CHIRALPAK OJ-H column, 0.5 mL/min, 5% isopropanol in hexane, λ = 254 nm, t_R(minor) = 14.389 min, t_R(major) = 15.554 min.); $[\alpha]^{22}_D$ = +99.22 (c = 0.26, $CHCl_3$). HRMS (ESI) m/z calc'd for $C_{20}H_{24}O_5$ [M+H]: 345.1702; found 345.1692.

Table S5. Substrate Scope with β-ketoester Nucleophiles.

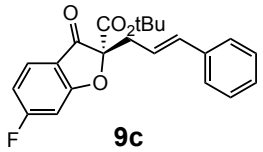




General procedure A for <u>β-ketoester 6</u> in Table S5: To a ½ dram borosilicate vial with stir bar was added ligand **L9** (5.2 mg, 0.01 mmol, 0.05 equiv) and $Pd(OAc)_2$ (2.2 mg, 0.01 mmol, 0.05 equiv). **Benzene** (0.2 mL) was added, and the vial was capped and stirred at 45˚C until all solids had dissolved. Separately, to a second 1 dram borosilicate vial with stir bar was added nucleophile **6** (94 mg, 0.4 mmol, 2.0 equiv), 2,6-dimethylbenzoquinone (40 mg, 0.3 mmol, 1.5 equiv) and $Zn(OAc)_2$ dihydrate (22 mg, 0.1 mmol, 0.5 equiv). The catalyst solution was subsequently added to the reaction flask, and Benzene (1.0 mL) was used to rinse the catalyst vial, also transferred and added to the reaction flask (total volume: 1.2 mL). The reaction vial was sealed with a Teflon cap and cooled at 5˚C for 10 min. Allylarene **8** (0.20 mmol, 1.0 equiv) was then added and the reaction was allowed to stir for 72 hours at 5˚C. Afterward, the reaction mixture was directly subjected to flash column chromatography to provide product.

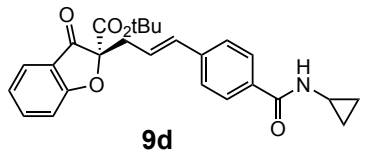


***Tert*-butyl (*R*)-2-cinnamyl-6-methoxy-3-oxo-2,3-dihydrobenzofuran-2-carboxylate (9b):** Allylbenzene (13.0 µL, 0.10 mmol, 1 equiv) reacted with nucleophile **6b** according to the **general procedure A**. Purification by flash column chromatography (5%→10% EtOAc/hexanes) provided the product as a clear oil: Run 1 (30.7 mg, 81% yield, 92% ee); Run 2 (32.5 mg, 85% yield, 92% ee); Run 3 (29.6 mg, 78% yield, 92% ee). **Average: 81% (±3.8%) yield, 92% ee.** The enantiomeric excess was determined by chiral HPLC analysis (CHIRALPAK OJ-H column, 1 mL/min, 2% isopropanol in hexanes, λ = 280 nm): t_R(minor) = 21.130 min, t_R(major) = 23.398 min. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.54 (d, *J* = 9.1 Hz, 1H), 7.29 – 7.25 (m, 4H), 7.22 – 7.17 (m, 1H), 6.67 – 6.62 (m, 2H), 6.56 (d, *J* = 15.8 Hz, 1H), 6.09 (dt, *J* = 15.8, 7.2 Hz, 1H), 3.88 (s, 3H), 3.17 (dd, *J* = 14.6, 7.7 Hz, 1H), 2.88 (dd, *J* = 14.6, 6.8, 1H), 1.45 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.43, 174.84, 168.65, 164.54, 136.94, 134.98, 128.44, 127.45, 126.27, 125.91, 121.62, 112.64, 112.30, 96.16, 92.28, 83.65, 55.92, 37.52, 27.85. HRMS (ESI) m/z calc'd for $C_{23}H_{24}O_5$ [M+H]+: 381.1702; found 381.1690. $[\alpha]^{22}_D$ = -33.0^o (c = 1.2, $CHCl_3$).



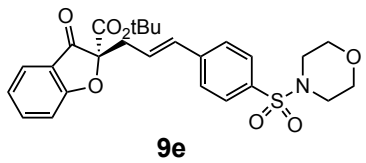
9c

***Tert*-butyl (*R*)-2-cinnamyl-6-fluoro-3-oxo-2,3-dihydrobenzofuran-2-carboxylate (9c):** Allylbenzene (13.0 μL, 0.10 mmol, 1 equiv) reacted with nucleophile **6c** according to the **general procedure A**. Purification by flash column chromatography (1%→2% EtOAc/hexanes) provided the product as a clear oil: Run 1 (34.7 mg, 94% yield, 90% ee); Run 2 (34.3 mg, 93% yield, 90% ee); Run 3 (33.8 mg, 92% yield, 90% ee). **Average: 93% (±1.2%) yield, 90% ee.** The enantiomeric excess was determined by chiral HPLC analysis (CHIRALPAK OJ-H column, 1 mL/min, 2% isopropanol in hexanes, λ = 280 nm): t_R(minor) = 6.422 min, t_R(major) = 11.157 min. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.66 (dd, *J* = 8.5, 5.7 Hz, 1H), 7.29 – 7.24 (m, 5H), 7.24 – 7.17 (m, 1H), 6.90 (dd, *J* = 9.0, 2.1 Hz, 1H), 6.82 (td, *J* = 8.7, 2.1 Hz, 1H), 6.57 (d, *J* = 15.9 Hz, 1H), 6.07 (dt, *J* = 15.6, 7.3 Hz, 1H), 3.18 (dd, *J* = 14.5, 7.1 Hz, 1H), 2.92 (dd, *J* = 14.5, 7.1 Hz, 1H), 1.46 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.97, 173.73 (d, *J* = 15.0 Hz), 169.52 (d, *J* = 259.2 Hz), 163.88, 136.75, 135.42, 128.49, 127.61, 126.79 (d, *J* = 12.2 Hz), 126.28, 120.94, 116.34, 111.40 (d, *J* = 24.4 Hz), 100.93 (d, *J* = 26.1 Hz). 92.64, 84.04, 37.37, 27.81. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -95.86. HRMS (ESI) m/z calc'd for $C_{22}H_{21}FO_4$ [M+Na]+: 391.1322; found 391.1321. $[\alpha]^{23}_D$ = +46.7° (c = 1.44, $CHCl_3$).



9d

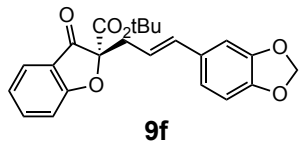
***Tert*-butyl (*R*,*E*)-2-(3-(4-(cyclopropylcarbamoyl)phenyl)allyl)-3-oxo-2,3-dihydrobenzofuran-2-carboxylate (9d):** 4-allyl-*N*-cyclopropylbenzamide (40.2 mg, 0.2 mmol, 1.0 equiv) reacted with nucleophile **6** according to the **general procedure A**. Purification by flash column chromatography (20%→30% Acetone/hexanes) provided the product as a colorless gel. Run 1 (78.9 mg, 91% yield, 94% ee); Run 2 (77.1 mg, 89% yield, 94% ee); Run 3 (79.0 mg, 91% yield, 94% ee). **Average: 90% (±1.2%) yield, 94% ee.** The enantiomeric excess was determined by chiral HPLC analysis (CHIRALPAK IA-3 column, 1 mL/min, 5% isopropanol in hexanes, λ = 254 nm): t_R(minor) = 53.437 min, t_R(major) = 57.398 min. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.67 – 7.59 (m, 4H), 7.26 (d, *J* = 8.3 Hz, 2H), 7.21 (dd, *J* = 9.0, 0.8 Hz, 1H), 7.09 (td, *J* = 7.5, 0.8 Hz, 1H), 6.56 (d, *J* = 16.1 Hz, 1H), 6.32 (br, 1H), 6.16 (ddd, *J* = 15.8, 7.7, 7.0 Hz, 1H), 3.18 (ddd, *J* = 14.6, 7.7, 1.3 Hz, 1H), 2.91 – 2.83 (m, 2H), 1.42 (s, 9H), 0.82 (m, 2H), 0.58 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.84, 172.23, 168.40, 164.11, 139.87, 138.56, 134.22, 133.20, 127.13, 126.27, 124.88, 123.67, 122.59, 119.55, 113.45, 91.26, 83.94, 37.50, 27.81, 23.12, 6.76. HRMS (ESI) m/z calc'd for $C_{26}H_{27}NO_5$ [M+H]+: 434.1967; found 434.1961. $[\alpha]^{22}_D$ = +84.1° (c = 1.1, $CHCl_3$).



9e

***Tert*-butyl (*R*,*E*)-2-(3-(4-(morpholinosulfonyl)phenyl)allyl)-3-oxo-2,3-dihydrobenzofuran-2-carboxylate (9e):** 4-((4-allylphenyl)sulfonyl)morpholine (54 mg, 0.2 mmol, 1.0 equiv) reacted with nucleophile **6** according to the **general procedure A**. Purification by flash column chromatography (20%→30% EtOAc/hexanes) provided the product as a white solid: Run 1 (89.2 mg, 89% yield, **92% ee**).

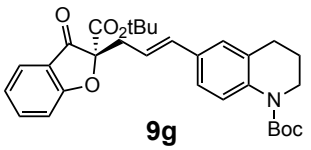
Using 2.5 mol% catalyst: **L9** (5.2 mg, 0.01 mmol, 0.05 equiv) and $Pd(OAc)_2$ (2.2 mg, 0.01 mmol, 0.05 equiv), nucleophile **6** (235 mg, 1 mmol, 2.0 equiv), 2,6-dimethylbenzoquinone (102 mg, 0.75 mmol, 1.5 equiv) and $Zn(OAc)_2$ dihydrate (55 mg, 0.25 mmol, 0.5 equiv). 4-((4-allylphenyl)sulfonyl)morpholine (135 mg, 0.5 mmol, 1.0 equiv) in Benzene (total reaction volume: 3 mL): Run 2 (184.6 mg, 74% yield, 92% ee); Run 3 (175 mg, 70% yield, 92% ee). **Average: 72% yield, 92% ee.** The enantiomeric excess was determined by chiral HPLC analysis (CHIRALPAK IB-3 column, 1 mL/min, 5% isopropanol in hexanes, λ = 280 nm): t_R(major) = 19.003 min, t_R(minor) = 21.562 min. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.66 (m,, 2H), 7.63 (dd, *J* = 8.1 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.5 Hz, 1H), 7.12 (t, *J* = 7.4 Hz, 1H), 6.60 (d, *J* = 15.9 Hz, 1H), 6.25 (dt, *J* = 15.8, 7.3 Hz, 1H), 3.75 – 3.67 (m, 4H), 3.21 (dd, *J* = 14.6, 7.5 Hz, 1H), 2.99 – 2.95 (m, 4H), 2.92 (dd, *J* = 14.7, 7.1 Hz, 1H), 1.44 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.74, 172.24, 164.05, 141.54, 138.62, 133.61, 133.43, 128.16, 126.73, 125.73, 124.95, 122.68, 119.54, 113.46, 91.05, 84.03, 66.09, 45.96, 37.33, 27.82. HRMS (ESI) m/z calc'd for $C_{26}H_{29}NO_7S$ [M+H]+: 500.1732; found 500.1736. $[\alpha]^{22}_D$ = +83.6° (c = 1.0, $CHCl_3$). ***Single crystals suitable for X-ray crystallography were grown by slow diffusion from Et_2O/Hexane. The absolute stereochemistry is determined by X-ray crystallography shown on page S33.***



9f

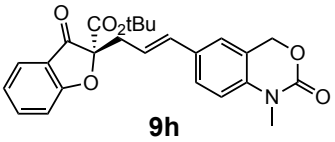
***Tert*-butyl (*R*,*E*)-2-(3-(benzo[*d*][1,3]dioxol-5-yl)allyl)-3-oxo-2,3-dihydrobenzofuran-2-carboxylate (9f):** Safrole (33 mg, 0.2 mmol, 1.0 equiv) reacted with nucleophile **6** according to the **general procedure A**. Purification by flash column chromatography (5%→8% EtOAc/hexanes) provided the product as a clear oil: Run 1 (69.3 mg, 88% yield, 92% ee); Run 2 (68.8 mg, 87% yield, 92% ee); Run 3 (69.4 mg, 88% yield, 92% ee). **Average: 88% (±0.4%) yield, 92% ee.** The enantiomeric excess was determined by chiral HPLC analysis (CHIRALPAK AD-RH column, 0.75 mL/min, 45% MeCN in H_2O, λ = 280 nm): t_R(minor) = 34.062 min, t_R(major) = 36.926 min. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.68 – 7.59 (m, 2H), 7.22 (d, *J* = 8.3 Hz, 1H), 7.09 (t, *J* = 7.4 Hz, 1H), 6.77 (s, 1H), 6.69 (d, *J* = 1.1 Hz, 2H), 6.46 (dd, *J* = 15.7, 1.2 Hz, 1H), 5.96 – 5.86 (m, 3H), 3.14 (dd, *J* = 14.6, 7.6 Hz, 1H), 2.85 (dd, *J* = 14.6, 7.0 Hz, 1H), 1.44 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.97, 172.27, 164.21, 147.89, 147.14, 138.44, 134.71, 131.35, 124.85, 122.46, 120.92,

119.67, 119.49, 113.45, 108.16, 105.57, 101.00, 91.53, 83.77, 37.48, 27.83. HRMS (ESI) m/z calc'd for $C_{23}H_{22}O_6$ [M+Na]+: 417.1314; found 417.1320. $[\alpha]^{23}_D$ = +107.2° (c = 0.87, $CHCl_3$).



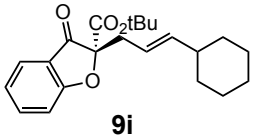
9g

***Tert*-butyl (*R*,*E*)-6-(3-(2-(*tert*-butoxycarbonyl)-3-oxo-2,3-dihydrobenzofuran-2-yl)prop-1-en-1-yl)-3,4-dihydroquinoline-1(2*H*)-carboxylate (9g):** *Tert*-butyl 6-allyl-3,4-dihydroquinoline-1(2*H*)-carboxylate **8d** (55 mg, 0.2 mmol, 1.0 equiv) reacted with nucleophile **6** according to the **general procedure A**. Purification by flash column chromatography (5%→10%→15% EtOAc/hexanes) provided the product as a clear oil: Run 1 (94.5 mg, 93% yield, 90% ee); Run 2 (98.3 mg, 97% yield, 90% ee); Run 3 (97.8 mg, 97% yield, 90% ee). **Average: 96% (±2.0%) yield, 90% ee.** The enantiomeric excess was determined by chiral HPLC analysis (CHIRALPAK IB-3 column, 1 mL/min, 1% isopropanol in hexanes, λ = 280 nm): t_R(major) = 6.752 min, t_R(minor) = 9.283 min. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.66 – 7.60 (m, 2H), 7.55 (d, *J* = 8.6 Hz, 1H), 7.21 (d, *J* = 8.5 Hz, 1H), 7.09 (t, *J* = 7.4 Hz, 1H), 7.02 (dd, *J* = 8.6, 2.1 Hz, 1H), 6.95 (d, *J* = 2.1 Hz, 1H), 6.47 (d, *J* = 15.6 Hz, 1H), 5.98 (dt, *J* = 15.7, 7.3 Hz, 1H), 3.69 – 3.64 (m, 2H), 3.15 (dd, *J* = 14.6, 7.8 Hz, 1H), 2.87 (dd, *J* = 14.7, 6.9 Hz, 1H), 2.69 (t, *J* = 6.6 Hz, 2H), 1.88 (p, *J* = 6.4 Hz, 2H), 1.50 (s, 9H), 1.44 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.02, 172.29, 164.24, 153.83, 138.42, 138.00, 134.68, 131.81, 129.69, 126.42, 124.84, 123.93, 123.70, 122.44, 120.01, 119.69, 113.46, 91.57, 83.75, 80.81, 44.75, 37.60, 28.38, 27.84, 27.54, 23.44. HRMS (ESI) m/z calc'd for $C_{30}H_{35}NO_6$ [M+H]+: 506.2543; found 506.2551. $[\alpha]^{23}_D$ = +83.4° (c = 1.1, $CHCl_3$).



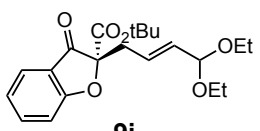
9h

***Tert*-butyl (*R*,*E*)-2-(3-(1-methyl-2-oxo-1,4-dihydro-2*H*-benzo[*d*][1,3]oxazin-6-yl)allyl)-3-oxo-2,3-dihydrobenzofuran-2-carboxylate (9h):** 6-allyl-1-methyl-1,4-dihydro-2*H*-benzo[*d*][1,3]oxazin-2-one (41 mg, 0.2 mmol, 1.0 equiv) reacted with nucleophile **6** according to the **general procedure A**. Purification by flash column chromatography (10%→20%→30%→40% EtOAc/hexanes) provided the product as a clear oil: Run 1 (78.5 mg, 90% yield, 93% ee); Run 2 (78.3 mg, 90% yield, 93% ee); Run 3 (81.3 mg, 93% yield, 93% ee). **Average: 91% (±1.9%) yield, 93% ee.** The enantiomeric excess was determined by chiral HPLC analysis (CHIRALPAK OJ-H column, 1 mL/min, 30% isopropanol in hexanes, λ = 280 nm): t_R(minor) = 21.957 min, t_R(major) = 27.179 min. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.63 (m, 2H), 7.23 – 7.18 (m, 2H), 7.09 (t, *J* = 7.4 Hz, 1H), 7.01 (d, *J* = 1.9 Hz, 1H), 6.80 (d, *J* = 8.4 Hz, 1H), 6.49 (d, *J* = 16.1 Hz, 1H), 6.02 (dt, *J* = 15.6, 7.3 Hz, 1H), 5.12 (s, 2H), 3.32 (s, 3H), 3.15 (dd, *J* = 14.6, 7.7 Hz, 1H), 2.87 (dd, *J* = 14.5, 6.9 Hz, 1H), 1.42 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.86, 172.23, 164.15, 153.12, 138.51, 137.62, 133.74, 132.04, 127.17, 124.87, 122.55, 121.86, 121.18, 120.68, 119.62, 113.44, 112.92, 91.37, 83.86, 67.28, 37.43, 31.55, 27.82. HRMS (ESI) m/z calc'd for $C_{25}H_{25}NO_6$ [M+H]+: 436.1760; found 436.1767. $[\alpha]^{23}_D$ = +90.3° (c = 0.8, $CHCl_3$).



9i

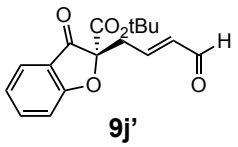
***Tert*-butyl (*R*,*E*)-2-(3-cyclohexylallyl)-3-oxo-2,3-dihydrobenzofuran-2-carboxylate (9i):** To a ½ dram borosilicate vial with stir bar was added ligand **L9** (5.2 mg, 0.01 mmol, 0.1 equiv) and $Pd(OAc)_2$ (2.2 mg, 0.01 mmol, 0.1 equiv). Benzene (0.2 mL) was added, and the vial was capped and stirred at 45˚C for 10 mins. Separately, to a ½ dram borosilicate vial with stir bar was added $Zn(OAc)_2$ dihydrate (11 mg, 0.05 mmol, 0.5 equiv), 2,6-dimethylbenzoquinone (20 mg, 0.15 mmol, 1.5 equiv) and **6** (47 mg, 0.20 mmol, 2 equiv). The catalyst solution was subsequently added to the reaction flask, and benzene (0.4 mL) was used to rinse the catalyst vial, also transferred and added to the reaction flask. Allylcyclohexane (12.4 mg, 0.1 mmol, 1.0 equiv) was added. The vial was sealed with a Teflon cap, and allowed to stir **for 72 hours** at **room temperature**. Afterward, the reaction mixture was directly subjected to flash column chromatography (1%→2% EtOAc/hexanes) to provide product **9i** as a colorless oil. Run 1 (29.6 mg, 83% yield, 79% ee); Run 2 (30.4 mg, 85% yield, 79% ee); Run 3 (28.7 mg, 81% yield, 79% ee); **Average: 83% (±2.4%) yield, 79% ee.** The enantiomeric excess was determined to be 79% by chiral HPLC analysis (CHIRALPAK AD-RH column, 0.5 mL/min, 55% MeCN in H_2O, λ = 254 nm): t_R(minor) = 30.213 min, t_R(major) = 33.981 min. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.65 – 7.58 (m, 2H), 7.19 (d, *J* = 8.9 Hz, 1H), 7.08 (t, *J* = 7.4 Hz, 1H), 5.55 (dd, *J* = 15.5, 6.9 Hz, 1H), 5.23 (ddd, *J* = 15.6, 7.9, 6.7 Hz, 1H), 2.92 (dd, *J* = 14.4, 7.8 Hz, 1H), 2.69 (dd, *J* = 14.4, 6.7 Hz, 1H), 1.87 – 1.75 (m, 1H), 1.67 – 1.48 (m, 5H), 1.44 (s, 9H), 1.20 – 1.01 (m, 3H), 0.92 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.25, 172.32, 164.38, 142.60, 138.23, 124.64, 122.23, 119.96, 118.43, 113.36, 91.73, 83.49, 40.55, 37.19, 32.62, 27.82, 26.08, 25.82. HRMS (ESI) m/z calc'd for $C_{22}H_{28}O_4$ [M+H]+: 357.2066; found 357.2062. $[\alpha]^{23}_D$ = +75.5° (c = 0.67, $CHCl_3$).



9j

***Tert*-butyl (*R*,*E*)-2-(4,4-diethoxybut-2-en-1-yl)-3-oxo-2,3-dihydrobenzofuran-2-carboxylate (9j):** To a ½ dram borosilicate vial with stir bar was added ligand **L9** (5.2 mg, 0.01 mmol, 0.1 equiv) and $Pd(OAc)_2$ (2.2 mg, 0.01 mmol, 0.1 equiv). Benzene (0.2 mL) was added, and the vial was capped and stirred at 45˚C for 10 mins. Separately, to a ½ dram borosilicate vial with stir bar was added $Zn(OAc)_2$ dihydrate (11 mg, 0.05 mmol, 0.5 equiv), 2,6-dimethylbenzoquinone (20 mg, 0.15 mmol, 1.5 equiv) and **6** (47 mg, 0.20 mmol, 2 equiv). The catalyst solution was subsequently added to the reaction flask, and benzene (0.4 mL) was used to rinse the catalyst vial, also transferred and added to the reaction flask. 3-Butenal diethyl acetal (14.4 mg, 0.1 mmol, 1.0 equiv) was added. The vial was sealed with a Teflon cap, and allowed to stir **for 48 hours** at

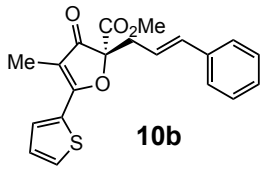
room temperature. Afterward, the reaction mixture was directly subjected to flash column chromatography (silica neutralized with 1% Et_3N in 5% EtOAc/hexanes, flushed with 5%→8%→10% EtOAc/hexanes) to provide product **9j** as a colorless oil. Run 1 (31.6 mg, 84% yield, 79% ee); Run 2 (29.7 mg, 79% yield, 79% ee); Run 3 (30.3 mg, 80% yield, 79% ee); **Average: 81% (±2.6%) yield, 79% ee.** The product is converted into aldehyde **9j'** (see below) for chiral HPLC analysis. The enantiomeric excess was determined to be 79% by chiral HPLC analysis (CHIRALPAK OJ-H column, 1 mL/min, 10% isopropanol in hexanes, λ = 254 nm): t_R(minor) = 5.381 min, t_R(major) = 8.786 min. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.68 – 7.62 (m, 2H), 7.22 (d, *J* = 9.0 Hz, 1H), 7.12 (t, *J* = 7.5 Hz, 1H), 5.75 – 5.65 (m, 2H), 4.75 – 4.72 (m, 1H), 3.55 – 3.43 (m, 2H), 3.39 – 3.26 (m, 2H), 3.04 (dd, *J* = 14.4, 5.3 Hz, 1H), 2.80 (dd, *J* = 14.4, 5.3 Hz, 1H), 1.46 (s, 9H), 1.13 (dt, *J* = 11.1, 7.0 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.95, 172.33, 164.14, 138.36, 133.32, 125.62, 124.77, 122.40, 119.72, 113.45, 100.98, 91.11, 83.85, 60.98, 60.91, 36.40, 27.76, 15.12, 15.10. HRMS (ESI) m/z calc'd for $C_{21}H_{28}O_6$ [M+Na]+: 399.1784; found 399.1783. $[\alpha]^{23}_D$ = +37.2° (c = 1.6, $CHCl_3$).



9j'

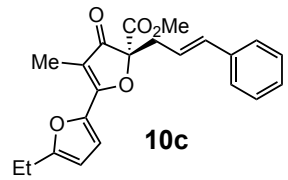
***Tert*-butyl (*R*,*E*)-3-oxo-2-(4-oxobut-2-en-1-yl)-2,3-dihydrobenzofuran-2-carboxylate (9j'):** ^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.44 (d, *J* = 7.8 Hz, 1H), 7.71 – 7.65 (m, 2H), 7.22 (d, *J* = 8.7 Hz, 1H), 7.15 (t, *J* = 7.5 Hz, 1H), 6.78 – 6.68 (m, 1H), 6.25 (dd, *J* = 15.8, 7.8 Hz, 1H), 3.29 (dd, *J* = 15.1, 7.4 Hz, 1H), 2.96 (dd, *J* = 15.2, 7.0 Hz, 1H), 1.43 (s, *J* = 1.0 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.27, 193.13, 172.22, 163.66, 148.59, 138.85, 136.75, 125.08, 122.95, 119.24, 113.52, 89.92, 84.50, 36.37, 27.75. HRMS (ESI) m/z calc'd for $C_{17}H_{18}O_5$ [M+Na]+: 325.1052; found 325.1055.

General procedure B for β-ketoester 7 in Table S5: To a ½ dram borosilicate vial with stir bar was added ligand **L10** (6.1 mg, 0.01 mmol, 0.1 equiv) and $Pd(OAc)_2$ (2.2 mg, 0.01 mmol, 0.1 equiv). **Dioxane** (0.3 mL) was added, and the vial was capped and stirred at 45˚C until all solids had dissolved. Separately, to a second ½ dram borosilicate vial with stir bar was added nucleophile, 2,6-dimethylbenzoquinone (20.8 mg, 0.15 mmol, 1.5 equiv) and $Zn(OAc)_2$ dihydrate (11 mg, 0.05 mmol, 0.5 equiv). The catalyst solution was subsequently added to the reaction flask, and dioxane (volume specified below) was used to rinse the catalyst vial, also transferred and added to the reaction flask. The reaction vial was sealed with a Teflon cap and cooled at 5˚C for 10 min. Allylarene **8** (0.10 mmol, 1 equiv) was then added and the reaction was allowed to stir for 72 hours at 5˚C. Afterward, the reaction mixture was directly subjected to flash column chromatography to provide product.



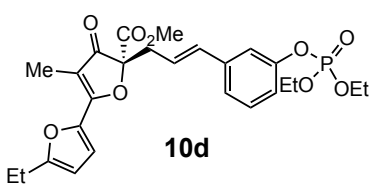
10b

Methyl (*R*)-2-cinnamyl-4-methyl-3-oxo-5-(thiophen-2-yl)-2,3-dihydrofuran-2-carboxylate (10b): Allylbenzene (13.0 µL, 0.10 mmol, 1 equiv) was reacted with nucleophile **7b** (24 mg, 0.10 mmol, 1 equiv) in Dioxane (**1.5 mL** total volume) using 1 dram vial according to the **general procedure B**. Purification by flash column chromatography (10%→20%→30%→50% EtOAc/hexanes) provided the product as a clear oil. Run 1 (29.1 mg, 82% yield, 91% ee); Run 2 (28.6 mg, 81% yield, 91% ee); Run 3 (30.1 mg, 85% yield, 91% ee). **Average: 83% (±2.2%) yield, 91% ee.** The enantiomeric excess was determined to be 91% by chiral HPLC analysis (CHIRALPAK IB-3 column, 0.5 mL/min, 10% isopropanol in hexane, λ = 254 nm, t_R(minor) = 9.52 min, t_R(major) = 10.04 min.). ^{1}H NMR (500MHz, $CDCl_3$) δ 7.80 (dd, *J* = 3.9, 1.2 Hz, 1H), 7.71 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.35 – 7.16 (m, 6H), 6.56 (d, *J* = 15.8 Hz, 1H), 6.07 (dt, *J* = 15.2, 7.3 Hz, 1H), 3.78 (s, 3H), 3.20 (dd, *J* = 15.4, 7.4 Hz, 1H), 2.95 (dd, *J* = 14.6, 7.2 Hz, 1H), 2.00 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.0, 174.9, 166.1, 137.1, 135.4, 132.1, 132.0, 131.1, 128.6, 128.5, 127.7, 126.5, 121.3, 107.9, 89.8, 53.5, 37.9, 7.2; HRMS (ESI) m/z calc'd for $C_{20}H_{18}O_4S$ [M+H]: 355.1004; found 355.0998. $[\alpha]^{22}_D$ = +93.19 (c = 0.13, $CHCl_3$).



10c

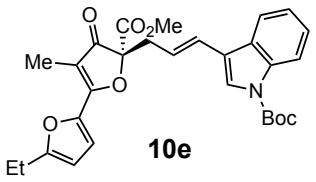
Methyl (*R*)-5-cinnamyl-5'-ethyl-3-methyl-4-oxo-4,5-dihydro-[2,2'-bifuran]-5-carboxylate (10c): Allylbenzene (13.0 µL, 0.10 mmol, 1 equiv) was reacted with nucleophile **7c** (25 mg, 0.10 mmol, 1 equiv) in Dioxane (**0.6 mL** total volume) according to the **general procedure B**. Purification by flash column chromatography (10%→20%→30%→50% EtOAc/hexanes) provided the product as a clear oil. Run 1 (23.2 mg, 63% yield, 93% ee); Run 2 (24.5 mg, 67% yield, 93% ee); Run 3 (25.6 mg, 70% yield, 93% ee). **Average: 67% (±3.3%) yield, 93% ee.** The enantiomeric excess was determined to be 93% by chiral HPLC analysis (CHIRALPAK OJ-H column, 0.5 mL/min, 20% isopropanol in hexane, λ = 230 nm, t_R(minor) = 10.82 min, t_R(major) = 12.83 min.) ^{1}H NMR (500MHz, $CDCl_3$) δ 7.33 – 7.24 (m, 4H), 7.24 – 7.16 (m, 1H), 7.11 (d, *J* = 3.5 Hz, 1H), 6.54 (d, *J* = 15.8 Hz, 1H), 6.25 (d, *J* = 3.4 Hz, 1H), 6.06 (dt, *J* = 15.2, 7.3 Hz, 1H), 3.77 (s, 3H), 3.17 (dd, *J* = 14.7, 7.5 Hz, 1H), 2.94 (dd, *J* = 14.4, 7.2 Hz, 1H), 2.77 (q, *J* = 7.6 Hz, 2H), 1.99 (s, 3H), 1.30 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.8, 170.8, 166.2, 163.6, 143.9, 137.1, 135.2, 128.6, 127.6, 126.5, 121.4, 117.7, 107.7, 107.2, 89.6, 53.4, 37.9, 21.9, 11.9, 6.4; HRMS (ESI) m/z calc'd for $C_{22}H_{22}O_5$ [M+H]: 367.1545; found 367.1541. $[\alpha]^{22}_D$ = +135.15 (c = 0.11, $CHCl_3$).



10d

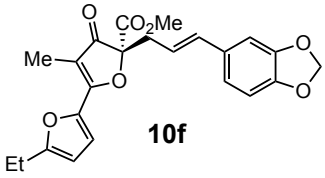
Methyl (*R*,*E*)-5-(3-(3-((diethoxyphosphoryl)oxy)phenyl)allyl)-5'-ethyl-3-methyl-4-oxo-4,5-dihydro-[2,2'-bifuran]-5-carboxylate (10d): 3-allylphenyl diethyl phosphate (27 mg, 0.10 mmol, 1 equiv) was reacted with nucleophile **7c** (25 mg, 0.10 mmol, 1 equiv) in Dioxane (**0.6 mL** total volume) according to the **general procedure B**.

Purification by flash column chromatography (10%→20%→30%→50% EtOAc/hexanes) provided the product as a clear oil. Run 1 (39.1 mg, 75% yield, 93% ee); Run 2 (37.2 mg, 72% yield, 93% ee); Run 3 (38.8 mg, 75% yield, 93% ee). **Average: 74% (±2.0%) yield, 93% ee.** The enantiomeric excess was determined to be 93% by chiral HPLC analysis (CHIRALPAK IB-3 column, 0.5 mL/min, 5% isopropanol in hexane, λ = 254 nm, t_R(minor) = 36.87 min, t_R(major) = 38.83 min). ^{1}H NMR (500MHz, $CDCl_3$) δ 7.22 (t, *J* = 7.9 Hz, 1H), 7.13 – 7.05 (m, 4H), 6.50 (d, *J* = 15.7 Hz, 1H), 6.25 (d, *J* = 3.4 Hz, 1H), 6.06 (dt, *J* = 15.2, 7.3 Hz, 1H), 4.27 – 4.14 (m, 4H), 3.76 (s, 3H), 3.15 (dd, *J* = 14.6, 7.5 Hz, 1H), 2.92 (dd, *J* = 14.7, 7.2 Hz, 1H), 2.77 (q, *J* = 7.6 Hz, 2H), 1.99 (s, 3H), 1.33 (t, *J* = 7.3 Hz, 6H), 1.29 (t, *J* = 9.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.6, 170.8, 166.2, 163.7, 151.0 (d, J_P = 6.3 Hz), 143.8, 139.0, 134.3, 129.7, 123.2, 122.7, 119.0 (d, J_P = 5.0 Hz), 117.8 (d, J_P = 5.0 Hz), 117.8, 107.7, 107.1, 89.4, 64.7 (d, J_P = 6.3 Hz), 53.4, 37.8, 21.9, 16.2 (d, J_P = 5.0 Hz), 11.9, 6.4; ^{31}P NMR (202MHz, $CDCl_3$) δ –5.2; HRMS (ESI) m/z calc'd for $C_{26}H_{31}O_9P$ [M+H]: 519.1784; found 519.1786. $[\alpha]^{23}_D$ = +121.00 (c = 0.10, $CHCl_3$).



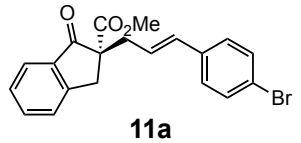
10e

***Tert*-butyl (*R*,*E*)-3-(3-(5'-ethyl-5-(methoxycarbonyl)-3-methyl-4-oxo-4,5-dihydro-[2,2'-bifuran]-5-yl)prop-1-en-1-yl)-1*H*-indole-1-carboxylate (10e):** Tert-butyl 3-allyl-1H-indole-1-carboxylate (25.7 mg, 0.10 mmol, 1 equiv) was reacted with nucleophile **7c** (25 mg, 0.10 mmol, 1 equiv) in Dioxane (**0.6 mL** total volume) according to the **general procedure B**. Purification by flash column chromatography (10%→20%→30%→50% EtOAc/hexanes) provided the product as a clear oil. Run 1 (29.0 mg, 57% yield, 95% ee); Run 2 (28.3 mg, 56% yield, 95% ee); Run 3 (30.8 mg, 61% yield, 95% ee). **Average: 58% (±2.6%) yield, 95% ee.** The enantiomeric excess was determined to be 95% by chiral HPLC analysis (CHIRALPAK IA-3 column, 0.5 mL/min, 10% isopropanol in hexane, λ = 330 nm, t_R(major) = 3.76 min, t_R(minor) = 4.48 min). ^{1}H NMR (500MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.3 Hz, 1H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.51 (s, 1H), 7.30 (t, *J* = 8.4 Hz, 1H), 7.19 (t, *J* = 8.9 Hz, 1H), 7.12 (d, *J* = 3.5 Hz, 1H), 6.63 (d, *J* = 16.0 Hz, 1H), 6.25 (d, *J* = 3.5 Hz, 1H), 6.10 (dt, *J* = 15.3, 7.3 Hz, 1H), 3.78 (s, 3H), 3.19 (dd, *J* = 14.7, 7.5 Hz, 1H), 3.02 (dd, *J* = 14.3, 6.9 Hz, 1H), 2.77 (q, *J* = 7.6 Hz, 2H), 1.99 (s, 3H), 1.65 (s, 9H), 1.29 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.9, 170.8, 166.3, 163.6, 149.7, 143.9, 135.9, 128.8, 126.4, 124.7, 123.7, 122.9, 121.9, 119.9, 118.6, 117.7, 115.4, 107.7, 107.3, 89.6, 84.0, 53.4, 38.4, 28.3, 21.9, 11.9, 6.4; HRMS (ESI) m/z calc'd for $C_{29}H_{31}NO_7$ [M+H]: 506.2179; found 506.2178. $[\alpha]^{23}_D$ = +109.85 (c = 0.31, $CHCl_3$).



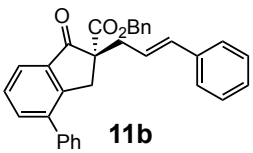
10f

Methyl (*R*,*E*)-5-(3-(benzo[*d*][1,3]dioxol-5-yl)allyl)-5'-ethyl-3-methyl-4-oxo-4,5-dihydro-[2,2'-bifuran]-5-carboxylate (10f): Safrole (14.8 mg, 0.10 mmol, 1 equiv) was reacted with nucleophile **7c** (25 mg, 0.10 mmol, 1 equiv) in Dioxane (**0.6 mL** total volume) according to the **general procedure B**. Purification by flash column chromatography (10%→20%→30%→50% EtOAc/hexanes) provided the product as a clear oil. Run 1 (37.8 mg, 92% yield, 91% ee); Run 2 (35.7 mg, 87% yield, 91% ee); Run 3 (37.3 mg, 91% yield, 91% ee). **Average: 90% (±2.7%) yield, 91% ee.** The enantiomeric excess was determined to be 91% by chiral HPLC analysis (CHIRALPAK OJ-H column, 0.5 mL/min, 40% isopropanol in hexane, λ = 260 nm, t_R(major) = 12.82 min, t_R(minor) = 16.11 min). ^{1}H NMR (500MHz, $CDCl_3$) δ 7.10 (d, *J* = 3.5 Hz, 1H), 6.82 (s, 1H), 6.76 – 6.67 (m, 2H), 6.44 (d, *J* = 15.6 Hz, 1H), 6.25 (d, *J* = 3.2 Hz, 1H), 5.92 (s, 2H), 5.87 (dt, *J* = 15.9, 7.3 Hz, 1H), 3.76 (s, 3H), 3.13 (dd, *J* = 14.7, 7.5 Hz, 1H), 2.91 (dd, *J* = 14.6, 7.2 Hz, 1H), 2.77 (q, *J* = 7.6 Hz, 2H), 1.98 (s, 3H), 1.30 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.8, 170.8, 166.2, 163.6, 148.0, 147.2, 143.9, 134.8, 131.6, 121.1, 119.5, 117.7, 108.3, 107.7, 107.2, 105.8, 101.1, 89.6, 53.4, 37.8, 21.9, 11.9, 6.4; HRMS (ESI) m/z calc'd for $C_{23}H_{22}O_7$ [M+H]: 411.1444; found 411.1443. $[\alpha]^{23}_D$ = +113.49 (c = 0.23, $CHCl_3$).

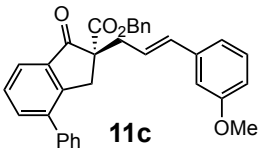


11a

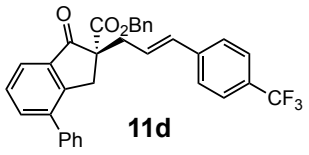
Methyl (*E*)-2-(3-(4-bromophenyl)allyl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (11a): 4-Bromoallylbenzene (19.7 mg, 0.1 mmol, 1.0 equiv) reacted with nucleophile **7d** (38 mg, 0.20 mmol, 2 equiv.) in Dioxane (**0.6 mL** total volume) according to the general procedure **B**. Purification by flash column chromatography (5%→8%→10% EtOAc/hexanes) provided the product as a clear oil: Run 1 (32.6 mg, 85% yield, 79% ee); Run 2 (31.9mg, 83% yield, 79% ee); Run 3 (34.7 mg, 90% yield, 79% ee). **Average: 86% (±3.8%) yield, 79% ee.** The enantiomeric excess was determined by chiral HPLC analysis (CHIRALPAK OJ-H column, 1 mL/min, 10% isopropanol in hexanes, λ = 260 nm): t_R(minor) = 23.800 min, t_R(major) = 31.201 min. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.79 (d, *J* = 7.6 Hz, 1H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.36 (d, *J* = 8.5 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 6.41 (d, *J* = 15.6 Hz, 1H), 6.04 (dt, *J* = 15.6, 7.4 Hz, 1H), 3.72 (s, 3H), 3.67 (d, *J* = 17.3 Hz, 1H), 3.18 (d, *J* = 17.3 Hz, 1H), 3.03 (dd, *J* = 14.1, 7.3 Hz, 1H), 2.73 (dd, *J* = 14.1, 7.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 201.92, 171.20, 152.92, 135.82, 135.55, 135.01, 133.12, 131.56, 127.89, 127.73, 126.45, 125.27, 124.87, 121.19, 60.25, 52.88, 38.29, 36.14. HRMS (ESI) m/z calc'd for $C_{20}H_{17}BrO_3$ [M+H]+: 385.0439; found 385.0433. $[\alpha]^{23}_D$ = +103.1^o (c = 0.385, $CHCl_3$).



Benzyl (*R*)-2-cinnamyl-1-oxo-4-phenyl-2,3-dihydro-1*H*-indene-2-carboxylate (11b): Allylbenzene (13.0 μL, 0.10 mmol, 1 equiv) reacted with nucleophile **7e** (68 mg, 0.20 mmol, 2 equiv.) in Dioxane (**0.6 mL** total volume) according to the general procedure **B**. Purification by flash column chromatography (5%→8%→10% EtOAc/hexanes) provided the product as a clear oil: Run 1 (36.4 mg, 79% yield, 91% ee); Run 2 (37.7 mg, 82% yield, 91% ee); Run 3 (38.9 mg, 85% yield, 91% ee). **Average: 82% (±2.7%) yield, 91% ee.** The enantiomeric excess was determined by chiral HPLC analysis (CHIRALPAK OJ-H column, 1 mL/min, 5% isopropanol in hexanes, λ = 254 nm): t_R(major) = 5.261 min, t_R(minor) = 7.151 min. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 7.7 Hz, 1H), 7.53 (d, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.39 – 7.35 (m, 2H), 7.33 – 7.29 (m, 3H), 7.25 – 7.20 (m, 5H), 7.18 – 7.05 (m, 5H), 6.34 (d, *J* = 15.7 Hz, 1H), 5.90 (dt, *J* = 15.8, 7.4 Hz, 1H), 5.10 (s, 2H), 3.66 (d, *J* = 17.4 Hz, 1H), 3.06 (d, *J* = 17.4 Hz, 1H), 2.99 (dd, *J* = 14.1, 7.6 Hz, 1H), 2.69 (dd, *J* = 14.1, 7.3 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 201.92, 170.38, 150.53, 140.33, 138.72, 136.83, 135.71, 135.56, 135.54, 134.22, 128.72, 128.56, 128.47, 128.43, 128.21, 127.91, 127.83, 127.43, 126.21, 124.18, 123.80, 67.27, 60.98, 38.33, 35.88. (missing one carbon in the aromatic region, possibly due to overlapping). HRMS (ESI) m/z calc'd for $C_{32}H_{36}O_3$ [M+H]+: 459.1960; found 459.1945. $[\alpha]^{23}_D$ = +16.0° (c = 0.68, $CHCl_3$).

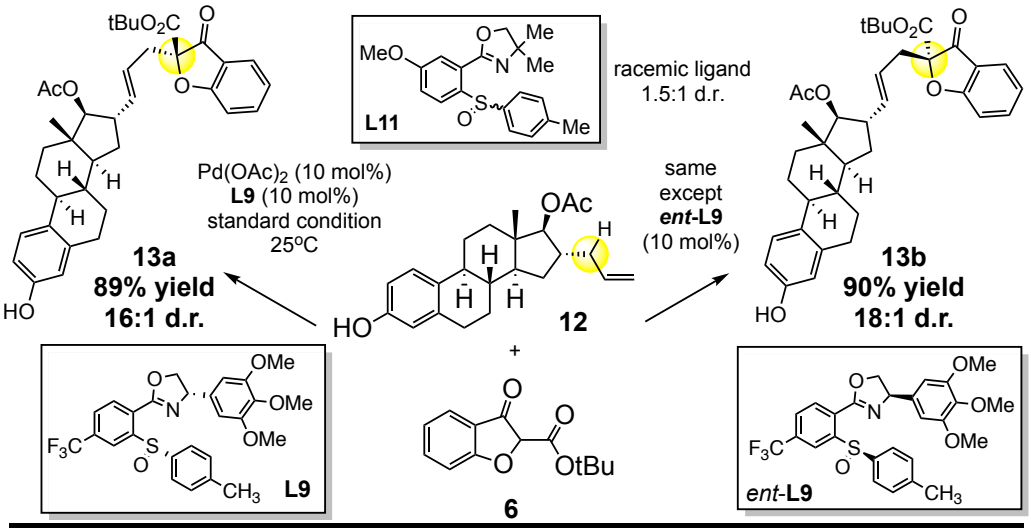


Benzyl (*R*,*E*)-2-(3-(3-methoxyphenyl)allyl)-1-oxo-4-phenyl-2,3-dihydro-1*H*-indene-2-carboxylate (11c): 3-allylanisole (14.8 mg, 0.10 mmol, 1 equiv) reacted with nucleophile **7e** (68 mg, 0.20 mmol, 2 equiv.) in Dioxane (**0.6 mL** total volume) according to the general procedure **B**. Purification by flash column chromatography (5%→8%→10% EtOAc/hexanes) provided the product as a clear oil: Run 1 (36.8 mg, 75% yield, 92% ee); Run 2 (33.4 mg, 68% yield, 93% ee); Run 3 (33.5 mg, 69% yield, 93% ee). **Average: 71% (±3.9%) yield, 93% ee.** The enantiomeric excess was determined by chiral HPLC analysis (CHIRALPAK OJ-H column, 1 mL/min, 30% isopropanol in hexanes, λ = 254 nm): t_R(major) = 18.424 min, t_R(minor) = 23.131 min. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 7.6 Hz, 1H), 7.61 (d, *J* = 7.3 Hz, 1H), 7.52 – 7.36 (m, 7H), 7.34 – 7.27 (m, 4H), 7.15 (t, *J* = 7.9 Hz, 1H), 6.77 – 6.72 (m, 2H), 6.69 (s, 1H), 6.39 (d, *J* = 15.7 Hz, 1H), 5.97 (dt, *J* = 15.3, 7.4 Hz, 1H), 5.17 (s, 2H), 3.76 (s, 3H), 3.73 (d, *J* = 17.8 Hz, 1H), 3.14 (d, *J* = 17.4 Hz, 1H), 3.06 (dd, *J* = 14.2, 7.7 Hz, 1H), 2.78 (dd, *J* = 13.9, 7.2 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 201.95, 170.40, 159.65, 150.55, 140.34, 138.72, 138.30, 135.73, 135.56, 134.16, 129.42, 128.73, 128.56, 128.51, 128.48, 128.44, 128.22, 127.87, 127.84, 124.53, 123.80, 118.88, 113.06, 111.49, 67.27, 60.94, 55.22, 38.27, 35.87. HRMS (ESI) m/z calc'd for $C_{33}H_{28}O_4$ [M+H]+: 489.2066; found 489.2057. $[\alpha]^{23}_D$ = +14.3° (c = 0.7, $CHCl_3$).



Benzyl (*R*,*E*)-1-oxo-4-phenyl-2-(3-(4-(trifluoromethyl)phenyl)allyl)-2,3-dihydro-1*H*-indene-2-carboxylate (11d): 4-trifluoromethylallylbenzene (18.6 mg, 0.10 mmol, 1 equiv) reacted with nucleophile **7e** (68 mg, 0.20 mmol, 2 equiv.) in Dioxane (**0.6 mL** total volume) according to the general procedure **B**. Purification by flash column chromatography (5%→8% EtOAc/hexanes) provided the product as a clear oil: Run 1 (40.5 mg, 77% yield, 91% ee); Run 2 (39.6 mg, 75% yield, 91% ee); Run 3 (39.3 mg, 75% yield, 91% ee). **Average: 76% (±1.2%) yield, 91% ee.** The enantiomeric excess was determined by chiral HPLC analysis (CHIRALPAK OJ-H column, 1 mL/min, 10% isopropanol in hexanes, λ = 254 nm): t_R(major) = 10.815 min, t_R(minor) = 15.988 min. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 7.6 Hz, 1H), 7.64 (d, *J* = 7.4 Hz, 1H), 7.55 – 7.39 (m, 9H), 7.35 – 7.29 (m, 4H), 7.24 (d, *J* = 8.1 Hz, 2H), 6.45 (d, *J* = 15.7 Hz, 1H), 6.10 (dt, *J* = 15.4, 7.4 Hz, 1H), 5.24 – 5.16 (m, 2H), 3.79 (d, *J* = 17.4 Hz, 1H), 3.13 (d, *J* = 17.4 Hz, 1H), 3.10 (dd, *J* = 14.1, 7.3 Hz, 1H), 2.80 (ddd, *J* = 14.1, 7.3 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 201.71, 170.27, 150.34, 140.34, 140.22, 138.65, 135.81, 135.49, 135.47, 132.90, 129.18 (q, *J* = 32.4 Hz), 128.76, 128.58, 128.56, 128.45, 128.29, 127.99, 127.90, 127.10, 126.35, 125.38 (q, *J* = 3.8 Hz), 124.15 (q, *J* = 271.9 Hz), 123.86, 67.35, 60.78, 38.30, 36.07. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -62.46. HRMS (ESI) m/z calc'd for $C_{33}H_{25}O_3F_3$ [M+H]+: 527.1834; found 527.1820. $[\alpha]^{23}_D$ = +10.4° (c = 1.51, $CHCl_3$).

Scheme S4: Diastereoselective Allylic C–H Alkylation.



12b	Ligand	Yield	*d.r.*[b]
	L12[c]	35%	1:1.3
	L9	91%	8:1
	ent-L9	84%	1:17

12c	Ligand	Yield	*d.r.*
	L12[c]	21%	1:1
	L9	93%	5:1
	ent-L9	89%	1:4

12d	Ligand	Yield	*d.r.*
	L12[c]	44%	1:1.2
	L9	92%	3:1
	ent-L9	90%	1:20

12e	Ligand	Yield	*d.r.*[b]
	L11	31%	1:1
	L9	90%	4:1
	ent-L9	93%	1:5

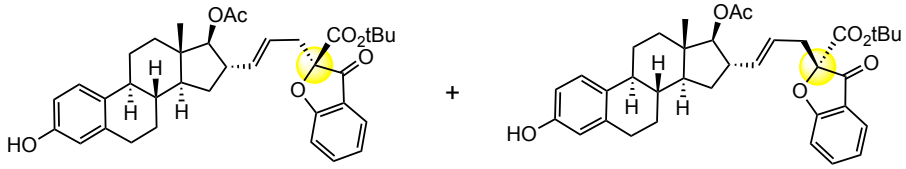
Notes on indication of absolute stereochemistry at the newly formed stereocenter*:** Crystal structure of **9e** unambiguously showed that ArSOX **L9** led to (R***) at β-ketoester **6** (vide supra). Crystsal structure of **13b** corroborated this observation by showing ArSOX ***ent*-L9** led to (***S***), when estrone derivative 12 was used for alkylation of β-ketoester **6** (vide infra). Therefore, when chiral substrates **12b**, **12c**, **12d** and **12e** were evaluated, the absolute stereochemistry of the newly formed stereocenter was inferred from the ligand of choice: **L9** leads to (***R***), ***ent*-L9** leads to (***S***).

General procedure for Scheme S4: To a ½ dram borosilicate vial with stir bar was added ligand **L9** or ***ent*-L9** (10.4 mg, 0.02 mmol, 0.1 equiv) and $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 0.1 equiv). **Benzene** (0.4 mL) was added, and the vial was capped and stirred at 45˚C until all solids had dissolved. Separately, to a second 1 dram borosilicate vial with stir bar was added nucleophile **6** (94 mg, 0.4 mmol, 2.0 equiv), 2,6-dimethylbenzoquinone (40 mg, 0.3 mmol, 1.5 equiv) and $Zn(OAc)_2$ dihydrate (22 mg, 0.1 mmol, 0.5 equiv). The catalyst solution was subsequently added to the reaction flask, and Benzene (0.8 mL) was used to rinse the catalyst vial, also transferred and added to the reaction flask (total volume: 1.2 mL). Terminal olefin substrate **12** (0.20 mmol, 1.0 equiv) was then added and the reaction was allowed to stir for 72 hours at **room temperature** (**25˚C**). Afterward, the reaction mixture was directly subjected to flash column chromatography to provide the product.

Racemic reaction condition A for Scheme S4:[1] A ½ dram oven dried borosilicate vial equipped with a Teflon magnetic stir bar was charged with nucleophile **6** (47 mg, 0.2 mmol, 2.0 equiv), 2,6-dimethylbenzoquinone (DMBQ) (20.4 mg, 0.15 mmol, 1.5 equiv) and $Pd(OAc)_2$/bis-sulfoxide catalyst (5.0 mg, 0.010 mmol, 0.1 equiv.). To the reaction vial was sequentially added DMSO (0.24 mL) and Dioxane (0.06 mL). Terminal olefin substrate **12** (0.10 mmol, 1.0 equiv) was then added and the reaction was allowed to stir for 24 hours at **45˚C**. The reaction mixture was quenched with saturated aqueous NH_4Cl solution (10 mL) and extracted with ethyl acetate (EtOAc) (3 x 10 mL). The combined organic extracts were dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The crude reaction mixture was purified by flash column chromatography to provide the racemic standard.

Racemic reaction condition B for Scheme S4: To a 1 dram borosilicate vial with stir bar was added racemic SOX ligand **L11** (6.8 mg, 0.02 mmol, 0.1 equiv), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 0.1 equiv), 2,6-dimethylbenzoquinone (40 mg, 0.3 mmol, 1.5 equiv), $Zn(OAc)_2$ dihydrate (22 mg, 0.1 mmol, 0.5 equiv), nucleophile **6** (94 mg, 0.4 mmol, 2.0 equiv) and

benzene (1.2 mL). Terminal olefin substrate **12** (0.20 mmol, 1.0 equiv) was then added and the reaction was allowed to stir for 24 hours at **45**°**C**. Afterward, the reaction mixture was directly subjected to flash column chromatography to provide the product.



13a **13b**

Tert-butyl (R)-2-((E)-3-((8R,9S,13S,14S,16S,17S)-17-acetoxy-3-hydroxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-16-yl)allyl)-3-oxo-2,3-dihydrobenzofuran-2-carboxylate (13a)

***Tert*-butyl (*S*)-2-((*E*)-3-((8*R*,9*S*,13*S*,14*S*,16*S*,17*S*)-17-acetoxy-3-hydroxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-16-yl)allyl)-3-oxo-2,3-dihydrobenzofuran-2-carboxylate (13b)**

Estrone derivative **12a**[4] (71 mg, 0.2 mmol, 1.0 equiv) was reacted with nucleophile **6** according to the general procedure. Purification by flash column chromatography (10%→20%→30% EtOAc/hexanes) provided the diastereomeric product **13a** and **13b** as a white solid.

With **L9**: Run 1 (103.8 mg, 88% yield); Run 2 (105.2 mg, 90% yield). **Average: 89% yield, 16:1 *d.r.*** The diastereomeric ratio was determined by 1H NMR, after purification of an inseparable mixture of diastereomers.

With ***ent*-L9**: Run 1 (104.7 mg, 89% yield); Run 2 (105.2 mg, 90% yield). **Average: 90% yield, 1:18 *d.r.*** The diastereomeric ratio was determined by 1H NMR, after purification of an inseparable mixture of diastereomers.

With **racemic condition B:** Run 1 (102.0 mg, 87% yield); Run 2 (96.1 mg, 82% yield). **Average: 85% yield, 1.5:1 *d.r.*** The diastereomeric ratio was determined by 1H NMR, after purification of an inseparable mixture of diastereomers.

13a: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.68 – 7.58 (m, 2H), 7.20 (d, *J* = 8.3 Hz, 1H), 7.12 – 7.05 (m, 2H), 6.63 (dd, *J* = 8.5, 2.7 Hz, 1H), 6.57 (d, *J* = 2.8 Hz, 1H), 5.67 (dd, *J* = 15.3, 8.0 Hz, 1H), 5.59 (br, 1H), 5.26 (dt, *J* = 14.3, 6.8 Hz, 1H), 4.59 (d, *J* = 8.0 Hz, 1H), 2.94 (dd, *J* = 14.6, 7.3 Hz, 1H), 2.83 – 2.77 (m, 3H), 2.58 – 2.48 (m, 1H), 2.25 – 2.18 (m, 1H), 2.16 – 2.08 (m, 1H), **1.93 (s, 3H)**, 1.77 – 1.69 (m, 2H), 1.61 (m, 1H), 1.49 – 1.22 (m, 15H), 0.74 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.46, 172.42, 170.96, 164.44, 153.71, 139.09, 138.45, 137.97, 132.09, 126.45, 124.71, 122.34, 120.54, 119.93, 115.30, 113.49, 112.80, 91.57, 86.35, 83.78, 77.27, 48.53, 44.19, 43.69, 38.42, 36.95, 36.82, 30.62, 29.57, 27.80, 27.03, 26.10, 21.04, 12.53. HRMS (ESI) m/z calc'd for $C_{36}H_{42}O_7$ [M+Na]+: 609.2821; found 609.2826. $[\alpha]^{23}_D$ = +30.1° (c = 0.81, $CHCl_3$).

13b: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.66 – 7.60 (m, 2H), 7.22 (d, *J* = 8.3 Hz, 1H), 7.14 – 7.05 (m, 2H), 6.64 (dd, *J* = 8.4, 2.7 Hz, 1H), 6.57 (d, *J* = 2.7 Hz, 1H), 5.66 (dd, *J* = 15.2, 8.1 Hz, 1H), 5.60 (br, 1H), 5.27 (dt, *J* = 14.4, 7.0 Hz, 1H), 4.56 (d, *J* = 8.0 Hz, 1H), 2.95 (dd, *J* = 14.6, 7.3 Hz, 1H), 2.81 – 2.71 (m, 3H), 2.58 – 2.50 (m, 1H), 2.25 – 2.18 (m, 1H), 2.14 – 2.08 (m, 1H), **1.97 (s, 3H)**, 1.77 – 1.69 (m, 2H), 1.64 – 1.54 (m, 1H), 1.49 – 1.14 (m, 15H), 0.75 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.36, 172.42, 171.02, 164.41, 153.73, 139.18, 138.41, 137.95, 132.05, 126.45, 124.78, 122.38, 120.55, 119.88, 115.31, 113.48, 112.82, 91.51, 86.32, 83.76, 77.26, 48.55, 44.02, 43.72, 38.37, 36.91, 36.87, 30.25, 29.55, 27.83, 27.04, 26.07, 21.05, 12.53. $[\alpha]^{23}_D$ = -43.8° (c = 1.05, $CHCl_3$). ***Single crystals of 13b suitable for X-ray crystallography were grown by slow diffusion from Et_2O/Hexane. The absolute stereochemistry is determined by X-ray crystallography shown on page S35.***

14a **14b**

***Tert*-butyl (*S*)-2-((*E*)-3-((*R*)-2-(*tert*-butoxycarbonyl)-3-oxo-2,3-dihydrobenzofuran-2-yl)prop-1-en-1-yl)pyrrolidine-1-carboxylate (14a)**

***Tert*-butyl (*S*)-2-((*E*)-3-((*S*)-2-(*tert*-butoxycarbonyl)-3-oxo-2,3-dihydrobenzofuran-2-yl)prop-1-en-1-yl)pyrrolidine-1-carboxylate (14b)**

Tert-butyl (*S*)-2-allylpyrrolidine-1-carboxylate **12b**[5] (42 mg, 0.2 mmol, 1.0 equiv) was reacted with nucleophile **6** according to the general procedure. Purification by flash column chromatography (5%→10% Acetone/hexanes) provided the diastereomeric product **14a** and **14b** as a colorless oil, which solidifies upon refrigeration.

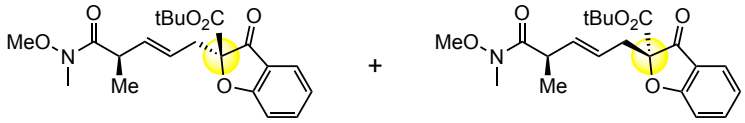
With **L9**: Run 1 (82.5 mg, 93% yield); Run 2 (78.2 mg, 88% yield). **Average: 91% yield, 8:1 *d.r.*** The diastereomeric ratio was determined by chiral HPLC analysis (CHIRALPAK IA-3 column, 1 mL/min, 2% isopropanol in Hexanes, λ = 325 nm): t_R(major) = 8.984 min, t_R(minor) = 11.421 min.

With ***ent*-L9**: Run 1 (75.4 mg, 85% yield); Run 2 (73.6 mg, 83% yield). **Average: 84% yield, 1:17 *d.r.*** The diastereomeric ratio was determined by chiral HPLC analysis (CHIRALPAK IA-3 column, 1 mL/min, 2% isopropanol in Hexanes, λ = 325 nm): t_R(minor) = 8.946 min, t_R(major) = 11.194 min.
With **racemic condition A:** Run 1 (33.6 mg, 38% yield); Run 2 (28.7 mg, 32% yield). **Average: 35% yield, 1:1.3 *d.r.*** The diastereomeric ratio was determined by chiral HPLC analysis (CHIRALPAK IA-3 column, 1 mL/min, 2% isopropanol in Hexanes, λ = 325 nm): t_R(minor) = 9.096 min, t_R(major) = 11.528 min.

14a and **14b** gave identical 1H and 13C NMR, therefore the spectral data of **14b** (1:17 *d.r.*) was reported below:

14a: 8:1 *diastereomeric mixture*, $[\alpha]^{22}_D$ = +10.6° (c = 0.75, $CHCl_3$).

14b: 1:17 *diastereomeric mixture,* ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.60 – 7.53 (m, 2H), 7.12 (d, *J* = 8.6 Hz, 1H), 7.02 (t, *J* = 7.4 Hz, 1H), 5.46 (d, *J* = 14.5 Hz, 1H), 5.24 (dt, *J* = 14.5 Hz, 7.3 Hz, 1H), 4.22 – 4.00 (br, 1H), 3.26 – 3.02 (m, 2H), 2.90 (dd, *J* = 14.4, 7.2 Hz, 1H), 2.78 – 2.64 (br, 1H), 1.85 – 1.48 (m, 4H), 1.37 (s, 9H), 1.32 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.17, 172.38, 164.28, 154.50, 138.33, 136.76 (br), 124.67, 122.33, 120.65 (br), 119.88, 113.37, 91.42, 83.62, 79.04, 58.11 (br), 45.88 (br), 36.36, 31.92, 29.70, 28.45, 27.79. HRMS (ESI) m/z calc'd for $C_{25}H_{33}NO_6$ [M+Na]+: 466.2206; found 466.2202. $[\alpha]^{22}_D$ = -103.5° (c = 0.85, $CHCl_3$).



15a **15b**

***Tert*-butyl (*R*)-2-((*S*,*E*)-5-(methoxy(methyl)amino)-4-methyl-5-oxopent-2-en-1-yl)-3-oxo-2,3-dihydrobenzofuran-2-carboxylate (15a)**
***Tert*-butyl (*S*)-2-((*S*,*E*)-5-(methoxy(methyl)amino)-4-methyl-5-oxopent-2-en-1-yl)-3-oxo-2,3-dihydrobenzofuran-2-carboxylate (15b)**
Weinreb amide substrate **12c**[6] (31.4 mg, 0.2 mmol, 1.0 equiv) was reacted with nucleophile **6** according to the general procedure. Purification by flash column chromatography (10%→20% EtOAc/hexanes) provided the diastereomeric product **15a** and **15b** as a colorless oil.
With **L9**: Run 1 (70.1 mg, 90% yield); Run 2 (74.3 mg, 95% yield). **Average: 93% yield, 5:1 *d.r.*** The diastereomeric ratio was determined by 1H NMR, after purification of an inseparable mixture of diastereomers.
With ***ent*-L9**: Run 1 (68.5 mg, 88% yield); Run 2 (69.9 mg, 90% yield). **Average: 89% yield, 1:4 *d.r.*** The diastereomeric ratio was determined by 1H NMR, after purification of an inseparable mixture of diastereomers.
With **racemic condition A:** Run 1 (16.8 mg, 22% yield); Run 2 (14.6 mg, 19% yield). **Average: 21% yield, 1:1 *d.r.*** The diastereomeric ratio was determined by 1H NMR, after purification of an inseparable mixture of diastereomers.
15a: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.65 – 7.59 (m, 2H), 7.18 (d, *J* = 8.7 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 5.72 (dd, *J* = 15.4, 8.2 Hz, 1H), 5.41 (dt, *J* = 15.0, 7.3 Hz, 1H), **3.55 (s, 3H)**, **3.09 (s, 3H)**, 2.94 (dd, *J* = 14.3, 8.2 Hz, 1H), 2.72 (dd, *J* = 14.5, 6.5 Hz, 1H), 1.42 (s, 9H), **1.02 (d, *J* = 6.9 Hz, 3H)**. ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.01, 175.13, 172.29, 164.18, 138.34, 136.10, 124.70, 122.67, 122.34, 119.80, 113.42, 91.29, 83.70, 61.37, 38.95, 36.79, 32.18, 27.79, 17.66. HRMS (ESI) m/z calc'd for $C_{21}H_{27}NO_6$ [M+H]+: 390.1917; found 390.1911. $[\alpha]^{22}_D$ = +33.4° (c = 1.45, $CHCl_3$).

15b: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.65 – 7.59 (m, 2H), 7.17 (d, *J* = 8.6 Hz, 1H), 7.08 (t, *J* = 7.4 Hz, 1H), 5.72 (dd, *J* = 15.5, 8.1 Hz, 1H), 5.38 (ddd, *J* = 15.4, 7.7 Hz, 6.8 Hz, 1H), **3.51 (s, 3H)**, **3.05 (s, 3H)**, 2.94 (dd, *J* = 14.6, 7.5 Hz, 1H), 2.73 (dd, *J* = 14.5, 6.7 Hz, 1H), 1.41 (s, 9H), **1.06 (d, *J* = 6.9 Hz, 3H)**. ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.06, 175.10, 172.32, 164.21, 138.26, 136.16, 124.68, 122.51, 122.30, 119.85, 113.44, 91.35, 83.70, 61.33, 38.81, 36.79, 32.13, 27.75, 17.70. $[\alpha]^{22}_D$ = -66.2° (c = 1.48, $CHCl_3$).

16a **16b**

***Tert*-butyl (*R*)-2-((*R*,*E*)-4-((*tert*-butyldimethylsilyl)oxy)-5-((4-methoxybenzyl)oxy)pent-2-en-1-yl)-3-oxo-2,3-dihydrobenzofuran-2-carboxylate (16a)**
***Tert*-butyl (*S*)-2-((*R*,*E*)-4-((*tert*-butyldimethylsilyl)oxy)-5-((4-methoxybenzyl)oxy)pent-2-en-1-yl)-3-oxo-2,3-dihydrobenzofuran-2-carboxylate (16b)**

Chiral diol substrate **12d**[7] (67.3 mg, 0.2 mmol, 1.0 equiv) was reacted with nucleophile **6** according to the general procedure. Purification by flash column chromatography (2%→5%→10% EtOAc/hexanes) provided the diastereomeric product **16a** and **16b** as a colorless oil.

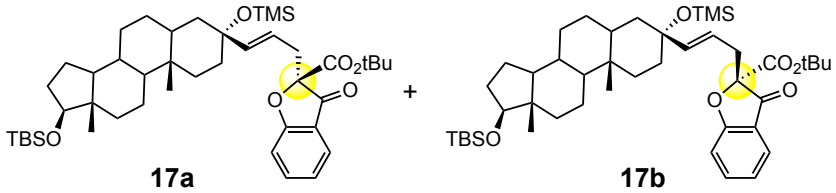
With **L9**: Run 1 (102.3 mg, 90% yield); Run 2 (106.8 mg, 94% yield). **Average: 92% yield, 3:1 *d.r.*** The diastereomeric ratio was determined by 1H NMR, after purification of an inseparable mixture of diastereomers.

With ***ent*-L9**: Run 1 (100.2 mg, 88% yield); Run 2 (104.5 mg, 92% yield). **Average: 90% yield, 1:20 *d.r.*** The diastereomeric ratio was determined by 1H NMR, after purification of an inseparable mixture of diastereomers.

With **racemic condition A:** Run 1 (51.4 mg, 45% yield); Run 2 (48.8 mg, 43% yield). **Average: 44% yield, 1:1.2 *d.r.*** The diastereomeric ratio was determined by 1H NMR, after purification of an inseparable mixture of diastereomers.

16a: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.63 – 7.54 (m, 2H), 7.21 (d, *J* = 8.7 Hz, 2H), 7.16 (d, *J* = 8.9 Hz, 1H), 7.07 (t, *J* = 7.5 Hz, 1H), 6.86 (d, *J* = 8.5 Hz, 2H), 5.67 (dd, *J* = 8.9 Hz, 1H), 5.57 – 5.48 (m, 1H), 4.42 – 4.35 (m, 2H), 4.17 – 4.12 (m, 1H), 3.80 (s, 3H), 3.27 – 3.15 (m, 2H), 2.98 (dd, *J* = 14.7, 6.4 Hz, 1H), 2.87 (dd, *J* = 14.7, 7.8 Hz, 1H), 1.42 (s, 9H), **0.78 (s, 9H)**, **-0.10 (s, 3H)**, **-0.18 (s, 3H)**. ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.28, 172.47, 164.43, 159.06, 138.26, 136.22, 130.50, 129.10, 124.71, 122.33, 121.73, 119.99, 113.68, 113.46, 91.41, 83.62, 74.67, 72.89, 71.73, 55.27, 36.33, 27.78, 25.78, 18.18, -4.96, -4.98. HRMS (ESI) m/z calc'd for $C_{32}H_{44}O_7Si$ [M+Na]+: 591.2754; found 591.2759. $[\alpha]^{24}_D$ = +18.5° (c = 1.12, $CHCl_3$).

16b: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.63 – 7.57 (m, 2H), 7.21 (d, *J* = 8.6 Hz, 2H), 7.16 (d, *J* = 8.1 Hz, 1H), 7.07 (t, *J* = 7.4, 1H), 6.86 (d, *J* = 8.6 Hz, 2H), 5.67 (dd, *J* = 15.4, 5.4 Hz, 1H), 5.58 – 5.48 (m, 1H), 4.39 (d, *J* = 2.9 Hz, 2H), 4.15 (q, *J* = 5.1 Hz, 1H), 3.80 (s, 3H), 3.27 – 3.16 (m, 2H), 2.98 (dd, *J* = 14.5, 7.5 Hz, 1H), 2.81 (dd, *J* = 14.5, 6.8 Hz, 1H), 1.42 (s, 9H), **0.80 (s, 9H)**, **-0.08 (s, 3H)**, **-0.12 (s, 3H)**. ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.15, 172.44, 164.33, 159.06, 138.30, 136.29, 130.52, 129.11, 124.76, 122.30, 122.09, 119.87, 113.68, 113.40, 91.27, 83.59, 74.74, 72.92, 71.98, 55.26, 36.54, 27.77, 25.79, 18.19, -4.87, -4.93. $[\alpha]^{24}_D$ = -36.0° (c = 1.23, $CHCl_3$).



17a **17b**

***Tert*-butyl (2*R*)-2-((*E*)-3-((3*R*,10*S*,13*S*,17*S*)-17-((*tert*-butyldimethylsilyl)oxy)-10,13-dimethyl-3-((trimethylsilyl)oxy)hexadecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl)allyl)-3-oxo-2,3-dihydrobenzofuran-2-carboxylate (17a)**

***Tert*-butyl (2*S*)-2-((*E*)-3-((3*R*,10*S*,13*S*,17*S*)-17-((*tert*-butyldimethylsilyl)oxy)-10,13-dimethyl-3-((trimethylsilyl)oxy)hexadecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl)allyl)-3-oxo-2,3-dihydrobenzofuran-2-carboxylate (17b)**

Androsterone derivative **12e**[8] (103 mg, 0.2 mmol, 1.0 equiv) was reacted with nucleophile **6** according to the general procedure. Purification by flash column chromatography (2% EtOAc/hexanes) provided the diastereomeric product **17a** and **17b** as a colorless oil.

With **L9**: Run 1 (132.2 mg, 88% yield); Run 2 (138.5 mg, 92% yield). **Average: 90% yield, 4.3:1 *d.r.*** The diastereomeric ratio was determined by chiral HPLC analysis (CHIRALPAK IC-3 column, 0.8 mL/min, 0.3% isopropanol in Hexanes, λ = 254 nm): t_R(minor) = 4.252 min, t_R(major) = 4.524 min.

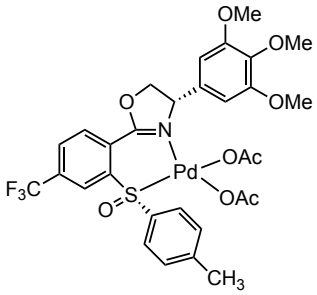
With ***ent*-L9**: Run 1 (136.7 mg, 91% yield); Run 2 (144.1 mg, 96% yield). **Average: 93% yield, 1:5 *d.r.*** The diastereomeric ratio was determined by chiral HPLC analysis (CHIRALPAK IC-3 column, 0.8 mL/min, 0.3% isopropanol in Hexanes, λ = 254 nm): t_R(major) = 4.373 min, t_R(minor) = 4.686 min.

With **racemic condition B:** Run 1 (47.0 mg, 31% yield); Run 2 (45.0 mg, 30% yield). **Average: 31% yield, 1:1 *d.r.*** The diastereomeric ratio was determined by chiral HPLC analysis (CHIRALPAK IC-3 column, 0.8 mL/min, 0.3% isopropanol in Hexanes, λ = 254 nm): t_R(major) = 4.374 min, t_R(minor) = 4.676 min.

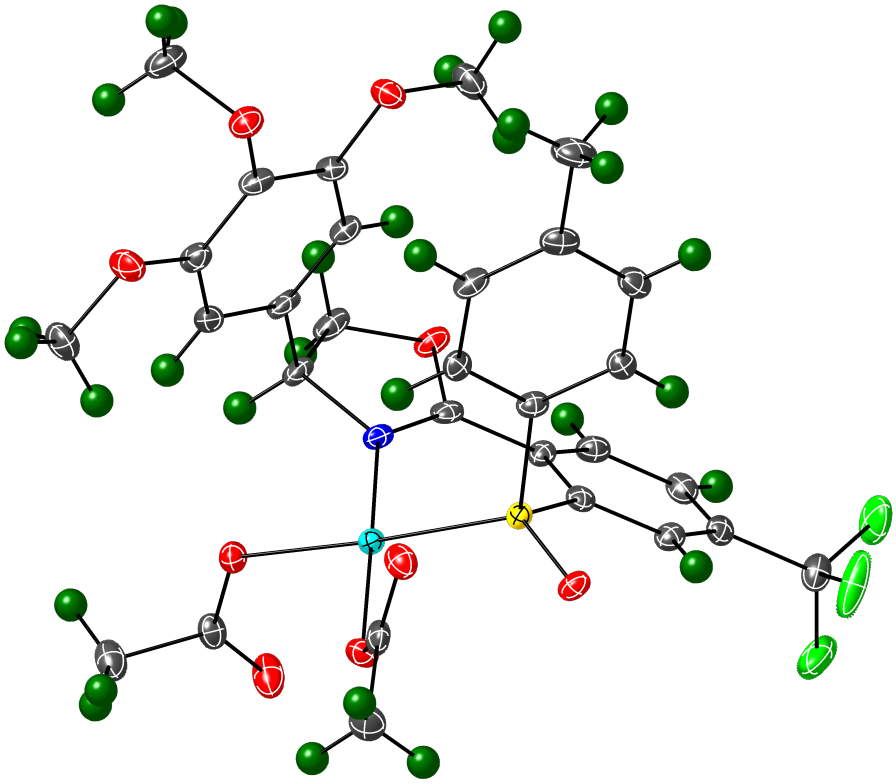
17a: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.64 – 7.59 (m, 2H), 7.17 (d, *J* = 8.3 Hz, 1H), 7.08 (t, *J* = 7.4 Hz, 1H), 5.70 (d, *J* = 15.7 Hz, 1H), 5.30 (dt, *J* = 15.8, 7.2 Hz, 1H), 3.52 (t, *J* = 8.3 Hz, 1H), 2.95 (dd, *J* = 14.4, 7.4 Hz, 1H), 2.80 (dd, *J* = 14.5, 7.1 Hz, 1H), 1.89 – 1.79 (m, 1H), 1.69 (m, 1H), 1.65 – 1.60 (m, 1H), 1.51 (m, 2H), 1.44 (s, 9H), 1.42 – 1.27 (m, 5H), 1.26 – 1.15 (m, 4H), 1.12 – 0.94 (m, 5H), 0.92 – 0.80 (m, 2H), 0.86 (s, 9H), 0.67 (s, 3H), 0.62 (m, 1H), 0.57 (s, 3H), -0.01 (s, 9H), -0.01 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.30, 172.38, 164.37, 144.82, 138.27, 124.65, 122.31, 119.98, 118.05, 113.39, 91.37, 83.62, 81.86, 74.20, 54.66, 50.68, 43.30, 40.66, 40.49, 37.18, 36.84, 35.59, 35.57, 33.78, 33.16, 31.69, 30.91, 28.19, 27.79, 25.86, 23.50, 20.60, 18.11, 11.48, 11.37, 2.42, -4.51, -4.82. HRMS (ESI) m/z calc'd for $C_{44}H_{70}O_6Si_2$ [M+Na]+: 773.4609; found 773.4595. $[\alpha]^{24}_D$ = +10.8° (c = 1.2, $CHCl_3$).

17b: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.64 – 7.59 (m, 2H), 7.18 (d, *J* = 8.2 Hz, 1H), 7.08 (t, *J* = 7.4 Hz, 1H), 5.70 (d, *J* = 15.7 Hz, 1H), 5.31 (dt, *J* = 15.5, 7.5 Hz, 1H), 3.52 (t, *J* = 8.3 Hz, 1H), 2.95 (dd, *J* = 14.7, 7.4 Hz, 1H), 2.79 (dd, *J* = 14.3, 7.1 Hz, 1H), 1.84 (m, 1H), 1.69 (m, 1H), 1.62 (m, 1H), 1.55 – 1.47 (m, 2H), 1.44 (s, 9H), 1.42 – 1.28 (m, 5H), 1.26 – 1.15 (m, 4H), 1.14 – 0.95 (m, 5H), 0.92 – 0.80 (m, 2H), 0.86 (s, 9H), 0.67 (s, 3H), 0.66 – 0.59 (m, 1H), 0.57 (s, 3H), -0.01 (s, 9H), -0.01 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.29, 172.37, 164.35, 144.82, 138.29, 124.66, 122.31, 119.96, 118.07, 113.39, 91.37, 83.62, 81.86, 74.18, 54.66, 50.69, 43.30, 40.52, 40.02, 37.19, 36.89, 35.60, 35.58, 33.80, 33.77, 31.72, 30.91, 28.22, 27.79, 25.86, 23.50, 20.60, 18.11, 11.47, 11.37, 2.41, -4.51, -4.82. $[\alpha]^{24}_{D}$ = -14.0^{o} (c = 1.0, $CHCl_3$).

Scheme S5. Crystal Structure of $Pd(OAc)_2$ / ArSOX L9 complex



co-crystallized with 1 equiv. dichloromethane

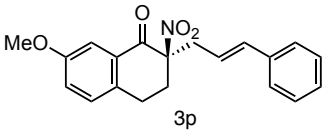


Crystal data and structure refinement for dd01ls .

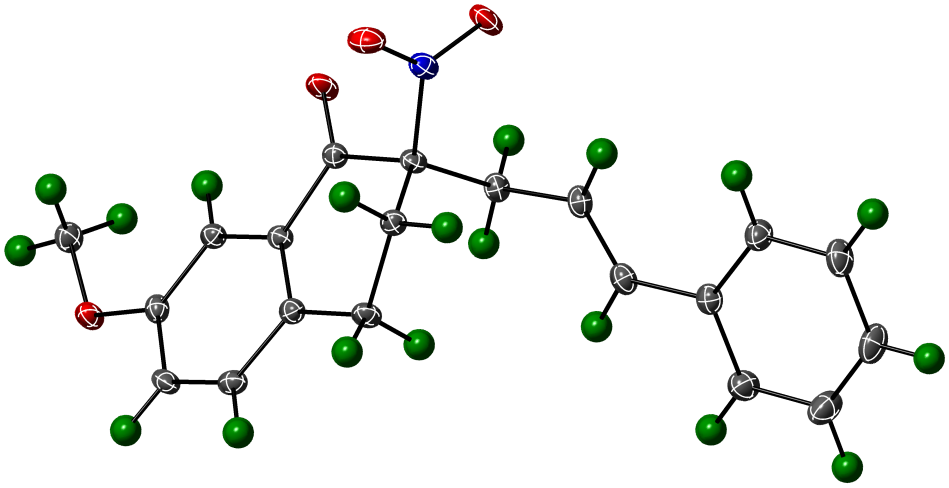
Identification code	dd01ls	
Empirical formula	C31 H32 Cl2 F3 N O9 Pd S	
Formula weight	828.93	
Temperature	100(2) K	
Wavelength	0.71073 ≈	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 11.5175(6) ≈	a= 90∞.
	b = 12.9029(7) ≈	b= 112.9346(17)∞.
	c = 12.3215(6) ≈	g = 90∞.
Volume	1686.34(15) $≈^3$	
Z	2	
Density (calculated)	1.633 Mg/m^3	

Absorption coefficient	0.841 mm^{-1}
F(000)	840
Crystal size	0.175 x 0.165 x 0.072 mm^3
Theta range for data collection	2.591 to 28.302∞.
Index ranges	-15<=h<=15, -17<=k<=17, -16<=l<=14
Reflections collected	21000
Independent reflections	8294 [R(int) = 0.0265]
Completeness to theta = 25.242∞	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7457 and 0.6863
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8294 / 1 / 440
Goodness-of-fit on F^2	1.091
Final R indices [I>2sigma(I)]	R1 = 0.0240, wR2 = 0.0498
R indices (all data)	R1 = 0.0262, wR2 = 0.0508
Absolute structure parameter	-0.029(8)
Extinction coefficient	0.0123(6)
Largest diff. peak and hole	0.497 and -0.463 e.≈$^{-3}$

Scheme S6. Crystal Structure of the Alkylation Product with Nitroketone (3p)



3p

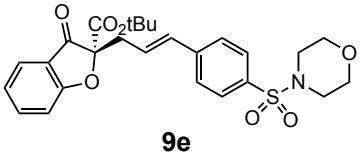


Crystal data and structure refinement for dd48fsa (**3p**).

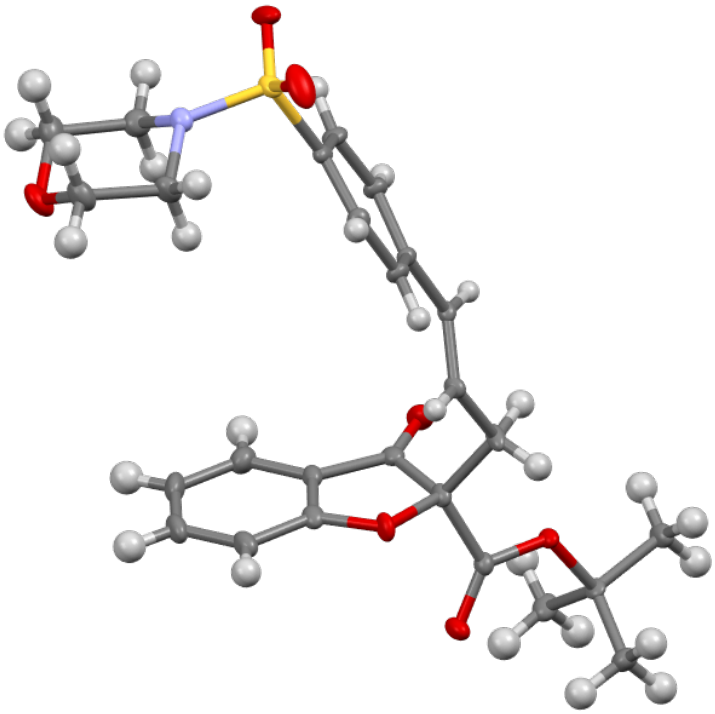
Identification code	dd48fsa	
Empirical formula	C20 H19 N O4	
Formula weight	337.36	
Temperature	110(2) K	
Wavelength	1.54178 ≈	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 7.2794(2) ≈	a= 90∞.
	b = 7.9760(2) ≈	b= 90∞.
	c = 28.9295(8) ≈	g = 90∞.
Volume	1679.66(8) $\approx^3$	
Z	4	
Density (calculated)	1.334 Mg/m^3	
Absorption coefficient	0.762 mm^{-1}	
F(000)	712	
Crystal size	0.574 x 0.185 x 0.157 mm^3	
Theta range for data collection	3.055 to 68.249∞.	
Index ranges	-8<=h<=8, -8<=k<=9, -32<=l<=34	
Reflections collected	15671	
Independent reflections	3063 [R(int) = 0.0410]	
Completeness to theta = 67.679∞	99.9 %	
Absorption correction	Integration	
Max. and min. transmission	1.0000 and 0.7163	

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3063 / 0 / 227
Goodness-of-fit on F^2	1.071
Final R indices [I>2sigma(I)]	R1 = 0.0293, wR2 = 0.0695
R indices (all data)	R1 = 0.0316, wR2 = 0.0709
Absolute structure parameter	-0.01(9)
Extinction coefficient	0.0060(5)
Largest diff. peak and hole	0.221 and -0.171 e.$\approx^{-3}$

Scheme S7. Crystal Structure of the Alkylation Product with β-ketoester (9e)



9e

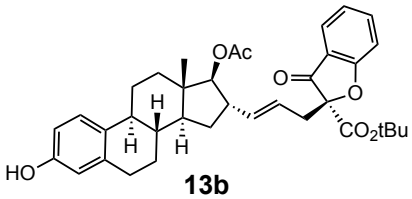


Crystal data and structure refinement for dd95is (**9e**).

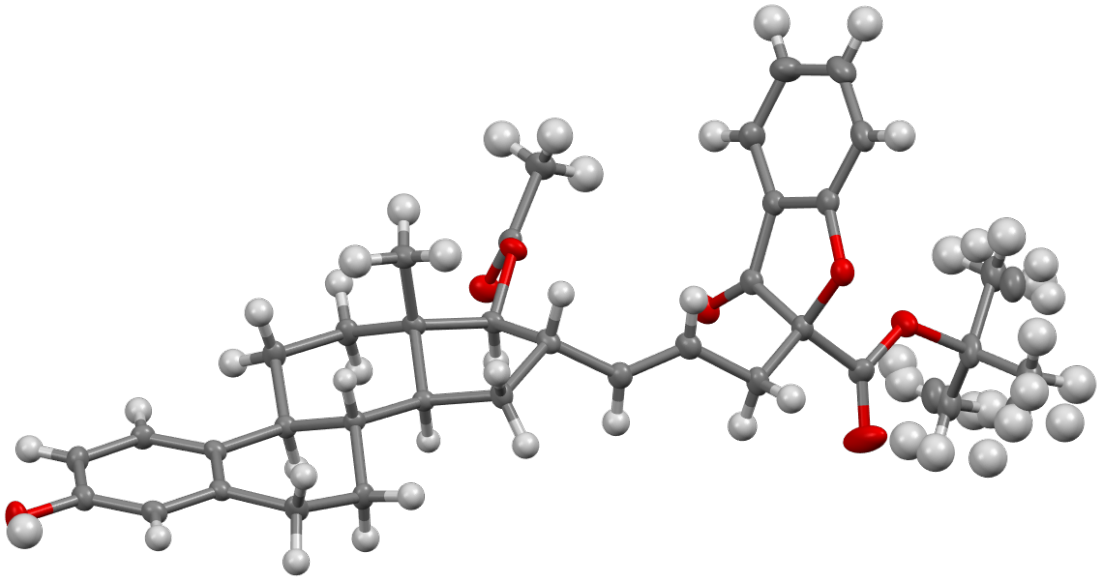
Identification code	dd95is	
Empirical formula	C26 H29 N O7 S	
Formula weight	499.56	
Temperature	100(2) K	
Wavelength	0.71073 ≈	
Crystal system	Triclinic	
Space group	P1	
Unit cell dimensions	a = 8.1073(3) ≈	a= 74.9956(16)∞.
	b = 12.6392(5) ≈	b= 81.3175(16)∞.
	c = 13.2065(6) ≈	g = 71.4936(14)∞.
Volume	1236.04(9) ≈^{3}	
Z	2	
Density (calculated)	1.342 Mg/m^3	
Absorption coefficient	0.177 mm^{-1}	
F(000)	528	
Crystal size	0.388 x 0.275 x 0.152 mm^3	
Theta range for data collection	2.620 to 28.350∞.	

Index ranges	-10<=h<=10, -16<=k<=16, -17<=l<=17
Reflections collected	102095
Independent reflections	12247 [R(int) = 0.0717]
Completeness to theta = 25.242∞	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7457 and 0.6562
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	12247 / 145 / 675
Goodness-of-fit on F^2	1.038
Final R indices [I>2sigma(I)]	R1 = 0.0376, wR2 = 0.0824
R indices (all data)	R1 = 0.0479, wR2 = 0.0874
Absolute structure parameter	-0.01(3)
Extinction coefficient	0.0170(14)
Largest diff. peak and hole	0.383 and -0.304 e.≈$^{-3}$

Scheme S8. Crystal Structure of the Alkylation Product with β-ketoesters (13b)



13b



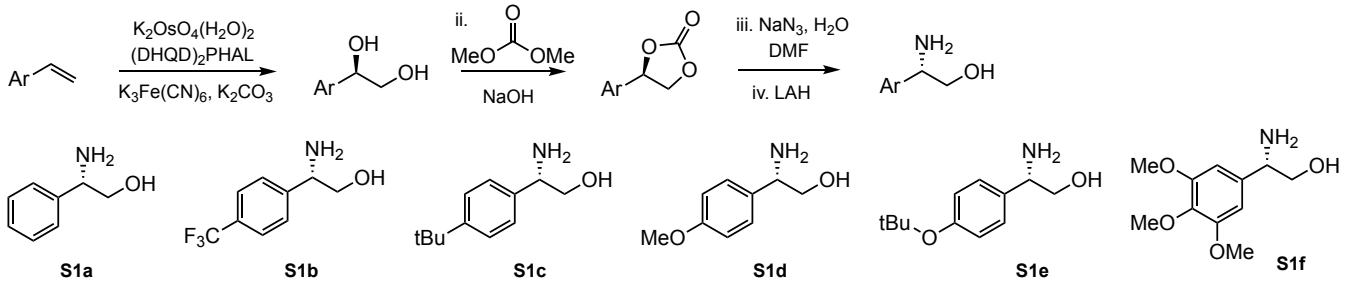
Crystal data and structure refinement for dd27esa (**13b**).

Identification code	dd27esa	
Empirical formula	C36 H42 O7	
Formula weight	586.69	
Temperature	100(2) K	
Wavelength	1.54178 ≈	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 12.9410(3) ≈	a= 90∞.
	b = 13.1806(3) ≈	b= 90∞.
	c = 18.8817(4) ≈	g = 90∞.
Volume	3220.65(12) $≈^3$	
Z	4	
Density (calculated)	1.210 Mg/m^3	
Absorption coefficient	0.670 mm^{-1}	
F(000)	1256	
Crystal size	0.354 x 0.163 x 0.116 mm^3	
Theta range for data collection	4.090 to 68.447∞.	
Index ranges	-15<=h<=15, -15<=k<=15, -22<=l<=22	
Reflections collected	26546	

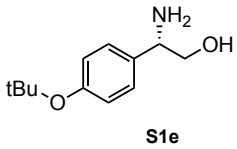
Independent reflections	5895 [R(int) = 0.0365]
Completeness to theta = 67.679∞	100.0 %
Absorption correction	Integration
Max. and min. transmission	0.9388 and 0.8218
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5895 / 31 / 397
Goodness-of-fit on F^2	1.165
Final R indices [I>2sigma(I)]	R1 = 0.0391, wR2 = 0.0943
R indices (all data)	R1 = 0.0427, wR2 = 0.0971
Absolute structure parameter	0.08(8)
Extinction coefficient	n/a
Largest diff. peak and hole	0.293 and -0.328 e.≈$^{-3}$

Scheme S9. Ligand Synthesis

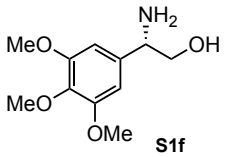
1. Amino alcohol synthesis



Chiral amino alcohol was synthesized based on the procedure by Sharpless,[9] except step iv reduction[10]. The asymmetric dihydroxylation was based on the procedure by Sharpless.[11] Compound **S1a** is commercial available. Compound **S1b**,[12] **S1c**,[10] **S1d**[10] was synthesized and matched with previous reports.

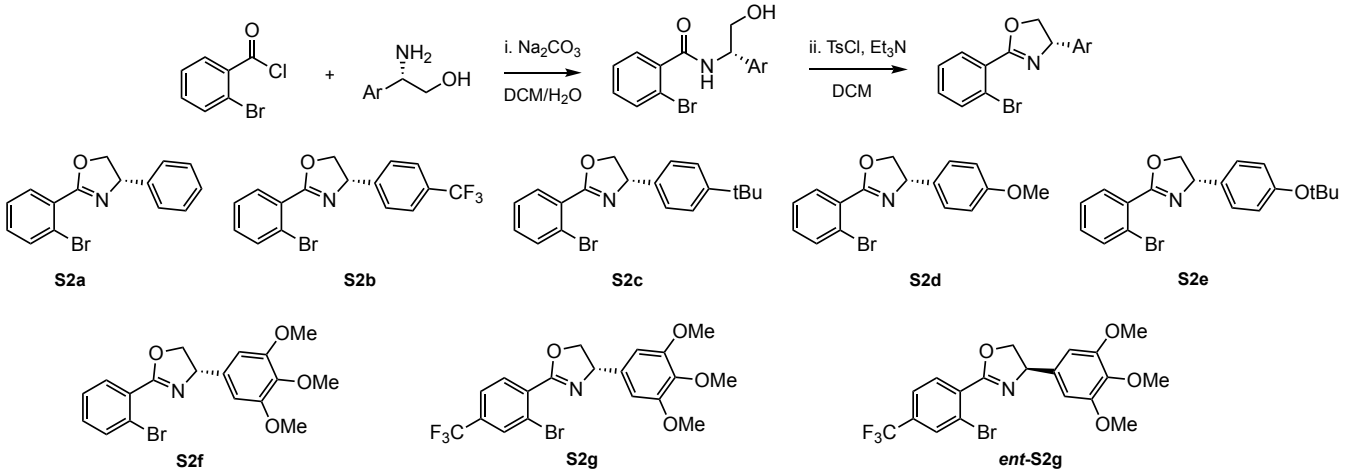


(*S*)-2-amino-2-(4-(*tert*-butoxy)phenyl)ethan-1-ol (S1e): White solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.20 (d, *J* = 8.4 Hz, 2H), 6.96 (d, *J* = 8.3 Hz, 2H), 4.00 (dd, *J* = 8.3, 4.4 Hz, 1H), 3.72 (dd, *J* = 10.8, 4.5 Hz, 1H), 3.53 (dd, *J* = 10.7, 8.3 Hz, 1H), 1.96 (br, 3H), 1.33 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.70, 137.53, 126.83, 124.22, 78.47, 68.09, 56.81, 28.85. HRMS (ESI) m/z calc'd for $C_{12}H_{19}NO_2$ [M+H]+: 210.1494; found 210.1498. $[\alpha]^{22}_D$ = 32.8° (c = 0.92, $CHCl_3$).

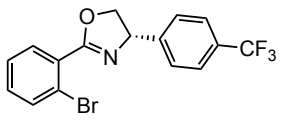


(*S*)-2-amino-2-(3,4,5-trimethoxyphenyl)ethan-1-ol (S1f): White solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.55 (s, 2H), 3.99 (dd, *J* = 8.2, 4.3 Hz, 1H), 3.84 (s, 6H), 3.81 (s, 3H), 3.70 (dd, *J* = 10.8, 4.3 Hz, 1H), 3.54 (dd, *J* = 10.8, 8.1 Hz, 1H), 2.30 (br, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.34, 138.31, 137.20, 103.43, 68.10, 60.81, 57.61, 56.13. HRMS (ESI) m/z calc'd for $C_{11}H_{17}NO_4$ [M+H]+: 228.1236; found 228.1232. $[\alpha]^{22}_D$ = 19.9° (c = 1.03, $CHCl_3$).

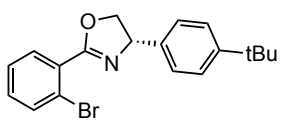
2. Oxazoline synthesis



Amino alcohol and benzoyl chloride was coupled to form the oxazoline according to published procedure.[13] Compound S2a was synthesized and matched with previous report.[14]

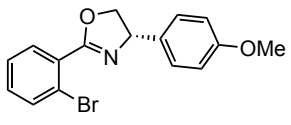


(*S*)-2-(2-bromophenyl)-4-(4-(trifluoromethyl)phenyl)-4,5-dihydrooxazole (S2b): colorless oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.79 (d, *J* = 7.6 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 8.1 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.34 (t, *J* = 7.7 Hz, 1H), 5.52 (dd, *J* = 10.3, 8.4 Hz, 1H), 4.68 (t, *J* = 9.9 Hz, 1H), 4.27 (t, *J* = 8.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.77, 146.05, 134.02, 132.02, 131.48, 129.96 (q, *J* = 32.05 Hz), 129.31, 127.23, 127.13, 125.75 (q, *J* = 3.9 Hz), 124.13 (q, *J* = 272.37 Hz), 121.98, 74.58, 70.06. ^{19}F NMR (470 MHz, $CDCl_3$) δ -62.86. HRMS (ESI) m/z calc'd for $C_{16}H_{11}ONOF_3Br$ [M+H]+: 370.0054; found 370.0059. $[\alpha]^{22}_D$ = -16.6° (c = 1.0, $CHCl_3$).



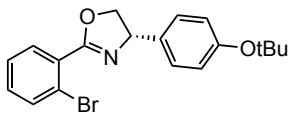
(*S*)-2-(2-bromophenyl)-4-(4-(*tert*-butyl)phenyl)-4,5-dihydrooxazole (S2c): colorless oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 7.6 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.41 (d, *J* = 8.3 Hz, 2H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.34 – 7.28 (m, 3H), 5.42 (dd, *J* = 10.2, 8.3 Hz, 1H), 4.81

(dd, *J* = 10.2, 8.4 Hz, 1H), 4.33 (t, *J* = 8.3 Hz, 1H), 1.32 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.04, 150.59, 139.04, 133.87, 131.75, 131.55, 129.83, 127.12, 126.49, 125.68, 121.95, 74.98, 70.16, 34.55, 31.37. HRMS (ESI) m/z calc'd for $C_{19}H_{20}BrNO$ [M]+: 358.0807; found 358.0810. $[\alpha]^{22}_D$ = -39.6° (c = 1.18, $CHCl_3$).



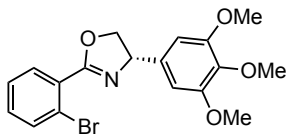
S2d

(*S*)-2-(2-bromophenyl)-4-(4-methoxyphenyl)-4,5-dihydrooxazole (S2d): colorless oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 7.7 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.31 – 7.27 (m, 3H), 6.94 – 6.87 (m, 2H), 5.39 (dd, *J* = 10.2, 8.3 Hz, 1H), 4.78 (dd, *J* = 10.2, 8.4 Hz, 1H), 4.26 (t, *J* = 8.3 Hz, 1H), 3.79 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.97, 159.13, 134.27, 133.88, 131.80, 131.53, 129.80, 127.95, 127.16, 121.95, 114.15, 75.12, 69.97, 55.32. HRMS (ESI) m/z calc'd for $C_{16}H_{14}BrO_2$ [M]+: 332.0286; found 332.0277. $[\alpha]^{22}_D$ = -41.9° (c = 1.16, $CHCl_3$).



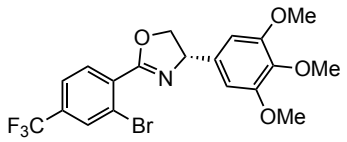
S2e

(*S*)-2-(2-bromophenyl)-4-(4-(*tert*-butoxy)phenyl)-4,5-dihydrooxazole (S2e): white solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 7.7 Hz, 1H), 7.67 (d, *J* = 7.9 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.30 (t, *J* = 7.7 Hz, 1H), 7.26 (d, *J* = 8.5 Hz, 2H), 6.99 (d, *J* = 8.4 Hz, 2H), 5.40 (dd, *J* = 10.2, 8.4 Hz, 1H), 4.80 (dd, *J* = 10.1, 8.3 Hz, 1H), 4.29 (t, *J* = 8.4 Hz, 1H), 1.33 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.12, 154.88, 136.87, 133.88, 131.79, 131.54, 129.75, 127.36, 127.14, 124.46, 121.93, 78.54, 75.11, 70.08, 28.85. HRMS (ESI) m/z calc'd for $C_{19}H_{20}BrNO_2$ [M+H]+: 374.0756; found 374.0744. $[\alpha]^{22}_D$ = -41.4° (c = 1.1, $CHCl_3$).



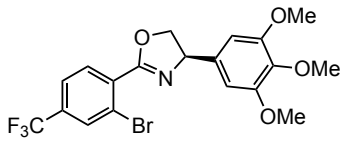
S2f

(*S*)-2-(2-bromophenyl)-4-(3,4,5-trimethoxyphenyl)-4,5-dihydrooxazole (S2f): white solid upon refrigeration. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 7.6 Hz, 1H), 7.68 (d, *J* = 7.9 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.32 (t, *J* = 7.7 Hz, 1H), 6.60 (s, 2H), 5.38 (dd, *J* = 10.2, 8.2 Hz, 1H), 4.80 (dd, *J* = 10.2, 8.4 Hz, 1H), 4.29 (t, *J* = 8.3 Hz, 1H), 3.86 (s, 6H), 3.83 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.23, 153.51, 137.87, 137.38, 133.89, 131.87, 131.41, 129.69, 127.23, 121.89, 103.65, 74.95, 70.63, 60.85, 56.18. HRMS (ESI) m/z calc'd for $C_{18}H_{18}NO_4Br$ [M+H]+: 392.0497; found 392.0504. $[\alpha]^{26}_D$ = -34.4° (c = 0.98, $CHCl_3$).



S2g

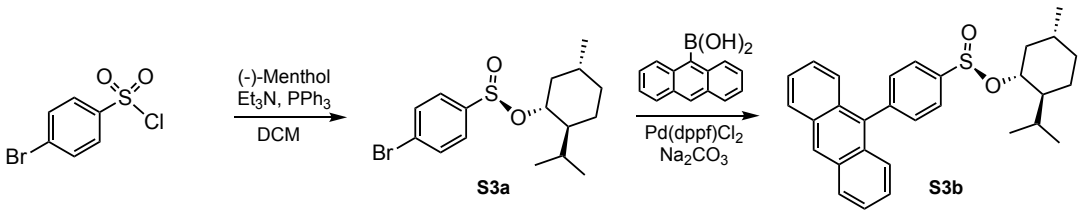
(*S*)-2-(2-bromo-4-(trifluoromethyl)phenyl)-4-(3,4,5-trimethoxyphenyl)-4,5-dihydrooxazole (S2g): white solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.98 – 7.93 (m, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.65 (d, *J* = 8.3 Hz, 1H), 6.59 (s, 2H), 5.41 (dd, *J* = 10.3, 8.4 Hz, 1H), 4.84 (dd, *J* = 10.3, 8.5 Hz, 1H), 4.33 (t, *J* = 8.4 Hz, 1H), 3.87 (s, 6H), 3.84 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.10, 153.59, 137.54, 137.38, 133.73 (q, *J* = 33.3 Hz), 133.08, 131.91, 130.94 (q, *J* = 3.9 Hz), 124.12 (q, *J* = 3.6 Hz), 122.73 (q, *J* = 273.67 Hz), 122.37, 103.63, 75.14, 70.74, 60.87, 56.19. ^{19}F NMR (470 MHz, $CDCl_3$) δ -63.49. HRMS (EI) m/z calc'd for $C_{19}H_{17}BrF_3NO_4$ [M+H]+: 460.0371; found 460.0376. $[\alpha]^{22}_D$ = -30.86° (c = 1.05, $CHCl_3$).



***ent*-S2g**

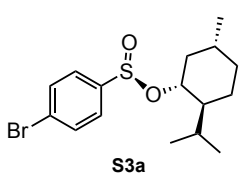
(*R*)-2-(2-bromo-4-(trifluoromethyl)phenyl)-4-(3,4,5-trimethoxyphenyl)-4,5-dihydrooxazole (*ent*-S2g): white solid. $[\alpha]^{22}_D$ = 31.74° (c = 1.4, $CHCl_3$).

3. Sulfinate synthesis



S3a **S3b**

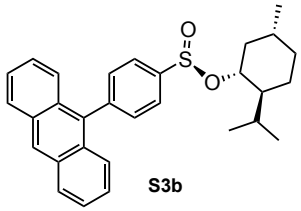
The synthesis of chiral sulfinate was based on previous reports.[15]



S3a

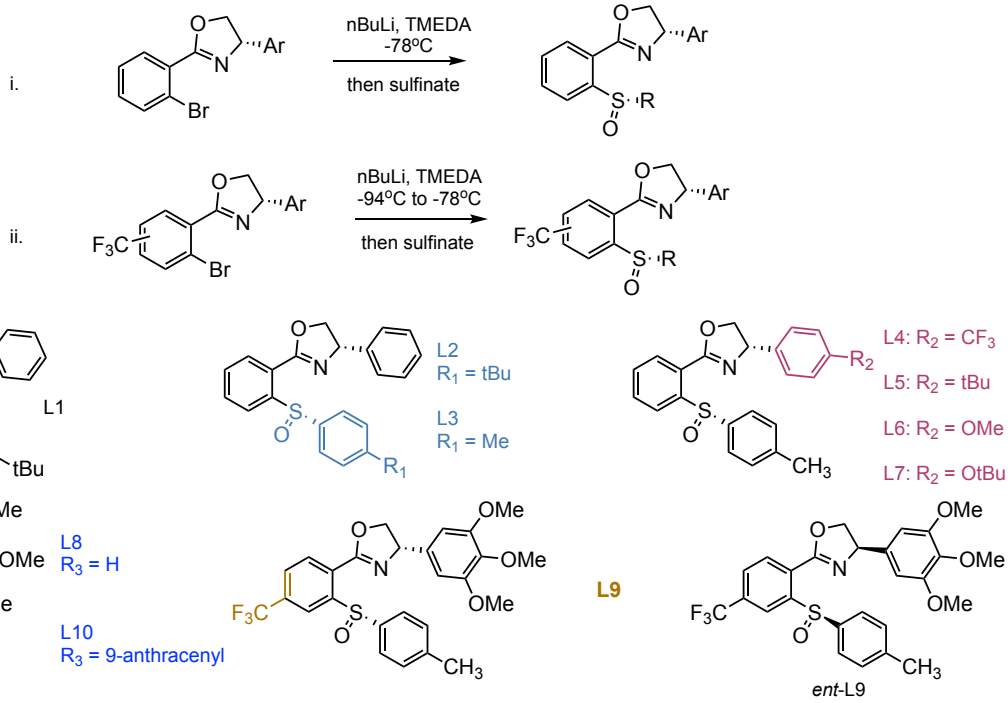
(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl (*S*)-4-bromobenzenesulfinate (S3a): To a mixture of 4-bromosulfonyl chloride (5 g, 19.5 mmol, 1.01 equiv.) and (–)-menthol (3.02 g, 19.3 mmol, 1 equiv.) in CH_2Cl_2 (50 mL) at 0˚C under argon was added Et_3N (26.9 mL, 193 mmol, 10 equiv.), and the reaction was stirred 15 minutes at 0˚C. A solution of triphenylphosphine (5.06 g, 19.3 mmol, 1 equiv.) in CH_2Cl_2 (10 mL) was added dropwise at 0˚C, and the reaction was stirred 3 hours at 0˚C. The mixture was washed with 1M HCl (2x30 mL) and brine (1x30 mL), the organic layer was dried

over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude mixture was purified by silica gel column chromatography (10% EtOAc in hexanes) to afford the product as a mixture of diastereomers. The diastereomeric mixture was dissolved in a minimal amount of acetone and one drop of HCl (conc.) was added. Recrystallization at **0˚C** afforded the product as a single diastereomer (2.3 g, 6.4 mmol, 33% yield). ^{1}H NMR (500MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.5 Hz, 2H), 7.58 (d, *J* = 8.5 Hz, 2H), 4.13 (td, *J* = 10.7, 4.5 Hz, 1H), 2.32 – 2.22 (m, 1H), 2.10 (qd, *J* = 7.4, 4.9 Hz, 1H), 1.76 – 1.58 (m, 2H), 1.56 – 1.43 (m, 1H), 1.41 – 1.30 (m, 1H), 1.22 (m, 1H), 1.12 – 0.99 (m, 1H), 0.96 (d, *J* = 6.5 Hz, 3H), 0.93 – 0.81 (m, 4H), 0.72 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.3, 132.3, 126.8, 126.8, 80.8, 48.0, 43.0, 34.1, 31.9, 25.4, 23.3, 22.2, 21.0, 15.6; HRMS (ESI) m/z calc'd for $C_{16}H_{124}O_2SBr$ [M+H]: 359.0680; found 359.0685. $[\alpha]^{23}_D$ = –151.98 (c = 0.76, $CHCl_3$).



Isopropyl 2-cinnamyl-5-isopropoxy-3-oxo-2,3-dihydrofuran-2-carboxylate (S3b): To a round bottom flask with a reflux condenser was added sulfinate **S3a** (1.2 g, 3.34 mmol, 1 equiv.), 9-anthraceneboronic acid (1.11 g, 5.01 mmol, 1.5 equiv.), Pd(dppf)Cl_2 (366 mg, 0.5 mmol, 0.15 equiv.), and Na_2CO_3 (1.42 g, 13.36 mmol, 4 equiv.). The atmosphere in the flask was replaced with argon, and a mixture of degassed 1:1:1 CH_3CN : H_2O : toluene (45 mL) was added to the flask. The reaction was stirred at 80˚C for 18 hours. After cooling to room temperature, the mixture was partitioned with EtOAc (100 mL) and H_2O (100 mL), and the layers were separated. The aqueous layer was extracted with EtOAc (2x100 mL), and the combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude material was purified by silica gel chromatography (5%→10% EtOAc in hexanes) to afford the product as an off-white solid (1.2 g, 79 % yield). ^{1}H NMR (500MHz, $CDCl_3$) δ 8.54 (s, 1H), 8.06 (d, *J* = 8.5 Hz, 2H), 7.95 (d, *J* = 8.2 Hz, 2H), 7.65 – 7.55 (m, 4H), 7.48 (t, *J* = 7.0 Hz, 2H), 7.37 (t, *J* = 7.7 Hz, 2H), 4.28 (td, *J* = 10.8, 4.5 Hz, 1H), 2.44 – 2.34 (m, 1H), 2.28 (m, 1H), 1.82 – 1.69 (m, 2H), 1.63 – 1.41 (m, 2H), 1.35 (m, 1H), 1.12 (qd, *J* = 13.0, 3.6 Hz, 1H), 1.01 (d, *J* = 6.5 Hz, 3H), 0.98 – 0.88 (m, 4H), 0.83 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.5, 143.1, 135.4, 132.1, 131.4, 130.1, 128.6, 127.4, 126.5, 125.9, 125.5, 125.36, 80.9, 48.1, 43.2, 34.2, 32.0, 25.4, 23.3, 22.3, 21.1, 15.7; HRMS (ESI) m/z calc'd for $C_{30}H_{33}O_2S$ [M+H]: 457.2201; found 457.2197. $[\alpha]^{23}_D$ = –103.60 (c = 0.275, $CHCl_3$).

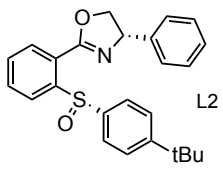
4. Ligand synthesis



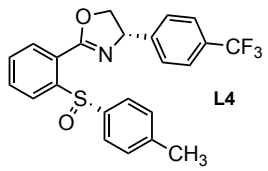
i. For ligands <u>without CF_3 group</u>: Oxazoline (synthesized from Scheme **S9.2**) was coupled with sulfinate (commercial available or synthesized from Scheme **S9.3**) using previously reported procedure.[14]

ii. For ligands <u>with CF_3 group (**L4, L9, ent-L9**)</u>: To a flame-dried flask under nitrogen was added the oxazoline (1 equiv.), THF (0.1 M), and TMEDA (1.0 equiv.). The solution was cooled to -94°C (acetone/liquid N_2 bath) with stirring, and n-butyllithium (1.6 M in hexane, 1.0 equiv.) was added **slowly** via syringe ***dropwise***. The reaction was stirred at -94°C for 5 minutes. (*NOTE: maintaining the temperature at -94°C was critical for this reaction. It was found to be effective by keeping the acetone bath frozen by liquid N_2*). The reaction was warmed to -78°C by switching to acetone/dry ice bath, upon which

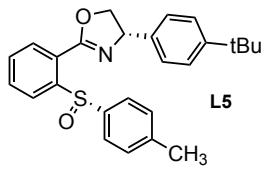
the sulfinate (3.0 equiv.) was added slowly as a solution in THF (0.5 M) dropwise via syringe. The reaction was stirred at -78°C for 30 minutes, then 0°C for 1 hour, and room temperature for 2 hours. The reaction was quenched with sat. NH_4Cl (aq.) solution and diluted with EtOAc. The layers were separated and the aqueous layer was extracted with EtOAc two times. The combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The crude residue was purified via column chromatography (acetone/hexane) to afford the desired product.
Ligand **L1**, **L3** was synthesized and matched with previous report.[14]



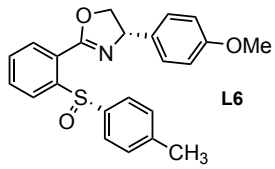
(*S*)-2-(2-((*S*)-(4-(*tert*-butyl)phenyl)sulfinyl)phenyl)-4-phenyl-4,5-dihydrooxazole (L2): white solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.49 – 8.45 (m, 1H), 8.01 (dd, *J* = 7.7 Hz, 1H), 7.79 (t, *J* = 7.5 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.29 – 7.23 (m, 3H), 7.22 – 7.19 (m, 2H), 7.05 – 6.99 (m, 2H), 5.43 (dd, *J* = 10.2, 8.6 Hz, 1H), 4.73 (dd, *J* = 10.2, 8.4 Hz, 1H), 4.18 (t, *J* = 8.5 Hz, 1H), 1.25 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.72, 153.78, 146.67, 143.28, 141.52, 132.11, 130.23, 129.94, 128.59, 127.59, 126.83, 126.80, 125.79, 125.29, 124.89, 74.40, 70.72, 34.80, 31.17. HRMS (EI) m/z calc'd for $C_{25}H_{25}NO_2S$ [M+H]+: 404.1684; found 404.1690. $[\alpha]^{22}_D$ = -166.7° (c = 0.57, $CHCl_3$).



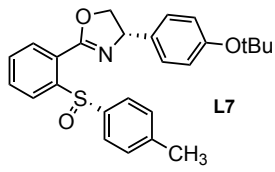
(*S*)-2-(2-((*S*)-*p*-tolylsulfinyl)phenyl)-4-(4-(trifluoromethyl)phenyl)-4,5-dihydrooxazole (L4): white solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.47 (d, *J* = 7.9 Hz, 1H), 8.02 (d, *J* = 7.8 Hz, 1H), 7.81 (t, *J* = 7.7 Hz, 1H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.47 (d, *J* = 8.1 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.05 (d, *J* = 8.2 Hz, 2H), 6.97 (d, *J* = 7.9 Hz, 2H), 5.46 (dd, *J* = 10.2, 8.1 Hz, 1H), 4.74 (dd, *J* = 10.2, 8.5 Hz, 1H), 4.16 (t, *J* = 8.3 Hz, 1H), 2.30 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.18, 146.49, 145.50, 145.49, 143.43, 140.95, 132.36, 130.34, 130.08, 129.83 (q, *J* = 32.4 Hz), 127.08, 126.95, 125.63, 125.48 (q, *J* = 3.8 Hz), 124.49, 124.04 (q, *J* = 272.46 Hz), 74.04, 70.24, 21.23. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.52. HRMS (EI) m/z calc'd for $C_{23}H_{18}NO_2SF_3$ [M+H]+: 430.1089; found 430.1080. $[\alpha]^{22}_D$ = -116.8° (c = 0.64, $CHCl_3$).



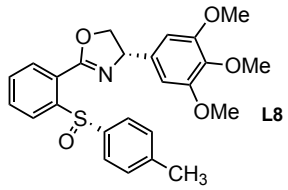
(*S*)-4-(4-(*tert*-butyl)phenyl)-2-(2-((*S*)-*p*-tolylsulfinyl)phenyl)-4,5-dihydrooxazole (L5): white solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.44 (d, *J* = 8.0 Hz, 1H), 8.00 (d, *J* = 7.7 Hz, 1H), 7.77 (t, *J* = 7.7 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.44 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.3 Hz, 2H), 6.97 (m, 4H), 5.39 (dd, *J* = 10.2, 8.4 Hz, 1H), 4.69 (dd, *J* = 10.1, 8.4 Hz, 1H), 4.22 (t, *J* = 8.3 Hz, 1H), 2.30 (s, 3H), 1.33 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.52, 150.52, 146.81, 143.50, 140.60, 138.49, 132.07, 130.21, 129.98, 129.42, 126.90, 126.57, 125.44, 125.15, 124.91, 74.32, 70.37, 34.53, 31.38, 21.37. HRMS (EI) m/z calc'd for $C_{26}H_{27}NO_2S$ [M+H]+: 418.1841; found 418.1836. $[\alpha]^{22}_D$ = -171.4° (c = 1.34, $CHCl_3$).



(*S*)-4-(4-methoxyphenyl)-2-(2-((*S*)-*p*-tolylsulfinyl)phenyl)-4,5-dihydrooxazole (L6): white solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.44 (d, *J* = 7.9 Hz, 1H), 7.99 (d, *J* = 7.9 Hz, 1H), 7.76 (t, *J* = 7.6 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.43 (d, *J* = 8.2 Hz, 2H), 6.99 (d, *J* = 8.0 Hz, 2H), 6.93 (d, *J* = 8.6 Hz, 2H), 6.78 (d, *J* = 8.6 Hz, 2H), 5.35 (dd, *J* = 10.1, 8.3 Hz, 1H), 4.67 (dd, *J* = 10.1, 8.4 Hz, 1H), 4.15 (t, *J* = 8.4 Hz, 1H), 3.81 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.46, 159.04, 146.75, 143.51, 140.70, 133.70, 132.08, 130.23, 129.98, 129.42, 127.97, 126.86, 125.19, 124.89, 113.90, 74.46, 70.20, 55.31, 21.34. HRMS (EI) m/z calc'd for $C_{23}H_{21}NO_3S$ [M+H]+: 392.1320; found 392.1324. $[\alpha]^{22}_D$ = -191.6° (c = 1.0, $CHCl_3$).

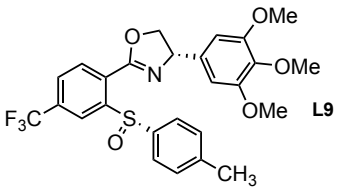


(*S*)-4-(4-(*tert*-butoxy)phenyl)-2-(2-((*S*)-*p*-tolylsulfinyl)phenyl)-4,5-dihydrooxazole (L7): white solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.43 (d, *J* = 8.0 Hz, 1H), 8.00 (d, *J* = 7.7 Hz, 1H), 7.77 (t, *J* = 7.6 Hz, 1H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.49 – 7.44 (m, 2H), 7.02 (d, *J* = 8.4 Hz, 2H), 6.94 – 6.85 (m, 4H), 5.38 (dd, *J* = 10.1, 8.6 Hz, 1H), 4.70 (dd, *J* = 10.2, 8.4 Hz, 1H), 4.18 (t, *J* = 8.5 Hz, 1H), 2.30 (s, 3H), 1.35 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.63, 154.84, 146.76, 143.51, 140.78, 136.27, 132.13, 130.24, 129.96, 129.44, 127.34, 126.84, 125.20, 124.92, 124.15, 78.54, 74.48, 70.27, 28.86, 21.32. HRMS (ESI) m/z calc'd for $C_{26}H_{27}NO_3S$ [M+H]+: 434.1790; found 434.1783. $[\alpha]^{23}_D$ = -219.1° (c = 1.1, $CHCl_3$).



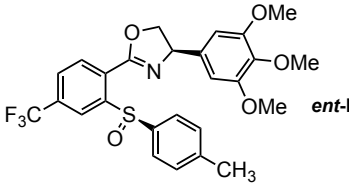
(*S*)-2-(2-((*S*)-*p*-tolylsulfinyl)phenyl)-4-(3,4,5-trimethoxyphenyl)-4,5-dihydrooxazole (L8): white solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.43 (d, *J* = 8.0 Hz, 1H), 8.00 (d, *J* = 7.8 Hz, 1H), 7.78 (t, *J* = 7.8 Hz, 1H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.44 (d, *J* = 8.2 Hz, 2H), 6.98 (d, *J* = 8.2 Hz, 2H), 6.30 (s, 2H), 5.34 (dd, *J* = 10.1, 8.6 Hz, 1H), 4.72 (dd, *J* = 10.2, 8.5 Hz, 1H), 4.21 (t, *J* = 8.5 Hz, 1H), 3.86 (s, 3H), 3.73 (s, 6H), 2.28 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.73, 153.38, 147.24, 143.46, 140.81, 137.42, 137.12, 132.22, 130.25, 129.96, 129.31, 126.93, 125.15, 124.75, 103.79, 74.35, 71.04, 60.86, 55.98, 21.26; HRMS (ESI) m/z calc'd for

$C_{25}H_{25}NO_5S$ [M+H]+: 452.1532; found 452.1532. $[\alpha]^{22}_D$ = -111.9° (c = 1.1, $CHCl_3$).



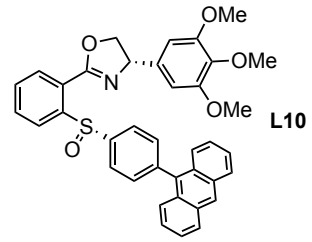
L9

(*S*)-2-(2-((*S*)-*p*-tolylsulfinyl)-4-(trifluoromethyl)phenyl)-4-(3,4,5-trimethoxyphenyl)-4,5-dihydrooxazole (L9): white foam. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.76 (s, 1H), 8.12 (d, *J* = 8.0 Hz, 1H), 7.81 (d, *J* = 7.9 Hz, 1H), 7.40 (d, *J* = 8.3 Hz, 2H), 6.97 (d, *J* = 8.0 Hz, 2H), 6.27 (s, 2H), 5.38 (dd, *J* = 10.2, 8.5 Hz, 1H), 4.75 (dd, *J* = 10.3, 8.6 Hz, 1H), 4.26 (t, *J* = 8.6 Hz, 1H), 3.87 (s, 3H), 3.72 (s, 6H), 2.28 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.71, 153.44, 149.18, 142.67, 141.33, 137.58, 136.60, 134.12 (q, *J* = 33.5 Hz), 130.56, 129.44, 127.75, 127.10, 127.06 (q, *J* = 3.7 Hz), 123.36 (q, *J* = 273.67 Hz), 122.42 (q, *J* = 3.8 Hz), 103.84, 74.56, 71.27, 60.87, 55.97, 21.27. ^{19}F NMR (470 MHz, $CDCl_3$) δ -63.25. HRMS (ESI) m/z calc'd for $C_{26}H_{24}F_3NO_5S$ [M+H]+: 520.1406; found 520.1414. $[\alpha]^{22}_D$ = -68.1° (c = 0.71, $CHCl_3$).



***ent*-L9**

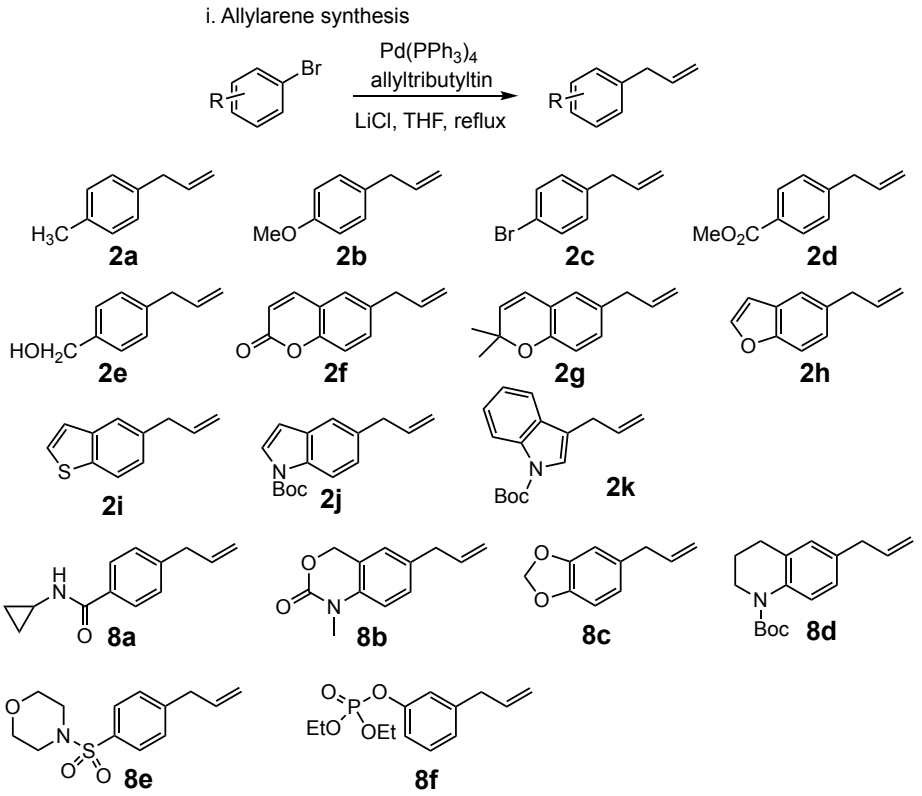
(*R*)-2-(2-((*R*)-*p*-tolylsulfinyl)-4-(trifluoromethyl)phenyl)-4-(3,4,5-trimethoxyphenyl)-4,5-dihydrooxazole (*ent*-L9): white foam. $[\alpha]^{22}_D$ = 68.7° (c = 1.31, $CHCl_3$).



L10

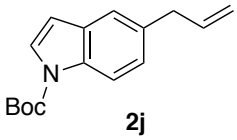
(*S*)-2-(2-((*S*)-(4-(anthracen-9-yl)phenyl)sulfinyl)phenyl)-4-(3,4,5-trimethoxyphenyl)-4,5-dihydrooxazole (L10): white solid. ^{1}H NMR (500MHz, $CDCl_3$) δ 8.55 – 8.46 (m, 2H), 8.10 (d, *J* = 7.8 Hz, 1H), 8.03 (d, *J* = 8.5 Hz, 2H), 7.98 (d, *J* = 7.5 Hz, 2H), 7.85 (t, *J* = 7.7 Hz, 1H), 7.63 (t, J = 7.6 Hz, 1H), 7.50 – 7.40 (m, 4H), 7.36 (d, *J* = 7.7 Hz, 2H), 7.31 (d, *J* = 7.5 Hz, 2H), 6.51 (s 2H), 5.46 (t, *J* = 9.7 Hz, 1H), 4.84 (d, *J* = 9.6 Hz, 1H), 4.31 (t, *J* = 9.0 Hz, 1H), 3.73 (s, 6H), 3.68 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.4, 153.7, 147.8, 146.0, 141.6, 137.6, 137.1, 135.4, 132.8, 131.8, 131.4, 130.7, 130.1, 130.0, 128.6, 127.3, 126.7, 126.4, 125.8, 125.4, 125.3, 125.2, 103.9, 74.8, 71.2, 60.9, 56.3; HRMS (ESI) m/z calc'd for $C_{38}H_{32}NO_5S$ [M+H]: 614.2015; found 614.2010. $[\alpha]^{21}_D$ = –229.29 (c = 0.2, $CHCl_3$).

Scheme S10. Substrate Synthesis: Allylarenes.

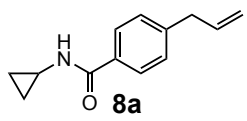


General procedure for Stille coupling (**S5**): To a flamed-dried RBF was added bromoarene (1 equiv), lithium chloride (5 equiv), dry THF (0.1 M) and finally allyltributylstannane (1.1 equiv). The solution was stirred and degassed under dry argon for 15 mins. Then, $Pd(PPh_3)_4$ (0.1 equiv) was added as a solid and the reaction flask was fitted with an oven-dried condenser. The reaction was heated in 80°C oil bath for 22 hours under argon. After cooled down to RT, the reaction was diluted with water, which was then partition into a separatory funnel. The aqueous layer was extracted with EtOAc 3 times. The organic layers were combined and dried over anhydrous $MgSO_4$. The solid was filtered off and the solvent was removed under reduced pressure. The crude was purified via silica column chromatography.

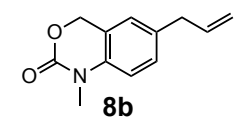
4-allyltoluene (**2a**), 4-allylanisole (**2b**), 4-allylbromobenzene (**2c**), safrole (**8c**) are commercially available. Substrate **2d**,[16] **2e**,[17] **2f**,[18] **2g**,[1] **2h**,[19] **2i**,[20] **2k**[1] has been reported in literature and synthesized accordingly or based on general procedure (**S5**).



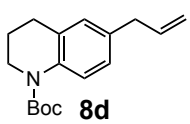
***Tert*-butyl 5-allyl-1*H*-indole-1-carboxylate (2j):** colorless liquid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.12 (m, 1H), 7.63 (m, 1H), 7.42 (m, 1H), 7.20 (d, *J* = 8.3 Hz, 1H), 6.56 (d, *J* = 3.7 Hz, 1H), 6.07 (ddd, *J* = 16.8, 12.8, 5.4 Hz, 1H), 5.21 – 5.09 (m, 2H), 3.53 (d, *J* = 5.5 Hz, 2H), 1.72 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.82, 138.09, 134.37, 133.82, 130.89, 126.06, 125.13, 120.58, 115.47, 115.02, 107.17, 83.52, 40.16, 28.24. HRMS (ESI) m/z calc'd for $C_{16}H_{19}NO_2$ [M+Na]+: 280.0963; found 280.0966.



4-allyl-*N*-cyclopropylbenzamide (8a): White solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 8.2 Hz, 2H), 7.22 (d, *J* = 8.3 Hz, 2H), 6.28 (br, 1H), 5.94 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.13 – 5.02 (m, 2H), 3.41 (d, *J* = 6.6 Hz, 2H), 2.89 (m, 1H), 0.85 (m, 2H), 0.64 – 0.57 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.72, 143.84, 136.56, 132.28, 128.74, 127.00, 116.44, 39.97, 23.10, 6.80. HRMS (ESI) m/z calc'd for $C_{13}H_{15}NO$ [M+Na]+: 224.1051; found 220.1048.

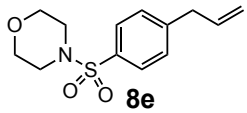


6-allyl-1-methyl-1,4-dihydro-2*H*-benzo[*d*][1,3]oxazin-2-one (8b): Yellowish solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.16 (d, *J* = 8.3 Hz, 1H), 6.96 (s, 1H), 6.86 (d, *J* = 8.2 Hz, 1H), 5.93 (ddt, *J* = 16.9, 10.3, 6.7 Hz, 1H), 5.17 (s, 2H), 5.12 – 5.02 (m, 2H), 3.36 (s, 3H), 3.35 (d, *J* = 6.7 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.40, 136.98, 136.64, 134.96, 129.16, 124.47, 120.67, 116.21, 112.86, 67.39, 39.32, 31.53. HRMS (ESI) m/z calc'd for $C_{12}H_{13}NO_2$ [M+H]+: 204.1025; found 204.1028.



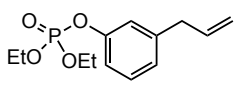
8d

***Tert*-butyl 6-allyl-3,4-dihydroquinoline-1(2*H*)-carboxylate (8d):** Colorless oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.57 (d, *J* = 8.4 Hz, 1H), 6.96 (dd, *J* = 8.5 Hz, 1H), 6.89 (s, 1H), 5.95 (ddt, *J* = 16.8, 10.0, 6.7 Hz, 1H), 5.13 – 5.00 (m, 2H), 3.74 – 3.64 (m, 2H), 3.31 (d, *J* = 6.8 Hz, 2H), 2.74 (t, *J* = 6.6 Hz, 2H), 2.04 – 1.82 (m, 2H), 1.52 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.98, 137.61, 136.70, 134.83, 129.77, 128.49, 125.93, 124.11, 115.57, 80.61, 44.63, 39.59, 28.42, 27.48, 23.59. HRMS (ESI) m/z calc'd for $C_{17}H_{23}NO_2$ [M+Na]+: 296.1626; found 296.1632.



8e

4-((4-allylphenyl)sulfonyl)morpholine (8e): White solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.68 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 8.1 Hz, 2H), 5.95 (ddt, *J* = 16.9, 10.1, 6.7 Hz, 1H), 5.18 – 5.09 (m, 2H), 3.76 – 3.72 (m, 4H), 3.48 (d, *J* = 6.7 Hz, 2H), 3.05 – 2.95 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.90, 135.75, 132.79, 129.30, 128.06, 117.21, 66.12, 46.00, 39.96. HRMS (ESI) m/z calc'd for $C_{13}H_{17}NO_3S$ [M+H]+: 268.1007; found 268.1001.

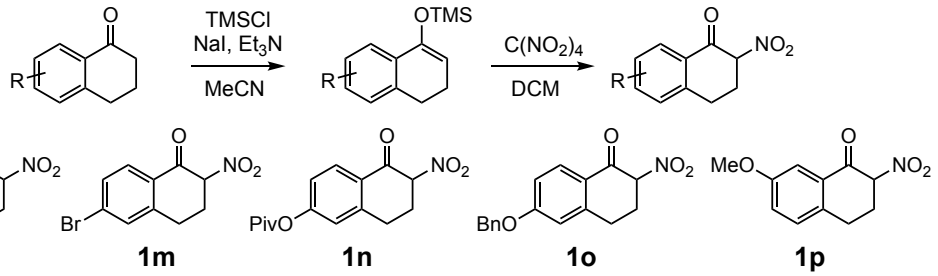


8f

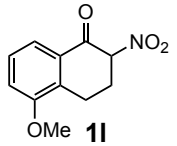
3-allylphenyl diethyl phosphate (8f): To a flame-dried RBF under argon was added 3-allylphenol (350 mg, 2.5 mmol, 1 equiv.), anhydrous THF (8 mL), and DABCO (420 mg, 3.75 mmol, 1.5 equiv.) at room temperature. To this mixture was added diethylchlorophosphate (540 mg, 3.75 mmol, 1.5 equiv.) dissolved in THF (2 mL) dropwise via syringe. The reaction was stirred at room temperature overnight. Afterward, the reaction was poured into CH_2Cl_2 and washed with HCl (5% aq.), $NaHCO_3$ (sat. aq.), and brine. The organic layer was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude mixture was purified by silica gel chromatography (20%→30%→50% EtOAc in hexanes) to afford the product as a clear oil (450 mg, 67% yield). ^{1}H NMR (500MHz, $CDCl_3$) δ 7.33 – 7.19 (m, 1H), 7.09 – 7.02 (m, 2H), 7.00 (d, *J* = 7.7 Hz, 1H), 6.03 – 5.86 (m, 1H), 5.14 – 5.02 (m, 2H), 4.26 – 4.17 (m, 4H), 3.38 (d, *J* = 6.7 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.9 (d, J_P = 7.5 Hz), 142.3, 136.8, 129.7, 125.4, 120.3 (d, J_P = 5.0 Hz) 117.7 (d, J_P = 5.0 Hz), 116.5, 64.7 (d, J_P = 6.3 Hz), 40.0, 16.2 (d, J_P = 6.3 Hz); ^{31}P NMR (202MHz, $CDCl_3$) δ –5.2; HRMS (ESI) m/z calc'd for $C_{13}H_{20}O_4P$ [M+H]: 271.1099; found 271.1105.

Scheme S11. Substrate Synthesis: Nucleophiles.

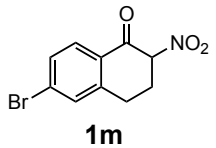
i. 2-Nitrotetralone synthesis



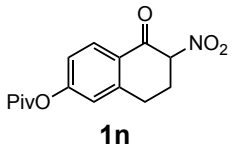
General procedure for the synthesis of 2-nitroketone nucleophiles: the silyl enol ether was synthesized using a previous procedure[21]; the silyl enol ether was purified via silica gel column chromatography (**NOTE**: fast elution to minimize product decomposition on silica). The 2-nitroketone nucleophile was synthesized via the nitration of silyl enol ether based on a previous method[22] (**NOTE**: the crude material was purified via recrystallization from Et_2O/Hexane or DCM/Hexane).



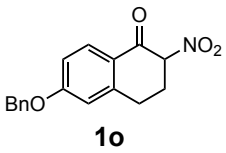
5-methoxy-2-nitro-3,4-dihydronaphthalen-1(2*H*)-one (1l): White solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 8.0 Hz, 1H), 7.35 (t, *J* = 8.0 Hz, 1H), 7.10 (d, *J* = 8.1 Hz, 1H), 5.43 (dd, *J* = 12.5, 4.9 Hz, 1H), 3.89 (s, 3H), 3.28 (dt, *J* = 16.2, 3.8 Hz, 1H), 2.92 – 2.74 (m, 2H), 2.71 – 2.65 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 186.68, 156.66, 131.71, 131.36, 128.02, 119.66, 115.58, 89.56, 55.82, 27.44, 20.67. HRMS (ESI) m/z calc'd for $C_{11}H_{11}NO_4$ [M+H]+: 222.0766; found 222.0762.



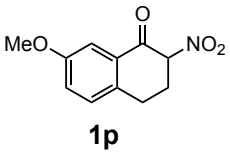
6-bromo-2-nitro-3,4-dihydronaphthalen-1(2*H*)-one (1m): White solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 8.4 Hz, 1H), 7.55 (d, *J* = 8.4 Hz, 1H), 7.50 (s, 1H), 5.43 (dd, *J* = 12.1, 4.6 Hz, 1H), 3.13 (m, 2H), 2.88 (m, 1H), 2.69 (dq, *J* = 13.6, 4.6 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 185.48, 144.14, 131.91, 131.23, 130.59, 130.01, 129.28, 89.16, 28.02, 26.32. HRMS (ESI) m/z calc'd for $C_{10}H_8NO_3Br$[M+Na]+: 291.9585; found 291.9580.



6-nitro-5-oxo-5,6,7,8-tetrahydronaphthalen-2-yl pivalate (1n): White solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.12 (d, *J* = 8.6 Hz, 1H), 7.09 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.05(d, *J* = 2.2 Hz, 1H), 5.44 (dd, *J* = 12.1, 4.6 Hz, 1H), 3.19 – 3.11 (m, 2H), 2.89 (m, 1H), 2.70 (dq, *J* = 13.4, 4.5 Hz, 1H), 1.37 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 185.21, 176.35, 156.20, 144.50, 130.45, 127.94, 121.65, 121.31, 89.38, 39.31, 28.16, 27.03, 26.69. HRMS (ESI) m/z calc'd for $C_{15}H_{17}NO_5$ [M+H]+: 292.1174; found 292.1175.

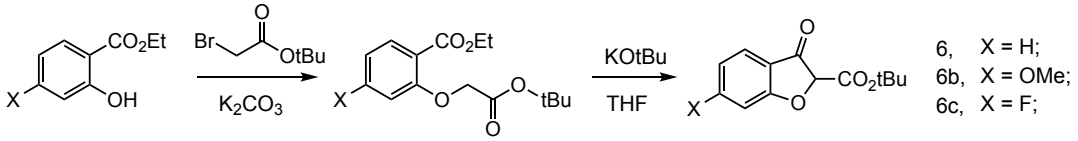


6-(benzyloxy)-2-nitro-3,4-dihydronaphthalen-1(2*H*)-one (1o): Pink solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.06 (d, *J* = 8.7 Hz, 1H), 7.44 – 7.33 (m, 5H), 6.97 (d, *J* = 8.7 Hz, 1H), 6.81 (s, 1H), 5.40 (dd, *J* = 12.1, 4.5 Hz, 1H), 5.14 (s, 2H), 3.13 – 3.07 (m, 2H), 2.85 (m, 1H), 2.66 (dq, *J* = 13.3, 4.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 184.81, 163.96, 145.27, 135.70, 131.09, 128.78, 128.43, 127.46, 123.98, 114.91, 113.74, 89.55, 70.34, 28.32, 26.96. HRMS (ESI) m/z calc'd for $C_{17}H_{15}NO_4$ [M+H]+: 298.1069; found 298.1066.



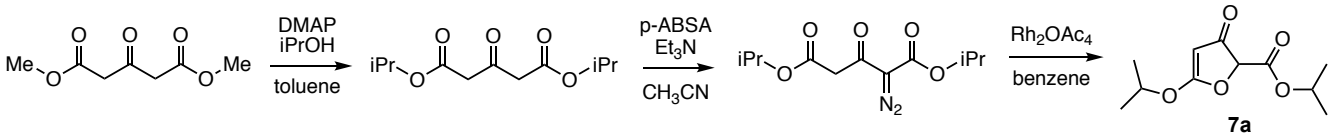
7-methoxy-2-nitro-3,4-dihydronaphthalen-1(2*H*)-one (1p): White solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.51 (d, *J* = 2.8 Hz, 1H), 7.21 (d, *J* = 8.4 Hz, 1H), 7.15 (dd, *J* = 8.5, 2.8 Hz, 1H), 5.43 (dd, *J* = 12.2, 4.6 Hz, 1H), 3.84 (s, 3H), 3.12 – 3.06 (m, 2H), 2.85 (m, 1H), 2.68 (dq, *J* = 13.2, 4.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 186.40, 158.89, 135.38, 131.21, 130.17, 123.58, 109.91, 89.75, 55.63, 28.59, 25.93. HRMS (ESI) m/z calc'd for $C_{11}H_{11}NO_4$ [M-H]+: 220.0610; found 220.0614.

ii. β-ketoester **6** synthesis



The synthesis of benzofuranone-type β-ketoester nucleophile **6** was based on a previous procedure.[23]

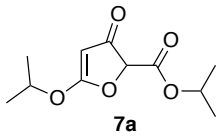
iii. β-ketoester **7a** synthesis



To a flame-dried round bottom flask equipped with a reflux condenser was added dimethyl 3-oxoglutarate (1 equiv.), isopropanol (2.5 equiv.), toluene (0.8 M) and DMAP (0.1 equiv.). The mixture was refluxed for 24 hours. Afterward, the mixture was cooled and concentrated under reduced pressure. The crude mixture was purified by silica gel column chromatography (5% EtOAc in hexanes) to afford the isopropyl ester product.

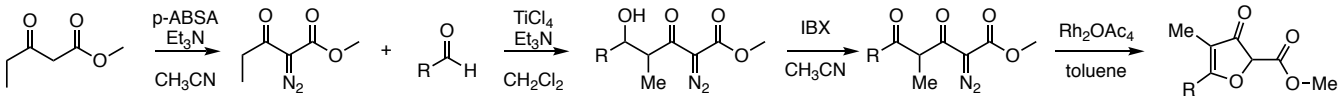
To a flame-dried round bottom flask was added the isopropyl ester substrate (1 equiv.) and CH_3CN (0.1 M). Et_3N (1.5 equiv) was added, and the reaction was cooled to 0˚C. 4-Acetamidobenzenesulfonyl azide (1.0 equiv.) was added, and the reaction was warmed to room temperature and stirred 4 hours. Afterward, the suspension was filtered through celite and rinsed with EtOAc. The mixture was concentrated under reduced pressure and purified by silica gel column chromatography (20% EtOAc in hexanes) to afford the diazo ester which was taken on to the next step.

To a flame-dried RBF in a glove box was added a catalytic amount of Rh_2OAc_4. The flask was sealed with a septum and taken out of the glove box, after which an argon balloon was added. Benzene (0.1M) was added, and the mixture was heated to 50˚C. A 1M solution of the ketone substrate in benzene was added under slow addition conditions, and the reaction was stirred for 1 hour after completion of addition. Evolution of nitrogen gas was observed. The reaction was subsequently rapidly cooled in an ice bath, and filtered through celite (rinsing with EtOAc) to remove the majority of the catalyst. The crude mixture was concentrated under reduced pressure and was purified by silica gel column chromatography (20%→30% →50% EtOAc in hexanes) to afford the β-ketoester product. NOTE: The product was moderately unstable to silica gel, so the column purification was performed in a rapid manner. Additionally the β-ketoester product was observed to decompose after prolonged exposure to the atmosphere, however it was stable when stored either under vacuum, or in a glovebox freezer under argon atmosphere.


7a

Isopropyl 5-isopropoxy-4-methyl-3-oxo-2,3-dihydrofuran-2-carboxylate (7a): ^{1}H NMR (500MHz, $CDCl_3$) δ 5.13 (hept, *J* = 6.2 Hz, 1H), 5.04 (s, 1H), 4.80 (hept, *J* = 6.2 Hz, 1H), 4.74 (s, 1H), 1.45 (dd, *J* = 6.6, 1.9 Hz, 6H), 1.32 (dd, *J* = 6.3, 2.5 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.2, 185.2, 163.3, 82.7, 79.6, 77.6, 70.8, 22.0, 21.84, 21.82, 21.78; HRMS (ESI) m/z calc'd for $C_{11}H_{17}O_5$ [M+H]: 229.1076; found 229.1079.

iv. β-ketoester **7b**, **7c** synthesis



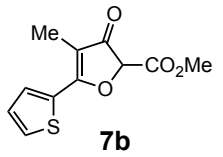
To a flame-dried round bottom flask was added methyl 3-oxopentanoate (1 equiv.) and CH_3CN (0.4 M). 4-Acetamidobenzenesulfonyl azide (1.1 equiv.) was added, and the reaction was cooled to 0˚C. Et_3N (1.2 equiv) was added, and the reaction was stirred at 0˚C for 30 minutes before warming to room temperature. The reaction was stirred overnight. Afterward, the suspension was filtered through celite and rinsed with EtOAc. The mixture was concentrated under reduced pressure and purified by silica gel column chromatography (20% Et_2O in petroleum ether) to afford the diazo ester which was taken on to the next step.

To a flame-dried RBF under argon was added the diazo ester (1 equiv.) and CH_2Cl_2 (0.1 M), and the reaction was cooled to –78˚C. Et_3N (1.1 equiv.) was added, followed by $TiCl_4$ dropwise (1M solution in CH_2Cl_2, 1.1 equiv), and the reaction was stirred at –78˚C for two hours. A solution of the aldehyde (1 equiv.) in CH_2Cl_2 (1M) was added dropwise, and the reaction was stirred for 1 hour at –78˚C. After complete conversion of the starting material was observed by TLC, NH_4Cl (sat. aq.) was added dropwise at –78˚C, and the reaction was allowed to warm to room temperature. The quenched reaction mixture was then extracted with CH_2Cl_2 (3x) and the combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude mixture was purified by silica gel column chromatography (20%→30% EtOAc in hexanes) to afford the alcohol product that was taken on to the next step.

To a flame-dried RBF equipped with a reflux condenser was added the alcohol substrate (1 equiv.) and CH_3CN (0.1 M) under argon. Freshly prepared IBX (1.5 equiv.) was added, and the reaction was stirred for 2 hours at 80˚C. After the flask was cooled, cold Et_2O was added, and the suspension was filtered through celite and rinsed with cold Et_2O. The filtrate was concentrated under reduced pressure, and the crude mixture was purified by silica gel column chromatography (20%→30% EtOAc in hexanes) to afford the ketone product that was taken on to the next step.

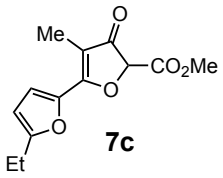
To a flame-dried RBF in a glove box was added a catalytic amount of Rh_2OAc_4. The flask was sealed with a septum and taken out of the glove box, after which an argon balloon was added. Toluene (0.1M) was added, and the mixture was heated to 80˚C. A 1M solution of the ketone substrate in toluene was added, and the reaction was stirred for ten minutes.

Evolution of nitrogen gas was observed. The reaction was subsequently rapidly cooled in an ice bath, and filtered through celite (rinsing with EtOAc) to remove the majority of the catalyst. The crude mixture was concentrated under reduced pressure and was purified by silica gel column chromatography (20% EtOAc in hexanes) to afford the β-ketoester product. NOTE: The products were moderately unstable to silica gel, so the column purification was performed in a rapid manner. Additionally the β-ketoester products were observed to decompose after prolonged exposure to the atmosphere, however they were stable when stored either under vacuum, or in a glovebox freezer under argon atmosphere.



7b

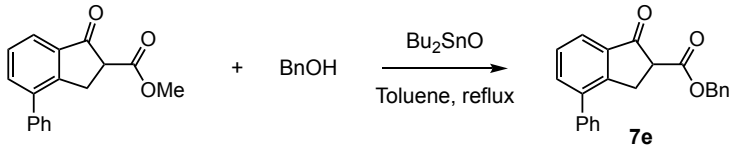
Methyl 4-methyl-3-oxo-5-(thiophen-2-yl)-2,3-dihydrofuran-2-carboxylate (7b): product exists in solution as an enol:keto-tautomeric mixture: ^{1}H NMR (500MHz, $CDCl_3$) *enol-tautomer*: δ 7.95-7.50 (br. s, 1H), 7.44 (d, *J* = 3.2 Hz, 1H), 7.40 (d, *J* = 4.8 Hz, 1H), 7.12 (dd, *J* = 5.0, 3.6 Hz, 1H), 3.94 (s, 3H), 2.19 (s, 3H); *keto-tautomer*: δ 3.94 (s, 3H), 2.09 (s, 3H); ^{13}C NMR (126 MHz, CD_2Cl_2) *enol-tautomer*: δ 132.45, 132.03, 130.90, 128.38, 127.75, 126.55, 125.56, 124.01, 108.90, 51.42, 7.09; *keto-tautomer*: δ 195.34, 175.16, 164.26, 147.99, 131.60, 126.83, 126.12, 108.00, 81.13, 53.02, 6.64. HRMS (EI) m/z calc'd for $C_{11}H_{11}O_4S$ [M+H]: 239.0378; found 239.0382.



7c

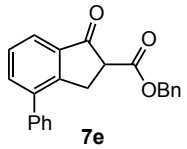
Methyl 5'-ethyl-3-methyl-4-oxo-4,5-dihydro-[2,2'-bifuran]-5-carboxylate (7c): product exists in solution as an approx. 10:1 enol:keto-tautomeric mixture: ^{1}H NMR (500MHz, $CDCl_3$) *enol-tautomer* δ 8.11 – 7.36 (br. s, 1H), 6.65 (d, *J* = 3.4 Hz, 1H), 6.10 (d, *J* = 3.4 Hz, 1H), 3.93 (s, 3H), 2.72 (q, *J* = 7.6 Hz, 2H), 2.18 (s, 3H), 1.27 (t, *J* = 7.5 Hz, 3H); *keto-tautomer* δ 7.09 (d, *J* = 3.6 Hz, 1H), 6.26 (d, *J* = 3.5 Hz, 1H), 3.86 (s, 3H), 2.00 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) (enol:keto-tautomeric mixture) δ 164.6, 163.7, 159.3, 144.3, 123.9, 117.9, 110.2, 108.4, 107.8, 106.4, 81.1, 53.3, 51.6, 21.9, 21.6, 12.1, 11.9, 6.9, 6.3; HRMS (ESI) m/z calc'd for $C_{13}H_{15}O_5$ [M+H]: 251.0919; found 251.0921.

v. β-ketoester **7e** synthesis



7e

β-ketoester **7e** was synthesized from the trans-esterification reaction[24] of the methyl ester[25].



7e

Benzyl 1-oxo-4-phenyl-2,3-dihydro-1*H*-indene-2-carboxylate (7e): product exists in solution as an enol:keto-tautomeric mixture: ^{1}H NMR (500 MHz, Chloroform-*d*) *keto-tautomer:* δ 7.80 (d, *J* = 7.6 Hz, 1H), 7.63 (dd, *J* = 7.4 Hz, 1H), 7.56 – 7.29 (m, 11H), 5.30 (s, 1H), 5.24 (s, 1H), 3.78 (dd, *J* = 8.2, 4.2 Hz, 1H), 3.63 (dd, *J* = 17.4, 4.2 Hz, 1H), 3.37 (dd, *J* = 17.4, 8.2 Hz, 1H). *enol-tautomer:* δ 7.67 (d, *J* = 7.4 Hz, 1H), 7.56 – 7.29 (m, 12H), 5.24 (s, 2H), 3.61 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) *keto-tautomer:* δ 199.33, 168.99, 150.97, 140.47, 138.68, 135.56, 128.72, 128.63, 128.59, 128.49, 128.47, 128.31, 128.20, 128.16, 127.90, 123.66, 67.39, 53.49, 30.18. *enol-tautomer:* δ 169.54, 140.83, 139.81, 138.80, 137.38, 136.03, 135.75, 130.11, 127.64, 127.56, 119.88, 102.57, 65.79, 32.51 (incomplete number of carbons, presumably due to overlapping). HRMS (ESI) m/z for $C_{23}H_{18}O_3$ [M+Na]: 365.1154.

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