Nitro-enabled catalytic enantioselective formal umpolung alkenylation of β-ketoesters

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**General information:** Unless stated otherwise, all reactions were carried out with distilled and dried solvents under an atmosphere of N₂ or argon, oven (120 °C) dried glassware with standard vacuum line techniques were used. Organic solvents used for carrying out reactions were dried using standard methods. All work up and purification were carried out with reagent grade solvents in air. Organometallic reagents were titrated using standard procedure¹ to determine their concentration. Thin-layer chromatography was performed using Merck silica gel 60 F₂₅₄ pre-coated plates (0.25 mm). Column chromatography was performed using silica gel (230-400 or 100-200 mesh). Infrared (FT-IR) spectra were recorded on a Perkin Elmer Spectrum BX spectrophotometer in cm⁻¹ and the bands are characterized as broad (br), strong (s), medium (m), and weak (w). NMR spectra were recorded on Bruker Ultrashield spectrometer at 400MHz (¹H) and 100 MHz (¹³C). Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as internal standard (CDCl₃: δ 7.26 for ¹H-NMR and CDCl₃: δ 77.0 for ¹³C NMR). For ¹H NMR, data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = double doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz) and integration. High-resolution mass spectrometry was performed on Micromass Q-TOF Micro instrument. Optical rotations were measured on JASCO P-2000 polarimeter. Melting points were measured using ANALAB µ-Thermocal 10 melting point apparatus. All melting points were measured in open glass capillary and values are uncorrected. Enantiomeric ratios were determined by HPLC analysis using chiral columns in comparison with authentic racemic materials. Racemic products were prepared by the reaction of cyclic β-ketoester with β-nitroenone in the presence of rac-Takemoto thiourea catalyst at ambient temperature followed by treatment with DBU. 1-Indanone derivatives apart from 5'-phenyl 1-indanone (S₁) were obtained from commercial source and used without any further purification. All acetophenone derivatives were obtained from commercial source and used without any further purification.

**A. Preparation of 5'-phenyl 1-indanone (S₁):**

5'-Phenyl 1-indanone (S₁) was prepared according to the modified literature procedure.²

\[
\text{Br} \quad \text{Na₂CO₃} \quad \text{Pb(OH)₂, Pd(OAc)₂} \quad \text{PhMe/EtOH/H₂O (5:1:1)} \quad \text{Ph} \quad \text{S₁}
\]

In an oven-dried 25 mL round-bottom flask equipped with a reflux condenser and an argon inlet, 5'-bromo 1-indanone (422 mg, 2.0 mmol, 1.0 equiv.), sodium carbonate (424 mg, 4.0 mmol, 2.0 equiv.), phenyl boronic acid (244 mg, 2.0 mmol, 1.0 equiv.) was taken in 14 mL toluene/EtOH/H₂O (5:1:1) and degassed for 15 min. Palladium(II) acetate (4.5 mg, 0.02 mmol, ¹

0.01 equiv.) and triphenyl phosphine (105 mg, 0.40 mmol, 0.2 equiv.) was added at 25 °C. The resulting mixture was refluxed at 105 °C for 12 h. The reaction mixture was cooled to 25 °C and ethanol was evaporated in vacuo. A 0.5 (M) aqueous NaOH solution (5 mL) was added and the resulting mixture was stirred at 25 °C for 15 min. Then it was extracted with toluene and the combined organic layer was dried over anh. Na$_2$SO$_4$, concentrated in vacuo to obtain a red oil which was purified by silica gel (100-200 mesh) column chromatography using 20% EtOAc in petroleum ether as eluent to obtain pure S1 as a yellow solid. (375 mg, 1.800 mmol; 90% yield). 

\[ R_f = 0.25 \] (20% EtOAc in petroleum ether). 

$^1$H-NMR (400 MHz, CDCl$_3$): \( \delta \) 7.82 (d, \( J = 8.1 \) Hz; 1H), 7.59-7.68 (m; 4H), 7.39-7.50 (m; 3H), 3.19-3.21 (m; 2H), 2.73-2.76 (m; 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): \( \delta \) 206.54, 155.82, 147.69, 140.22, 135.99, 128.94, 128.31, 127.47, 126.77, 125.15, 124.07, 36.51, 25.86. The spectral data are in agreement with the literature. 

B. Preparation of cyclic β-ketoesters:

**Preparation of methyl 1-oxo-2,3-dihydro-1H-indene-2-carboxylate (S2)**

Methyl 1-oxo-2,3-dihydro-1H-indene-2-carboxylate (S2) was prepared following a modified literature procedure.

\[ \text{Methyl 1-oxo-2,3-dihydro-1H-indene-2-carboxylate (S2)} \]

In an oven-dried 50 mL round-bottom flask equipped with a reflux condenser and an argon inlet, 60% sodium hydride in mineral oil (1.2 g, 30.11 mmol, 2.2 equiv.) was taken in 5 mL dimethyl carbonate. 1-Indanone (2.0 g, 13.68 mmol, 1.0 equiv.) in 15 mL dimethyl carbonate was added at 25 °C and the resulting mixture was refluxed at 80 °C. After 30 min, another 10 mL dimethyl carbonate was added and refluxing was continued at 80 °C for 3 h. Then the reaction mixture was cooled to 0 °C, quenched with 1 (M) aqueous HCl solution, extracted with CHCl$_3$. The combined organic layer was dried over anh. Na$_2$SO$_4$, concentrated in vacuo to obtain a red crude oil which was purified by silica gel (100-200 mesh) column chromatography using 15% EtOAc in petroleum ether as eluent to obtain pure S2 as an orange oil (2.2 g, 11.567 mmol; 85% yield). 

\[ R_f = 0.55 \] (20% EtOAc in petroleum ether). 

FT-IR (neat): \( \nu \) 2952 (w), 1743 (s), 1713 (s), 1655 (w), 1438 (m), 1212 (m), 1157 (m), 1023 (w) cm$^{-1}$; $^1$H-NMR (400 MHz, CDCl$_3$): The compound exists as a 5.9:1 mixture of keto/enol tautomer. \( \delta \) 7.77 (d, \( J = 7.7 \) Hz; 1H), 7.60-7.64 (m; 1H), 7.50 (d, \( J = 7.9 \) Hz; 1H), 7.37-7.41 (m;

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1H), 3.79 (s; 3H), 3.74 (dd, J = 4.0, 8.3 Hz; 1H), 3.56 (dd, J = 4.0, 17.3 Hz; 1H), 3.37 (dd, J = 8.3, 17.3 Hz; 1H); Representative signals corresponding to the enol tautomer: δ 3.85 (s; 3H), 3.51 (s; 2H); 13C-NMR (100 MHz, CDCl3): Signals corresponding to both tautomers: δ 199.36, 169.51, 153.54, 135.42, 135.19, 129.37, 127.79, 126.51, 124.67, 53.11, 52.73, 30.23; HRMS (ESI+): Calculated for C11H10O3Na ([M + Na]+): 213.0528, found: 213.0529.

Preparation of substituted 1-indanone 2-butyrate: Representative procedure for the synthesis of tert-butyl 1-oxo-2,3-dihydro-1H-indene-2-carboxylate (1a)

tert-Butyl 1-oxo-2,3-dihydro-1H-indene-2-carboxylate (1a) was prepared following a modified literature procedure.5

In an oven-dried 100 mL 2-neck round-bottom flask equipped with a reflux condenser, 60% sodium hydride in mineral oil (605 mg, 15.13 mmol, 2.0 equiv.) was taken in 30 mL THF under positive argon pressure. To this suspension, 1-indanone (1.0 g, 7.56 mmol, 1.0 equiv.) in 7.5 mL THF was added at 25 °C. The resulting mixture was allowed to reflux at 85 °C for 10 min. Then N-Boc pyrrole (2.5 g, 15.13 mmol, 2.0 equiv.) in 3 mL THF was added while refluxing. The resulting mixture was refluxed at 85 °C for 24 h. Then the reaction mixture was cooled to 0 °C and quenched by addition of 1 (M) aqueous HCl solution, extracted with Et2O. The combined organic layer was dried over anh. Na2SO4, concentrated in vacuo to obtain a brown oil which was purified by silica gel (100-200 mesh) column chromatography using 2% EtOAc in petroleum ether as eluent to obtain pure 1a as a colorless oil (1.6 g, 6.889 mmol; 91% yield). Rf = 0.45 (5% EtOAc in petroleum ether). FT-IR (neat): ν 2978 (m), 1712 (s), 1643 (w), 1150 (s) cm⁻¹; 1H-NMR (400 MHz, CDCl3): The compound exists as a 6.5:1 mixture of keto/enol tautomer. Signals corresponding to the keto tautomer: δ 7.76 (d, J = 7.8 Hz; 1H), 7.59-7.63 (m; 1H), 7.49 (d, J = 7.8 Hz; 1H), 7.36-7.40 (m; 1H), 3.62 (dd, J = 4.0, 8.2 Hz; 1H), 3.62 (dd, J = 4.0, 17.4 Hz; 1H), 3.33 (dd, J = 8.2, 17.4 Hz; 1H), 1.49 (s; 9H); Representative signals corresponding to the enol tautomer: δ 3.47 (s; 2H), 1.57 (s; 9H); 13C-NMR (100 MHz, CDCl3): Signals corresponding to both tautomers: δ 199.99, 168.32, 153.66, 135.47, 135.19, 127.65, 126.50, 124.55, 82.04, 54.37, 30.32, 28.01; HRMS (ESI+): Calculated for C14H16O3Na ([M + Na]+): 255.0997, found: 255.0997.

Similar procedure was followed for the synthesis of 1b-m.

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**tert-Butyl 5-bromo-1-oxo-2,3-dihydro-1H-indene-2-carboxylate 1b:** Purification by silica gel (100-200 mesh) column chromatography (1% EtOAc in petroleum ether) afforded pure 1b as an off-white solid (280 mg, 0.900 mmol; 45% yield). \( \text{Rf} = 0.50 \) (5% EtOAc in petroleum ether). **M.P.** = 84-85 °C; **FT-IR (neat):** ν 2977 (m), 1714 (s), 1647 (m), 1153 (s) cm\(^{-1}\); **\(^1\)H-NMR (400 MHz, CDCl\(_3\)):** The compound exists as a 4.2:1 mixture of keto/enol tautomer. Signals corresponding to the keto tautomer: δ 7.66-7.67 (m; 1H), 7.60 (d, \( J = 8.1 \) Hz; 1H), 3.61 (dd, \( J = 3.9, 8.2 \) Hz; 1H), 3.47 (dd, \( J = 3.9, 17.3 \) Hz; 1H), 3.30 (dd, \( J = 8.2, 17.3 \) Hz; 1H), 1.48 (s; 9H); Representative signals corresponding to the enol tautomer: δ 3.43 (s; 2H), 1.56 (s; 9H); **\(^{13}\)C-NMR (100 MHz, CDCl\(_3\)):** Signals corresponding to both tautomers: δ 198.64, 167.79, 155.17, 134.29, 131.34, 130.63, 129.80, 125.67, 121.69, 82.28, 54.32, 29.95, 28.43, 27.96; **HRMS (ESI+):** Calculated for C\(_{14}\)H\(_{15}\)BrO\(_3\)Na ([M + Na]+): 333.0102, found: 333.0101.

**tert-Butyl 5-chloro-1-oxo-2,3-dihydro-1H-indene-2-carboxylate 1c:** Purification by silica gel (100-200 mesh) column chromatography (1% EtOAc in petroleum ether) afforded pure 1c as a light yellow oil (380 mg, 1.425 mmol; 71% yield) which gradually solidified. **M.P.** = 69-70 °C; **FT-IR (neat):** ν 2978 (m), 1715 (s), 1649 (w), 1251 (s), 1152 (s), 1084 (m) cm\(^{-1}\); **\(^1\)H-NMR (400 MHz, CDCl\(_3\)):** The compound exists as a 4.6:1 mixture of keto/enol tautomer. Signals corresponding to the keto tautomer: δ 7.66 (d, \( J = 8.2 \) Hz; 1H), 7.47-7.51 (m; 1H), 7.32-7.40 (m; 1H), 3.62 (dd, \( J = 4.1, 8.3 \) Hz; 1H), 3.46 (dd, \( J = 4.1, 17.5 \) Hz; 1H), 3.29 (dd, \( J = 8.3, 17.5 \) Hz; 1H), 1.47 (s; 9H); Representative signals corresponding to the enol tautomer: δ 3.43 (s; 2H), 1.55 (s; 9H); **\(^{13}\)C-NMR (100 MHz, CDCl\(_3\)):** Signals corresponding to both tautomers: δ 198.38, 167.83, 155.05, 141.74, 133.88, 128.47, 126.17, 125.56, 82.23, 54.38, 29.98, 28.40, 27.94; **HRMS (ESI+):** Calculated for C\(_{14}\)H\(_{15}\)ClO\(_3\)Na ([M + Na]+): 289.0607, found: 289.0607.

**tert-Butyl 5-fluoro-1-oxo-2,3-dihydro-1H-indene-2-carboxylate 1d:** Purification by silica gel (100-200 mesh) column chromatography (1% EtOAc in petroleum ether) afforded pure 1d as a light brown solid (325 mg, 1.299 mmol; 65% yield). **Rf = 0.45** (5% EtOAc in petroleum ether). **M.P.** = 52-54 °C. **FT-IR (neat):** ν 2979 (m), 1714 (s), 1645 (w), 1251 (s), 1152 (s), 1084 (m) cm\(^{-1}\); **\(^1\)H-NMR (400 MHz, CDCl\(_3\)):** The compound exists as a 10.8:1 mixture of keto/enol tautomer. Signals corresponding to the keto tautomer: δ 7.72-7.75 (m; 1H), 7.12-7.14 (m; 1H), 7.04-7.08 (m; 1H), 3.62 (dd, \( J = 4.0, 8.2 \) Hz; 1H), 3.46 (dd, \( J = 4.0, 17.4 \) Hz; 1H), 3.29 (dd, \( J = 8.2, 17.4 \) Hz; 1H), 1.47 (s; 9H); Representative signals corresponding to the enol tautomer: δ 3.44 (s; 2H), 1.55 (s; 9H); **\(^{13}\)C-NMR (100 MHz, CDCl\(_3\)):** Signals corresponding to both tautomers: δ 197.94,
167.95, 167.33 (d, J = 257.6 Hz), 156.57 (d, J = 10.6 Hz), 131.80, 126.80 (d, J = 10.6 Hz), 116.02 (d, J = 23.8 Hz), 113.13 (d, J = 22.5 Hz), 82.17, 54.51, 30.12, 28.41, 27.94; HRMS (ESI+): Calculated for C$_{14}$H$_{15}$FO$_3$Na ([M + Na]$^+$): 273.0903, found: 273.0900.

**tert-Butyl 5-methyl-1-oxo-2,3-dihydro-1H-indene-2-carboxylate 1e:** Purification by silica gel (100-200 mesh) column chromatography (2% EtOAc in petroleum ether) afforded pure 1e as a light yellow solid (225 mg, 0.913 mmol; 46% yield). $R_f$ = 0.50 (5% EtOAc in petroleum ether). M.P. = 83-84 °C. FT-IR (neat): ν 2977 (m), 1711 (s), 1609 (m), 1149 (s) cm$^{-1}$; $^1$H-NMR (400 MHz, CDCl$_3$): The compound exists as an 18.1:1 mixture of keto/enol tautomer. Signals corresponding to the keto tautomer: δ 7.63 (d, J = 7.9 Hz; 1H), 7.27 (s; 1H), 7.17 (d, J = 7.9 Hz; 1H), 3.58 (dd, J = 3.9, 8.2 Hz; 1H), 3.42 (dd, J = 3.9, 16.9 Hz; 1H), 3.25 (dd, J = 8.2, 16.9 Hz; 1H), 2.43 (s; 3H), 1.47 (s; 9H); Representative signals corresponding to the enol tautomer: δ 3.41 (s; 2H), 1.56 (s; 9H); $^{13}$C-NMR (100 MHz, CDCl$_3$): Signals corresponding to both tautomers: δ 199.45, 168.52, 154.21, 146.52, 133.21, 128.94, 126.82, 124.35, 81.89, 54.55, 30.17, 28.01, 22.08; HRMS (ESI+): Calculated for C$_{15}$H$_{18}$O$_3$Na ([M + Na]$^+$): 269.1154, found: 269.1162.

**tert-Butyl 1-oxo-5-phenyl-2,3-dihydro-1H-indene-2-carboxylate 1f:** Purification by silica gel (100-200 mesh) column chromatography (5% EtOAc in petroleum ether) afforded pure 1f as a yellow oil (312 mg, 1.012 mmol; 51% yield). $R_f$ = 0.30 (50% EtOAc in petroleum ether). FT-IR (neat): ν 2977 (w), 1710 (s), 1605 (m), 1150 (s) cm$^{-1}$; $^1$H-NMR (400 MHz, CDCl$_3$): The compound exists as a 7.5:1 mixture of keto/enol tautomer. Signals corresponding to the keto tautomer: δ 7.82 (d, J = 7.9 Hz; 1H), 7.68-7.69 (m; 1H), 7.60-7.64 (m; 3H), 7.42-7.50 (m; 3H), 3.67 (dd, J = 4.1, 8.3 Hz; 1H), 3.55 (dd, J = 4.1, 17.1 Hz; 1H), 3.38 (dd, J = 8.3, 17.1 Hz; 1H), 1.51 (s; 9H); Representative signals corresponding to the enol tautomer: δ 3.54 (s; 2H), 1.59 (s; 9H); $^{13}$C-NMR (100 MHz, CDCl$_3$): Signals corresponding to both tautomers: δ 199.45, 168.52, 154.21, 146.52, 133.21, 128.94, 126.82, 124.35, 81.89, 54.55, 30.17, 28.01, 22.08; HRMS (ESI+): Calculated for C$_{20}$H$_{20}$O$_3$Na ([M + Na]$^+$): 331.1310, found: 331.1313.

**tert-Butyl 6-bromo-1-oxo-2,3-dihydro-1H-indene-2-carboxylate 1g:** Purification by silica gel (100-200 mesh) column chromatography (1% EtOAc in petroleum ether) afforded pure 1g as an off-white solid (275 mg, 0.884 mmol; 44% yield). $R_f$ = 0.35 (5% EtOAc in petroleum ether). M.P. = 66-68 °C; FT-IR (neat): ν 2977 (m), 1715 (s), 1648 (s), 1401 (s), 1256 (s), 1160 (s), 1136 (s) cm$^{-1}$; $^1$H-NMR (400 MHz, CDCl$_3$): The compound exists as a 2.8:1 mixture of keto/enol tautomer. Signals corresponding to the keto tautomer: δ 7.86 (d, J = 1.6 Hz; 1H), 7.69 (dd, J = 1.9, 8.1 Hz; 1H), 7.37 (d, J = 8.0 Hz; 1H), 3.64 (dd, J = 3.9, 8.2 Hz; 1H), 3.43 (dd, J = 3.9, 17.2
Hz; 1H), 3.26 (dd, J = 8.2, 17.2 Hz; 1H), 1.48 (s; 9H); Representative signals corresponding to the enol tautomer: δ 7.73 (d, J = 1.6 Hz; 1H), 7.49 (dd, J = 1.9, 8.1 Hz; 1H), 7.29 (d, J = 8.0 Hz; 1H), 3.41 (s; 2H), 1.56 (s; 9H); ¹³C-NMR (100 MHz, CDCl₃): Signals corresponding to both tautomers: δ 198.44, 167.74, 152.15, 141.49, 137.92, 137.26, 131.73, 128.02, 127.39, 125.99, 123.59, 121.82, 120.67, 105.31, 82.31, 81.34, 54.64, 32.61, 29.95, 28.42, 27.96; HRMS (ESI+): Calculated for C₁₄H₁₅BrO₃Na ([M + Na]+): 333.0102, found: 333.0103.

**tert-Butyl 6-methyl-1-oxo-2,3-dihydro-1H-indene-2-carboxylate 1h:** Purification by silica gel (100-200 mesh) column chromatography (1% EtOAc in petroleum ether) afforded pure 1h as a colorless solid (320 mg, 1.299 mmol; 65% yield). Rᵣ = 0.40 (5% EtOAc in petroleum ether). M.P. = 62-63 °C; FT-IR (neat): ν 2977 (m), 1712 (s), 1644 (m), 1275 (m), 1147 (s) cm⁻¹; ¹H-NMR (400 MHz, CDCl₃): The compound exists as a 9.5:1 mixture of keto/enol tautomer. Signals corresponding to the keto tautomer: δ 7.52 (s; 1H), 7.40 (d, J = 7.9 Hz; 1H), 3.58 (dd, J = 3.8, 8.1 Hz; 1H), 3.41 (dd, J = 3.8, 17.2 Hz; 1H), 3.25 (dd, J = 8.1, 17.2 Hz; 1H), 2.37 (s; 3H), 1.46 (s; 9H); Representative signals corresponding to the enol tautomer: δ 3.39 (s; 2H), 2.39 (s; 3H), 1.55 (s; 9H); ¹³C-NMR (100 MHz, CDCl₃): Signals corresponding to both tautomers: δ 199.95, 168.36, 150.99, 137.53, 136.38, 135.56, 126.07, 124.31, 81.80, 54.64, 29.90, 27.92, 20.92; HRMS (ESI+): Calculated for C₁₅H₁₈O₃Na ([M + Na]+): 269.1154, found: 269.1155.

**tert-Butyl 6-methoxy-1-oxo-2,3-dihydro-1H-indene-2-carboxylate 1i:** Purification by silica gel (100-200 mesh) column chromatography (5% EtOAc in petroleum ether) afforded pure 1i as an off-white solid (317 mg, 1.208 mmol; 60% yield). Rᵣ = 0.15 (5% EtOAc in petroleum ether). M.P. = 85-87 °C; FT-IR (neat): ν 2976 (m), 1710 (s), 1645 (w), 1149 (s) cm⁻¹; ¹H-NMR (400 MHz, CDCl₃): The compound exists as a 10:1 mixture of keto/enol tautomer. Signals corresponding to the keto tautomer: δ 7.37 (d, J = 8.2 Hz; 1H), 7.17-7.21 (m; 2H), 3.82 (s; 3H), 3.63 (dd, J = 3.7, 7.9 Hz; 1H), 3.38 (dd, J = 3.7, 16.9 Hz; 1H), 3.25 (dd, J = 7.9, 16.9 Hz; 1H), 1.48 (s; 9H); Representative signals corresponding to the enol tautomer: δ 3.84 (s; 3H), 3.39 (s; 3H), 1.56 (s; 9H); ¹³C-NMR (100 MHz, CDCl₃): Signals corresponding to both tautomers: δ 199.97, 168.37, 159.60, 146.56, 136.38, 135.56, 126.07, 124.31, 81.80, 54.64, 29.90, 27.92, 20.92; HRMS (ESI+): Calculated for C₁₅H₁₈O₄Na ([M + Na]+): 285.1103, found: 269.1154, 285.1103.

**tert-Butyl 4-bromo-1-oxo-2,3-dihydro-1H-indene-2-carboxylate 1j:** Purification by silica gel (100-200 mesh) column chromatography (1% EtOAc in petroleum ether) afforded pure 1j as a colorless oil (565 mg, 1.816 mmol; 91% yield) which gradually solidified. Rᵣ = 0.45 (5% EtOAc in petroleum ether). M.P. =
75-77 °C; FT-IR (neat): ν 2977 (m), 1718 (s), 1370 (s), 1248 (s), 1159 (s) cm⁻¹; ¹H-NMR (400 MHz, CDCl₃): The compound exists as a 2.5:1 mixture of keto/enol tautomer. Signals corresponding to the keto tautomer: δ 7.76 (d, J = 7.7 Hz; 1H), 7.69 (d, J = 7.6 Hz; 1H), 7.24-7.30 (m; 1H), 3.64 (dd, J = 4.1, 8.3 Hz; 1H), 3.41 (dd, J = 4.1, 17.7 Hz; 1H), 3.26 (dd, J = 8.3, 17.7 Hz; 1H), 1.49 (s; 9H); Representative signals corresponding to the enol tautomer: δ 7.55 (d, J = 7.5 Hz; 1H), 7.51 (d, J = 7.9 Hz; 1H), 7.21-7.22 (m; 1H), 3.41 (s; 2H), 1.57 (s; 9H); ¹³C-NMR (100 MHz, CDCl₃): Signals corresponding to both tautomers: δ 199.06, 167.69, 153.26, 137.90, 137.40, 131.94, 129.40, 128.59, 123.31, 121.96, 119.90, 119.54, 111.76, 104.67, 82.32, 81.38, 54.27, 34.30, 31.41, 28.42, 27.96, 27.85; HRMS (ESI+): Calculated for C₁₄H₁₅BrO₃Na ([M + Na]⁺): 333.0102, found: 333.0103.

tert-Butyl 7-methyl-1-oxo-2,3-dihydro-1H-indene-2-carboxylate 1k: Purification by silica gel (100-200 mesh) column chromatography (2% EtOAc in petroleum ether) afforded pure 1k as a yellow oil (260 mg, 1.056 mmol; 41% yield). Rf = 0.35 (5% EtOAc in petroleum ether). FT-IR (neat): ν 2977 (m), 1718 (s), 1649 (s), 1370 (s), 1248 (s), 1159 (s) cm⁻¹; ¹H-NMR (400 MHz, CDCl₃): The compound exists as a 4.5:1 mixture of keto/enol tautomer. Signals corresponding to the keto tautomer: δ 7.60 (d, J = 7.7 Hz; 1H), 7.42 (d, J = 7.3 Hz; 1H), 7.30 (t, J = 7.4 Hz; 1H), 3.62 (dd, J = 4.0, 8.2 Hz; 1H), 3.37 (dd, J = 3.8, 13.7 Hz; 1H), 3.22 (dd, J = 8.2, 17.3 Hz; 1H), 2.37 (s; 3H), 1.50 (s; 9H); Representative signals corresponding to the enol tautomer: δ 3.34 (s; 2H), 1.58 (s; 9H); ¹³C-NMR (100 MHz, CDCl₃): Signals corresponding to both tautomers: δ 200.29, 168.46, 152.65, 135.77, 135.64, 135.25, 127.87, 121.94, 82.04, 54.31, 29.21, 28.03, 17.71; HRMS (ESI+): Calculated for C₁₅H₁₈O₃Na ([M + Na]⁺): 269.1154, found: 269.1154.

tert-Butyl 4-oxo-5,6-dihydro-4H-cyclopenta[b]thiophene-5-carboxylate 1l: Purification by silica gel (100-200 mesh) column chromatography (6% EtOAc in petroleum ether) afforded pure 1l as a yellow viscous oil (65 mg, 0.273 mmol; 38% yield). Rf = 0.25 (10% EtOAc in petroleum ether). FT-IR (neat): ν 2972 (m), 1722 (s), 1643 (s), 1370 (s), 1248 (s), 1159 (s) cm⁻¹; ¹H-NMR (400 MHz, CDCl₃): The compound exists as keto tautomer only. Signals corresponding to the keto tautomer: δ 7.32 (d, J = 5.2 Hz; 1H), 7.13 (d, J = 5.2 Hz; 1H), 3.90 (dd, J = 2.9, 7.2 Hz; 1H), 3.52 (dd, J = 2.9, 17.3 Hz; 1H), 3.35 (dd, J = 7.2, 17.3 Hz; 1H), 1.49 (s; 9H); ¹³C-NMR (100 MHz, CDCl₃): Signals corresponding to keto tautomer: δ 191.16, 169.82, 167.80, 144.19, 131.30, 119.83, 82.25, 59.62, 28.49, 27.99; HRMS (ESI+): Calculated for C₁₂H₁₄O₃SNa ([M + Na]⁺): 261.0564, found: 261.0564.
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*tert*-Butyl 3,4-dimethyl-2-oxocyclopent-3-ene-1-carboxylate 1m: Purification by silica gel (100-200 mesh) column chromatography (6% EtOAc in petroleum ether) afforded pure 1m as a brown oil (165 mg, 0.785 mmol; 62% yield).  

**Rf** = 0.25 (10% EtOAc in petroleum ether).  

**FT-IR (neat)**: ν 2977 (m), 1713 (s), 1649 (m), 1371 (m), 1267 (s), 1152 (s) cm⁻¹;  

**1H-NMR (400 MHz, CDCl3)**: The compound exists as keto tautomer only. Signals corresponding to the keto tautomer: δ 3.29 (dd, J = 2.6, 7.0 Hz; 1H), 2.81 (d, J = 18.2 Hz; 1H), 2.64 (dd, J = 6.9, 18.0 Hz; 1H), 2.06 (s; 3H), 1.68 (s; 3H), 1.46 (s; 9H);  

**13C-NMR (100 MHz, CDCl3)**:  

Signals corresponding to keto tautomer: δ 202.74, 169.70, 168.83, 134.67, 81.70, 52.17, 35.69, 27.99, 17.07, 8.15;  


**Preparation of benzyl 1-oxo-2,3-dihydro-1H-indene-2-carboxylate (S3)**  

Benzyl 1-oxo-2,3-dihydro-1H-indene-2-carboxylate (S3) was prepared following a modified literature procedure.⁶  

In an oven-dried 50 mL round-bottom flask equipped with a reflux condenser and an argon inlet, methyl 1-oxo-2,3-dihydro-1H-indene-2-carboxylate (500 mg, 3.783 mmol, 1.0 equiv.), benzyl alcohol (409 mg, 3.783 mmol, 1.0 equiv.) and dibutyl tin oxide (235 mg, 0.946 mmol, 0.25 equiv.) was taken in 15 mL toluene and refluxed for 44 h. Then the reaction mixture was cooled to 25 °C, diluted with EtOAc, washed with brine. The organic layer was dried over anh. Na₂SO₄, concentrated in vacuo to obtain a yellow oil which was purified by silica gel (230-400 mesh) column chromatography using 3% EtOAc in petroleum ether as eluent to obtain pure S3 as a yellow oil (525 mg, 1.971 mmol; 52% yield) which gradually solidified.  

**Rf** = 0.55 (10% EtOAc in petroleum ether).  

**M.P.** = 54-56 °C;  

**FT-IR (neat)**: ν 3034 (m), 1712 (s), 1653 (m), 1209 (m), 1153 (s) cm⁻¹;  

**1H-NMR (400 MHz, CDCl3)**: The compound exists as a 4.4:1 mixture of keto/enol tautomer. Signals corresponding to the keto tautomer: δ 7.78 (d, J = 7.5 Hz; 1H), 7.61-7.65 (m; 1H), 7.50 (d, J = 7.5 Hz; 1H), 7.32-7.42 (m; 6H), 5.24 (d, J = 2.0 Hz; 2H), 3.79 (dd, J = 4.3, 8.3 Hz; 1H), 3.58 (dd, J = 4.2, 17.1 Hz; 1H), 3.38 (dd, J = 8.3, 17.3 Hz; 1H);  

Representative signals corresponding to the enol tautomer: δ 5.32 (s; 2H), 3.56 (s; 2H);  

**13C-NMR (100 MHz, CDCl3)**: Signals corresponding to both tautomers: δ 199.19, 168.95, 153.48, 135.54, 135.39, 135.24, 129.45, 128.58, 128.26, 128.21, 128.11, 128.01, 127.80, 126.81,

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126.52, 124.68, 120.76, 67.29, 53.26, 30.25; **HRMS (ESI+)**: Calculated for C_{17}H_{14}O_{3}Na ([M + Na]^+): 289.0841, found: 289.0843.

**Compound S4**: Similar procedure as described for the preparation of S3 was followed. Purification by silica gel (100-200 mesh) column chromatography (2% EtOAc in petroleum ether) afforded pure (1S, 3S)-adamantan-1-yl 1-oxo-2,3-dihydro-1H-indene-2-carboxylate S4 as a white solid (500 mg, 1.687 mmol; 34% yield). \( R_f = 0.55 \) (10% EtOAc in petroleum ether). **M.P. = 100-102 °C; FT-IR (neat)**: \( \nu \) 2912 (s), 2854 (m), 1712 (s), 1210 (m), 1054 (m) cm\(^{-1}\); \(^1\)H-NMR (400 MHz, CDCl\(_3\))**: The compound exists as a 5.3:1 mixture of keto/enol tautomer. Signals corresponding to the keto tautomer: \( \delta \) 7.76 (d, \( J = 7.8 \) Hz; 1H), 7.59-7.63 (m; 1H), 7.49 (d, \( J = 7.8 \) Hz; 1H), 7.36-7.40 (m; 1H), 3.61 (dd, \( J = 3.9, 8.3 \) Hz; 1H), 3.47-3.52 (m; 1H), 3.33 (dd, \( J = 8.3, 17.3 \) Hz; 1H), 2.15 (s; 9H), 1.66 (s; 6H), 1.57 (s; 6H); Representative signals corresponding to the enol tautomer: \( \delta \) 3.47 (s; 2H), 1.65 (s; 9H), 1.71 (s; 6H), 1.62 (s; 6H); \(^{13}\)C-NMR (100 MHz, CDCl\(_3\))**: Signals corresponding to both tautomers: \( \delta \) 200.00, 167.96, 153.67, 135.50, 135.15, 127.62, 126.49, 124.54, 82.11, 54.52, 41.80, 41.21, 36.21, 36.12, 30.91, 30.87, 30.37; **HRMS (ESI+)**: Calculated for C\(_{20}\)H\(_{22}\)O\(_3\)Na ([M + Na]^+): 333.1467, found: 133.1467.

**C. Preparation of \( \beta \)-nitroenone**: Representative procedure for the synthesis of (\( \text{E} \))-3-nitro-1-phenylprop-2-en-1-one (2a)

In an oven-dried 250 mL round-bottom flask equipped with a reflux condenser and an argon inlet, selenium dioxide (9.51 g, 85.72 mmol, 2.0 equiv.) was taken in 90 mL 1,4-dioxane/H\(_2\)O (10:1) and refluxed at 110 °C for 20 min. Then the resulting solution was cooled to 50 °C and acetophenone (5.0 mL, 42.86 mmol, 1.0 equiv.) was added. The resulting solution was refluxed at 110 °C for 20 h. Then the reaction mixture was cooled 25 °C, filtered through a silica gel (100-200 mesh) bed, washed with EtOAc. The filtrate was dried over anh. Na\(_2\)SO\(_4\), concentrated in vacuo to obtain 2-oxo-2-phenylacetaldehyde as a viscous yellow oil (5.74 g, 42.79 mmol, >99% yield) which was used for the subsequent step without any further purification.

In an oven-dried 250 mL round-bottom flask, 2-oxo-2-phenylacetaldehyde (5.74 g, 42.79 mmol, 1.0 equiv.) was taken in 85 mL nitromethane along with basic alumina (10.7 g). The resulting mixture was stirred vigorously at 25 °C for 3 h. The reaction mixture was then filtered through a pad of celite and washed with EtOAc. The combined organic layer was concentrated in
vacuo to obtain 2-hydroxy-3-nitro-1-phenylpropan-1-one as a yellow oil (8.35 g, 42.78 mmol, >99% yield) which was used for the next step without any further purification.

In an oven-dried 100 mL 2-neck round-bottom flask equipped with an argon inlet, crude 2-hydroxy-3-nitro-1-phenylpropan-1-one (4.3 g, 22.023 mmol, 1.0 equiv.) was taken in 44 mL CH₂Cl₂ and cooled to –20 °C. Mesyl chloride (5.1 mL, 66.096 mmol, 3.0 equiv.) was added and stirred at –20 °C for 30 min. Then triethyl amine (9.23 mL, 66.96 mmol, 3.0 equiv.) was added and the resulting solution was stirred at –20 °C for 20 h. The reaction mixture was brought to 25 °C, quenched by the addition of water, extracted with CHCl₃. The combined organic layer was dried over anh. Na₂SO₄, concentrated in vacuo to obtain a yellow oil which was purified by silica gel (230-400 mesh) column chromatography using 1% EtOAc in petroleum ether as eluent to obtain pure 2a as a yellow solid (1.73 g, 9.767 mmol; 44% yield). Rf = 0.30 (5% EtOAc in petroleum ether). M.P. = 96-97 °C; FT-IR (neat): ν 3107 (w), 1673 (m), 1619 (m), 1530 (s), 1352 (m) cm⁻¹; ¹H-NMR (400 MHz, CDCl₃): δ 8.12 (d, J = 13.3 Hz; 1H), 8.00 (d, J = 7.5 Hz; 2H), 7.67-7.71 (m; 2H), 7.54-7.58 (m; 2H); ¹³C-NMR (100 MHz, CDCl₃): δ 186.99, 148.09, 135.85, 134.82, 129.62, 129.20, 128.91. Spectral data are in agreement with the literature.⁷

The same procedure as above was followed for the synthesis of 2b-p.

(E)-3-Nitro-1-(p-tolyl)prop-2-en-1-one 2b: Purification by silica gel (230-400 mesh) column chromatography (2% Et₂O in petroleum ether) afforded pure 2b as a yellow oil (125 mg, 0.654 mmol; 18% yield). Rf = 0.35 (5% EtOAc in petroleum ether). M.P. = 96-97 °C; FT-IR (neat): ν 3107 (w), 1673 (m), 1619 (m), 1530 (s), 1352 (m) cm⁻¹; ¹H-NMR (400 MHz, CDCl₃): δ 8.12 (d, J = 13.3 Hz; 1H), 8.00 (d, J = 7.5 Hz; 2H), 7.67-7.71 (m; 2H), 7.54-7.58 (m; 2H); ¹³C-NMR (100 MHz, CDCl₃): δ 186.99, 148.09, 135.85, 134.82, 129.62, 129.20, 128.91. Spectral data are in agreement with the literature.⁷

(E)-1-(4-Methoxyphenyl)-3-nitroprop-2-en-1-one 2c: Purification by silica gel (230-400 mesh) column chromatography (3% EtOAc in petroleum ether) afforded pure 2c as a yellow solid (612 mg, 2.718 mmol; 34% yield). Rf = 0.50 (10% EtOAc in petroleum ether). M.P. = 76-78 °C; FT-IR (neat): ν 3103 (w), 1677 (s), 1589 (m), 1533 (s), 1354 (m) cm⁻¹; ¹H-NMR (400 MHz, CDCl₃): δ 8.12 (d, J = 13.3 Hz; 1H), 7.98-8.00 (m; 2H), 7.68 (d, J = 13.3 Hz; 1H), 7.35 (d, J = 8.2 Hz; 2H), 2.46 (s; 3H); ¹³C-NMR (100 MHz, CDCl₃): δ 184.99, 147.92, 146.26, 133.49, 129.92, 129.81, 129.08, 21.86; HRMS (ESI+): Calculated for C₁₀H₉NO₃Na ([M + Na]⁺): 214.0480, found: 214.0479.

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(E)-1-(4-Chlorophenyl)-3-nitroprop-2-en-1-one 2d: Purification by silica gel (230-400 mesh) column chromatography (2% EtOAc in petroleum ether) afforded pure 2d as a yellow solid (310 mg, 1.465 mmol; 11% yield). Rf = 0.35 (5% EtOAc in petroleum ether). M.P. = 93-95 °C; FT-IR (neat): ν 3118 (w), 1669 (s), 1616 (m), 1579 (s), 1517 (s), 1351 (m) cm⁻¹;¹H-NMR (400 MHz, CDCl₃): δ 8.08 (d, J = 13.1 Hz; 1H), 7.94-7.96 (m; 2H), 7.69 (d, J = 13.1 Hz; 1H), 7.52-7.56 (m; 2H);¹³C-NMR (100 MHz, CDCl₃): δ 185.76, 148.41, 141.66, 134.17, 130.24, 129.62, 129.05.

(E)-1-(4-Fluorophenyl)-3-nitroprop-2-en-1-one 2e: Purification by silica gel (230-400 mesh) column chromatography (3% EtOAc in petroleum ether) afforded pure 2e as a yellow solid (320 mg, 1.640 mmol; 20% yield). Rf = 0.40 (5% EtOAc in petroleum ether). M.P. = 71-73 °C; FT-IR (neat): ν 3208 (w), 1676 (s), 1589 (s), 1519 (s), 1410 (w), 1352 (s) cm⁻¹;¹H-NMR (400 MHz, CDCl₃): δ 8.10 (d, J = 13.2 Hz; 1H), 8.04-8.09 (m; 2H), 7.69 (d, J = 13.2 Hz; 1H), 7.22-7.27 (m; 2H);¹³C-NMR (100 MHz, CDCl₃): δ 185.34, 166.79 (d, J = 263.7 Hz), 148.2, 132.33 (d, J = 2.9 Hz), 131.75 (d, J = 9.6 Hz), 129.25, 116.54 (d, J = 22.2 Hz).

(E)-1-(3-Methoxyphenyl)-3-nitroprop-2-en-1-one 2f: Purification by silica gel (230-400 mesh) column chromatography (3% EtOAc in petroleum ether) afforded pure 2f as a yellow oil (790 mg, 3.813 mmol; 39% yield) which solidified at −20 °C. Rf = 0.30 (5% EtOAc in petroleum ether). M.P. = 52-54 °C; FT-IR (neat): ν 3103 (w), 1677 (s), 1589 (m), 1533 (s), 1354 (m) cm⁻¹;¹H-NMR (400 MHz, CDCl₃): δ 8.08 (d, J = 13.2 Hz; 1H), 7.67 (d, J = 13.2 Hz; 1H), 7.54-7.56 (m; 1H), 7.49-7.50 (m; 1H), 7.43-7.47 (m; 1H), 7.20-7.23 (m; 1H), 3.88 (s; 3H);¹³C-NMR (100 MHz, CDCl₃): δ 186.76, 160.24, 148.05, 137.14, 130.14, 129.64, 121.68, 121.56, 112.65, 55.53; HRMS (ESI+): Calculated for C₁₀H₉NO₄Na ([M + Na]⁺): 230.0429, found: 230.0430.

(E)-3-Nitro-1-(m-tolyl)prop-2-en-1-one 2g: Purification by silica gel (230-400 mesh) column chromatography (2% EtOAc in petroleum ether) afforded pure 2g as a yellow oil (265 mg, 1.386 mmol; 13% yield). Rf = 0.35 (5% EtOAc in petroleum ether). FT-IR (neat): ν 3104 (m), 1677 (s), 1595 (m), 1532 (s), 1353 (s) cm⁻¹;¹H-NMR (400 MHz, CDCl₃): δ 8.10 (d, J = 13.1 Hz; 1H), 7.77-7.79 (m; 2H), 7.67 (d, J = 13.1 Hz; 1H), 7.49 (d, J = 7.5 Hz; 1H), 7.42-7.45 (m; 1H), 2.45 (s; 3H);¹³C-NMR (100 MHz, CDCl₃): δ 187.10, 147.95, 139.24, 135.89, 135.65, 129.82, 129.32, 129.04, 126.19, 21.27.
(E)-1-(3-Chlorophenyl)-3-nitroprop-2-en-1-one 2h: Purification by silica gel (230-400 mesh) column chromatography (3% EtOAc in petroleum ether) afforded pure 2h as a yellow solid (650 mg, 3.072 mmol; 43% yield). \( R_f = 0.40 \) (5% EtOAc in petroleum ether). M.P. = 58-59 °C; FT-IR (neat): ν 3105 (m), 1680 (s), 1625 (m), 1534 (s), 1423 (m), 1353 (s), 1253 (s) cm\(^{-1}\); \(^1\)H-NMR (400 MHz, CDCl\(_3\)): δ 8.07 (d, \( J = 13.4 \) Hz; 1H), 7.97-7.98 (m; 1H), 7.86-7.89 (m; 1H), 7.70 (d, \( J = 13.4 \) Hz; 1H), 7.65-7.68 (m; 1H), 7.50-7.54 (m; 1H); \(^1\)C-NMR (100 MHz, CDCl\(_3\)): δ 185.87, 148.58, 137.32, 135.77, 134.76, 130.52, 128.95, 128.86, 126.97.

(E)-3-Nitro-1-(m-tolyl)prop-2-en-1-one 2i: Purification by silica gel (230-400 mesh) column chromatography (2% EtOAc in petroleum ether) afforded pure 2i as a yellow solid (265 mg, 1.386 mmol; 13% yield). \( R_f = 0.35 \) (5% EtOAc in petroleum ether). M.P. = 52-53 °C; FT-IR (neat): ν 3104 (m), 1677 (s), 1595 (m), 1532 (s), 1353 (s) cm\(^{-1}\); \(^1\)H-NMR (400 MHz, CDCl\(_3\)): δ 8.10 (d, \( J = 13.1 \) Hz; 1H), 7.77-7.79 (m; 2H), 7.67 (d, \( J = 13.1 \) Hz; 1H), 7.49 (d, \( J = 7.5 \) Hz; 1H), 7.42-7.45 (m; 1H), 2.45 (s; 3H); \(^1\)C-NMR (100 MHz, CDCl\(_3\)): δ 187.10, 147.95, 139.24, 135.89, 135.78, 134.60, 131.09, 126.37, 121.23, 111.88, 55.86.

(E)-1-(2-Methoxyphenyl)-3-nitroprop-2-en-1-one 2j: Purification by silica gel (230-400 mesh) column chromatography (1% EtOAc in petroleum ether) afforded pure 2j as a yellow solid (250 mg, 1.207 mmol; 14% yield). \( R_f = 0.40 \) (10% EtOAc in petroleum ether). M.P. = 71-73 °C; FT-IR (neat): ν 3104 (w), 1669 (s), 1616 (s), 1595 (s), 1526 (s), 1479 (s), 1355 (m), 1242 (s) cm\(^{-1}\); \(^1\)H-NMR (400 MHz, CDCl\(_3\)): δ 8.08 (d, \( J = 13.4 \) Hz; 1H), 7.78 (dd, \( J = 1.8, 7.8 \) Hz; 1H), 7.56-7.61 (m; 2H), 7.02-7.09 (m; 2H), 3.96 (s; 3H); \(^1\)C-NMR (100 MHz, CDCl\(_3\)): δ 187.99, 159.54, 145.71, 135.78, 134.60, 131.09, 126.37, 121.23, 111.88, 55.86.

(E)-1-(Naphthalen-1-yl)-3-nitroprop-2-en-1-one 2k: Purification by silica gel (230-400 mesh) column chromatography (2% EtOAc in petroleum ether) afforded pure 2k as a yellow solid (100 mg, 0.440 mmol; 5% yield). \( R_f = 0.35 \) (5% EtOAc in petroleum ether). M.P. = 80-81 °C; FT-IR (neat): ν 3021 (m), 2921 (m), 1672 (s), 1533 (s), 1352 (s) cm\(^{-1}\); \(^1\)H-NMR (400 MHz, CDCl\(_3\)): δ 8.69 (d, \( J = 8.3 \) Hz; 1H), 8.13 (d, \( J = 8.3 \) Hz; 1H), 8.05 (d, \( J = 13.5 \) Hz; 1H), 7.93-7.96 (m; 2H), 7.57-7.70 (m; 4H); \(^1\)C-NMR (100 MHz, CDCl\(_3\)): δ 189.70, 148.04, 135.05, 133.98, 133.27, 132.92, 130.52, 130.32, 129.02, 128.80, 127.20, 125.41, 124.32.

(E)-1-(Naphthalen-2-yl)-3-nitroprop-2-en-1-one 2l: Similar procedure as described for the preparation of 2a was followed. Purification by silica gel (230-400 mesh) column chromatography (2% EtOAc in petroleum ether) afforded pure 2l as a yellow solid (470 mg, 2.068 mmol; 23% yield). \( R_f = 0.30 \) (5%
EtOAc in petroleum ether). M.P. = 70-72 °C; FT-IR (neat): ν 1669 (s), 1609, 1524 (s), 1353 (s) cm⁻¹; ¹H-NMR (400 MHz, CDCl₃): δ 8.49 (s; 1H), 8.27 (d, J = 13.2 Hz; 1H), 8.00-8.05 (m; 2H), 7.96 (d, J = 8.7 Hz; 1H), 7.91 (d, J = 8.1 Hz; 1H), 7.74 (d, J = 13.2 Hz; 1H), 7.66-7.70 (m; 1H), 7.60-7.64 (m; 1H); ¹³C-NMR (100 MHz, CDCl₃): δ 186.64, 148.04, 136.23, 133.32, 132.31, 131.62, 129.85, 129.68, 129.65, 129.36, 127.96, 127.44, 123.52.

(E)-3-Nitro-1-(thiophen-2-yl)prop-2-en-1-one 2m: Purification by silica gel (230-400 mesh) column chromatography (5% EtOAc in petroleum ether) afforded pure 2m as a yellow solid (230 mg, 1.256 mmol; 11% yield). Rr = 0.35 (5% EtOAc in petroleum ether). M.P. = 98-99 °C; FT-IR (neat): ν 3098 (m), 1659 (s), 1603 (s), 1533 (s), 1410 (m), 1352 (m) cm⁻¹; ¹H-NMR (400 MHz, CDCl₃): δ 7.90 (m; 1H), 7.60 (m; 1H); ¹³C-NMR (100 MHz, CDCl₃): δ 184.61, 153.55, 149.00, 147.79, 130.95, 129.71, 126.30, 108.29, 108.07, 102.40.

(E)-1-(2,4-Dimethoxyphenyl)-3-nitroprop-2-en-1-one 2n: Purification by silica gel (230-400 mesh) column chromatography (5% EtOAc in petroleum ether) afforded pure 2n as a yellow solid (100 mg, 0.422 mmol; 8% yield). Rr = 0.40 (5% EtOAc in petroleum ether). M.P. = 75-77 °C; FT-IR (neat): ν 3112 (m), 1585 (s), 1522 (s), 1351 (m) cm⁻¹; ¹H-NMR (400 MHz, CDCl₃): δ 8.15 (d, J = 13.4 Hz; 1H), 7.86 (d, J = 8.9 Hz; 1H), 7.56 (d, J = 13.4 Hz; 1H), 6.58-6.61 (m; 1H), 6.47-6.48 (m; 1H), 3.93 (s; 3H), 3.89 (s; 3H); ¹³C-NMR (100 MHz, CDCl₃): δ 185.65, 166.33, 161.75, 145.37, 135.41, 133.48, 119.67, 106.38, 98.30, 55.86, 55.73.

(E)-1-(Benzo[d][1,3]dioxol-5-yl)-3-nitroprop-2-en-1-one 2o: Purification by silica gel (230-400 mesh) column chromatography (5% EtOAc in petroleum ether) afforded pure 2o as an orange solid (125 mg, 0.565 mmol; 14% yield). Rr = 0.30 (10% EtOAc in petroleum ether). M.P. = 98-99 °C; FT-IR (neat): ν 3109 (m), 1661 (s), 1589 (s), 1516 (s), 1496 (s), 1440 (s), 1360 (s) cm⁻¹; ¹H-NMR (400 MHz, CDCl₃): δ 8.07 (d, J = 13.0 Hz; 1H), 7.66 (d, J = 13.0 Hz; 1H), 7.58-7.61 (m; 1H), 7.47 (d, J = 1.6 Hz; 1H), 6.93 (d, J = 8.1 Hz; 1H), 6.11 (s; 2H); ¹³C-NMR (100 MHz, CDCl₃): δ 184.61, 153.55, 149.00, 147.79, 130.95, 129.71, 126.30, 108.29, 108.07, 102.40.

(E)-4-Methyl-1-nitro-4-phenylpent-1-en-3-one 2p: Purification by silica gel (230-400 mesh) column chromatography (5% EtOAc in petroleum ether) afforded pure 2p as a yellow oil (430 mg, 1.961 mmol; 31% yield). Rr = 0.30 (5% EtOAc in petroleum ether). FT-IR (neat): ν 2982 (m), 1698 (s), 1621 (s), 1532 (s), 1468 (m), 1351 (m) cm⁻¹; ¹H-NMR (400 MHz, CDCl₃): δ 7.53 (d, J = 13.3 Hz; 1H), 7.40-7.44 (m; 2H), 7.34-7.37 (m; 1H), 7.24-7.28 (m; 2H), 7.13 (d, J = 13.3 Hz; 1H),
1.57 (s; 6H); $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 198.61, 147.34, 141.09, 129.44, 129.40, 127.95, 126.33, 52.23, 24.32.

D. Preparation of bifunctional (thio)urea catalysts

The bifunctional (thio)urea catalysts were prepared following reported literature procedure.$^8$

Purified by silica gel (100-200 mesh) column chromatography using 100:3:1 CH$_2$Cl$_2$/MeOH/Et$_3$N as eluent to afford thiourea VI as an off-white solid (320 mg, 0.524 mmol, 34% yield); M.P. = 123-125 °C. FT-IR (neat): $\nu$ 2932 (m), 1509 (m), 1384 (s), 1278 (s) cm$^{-1}$; $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 9.07 (br s; 1H), 8.73-8.75 (m; 1H), 7.55-8.12 (m; 6H), 7.37 (d, $J = 9.0$ Hz; 1H), 6.69 (br s; 1H), 4.80 (br s; 1H), 4.18 (br s; 2H), 3.96 (s; 3H), 3.52 (t, $J = 11.3$ Hz; 1H), 3.03-3.10 (m; 1H), 2.76-2.80 (m; 1H), 2.01-2.10 (m; 1H), 1.90 (br s; 2H), 1.77 (br s; 1H), 1.60-1.66 (m; 1H), 1.14-1.23 (m; 3H), 0.73-0.74 (m; 3H); $^{13}$C-NMR (100 MHz, CD$_3$OD): $\delta$ 160.23, 148.31, 145.39, 143.98, 132.50 (q, $J = 32.9$ Hz), 131.47, 131.37, 129.57, 129.00, 124.68 (q, $J = 270.8$ Hz), 124.67, 123.66, 121.71, 120.63, 104.01, 61.59, 57.43, 56.92, 44.70, 36.42, 27.38, 25.65, 25.49, 25.42, 11.88; HRMS (ESI+): Calculated for C$_{30}$H$_{32}$F$_6$N$_4$OSH ([M+H]$^+$): 611.2279, Found: 611.2279; $[\alpha]_D$ 24 $- 67.5$ (c 1.0, CHCl$_3$).

Purified by silica gel (100-200 mesh) column chromatography using 100:3:1 CH$_2$Cl$_2$/MeOH/Et$_3$N as eluent to afford thiourea VII as an off-white solid (550 mg, 1.179 mmol, 77% yield); M.P. = 105-107 °C. FT-IR (neat): $\nu$ 3257 (br m), 2931 (s), 1621 (m), 1508 (m), 1230 (s), 1029 (m) cm$^{-1}$; $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 8.70 (dd, $J = 1.4$, 4.3 Hz; 1H), 7.99 (dd, $J = 1.5$, 9.1 Hz; 1H), 7.71 (s; 1H), 7.64 (br s; 1H), 7.41 (d, $J = 4.5$ Hz; 1H), 7.35-7.37 (m; 1H), 5.58 (br s; 1H), 7.16 (br s; 1H), 3.96 (s; 3H), 3.84 (br s; 1H), 3.17-3.29 (m; 3H), 2.72-2.77 (m; 1H), 2.47-2.50 (m; 1H), 1.87-1.89 (m; 1H), 1.65-1.72 (m; 3H), 1.47-1.55 (m; 4H), 1.15-1.34 (m; 6H), 1.01-1.08 (m; 2H), 0.91-0.93 (m; 2H), 0.74-0.77 (m; 3H); $^{13}$C-NMR (100 MHz, CD$_3$OD): $\delta$ 159.58, 148.28, 148.10, 145.07, 131.12, 130.01, 123.77, 121.10, 104.32, 79.40, 61.53, 58.07, 56.55, 53.94, 42.98, 37.86, 33.60, 28.55, 28.08, 26.54, 26.34, 26.27, 25.82, 12.18; HRMS (ESI+): Calculated for C$_{27}$H$_{38}$N$_4$OSH ([M+H]$^+$): 467.2845, Found: 467.2845; $[\alpha]_D$ 24 $- 120.9$ (c 1.0, CHCl$_3$).

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E. Reaction conditions optimization

Optimization of ester substituents of β-ketoesters

![Chemical structure diagram]

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Solvent optimization

![Chemical structure diagram]

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\(^a\) Reactions were done in a 0.1 mmol. scale of 1a. \(^b\) Determined by \(^1\)H-NMR of the crude reaction mixture. \(^c\) Yields correspond to the isolated product after column chromatography. \(^d\) Determined by HPLC analysis using a stationary phase chiral column.
Additive and concentration optimization

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<sup>a</sup> Reactions were done in a 0.1 mmol. scale of 1a. <sup>b</sup> Yields correspond to the isolated product after column chromatography. <sup>c</sup> Determined by HPLC analysis using a stationary phase chiral column. <sup>d</sup> 4 Å MS used as additive.

F. Procedure for catalytic formal umpolung alkenylation reaction of 1a with 2a

In an oven-dried reaction tube equipped with an argon inlet, β-ketoester 1a (23.2 mg, 0.1 mmol, 1.0 equiv.) and the catalyst VII (4.7 mg, 0.01 mmol, 0.1 equiv.) was taken, put in vacuum, purged with argon. 2-MeTHF (0.5 mL) was added and the resulting solution was cooled to −60 °C. After 10 min, phenyl β-nitroenone 2a (21.2 mg, 0.12 mmol, 1.2 equiv.) in 0.5 mL 2-MeTHF was added dropwise and the resulting solution was stirred at −60 °C for 24 h. The reaction mixture was allowed to attain 25 °C and solvent was evaporated in vacuo to obtain a red oil. THF (0.5 mL) was added to it and the resulting solution was cooled to 0 °C. DBU (30.4 mg, 0.2 mmol, 2.0 equiv.) in 0.5 mL THF was added dropwise and the resulting reddish solution was stirred at 25 °C for 8 h. The reaction mixture was quenched by the addition of 3 M aqueous HCl solution and extracted with CHCl₃. The combined organic layer was dried over anh. Na₂SO₄, concentrated in vacuo to obtain a yellow crude oil which was purified by silica gel (100-200
mesh) column chromatography using 7% EtOAc in petroleum ether as eluent to obtain pure 4aa as a colorless oil (33 mg, 0.091 mmol; 91% yield).

G. Characterization data of the formal alkenylation products

**tert-Butyl (S)-1-oxo-2-(3-oxo-3-phenylprop-1-en-2-yl)-2,3-dihydro-1H-indene-2-carboxylate 4aa:** Purification by silica gel (100-200 mesh) column chromatography (7% EtOAc in petroleum ether) afforded pure 4aa as a colorless oil (33 mg, 0.091 mmol; 91% yield). $R_f = 0.35$ (10% EtOAc in petroleum ether). **FT-IR (neat):** $\nu$ 2978 (m), 1711 (s), 1659 (s), 1602 (s), 1256 (s), 1152 (s), 1029 (m) cm$^{-1}$; $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 7.83-7.86 (m; 3H), 7.63-7.67 (m; 1H), 7.54-7.58 (m; 1H), 7.50-7.52 (m; 1H), 7.39-7.48 (m; 3H), 5.88 (s; 1H), 5.76 (s; 1H), 4.28 (d, $J = 17.9$ Hz; 1H), 3.34 (d, $J = 17.9$ Hz; 1H), 1.32 (s; 9H); $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 201.15, 197.19, 167.96, 153.85, 147.66, 137.41, 135.73, 135.25, 132.37, 129.87, 128.19, 127.65, 127.40, 126.50, 124.70, 82.77, 65.61, 41.30, 27.65; HRMS (ESI+): Calculated for C$_{23}$H$_{22}$O$_4$Na ([M + Na]$^+$): 385.1416, found: 385.1415; $[\alpha]_D^{22} +214.1$ (c 1.00, CHCl$_3$) for an enantiomerically enriched sample with 97.5:2.5 er. Enantiomeric ratio was determined by HPLC analysis (Daicel Chiralpak AD-H column, 254 nm, $n$-Hexane/IPA = 90:10, 1.0 mL min$^{-1}$, $\tau_{\text{minor}} = 7.13$ min, $\tau_{\text{major}} = 8.28$ min). Absolute stereochemistry of 4aa is assigned in analogy with 4ba.

**tert-Butyl (S)-1-oxo-2-(3-oxo-3-(p-tolyl)prop-1-en-2-yl)-2,3-dihydro-1H-indene-2-carboxylate 4ab:** Purification by silica gel (100-200 mesh) column chromatography (6% EtOAc in petroleum ether) afforded pure 4ab as a colorless oil (34 mg, 0.090 mmol; 90% yield). $R_f = 0.35$ (10% EtOAc in petroleum ether). **FT-IR (neat):** $\nu$ 2976 (w), 1712 (s), 1655 (m), 1606 (m), 1257 (m), 1151 (s), 1027 (m) cm$^{-1}$; $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 7.83 (d, $J = 7.7$ Hz; 1H), 7.77 (d, $J = 8.2$ Hz; 2H), 7.62-7.66 (m; 1H), 7.50 (d, $J = 7.7$ Hz; 1H), 7.39-7.42 (m; 1H), 7.26 (s, $J = 8.2$ Hz; 2H), 5.84 (s; 1H), 5.74 (s; 1H), 4.28 (d, $J = 17.7$ Hz; 1H), 3.34 (d, $J = 17.7$ Hz; 1H), 2.42 (s; 3H), 1.31 (s; 9H); $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 201.22, 196.87, 167.97, 153.89, 147.74, 143.17, 135.68, 135.26, 134.68, 130.09, 128.86, 127.60, 126.71, 126.48, 124.67, 82.70, 65.70, 41.35, 27.46, 21.59; HRMS (ESI+): Calculated for C$_{24}$H$_{22}$O$_4$Na ([M + Na]$^+$): 399.1572, found: 399.1573; $[\alpha]_D^{22} +236.1$ (c 1.00, CHCl$_3$) for an enantiomerically enriched sample with 97:3 er. Enantiomeric ratio was determined by HPLC analysis (Daicel Chiralpak AS-H column, 254 nm, $n$-Hexane/EtOH = 95:5, 1.0 mL min$^{-1}$, $\tau_{\text{minor}} = 5.00$ min, $\tau_{\text{major}} = 5.90$ min). Absolute stereochemistry of 4ab is assigned in analogy with 4ba.
**tert-Butyl (S)-2-(3-(4-methoxyphenyl)-3-oxoprop-1-en-2-yl)-1-oxo,2,3-dihydro-1H-indene-2-carboxylate 4ac:** Purification by silica gel (100-200 mesh) column chromatography (10% EtOAc in petroleum ether) afforded pure 4ac as a colorless oil (32 mg, 0.082 mmol; 82% yield). *R*<sub>f</sub> = 0.25 (10% EtOAc in petroleum ether). **FT-IR (neat):** ν 2975 (m), 2927 (m), 1712 (s), 1651 (m), 1600 (s), 1257 (s), 1157 (s), 1028 (m) cm<sup>-1</sup>; **1H-NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.89 (d, *J* = 8.9 Hz; 2H), 7.83 (d, *J* = 7.6 Hz; 1H), 7.62-7.66 (m; 1H), 7.50 (d, *J* = 7.6 Hz; 1H), 7.39-7.43 (m; 1H), 6.94 (d, *J* = 9.0 Hz; 2H), 5.79 (s; 1H), 5.71 (s; 1H), 4.26 (d, *J* = 17.9 Hz; 1H), 3.88 (s; 3H), 3.37 (d, *J* = 17.9 Hz; 1H), 1.29 (s; 9H); **13C-NMR (100 MHz, CDCl<sub>3</sub>):** δ 201.26, 195.85, 167.99, 163.23, 153.92, 147.76, 135.67, 135.27, 132.35, 129.92, 127.59, 124.69, 124.65, 113.44, 82.70, 65.86, 55.44, 41.49, 27.63; **HRMS (ESI+):** Calculated for C<sub>24</sub>H<sub>24</sub>O<sub>5</sub>Na ([M + Na]<sup>+</sup>): 415.1521, found: 415.1520; [α]<sub>D</sub><sup>22</sup> +196.5 (c 1.00, CHCl<sub>3</sub>) for an enantiomerically enriched sample with 97:3 er. Enantiomeric ratio was determined by HPLC analysis (Daicel Chiralpak ID column, 254 nm, *n*-Hexane/IPA = 90:10, 1.0 mL min<sup>-1</sup>, *τ*<sub>major</sub> = 18.69 min, *τ*<sub>minor</sub> = 21.57 min). Absolute stereochemistry of 4ac is assigned in analogy with 4ba.

**tert-Butyl (S)-2-(3-(4-chlorophenyl)-3-oxoprop-1-en-2-yl)-1-oxo,2,3-dihydro-1H-indene-2-carboxylate 4ad:** Purification by silica gel (100-200 mesh) column chromatography (6% EtOAc in petroleum ether) afforded pure 4ad as a colorless oil (34 mg, 0.086 mmol; 86% yield). *R*<sub>f</sub> = 0.40 (10% EtOAc in petroleum ether). **FT-IR (neat):** ν 2976 (w), 1712 (s), 1659 (m), 1591 (m), 1257 (m), 1151 (s), 1023 (w) cm<sup>-1</sup>; **1H-NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.81-7.84 (m; 3H), 7.63-7.67 (m; 1H), 7.51 (d, *J* = 7.8 Hz; 1H), 7.40-7.45 (m; 3H), 5.86 (s; 1H), 5.71 (s; 1H), 4.25 (d, *J* = 18.0 Hz; 1H), 3.35 (d, *J* = 18.0 Hz; 1H), 1.31 (s; 9H); **13C-NMR (100 MHz, CDCl<sub>3</sub>):** δ 201.01, 196.03, 167.89, 153.79, 147.50, 138.91, 135.80, 135.66, 135.17, 131.33, 128.56, 127.70, 127.10, 126.48, 124.73, 82.90, 65.62, 41.31, 27.64; **HRMS (ESI+):** Calculated for C<sub>23</sub>H<sub>21</sub>ClO<sub>4</sub>Na ([M + Na]<sup>+</sup>): 419.1026, found: 419.1026; [α]<sub>D</sub><sup>22</sup> +230.4 (c 1.00, CHCl<sub>3</sub>) for an enantiomerically enriched sample with 98:2 er. Enantiomeric ratio was determined by HPLC analysis (Daicel Chiralpak AS-H column, 254 nm, *n*-Hexane/IPA = 90:10, 1.0 mL min<sup>-1</sup>, *τ*<sub>minor</sub> = 5.47 min, *τ*<sub>major</sub> = 6.45 min). Absolute stereochemistry of 4ad is assigned in analogy with 4ba.
tert-Butyl \((S)-2-(3-(4-fluorophenyl)-3-oxoprop-1-en-2-yl)-1-oxo-2,3-dihydro-1H-indene-2-carboxylate 4ae:\) Purification by silica gel (100-200 mesh) column chromatography (8% EtOAc in petroleum ether) afforded pure 4ae as a colorless oil (33 mg, 0.087 mmol; 87% yield). \(R_f = 0.40\) (10% EtOAc in petroleum ether). FT-IR (neat): \(\nu 2978\) (w), 1712 (s), 1659 (m), 1598 (m), 1253 (m), 1152 (s), 1027 (m) cm\(^{-1}\); \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta 7.89-7.93\) (m; 2H), 7.84 (d, \(J = 7.7\) Hz; 1H), 7.63-7.67 (m; 1H), 7.51 (d, \(J = 7.7\) Hz; 1H), 7.40-7.43 (m; 1H), 7.12-7.16 (m; 2H), 5.84 (s; 1H), 5.71 (s; 1H), 4.26 (d, \(J = 17.8\) Hz; 1H), 3.36 (d, \(J = 17.8\) Hz; 1H), 1.30 (s; 9H); \(^{13}\)C-NMR (100 MHz, CDCl\(_3\)): \(\delta 201.07, 195.77, 167.93, 165.38\) (d, \(J = 254.9\) Hz), 153.82, 147.60, 135.78, 135.19, 133.55 (d, \(J = 3.0\) Hz), 132.53 (d, \(J = 9.1\) Hz), 127.68, 126.79, 126.49, 124.72, 115.36 (d, \(J = 21.8\) Hz), 82.87, 65.70, 41.38, 27.63; HRMS (ESI+): Calculated for C\(_{23}\)H\(_{21}\)FO\(_4\)Na ([M + Na]+): 403.1322, found: 403.1320; \([\alpha]_{D}^{22} = +202.2\) (c 2.00, CHCl\(_3\)) for an enantiomerically enriched sample with 98:2 er. Enantiomeric ratio was determined by HPLC analysis (Daicel Chiralpak AS-H column, 254 nm, n-Hexane/EtOH = 95:5, 1.0 mL min\(^{-1}\), \(\tau_{minor} = 5.20\) min, \(\tau_{major} = 7.85\) min). Absolute stereochemistry of 4ae is assigned in analogy with 4ba.

tert-Butyl \((S)-2-(3-(3-methoxyphenyl)-3-oxoprop-1-en-2-yl)-1-oxo-2,3-dihydro-1H-indene-2-carboxylate 4af:\) Purification by silica gel (100-200 mesh) column chromatography (10% EtOAc in petroleum ether) afforded pure 4af as a colorless oil (34 mg, 0.087 mmol; 87% yield). \(R_f = 0.30\) (10% EtOAc in petroleum ether). FT-IR (neat): \(\nu 2975\) (m), 2927 (m), 1712 (s), 1651 (m), 1600 (m), 1257 (s), 1157 (s), 1028 (m) cm\(^{-1}\); \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta 7.83\) (d, \(J = 7.8\) Hz; 1H), 7.63-7.67 (m; 1H), 7.50 (d, \(J = 7.8\) Hz; 1H), 7.34-7.44 (m; 4H), 7.09-7.12 (m; 1H), 5.89 (s; 1H), 5.80 (s; 1H), 4.28 (d, \(J = 17.8\) Hz; 1H), 3.85 (s; 3H), 3.32 (d, \(J = 17.8\) Hz; 1H), 1.33 (s; 9H); \(^{13}\)C-NMR (100 MHz, CDCl\(_3\)): \(\delta 201.08, 196.90, 167.92, 159.47, 153.81, 147.58, 138.70, 135.72, 135.25, 129.14, 127.65, 127.57, 126.48, 124.70, 122.63, 118.85, 114.04, 82.75, 65.57, 55.42, 41.25, 27.66; HRMS (ESI+): Calculated for C\(_{24}\)H\(_{24}\)O\(_5\)Na ([M + Na]+): 415.1521, found: 415.1520; \([\alpha]_{D}^{22} = +202.2\) (c 1.00, CHCl\(_3\)) for an enantiomerically enriched sample with 97:3 er. Enantiomeric ratio was determined by HPLC analysis (Daicel Chiralpak AS-H column, 254 nm, n-Hexane/EtOH = 95:5, 1.0 mL min\(^{-1}\), \(\tau_{minor} = 5.76\) min, \(\tau_{major} = 8.63\) min). Absolute stereochemistry of 4af is assigned in analogy with 4ba.
**tert-Butyl**

(S)-1-oxo-2-(3-oxo-3-(m-tolyl)prop-1-en-2-yl)-2,3-dihydro-1H-indene-2-carboxylate 4ag: Purification by silica gel (100-200 mesh) column chromatography (6% EtOAc in petroleum ether) afforded pure 4ag as a colorless oil (31 mg, 0.082 mmol; 82% yield). Rf = 0.35 (10% EtOAc in petroleum ether). **FT-IR (neat):** ν 2977 (w), 1712 (s), 1657 (m), 1604 (m), 1255 (m), 1153 (s), 1036 (w) cm⁻¹; **¹H-NMR (400 MHz, CDCl₃):** δ 7.83 (d, J = 7.7 Hz; 1H), 7.63-7.66 (m; 3H), 7.50 (d, J = 7.7 Hz; 1H), 7.31-7.43 (m; 3H), 5.87 (s; 1H), 5.76 (s; 1H), 4.28 (d, J = 17.9 Hz; 1H), 3.32 (d, J = 17.9 Hz; 1H), 2.40 (s; 3H), 1.32 (s; 9H); **¹³C-NMR (100 MHz, CDCl₃):** δ 200.94, 195.85, 167.87, 153.87, 147.71, 138.01, 137.46, 135.71, 135.17, 133.11, 130.26, 128.02, 127.62, 127.38, 127.10, 126.48, 124.69, 82.71, 65.59, 41.29, 27.64, 21.28; **HRMS (ESI+):** Calculated for C₂₃H₂₄O₄Na ([M + Na⁺]): found: 419.1574; [α]D₂₂ +325.7 (c 1.00, CHCl₃) for an enantiomerically enriched sample with 97:3 er. Enantiomeric ratio was determined by HPLC analysis (Daicel Chiralpak IG column, 254 nm, n-Hexane/MeOH = 95:5, 1.0 mL min⁻¹, τminor = 21.56 min, τmajor = 23.07 min). Absolute stereochemistry of 4ag is assigned in analogy with 4ba.

**tert-Butyl**

(S)-2-(3-(3-chlorophenyl)-3-oxoprop-1-en-2-yl)-1-oxo-2,3-dihydro-1H-indene-2-carboxylate 4ah: Purification by silica gel (100-200 mesh) column chromatography (7% EtOAc in petroleum ether) afforded pure 4ah as a colorless oil (32 mg, 0.081 mmol; 81% yield). Rf = 0.35 (10% EtOAc in petroleum ether). **FT-IR (neat):** ν 2976 (w), 1712 (s), 1659 (m), 1591 (m), 1257 (m), 1151 (s), 1023 (w) cm⁻¹; **¹H-NMR (400 MHz, CDCl₃):** δ 7.82-7.85 (m; 2H), 7.72-7.74 (m; 1H), 7.64-7.68 (m; 1H), 7.50-7.55 (m; 2H), 7.38-7.44 (m; 2H), 5.90 (s; 1H), 5.75 (s; 1H), 4.26 (d, J = 17.7 Hz; 1H), 3.33 (d, J = 17.7 Hz; 1H), 1.32 (s; 9H); **¹³C-NMR (100 MHz, CDCl₃):** δ 200.94, 195.85, 167.87, 153.76, 147.35, 139.06, 135.82, 135.18, 134.50, 132.37, 129.76, 129.56, 129.77, 127.74, 127.73, 126.49, 124.76, 82.96, 65.52, 41.22, 27.66; **HRMS (ESI+):** Calculated for C₂₃H₂₂ClO₄Na ([M + Na⁺]): 419.1026, found: 419.1026; [α]D₂₂ +179.1 (c 1.00, CHCl₃) for an enantiomerically enriched sample with 96.5:3.5 er. Enantiomeric ratio was determined by HPLC analysis (Daicel Chiralpak IG column, 254 nm, n-Hexane/IPA = 90:10, 1.0 mL min⁻¹, τminor = 7.23 min, τmajor = 8.31 min). Absolute stereochemistry of 4ah is assigned in analogy with 4ba.

**tert-Butyl**

(S)-1-oxo-2-(3-oxo-3-(o-tolyl)prop-1-en-2-yl)-2,3-dihydro-1H-indene-2-carboxylate 4ai: Purification by silica gel (100-200 mesh) column chromatography (7% EtOAc in petroleum ether) afforded pure 4ai as a colorless oil (30 mg, 0.080 mmol; 80% yield). Rf = 0.45 (10% EtOAc in petroleum ether). **FT-IR (neat):** ν 2977 (w), 1711 (s), 1662 (m), 1605 (w), 1254 (m), 1152 (s), 1028 (w) cm⁻¹; **¹H-NMR (400 MHz, CDCl₃):** δ 7.82 (d, J = 7.7 Hz; 1H), 7.63-7.67 (m; 1H), 7.50-7.52 (m; 1H), 7.39-7.42 (m; 2H), 7.32-7.36 (m; 1H),...
7.19-7.25 (m; 2H), 5.99 (s; 1H), 5.75 (s; 1H), 4.35 (d, J = 17.8 Hz; 1H), 3.19 (d, J = 17.8 Hz; 1H), 2.37 (s; 3H), 1.41 (s; 9H); $^{13}$C-NMR (100 MHz, CDCl$_3$): δ 200.99, 198.93, 167.79, 153.57, 148.85, 137.83, 136.74, 135.71, 135.22, 130.86, 130.31, 130.18, 128.63, 127.64, 126.46, 124.98, 124.68, 82.55, 64.76, 40.70, 27.71, 19.62; HRMS (ESI+): Calculated for C$_2$H$_2$O$_3$Na ([M + Na$^+$]): 399.1572, found: 399.1572; [α]$_D^{22}$ +262.8 (c 2.00, CHCl$_3$) for an enantiomerically enriched sample with 97.5:2.5 er. Enantiomeric ratio was determined by HPLC analysis (Daicel Chiralpak AD-H column, 254 nm, n-Hexane/IPA = 90:10, 1.0 mL min$^{-1}$, $\tau$$_{minor}$ = 6.61 min, $\tau$$_{major}$ = 7.05 min). Absolute stereochemistry of 4ai is assigned in analogy with 4ba.

tert-Butyl (S)-2-(3-(2-methoxyphenyl)-3-oxoprop-1-en-2-yl)-1-oxo-2,3-dihydro-1H-indene-2-carboxylate 4aj: Purification by silica gel (100-200 mesh) column chromatography (10% EtOAc in petroleum ether) afforded pure 4aj as a colorless oil (34 mg, 0.087 mmol; 87% yield). Rf = 0.30 (10% EtOAc in petroleum ether). FT-IR (neat): ν 2976 (w), 1711 (s), 1660 (m), 1600 (m), 1253 (s), 1154 (s). 1026 (m) cm$^{-1}$; $^1$H-NMR (400 MHz, CDCl$_3$): δ 7.82 (d, J = 7.7 Hz; 1H), 7.62-7.66 (m; 1H), 7.50 (d, J = 7.7 Hz; 1H), 7.36-7.43 (m; 3H), 6.93-7.00 (m; 2H), 5.99 (s; 1H), 5.79 (s; 1H), 4.31 (d, J = 18.1 Hz; 1H), 3.78 (s; 3H), 3.23 (d, J = 18.1 Hz; 1H), 1.41 (s; 9H); $^{13}$C-NMR (100 MHz, CDCl$_3$): δ 201.11, 196.54, 167.81, 157.31, 153.80, 148.53, 135.61, 135.30, 131.66, 129.60, 128.00, 127.53, 126.44, 124.66, 120.03, 111.43, 82.34, 64.65, 55.66, 40.37, 27.70; HRMS (ESI+): Calculated for C$_{26}$H$_{22}$O$_3$Na ([M + Na$^+$]): 415.1521, found: 415.1519; [α]$_D^{22}$ +293.4 (c 1.00, CHCl$_3$) for an enantiomerically enriched sample with 98.5:1.5 er. Enantiomeric ratio was determined by HPLC analysis (Daicel Chiralpak AS-H column, 254 nm, n-Hexane/EtOH = 95:5, 1.0 mL min$^{-1}$, $\tau$$_{minor}$ = 6.13 min, $\tau$$_{major}$ = 6.58 min). Absolute stereochemistry of 4aj is assigned in analogy with 4ba.

tert-Butyl (S)-2-(3-(naphthalen-1-yl)-3-oxoprop-1-en-2-yl)-1-oxo-2,3-dihydro-1H-indene-2-carboxylate 4ak: Purification by silica gel (100-200 mesh) column chromatography (7% EtOAc in petroleum ether) afforded pure 4ak as a colorless oil (32 mg, 0.078 mmol; 78% yield). Rf = 0.35 (10% EtOAc in petroleum ether). FT-IR (neat): ν 2977 (w), 1711 (s), 1657 (m), 1606 (w), 1254 (m), 1152 (s), 1020 (w) cm$^{-1}$; $^1$H-NMR (400 MHz, CDCl$_3$): δ 8.20-8.22 (m; 1H), 7.97 (d, J = 8.1 Hz; 1H), 7.84-7.90 (m; 2H), 7.73-7.74 (m; 1H), 7.65-7.69 (m; 1H), 7.48-7.56 (m; 4H), 7.40-7.44 (m; 1H), 6.00 (s; 1H), 5.81 (s; 1H), 4.43 (d, J = 17.8 Hz; 1H), 3.34 (d, J = 17.8 Hz; 1H), 1.44 (s; 9H); $^{13}$C-NMR (100 MHz, CDCl$_3$): δ 201.09, 198.41, 167.93, 153.70, 149.55, 135.76, 135.60, 135.25, 133.63, 131.28, 130.94, 130.50, 128.33, 128.01, 127.68, 127.24, 126.50, 126.43, 125.46, 124.73, 124.21, 82.74, 65.07, 41.01, 27.77; HRMS (ESI+): Calculated for C$_{27}$H$_{22}$O$_3$Na ([M + Na$^+$]): 435.1572, found: 435.1570; [α]$_D^{22}$ +146.5 (c 2.00, CHCl$_3$) for an enantiomerically enriched sample with 98:2 er. Enantiomeric ratio was determined by HPLC analysis (Daicel Chiralpak AS-H column, 254 nm, n-Hexane/EtOH = 95:5, 1.0 mL
Absolute stereochemistry of 4ak is assigned in analogy with 4ba.

tert-Butyl (S)-2-(3-(naphthalen-2-yl)-3-oxoprop-1-en-2-yl)-1-oxo-2,3-dihydro-1H-indene-2-carboxylate 4al: Purification by silica gel (100-200 mesh) column chromatography (8% EtOAc in petroleum ether) afforded pure 4al as a colorless oil (37 mg, 0.090 mmol; 90% yield). Rf = 0.35 (10% EtOAc in petroleum ether). FT-IR (neat): v 2976 (w), 1711 (s), 1655 (m), 1602 (w), 1256 (m), 1152 (s), 1029 (m) cm⁻¹; ¹H-NMR (400 MHz, CDCl₃): δ 8.41 (s; 1H), 7.97 (d, J = 7.8 Hz; 1H), 7.85-7.92 (m; 4H), 7.64-7.68 (m; 1H), 7.52-7.62 (m; 3H), 7.41-7.45 (m; 1H), 5.92 (s; 1H), 5.84 (s; 1H), 4.33 (d, J = 17.7 Hz; 1H), 3.41 (d, J = 17.7 Hz; 1H), 1.32 (s; 9H); 1³C-NMR (100 MHz, CDCl₃): δ 201.26, 197.15, 168.00, 153.92, 147.83, 135.77, 135.28, 134.58, 132.21, 131.61, 129.39, 128.25, 128.19, 127.76, 127.66, 127.26, 126.78, 126.52, 125.61, 124.73, 82.83, 65.75, 41.41, 27.66; HRMS (ESI+): Calculated for C₂₇H₂₄O₄Na ([M + Na⁺]: 435.1572, found: 435.1576; [α]D²² +193.9 (c 1.00, CHCl₃) for an enantiomerically enriched sample with 97:3 er. Enantiomeric ratio was determined by HPLC analysis (Daicel Chiralpak AD-H column, 254 nm, n-Hexane/IPA = 90:10, 1.0 mL min⁻¹, τmajor = 9.91 min, τminor = 11.60 min). Absolute stereochemistry of 4al is assigned in analogy with 4ba.

tert-Butyl (S)-1-oxo-2-(3-oxo-3-(thiophen-2-yl)prop-1-en-2-yl)-2,3-dihydro-1H-indene-2-carboxylate 4am: Purification by silica gel (100-200 mesh) column chromatography (7% EtOAc in petroleum ether) afforded pure 4am as a colorless oil (29 mg, 0.079 mmol; 79% yield). Rf = 0.30 (10% EtOAc in petroleum ether). FT-IR (neat): v 2976 (w), 1711 (s), 1634 (m), 1256 (m), 1151 (s), 1022 (w) cm⁻¹; ¹H-NMR (400 MHz, CDCl₃): δ 7.83 (d, J = 7.7 Hz; 1H), 7.78-7.80 (m; 1H), 7.68-7.69 (m; 1H), 7.63-7.66 (m; 1H), 7.50 (d, J = 7.7 Hz; 1H), 7.39-7.43 (m; 1H), 7.13-7.15 (m; 1H), 6.00 (s; 1H), 5.80 (s; 1H), 4.22 (d, J = 17.7 Hz; 1H), 3.39 (d, J = 17.7 Hz; 1H), 1.27 (s; 9H); 1³C-NMR (100 MHz, CDCl₃): δ 200.86, 188.47, 167.74, 153.81, 147.66, 143.06, 135.74, 135.20, 134.54, 134.09, 127.83, 127.65, 126.50, 124.91, 124.72, 82.83, 65.80, 41.40, 27.55; HRMS (ESI+): Calculated for C₂₁H₂₀O₄Na ([M + Na⁺]: 391.0980, found: 391.0979; [α]D²² +248.0 (c 1.00, CHCl₃) for an enantiomerically enriched sample with 98.5:1.5 er. Enantiomeric ratio was determined by HPLC analysis (Daicel Chiralpak AD-H column, 254 nm, n-Hexane/EtOH = 95:5, 1.0 mL min⁻¹, τminor = 10.32 min, τmajor = 13.13 min). Absolute stereochemistry of 4am is assigned in analogy with 4ba.
tert-Butyl (S)-2-(3-(2,4-dimethoxyphenyl)-3-oxoprop-1-en-2-yl)-1-oxo-2,3-dihydro-1H-indene-2-carboxylate 4an: Purification by silica gel (100-200 mesh) column chromatography (15% EtOAc in petroleum ether) afforded pure 4an as a colorless oil (32 mg, 0.076 mmol; 76% yield). \( R_f = 0.20 \) (20% EtOAc in petroleum ether). FT-IR (neat): \( \nu 2974 \) (w), 1710 (s), 1659 (m), 1605 (s), 1263 (s), 1156 (s), 1028 (m) cm\(^{-1}\); \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \( \delta 7.81 \) (d, \( J = 7.6 \) Hz; 1H), 7.61-7.64 (m; 1H), 7.44-7.49 (m; 2H), 7.37-7.40 (m; 1H), 6.47-6.50 (m; 2H), 5.88 (s; 1H), 5.74 (s; 1H), 4.28 (d, \( J = 17.7 \) Hz; 1H), 3.77 (s; 3H), 3.27 (d, \( J = 17.7 \) Hz; 1H), 1.38 (s; 9H); \(^{13}\)C-NMR (100 MHz, CDCl\(_3\)): \( \delta 201.31, 195.55, 167.93, 163.12, 159.71, 153.91, 149.07, 135.55, 135.32, 127.99, 124.61, 120.61, 103.83, 98.95, 82.33, 65.08, 55.65, 55.46, 40.77, 27.70; HRMS (ESI+): Calculated for C\(_{25}\)H\(_{26}\)O\(_6\)Na ([M + Na]+): 445.1627, found: 445.1625; \([\alpha]_D^{22} +226.9 \) (c 1.00, CHCl\(_3\)) for an enantiomerically enriched sample with 94.5:5.5 er. Enantiomeric ratio was determined by HPLC analysis (Phenomenex C-1 column, 254 nm, n-Hexane/EtOH = 95:5, 1.0 mL min\(^{-1}\), \( \tau_{\text{minor}} = 9.55 \) min, \( \tau_{\text{major}} = 13.18 \) min). Absolute stereochemistry of 4an is assigned in analogy with 4ba.

tert-Butyl (S)-2-(3-(benzo[d][1,3]dioxol-5-y1)-3-oxoprop-1-en-2-yl)-1-oxo-2,3-dihydro-1H-indene-2-carboxylate 4ao: Purification by silica gel (100-200 mesh) column chromatography (10% EtOAc in petroleum ether) afforded pure 4ao as a colorless oil (36 mg, 0.089 mmol; 89% yield). \( R_f = 0.30 \) (10% EtOAc in petroleum ether). FT-IR (neat): \( \nu 2923 \) (w), 1712 (s), 1651 (m), 1606 (m), 1251 (s), 1153 (s), 1034 (m) cm\(^{-1}\); \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \( \delta 7.83 \) (d, \( J = 7.7 \) Hz; 1H), 7.49-7.53 (m; 2H), 7.40 (d, \( J = 1.5 \) Hz; 1H), 6.86 (d, \( J = 8.1 \) Hz; 1H), 6.05 (s; 2H), 5.79 (s; 1H), 5.72 (s; 1H), 4.25 (d, \( J = 17.6 \) Hz; 1H), 3.36 (d, \( J = 17.6 \) Hz; 1H), 1.30 (s; 9H); \(^{13}\)C-NMR (100 MHz, CDCl\(_3\)): \( \delta 201.14, 195.40, 167.95, 153.87, 151.51, 147.79, 147.64, 135.69, 135.24, 131.61, 127.62, 126.56, 126.48, 125.91, 124.68, 109.76, 107.63, 101.79, 82.76, 65.85, 41.48, 27.64; HRMS (ESI+): Calculated for C\(_{24}\)H\(_{22}\)O\(_6\)Na ([M + Na]^+): 429.1314, found: 429.1311; \([\alpha]_D^{22} +220.4 \) (c 1.00, CHCl\(_3\)) for an enantiomerically enriched sample with 95:5 er. Enantiomeric ratio was determined by HPLC analysis (Daicel Chiralpak AD-H column, 254 nm, n-Hexane/IPA = 90:10, 1.0 mL min\(^{-1}\), \( \tau_{\text{minor}} = 11.49 \) min, \( \tau_{\text{major}} = 13.72 \) min). Absolute stereochemistry of 4ao is assigned in analogy with 4ba.
tert-Butyl (S)-2-(4-methyl-3-oxo-4-phenylpent-1-en-2-yl)-1-oxo-2,3-dihydro-1H-indene-2-carboxylate 4ap: Purification by silica gel (100-200 mesh) column chromatography (4% EtOAc in petroleum ether) afforded pure 4ap as a colorless oil (23 mg, 0.057 mmol; 57% yield). \( R_t = 0.35 \) (10% EtOAc in petroleum ether). FT-IR (neat): \( \nu \) 2968 (m), 2924 (m), 1722 (s), 1614 (m), 1152 (s), 1013 (w) cm\(^{-1}\); \(^1\)H-NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.74 (d, \( J = 7.7 \) Hz; 1H), 7.61 (t, \( J = 7.1 \) Hz; 1H), 7.46 (d, \( J = 7.7 \) Hz; 1H), 7.29-7.37 (m; 3H), 7.19-7.25 (m; 3H), 5.63 (s; 1H), 5.42 (s; 1H), 4.25 (d, \( J = 18.1 \) Hz; 1H), 2.96 (d, \( J = 18.1 \) Hz; 1H), 1.67 (s; 3H), 1.50 (s; 3H), 1.42 (s; 3H); \(^1^3\)C-NMR (100 MHz, CDCl\(_3\)) \( \delta \) 203.32, 201.00, 168.02, 153.40, 144.45, 144.41, 135.56, 135.39, 128.92, 128.04, 127.52, 126.62, 126.38, 125.10, 124.57, 82.09, 65.93, 51.24, 40.72, 29.07, 27.78, 27.51; HRMS (ESI+): Calculated for C\(_{26}\)H\(_{28}\)O\(_4\)Na ([M + Na\(^+\)]: 427.4958, found: 427.4957; |\( \alpha \)|\(^22\) \(+\)123.9 (c 0.50, CHCl\(_3\)) for an enantiomerically enriched sample with 97.5:2.5 er. Enantiomeric ratio was determined by HPLC analysis (Daicel Chiralpak IE column, 254 nm, \( n \)-Hexane/IPA = 95:5, 1.0 mL min\(^{-1}\), \( \tau _{\text{minor}} = 7.56 \) min, \( \tau _{\text{major}} = 8.29 \) min). Absolute stereochemistry of 4ap is assigned in analogy with 4ba.

tert-butyl (E)-2-(4-methyl-3-oxo-4-phenylpent-1-en-1-yl)-1-oxo-2,3-dihydro-1H-indene-2-carboxylate S5: Purification by silica gel (100-200 mesh) column chromatography (5% EtOAc in petroleum ether) afforded pure S5 as a colorless oil (9 mg, 0.022 mmol; 22% yield). \( R_t = 0.30 \) (10% EtOAc in petroleum ether). FT-IR (neat): \( \nu \) 2977 (w), 2927 (w), 1614 (s), 1594 (m), 1450 (m), 1432 (m), 1350 (m), 128.04, 127.52, 126.82, 126.62, 126.38, 125.82, 124.57, 82.09, 65.93, 51.24, 40.72, 29.07, 27.78, 27.51; HRMS (ESI+): Calculated for C\(_{26}\)H\(_{28}\)O\(_4\)Na ([M + Na\(^+\)]: 427.4958, found: 427.4954; Enantiomeric ratio was determined by HPLC analysis (Daicel Chiralpak IE column, 254 nm, \( n \)-Hexane/IPA = 90:10, 1.0 mL min\(^{-1}\), \( \tau _{\text{minor}} = 16.88 \) min, \( \tau _{\text{major}} = 18.33 \) min) and found to be 52:48.

tert-Butyl (S)-5-bromo-1-oxo-2-(3-oxo-3-phenylprop-1-en-2-yl)-2,3-dihydro-1H-indene-2-carboxylate 4ba: Purification by silica gel (100-200 mesh) column chromatography (6% EtOAc in petroleum ether) afforded pure 4ba as a colorless oil (41 mg, 0.093 mmol; 93% yield). \( R_t = 0.30 \) (10% EtOAc in petroleum ether). M.P. = 97-98 °C. FT-IR (neat): \( \nu \) 2977 (w), 2927 (w), 1716 (s), 1658 (m), 1594 (w), 1250 (m), 1151 (s) cm\(^{-1}\); \(^1\)H-NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.69 (d, \( J = 7.7 \) Hz; 1H), 7.37 (m; 4H), 5.63 (s; 1H), 5.42 (s; 1H), 4.25 (d, \( J = 18.1 \) Hz; 1H), 2.96 (d, \( J = 18.1 \) Hz; 1H), 1.67 (s; 3H), 1.50 (s; 3H), 1.42 (s; 3H); \(^1^3\)C-NMR (100 MHz, CDCl\(_3\)) \( \delta \) 203.32, 201.00, 168.02, 153.40, 144.45, 144.41, 135.56, 135.39, 128.92, 128.04, 127.52, 126.62, 126.38, 125.82, 124.57, 82.09, 65.93, 51.24, 40.72, 29.07, 27.78, 27.51; HRMS (ESI+): Calculated for C\(_{26}\)H\(_{28}\)O\(_4\)Na ([M + Na\(^+\)]: 427.4958, found: 427.4954; Enantiomeric ratio was determined by HPLC analysis (Daicel Chiralpak IE column, 254 nm, \( n \)-Hexane/IPA = 90:10, 1.0 mL min\(^{-1}\), \( \tau _{\text{minor}} = 16.88 \) min, \( \tau _{\text{major}} = 18.33 \) min) and found to be 52:48.
tert-Butyl (S)-5-chloro-1-oxo-2-(3-oxo-3-phenylprop-1-en-2-yl)-2,3-dihydro-1H-indene-2-carboxylate 4ca: Purification by silica gel (100-200 mesh) column chromatography (5% EtOAc in petroleum ether) afforded pure 4ca as a colorless oil (37 mg, 0.093 mmol; 93% yield). \( R_f = 0.30 \) (10% EtOAc in petroleum ether). M.P. = 109-111 °C. FT-IR (neat): ν 2978 (w), 1715 (s), 1659 (m), 1594 (m), 1346 (m), 1298, 1185, 1152 (m), 1024 (w) cm\(^{-1}\); \(^1\)H-NMR (400 MHz, CDCl\(_3\)) : δ 7.82-7.86 (m; 3H), 7.54-7.70 (m; 2H), 4.26 (d, \( J = 18.1 \) Hz; 1H), 3.31 (d, \( J = 18.1 \) Hz; 1H), 1.31 (s; 9H); \(^{13}\)C-NMR (100 MHz, CDCl\(_3\)) : δ 199.17, 197.10, 167.91 (d, \( J = 8.4 \) Hz; 1H), 167.72, 156.82 (d, \( J = 10.6 \) Hz), 147.37, 137.28, 132.45, 131.62, 129.85, 128.21, 127.57, 127.07 (d, \( J = 10.6 \) Hz), 116.14 (d, \( J = 23.6 \) Hz), 113.11 (d, \( J = 22.4 \) Hz), 82.98, 65.85, 41.13, 27.62; HRMS (ESI+): Calculated for C\(_{23}\)H\(_{21}\)ClO\(_4\)Na ([M + Na\(^+\)]: 419.1026, found: 419.1027; \([\alpha]\)\(^D\)\(_{22}\) +226.7 (c 1.00, CHCl\(_3\)) for an enantiomerically enriched sample with >99.9:0.1 er. Enantiomeric ratio was determined by HPLC analysis (Daicel Chiralpak AD-H column, 254 nm, \( n\)-Hexane/EtOH = 95:5, 1.0 mL min\(^{-1}\), \( \tau_{\text{minor}} = 12.14 \) min, \( \tau_{\text{major}} = 14.55 \) min). Absolute stereochemistry of 4ba was assigned by single crystal X-ray diffraction analysis.

tert-Butyl (S)-5-fluoro-1-oxo-2-(3-oxo-3-phenylprop-1-en-2-yl)-2,3-dihydro-1H-indene-2-carboxylate 4da: Purification by silica gel (100-200 mesh) column chromatography (6% EtOAc in petroleum ether) afforded pure 4da as a colorless oil (36 mg, 0.095 mmol; 95% yield). \( R_f = 0.35 \) (10% EtOAc in petroleum ether). FT-IR (neat): ν 2978 (w), 1715 (s), 1659 (m), 1594 (m), 1251 (s), 1152 (s), 1028 (w) cm\(^{-1}\); \(^1\)H-NMR (400 MHz, CDCl\(_3\)) : δ 7.82-7.86 (m; 2H), 7.54-7.58 (m; 1H), 7.50 (s; 1H), 7.49 (m; 2H), 7.39 (d, \( J = 8.2 \) Hz; 1H), 5.88 (s; 1H), 5.79 (s; 1H), 4.25 (d, \( J = 17.8 \) Hz; 1H), 3.30 (d, \( J = 8.4 \) Hz; 1H), 1.32 (s; 9H); \(^{13}\)C-NMR (100 MHz, CDCl\(_3\)) : δ 199.63, 197.03, 167.61, 155.22, 147.32, 142.38, 137.25, 133.70, 132.46, 129.85, 128.54, 128.21, 127.60, 126.65, 125.76, 83.03, 65.76, 40.94, 27.62; HRMS (ESI+): Calculated for C\(_{23}\)H\(_{21}\)F\(_4\)O\(_4\)Na ([M + Na\(^+\)]: 403.1322, found: 403.1325; \([\alpha]\)\(^D\)\(_{22}\) +236.7 (c 2.00, CHCl\(_3\)) for an enantiomerically enriched sample with 98:2 er. Enantiomeric ratio was determined by HPLC analysis (Daicel Chiralpak AS-H column, 254 nm, \( n\)-Hexane/EtOH = 95:5, 1.0 mL min\(^{-1}\), \( \tau_{\text{minor}} = 5.13 \) min, \( \tau_{\text{major}} = 6.16 \) min). Absolute stereochemistry of 4ca is assigned in analogy with 4ba.
min\(^{-1}\), \(\tau_{\text{minor}} = 5.13\) min, \(\tau_{\text{major}} = 8.52\) min). Absolute stereochemistry of 4da is assigned in analogy with 4ba.

**tert-Butyl (S)-5-methyl-1-oxo-2-(3-oxo-3-phenylprop-1-en-2-yl)-2,3-dihydro-1H-indene-2-carboxylate 4ea:** Purification by silica gel (100-200 mesh) column chromatography (7% EtOAc in petroleum ether) afforded pure 4ea as a colorless oil (31 mg, 0.082 mmol; 82% yield). \(R_t = 0.30\) (10% EtOAc in petroleum ether). **FT-IR (neat):** \(\nu 2977\) (w), 1731 (s), 1710 (s), 1659 (m), 1607 (m), 1256 (m), 1153 (s), 1026 (m) cm\(^{-1}\); \(^1H\)-NMR (400 MHz, CDCl\(_3\)): \(\delta 7.84 - 7.86\) (m; 2H), 7.72 (d, \(J = 7.9\) Hz; 1H), 7.52 - 7.57 (m; 1H), 7.43 - 7.47 (m; 2H), 7.30 (s; 1H), 7.22 (d, \(J = 7.9\) Hz; 1H), 5.87 (s; 1H), 5.74 (s; 1H), 4.32 (d, \(J = 17.5\) Hz; 1H), 3.28 (d, \(J = 17.5\) Hz; 1H), 1.31 (s; 9H); \(^13C\)-NMR (100 MHz, CDCl\(_3\)): \(\delta 200.49, 197.26, 168.12, 154.35, 147.83, 147.20, 137.46, 133.03, 129.88, 128.98, 128.16, 127.27, 126.77, 124.54, 82.65, 65.78, 41.18, 27.65, 22.15; HRMS (ESI\(^+\)): Calculated for C\(_{24}\)H\(_{24}\)O\(_4\)Na ([M + Na\(^+\)]): 399.1572, found: 399.1571; \([\alpha]D\)\(_{22}\) +210.1 (c 1.00, CHCl\(_3\)) for an enantiomerically enriched sample with 98:2 er. Enantiomeric ratio was determined by HPLC analysis (Daicel Chiralpak AD-H column, 254 nm, \(n\)-Hexane/EtOH = 95:5, 1.0 mL min\(^{-1}\), \(\tau_{\text{major}} = 9.83\) min, \(\tau_{\text{minor}} = 10.79\) min). Absolute stereochemistry of 4ea is assigned in analogy with 4ba.

**tert-Butyl (S)-1-oxo-2-(3-oxo-3-phenylprop-1-en-2-yl)-5-phenyl-2,3-dihydro-1H-indene-2-carboxylate 4fa:** Purification by silica gel (100-200 mesh) column chromatography (7% EtOAc in petroleum ether) afforded pure 4fa as a colorless oil (33 mg, 0.075 mmol; 75% yield). \(R_t = 0.35\) (10% EtOAc in petroleum ether). **FT-IR (neat):** \(\nu 2925\) (w), 1709 (s), 1658 (m), 1604 (m), 1556 (s), 1547 (s), 137.46, 133.03, 129.88, 128.98, 128.16, 127.27, 126.77, 124.54, 82.65, 65.78, 41.18, 27.65, 22.15; **HRMS (ESI\(^+\)):** Calculated for C\(_{29}\)H\(_{26}\)O\(_4\)Na ([M + Na\(^+\)]): 461.1729, found: 461.1726; \([\alpha]D\)\(_{22}\) +114.6 (c 2.00, CHCl\(_3\)) for an enantiomerically enriched sample with 98:2 er. Enantiomeric ratio was determined by HPLC analysis (Daicel Chiralpak IB column, 254 nm, \(n\)-Hexane/IPA = 90:10, 1.0 mL min\(^{-1}\), \(\tau_{\text{major}} = 6.69\) min, \(\tau_{\text{minor}} = 12.06\) min). Absolute stereochemistry of 4fa is assigned in analogy with 4ba.
**tert-Butyl (S)-6-bromo-1-oxo-2-(3-oxo-3-phenylprop-1-en-2-yl)-2,3-dihydro-1H-indene-2-carboxylate 4ga:** Purification by silica gel (100-200 mesh) column chromatography (6% EtOAc in petroleum ether) afforded pure 4ga as a colorless oil (40 mg, 0.091 mmol; 91% yield). **Rf** = 0.35 (10% EtOAc in petroleum ether). **FT-IR** (neat): ν 2977 (w), 2927 (w), 1716 (s), 1658 (m), 1594 (w), 1250 (m), 1151 (s) cm⁻¹; **¹H-NMR** (400 MHz, CDCl₃): δ 7.95 (d, J = 1.5 Hz; 1H), 7.82-7.84 (m; 2H), 7.72-7.75 (m; 1H), 7.54-7.58 (m; 1H), 7.43-7.47 (m; 2H), 7.39 (d, J = 8.1 Hz; 1H), 5.88 (s; 1H), 5.79 (s; 1H), 4.20 (d, J = 17.8 Hz; 1H), 3.27 (d, J = 17.8 Hz; 1H), 1.31 (s; 9H); **¹³C-NMR** (100 MHz, CDCl₃): δ 199.72, 196.98, 167.44, 152.32, 147.24, 138.42, 137.21, 137.01, 132.48, 129.83, 128.22, 128.01, 127.63, 127.51, 121.78, 83.08, 66.02, 40.86, 27.61; **HRMS** (ESI⁺): Calculated for C₂₃H₂₁BrO₄Na ([M + Na⁺]: 463.0521, found: 463.0520; [α]ᵇ₂⁺ = 280.3 (c 2.00, CHCl₃) for an enantiomerically enriched sample with 99:1 er. Enantiomeric ratio was determined by HPLC analysis (Daicel Chiralpak AS-H column, 254 nm, n-Hexane/IPA = 90:10, 1.0 mL min⁻¹, τₘᵢₙᵢᵩ = 11.41 min, τₘᵢₖᵢᵩ = 18.12 min). Absolute stereochemistry of 4ga is assigned in analogy with 4ba.

**tert-Butyl (S)-6-methyl-1-oxo-2-(3-oxo-3-phenylprop-1-en-2-yl)-2,3-dihydro-1H-indene-2-carboxylate 4ha:** Purification by silica gel (100-200 mesh) column chromatography (6% EtOAc in petroleum ether) afforded pure 4ha as a colorless oil (36 mg, 0.096 mmol; 96% yield). **Rf** = 0.30 (10% EtOAc in petroleum ether). **FT-IR** (neat): ν 2977 (w), 1711 (s), 1659 (m), 1620 (w), 1150 (s), 1038 (m) cm⁻¹; **¹H-NMR** (400 MHz, CDCl₃): δ 7.83-7.85 (m; 2H), 7.63 (s; 1H), 7.53-7.57 (m; 1H), 7.43-7.47 (m; 3H), 7.39 (d, J = 7.6 Hz; 1H), 5.86 (s; 1H), 5.74 (s; 1H), 4.22 (d, J = 17.9 Hz; 1H), 3.28 (d, J = 17.9 Hz; 1H), 2.41 (s; 3H), 1.31 (s; 9H); **¹³C-NMR** (100 MHz, CDCl₃): δ 201.16, 197.19, 168.04, 151.26, 147.79, 137.62, 137.43, 137.05, 135.41, 132.32, 129.85, 128.15, 127.25, 126.15, 124.53, 82.64, 65.94, 40.95, 27.64, 21.01; **HRMS** (ESI⁺): Calculated for C₂₃H₂₄NaO₄ ([M + Na⁺]: 399.1570, found: 399.1572; [α]ᵇ₂⁺ = 280.3 (c 2.00, CHCl₃) for an enantiomerically enriched sample with 98.5:1.5 er. Enantiomeric ratio was determined by HPLC analysis (Daicel Chiralpak AS-H column, 254 nm, n-Hexane/EtOH = 95:5, 1.0 mL min⁻¹, τₘᵢₙᵢᵩ = 4.90 min, τₘᵢₖᵢᵩ = 5.26 min). Absolute stereochemistry of 4ha is assigned in analogy with 4ba.

**tert-Butyl (S)-6-methoxy-1-oxo-2-(3-oxo-3-phenylprop-1-en-2-yl)-2,3-dihydro-1H-indene-2-carboxylate 4ia:** Purification by silica gel (100-200 mesh) column chromatography (7% EtOAc in petroleum ether) afforded pure 4ia as a colorless oil (36 mg, 0.092 mmol; 92% yield). **Rf** = 0.25 (10% EtOAc in petroleum ether). **FT-IR** (neat): ν 2926 (w), 1709 (s), 1658 (s), 1619 (m), 1493 (s), 1263 (s), 1152 (s), 1029 (s) cm⁻¹; **¹H-NMR** (400 MHz, CDCl₃): δ 7.84-7.86 (m; 2H), 7.54-7.58 (m; 1H), 7.44-7.48 (m; 2H), 7.38-7.41 (m; 1H), 7.24-
7.27 (m; 2H), 5.88 (s; 1H), 5.76 (s; 1H), 4.19 (d, J = 17.5 Hz; 1H), 3.86 (s; 3H), 3.26 (d, J = 17.5 Hz; 1H), 1.33 (s; 9H); $^{13}$C-NMR (100 MHz, CDCl$_3$): δ 201.05, 197.14, 167.98, 159.62, 147.72, 146.84, 137.42, 136.35, 132.34, 129.85, 128.16, 127.26, 127.18, 125.33, 105.60, 82.71, 66.39, 55.60, 40.61, 27.65;

HRMS (ESI⁺): Calculated for C$_{24}$H$_{22}$O$_5$Na ([M + Na]$^+$): 415.1521, found: 415.1521; [α]$^D$ +178.3 (c 2.00, CHCl$_3$) for an enantiomerically enriched sample with 97.5:2.5 er. Enantiomeric ratio was determined by HPLC analysis (Daicel Chiralpak AS-H column, 254 nm, n-Hexane/EtOH = 95:5, 1.0 mL min$^{-1}$, $\tau_{\text{minor}}$ = 5.67 min, $\tau_{\text{major}}$ = 7.70 min). Absolute stereochemistry of 4ia is assigned in analogy with 4ba.

tert-Butyl (S)-4-bromo-1-oxo-2-(3-oxo-3-phenylprop-1-en-2-yl)-2,3-dihydro-1H-indene-2-carboxylate 4ja: Purification by silica gel (100-200 mesh) column chromatography (6% EtOAc in petroleum ether) afforded pure 4ja as a colorless oil (42 mg, 0.095 mmol; 95% yield). $R_t$ = 0.35 (10% EtOAc in petroleum ether). FT-IR (neat): ν 2977 (w), 1717 (s), 1658 (m), 1596 (w), 1253 (s), 1152 (s), 1028 (w) cm$^{-1}$; ¹H-NMR (400 MHz, CDCl$_3$): δ 7.77-7.85 (m; 4H), 7.54-7.59 (m; 1H), 7.44-7.48 (m; 2H), 7.30-7.48 (m; 1H), 5.89 (s; 1H), 5.80 (s; 1H), 4.21 (d, J = 18.2 Hz; 1H), 3.25 (d, J = 18.2 Hz; 1H), 1.33 (s; 9H);

HRMS (ESI⁺): Calculated for C$_{24}$H$_{22}$O$_5$Na ([M + Na]$^+$): 463.0521, found: 463.0520; [α]$^D$ +178.3 (c 2.00, CHCl$_3$) for an enantiomerically enriched sample with 96.5:3.5 er. Enantiomeric ratio was determined by HPLC analysis (Daicel Chiralpak AS-H column, 254 nm, n-Hexane/EtOH = 95:5, 1.0 mL min$^{-1}$, $\tau_{\text{minor}}$ = 4.99 min, $\tau_{\text{major}}$ = 5.78 min). Absolute stereochemistry of 4ja is assigned in analogy with 4ba.

tert-Butyl (S)-7-methyl-1-oxo-2-(3-oxo-3-phenylprop-1-en-2-yl)-2,3-dihydro-1H-indene-2-carboxylate 4ka: Purification by silica gel (100-200 mesh) column chromatography (7% EtOAc in petroleum ether) afforded pure 4ka as a colorless oil (34 mg, 0.090 mmol; 90% yield). $R_t$ = 0.35 (10% EtOAc in petroleum ether). FT-IR (neat): ν 2973 (w), 1715 (s), 1658 (m), 1590 (m), 1255 (m), 1151 (s), 1024 (m) cm$^{-1}$; ¹H-NMR (400 MHz, CDCl$_3$): δ 7.85-7.87 (m; 2H), 7.67 (d, J = 7.6 Hz; 1H), 7.54-7.58 (m; 1H), 7.44-7.48 (m; 3H), 7.32 (t, J = 7.6 Hz; 1H), 5.87 (s; 1H), 5.75 (s; 1H), 4.19 (d, J = 17.6 Hz; 1H), 3.20 (d, J = 17.6 Hz; 1H), 2.37 (s; 3H), 1.32 (s; 9H); $^{13}$C-NMR (100 MHz, CDCl$_3$): δ 201.45, 197.29, 168.03, 152.83, 147.86, 137.38, 136.20, 135.92, 134.99, 132.38, 129.87, 128.17, 127.88, 127.36, 122.06, 82.75, 65.57, 40.35, 27.63, 17.75; HRMS (ESI⁺): Calculated for C$_{24}$H$_{24}$O$_4$Na ([M + Na]$^+$): 399.1572, found: 399.1569; [α]$^D$ +153.6 (c 1.00, CHCl$_3$) for an enantiomerically enriched sample with 96.5:3.5 er. Enantiomeric ratio was determined by HPLC analysis (Daicel Chiralpak AS-H column, 254
nm, n-Hexane/EtOH = 98:2, 1.0 mL min⁻¹, τ_minor = 5.99 min, τ_major = 8.99 min). Absolute stereochemistry of 4ka is assigned in analogy with 4ba.

**tert-Butyl** (S)-5-bromo-2-(3-(4-chlorophenyl)-3-oxoprop-1-en-2-yl)-1-oxo-2,3-dihydro-1H-indene-2-carboxylate 4bd: Purification by silica gel (100-200 mesh) column chromatography (7% EtOAc in petroleum ether) afforded pure 4bd as a colorless oil (41 mg, 0.086 mmol; 86% yield). R_f = 0.50 (10% EtOAc in petroleum ether). FT-IR (neat): ν 2976 (w), 1715 (s), 1658 (m), 1591 (s), 1255 (m), 1151 (s), 1024 (m) cm⁻¹; ^1H-NMR (400 MHz, CDCl₃): δ 7.80 (d, J = 8.6 Hz; 2H), 7.68-7.70 (m; 2H), 7.55-7.57 (m; 1H), 7.44 (d, J = 17.9 Hz; 1H), 1.30 (s; 9H); ^13C-NMR (100 MHz, CDCl₃): δ 199.78, 195.89, 167.51, 155.26, 147.15, 139.04, 135.49, 134.02, 131.45, 131.41, 129.76, 128.61, 127.35, 125.85, 83.21, 65.69, 40.90, 27.63; HRMS (ESI+): Calculated for C_{23}H_{20}BrClO_{4}Na ([M + Na]⁺): 497.0131, found: 497.0134; [α]_D²²⁺173.6 (c 1.00, CHCl₃) for an enantiomerically enriched sample with 99:1 er. Enantiomeric ratio was determined by HPLC analysis (Daicel Chiralpak AS-H column, 254 nm, n-Hexane/EtOH = 95:5, 1.0 mL min⁻¹, τ_major = 5.45 min, τ_minor = 6.13 min). Absolute stereochemistry of 4bd is assigned in analogy with 4ba.

**tert-Butyl** (S)-4-oxo-5-(3-oxo-3-phenylprop-1-en-2-yl)-5,6-dihydro-4H-cyclopenta[b]thiophene-5-carboxylate 4la: Purification by silica gel (100-200 mesh) column chromatography (7% EtOAc in petroleum ether) afforded pure 4la as a colorless oil (32 mg, 0.087 mmol; 87% yield). R_f = 0.40 (10% EtOAc in petroleum ether). FT-IR (neat): ν 2976 (w), 1715 (s), 1591 (m), 1255 (m), 1151 (s), 1024 (m) cm⁻¹; ^1H-NMR (400 MHz, CDCl₃): δ 7.84-7.86 (m; 2H), 7.55-7.58 (m; 1H), 7.46 (t, J = 7.7 Hz; 2H), 7.36 (d, J = 5.2 Hz; 1H), 7.20 (d, J = 5.2 Hz; 1H), 5.94 (s; 1H), 5.80 (s; 1H), 4.31 (d, J = 17.9 Hz; 1H), 3.33 (d, J = 17.9 Hz; 1H), 1.32 (s; 9H); ^13C-NMR (100 MHz, CDCl₃): δ 197.25, 192.31, 170.85, 167.63, 147.25, 143.81, 137.26, 132.45, 131.46, 129.88, 128.21, 127.71, 119.90, 82.99, 71.24, 39.34, 27.65; HRMS (ESI+): Calculated for C_{21}H_{20}O₄SNa ([M + Na]⁺): 391.0980, found: 391.0980; [α]_D²²⁺123.1 (c 1.00, CHCl₃) for an enantiomerically enriched sample with 97:5:2.5 er. Enantiomeric ratio was determined by HPLC analysis (Daicel Chiralpak AS-H column, 254 nm, n-Hexane/EtOH = 95:5, 1.0 mL min⁻¹, τ_minor = 6.16 min, τ_major = 7.39 min). Absolute stereochemistry of 4la is assigned in analogy with 4ba.
tert-Butyl (S)-3,4-dimethyl-2-oxo-1-(3-oxo-3-phenylprop-1-en-2-yl)cyclopent-3-ene-1-carboxylate 4ma: Purification by silica gel (100-200 mesh) column chromatography (8% EtOAc in petroleum ether) afforded pure 4ma as a colorless oil (22 mg, 0.065 mmol; 65% yield). Rr = 0.40 (10% EtOAc in petroleum ether). FT-IR (neat): ν 2977 (w), 1712 (s), 1658 (m), 1593 (w), 1254 (s), 1151 (s), 1025 (m) cm⁻¹; ¹H-NMR (400 MHz, CDCl₃): δ 7.81-7.83 (m; 2H), 7.52-7.56 (m; 1H), 7.42-7.46 (m; 2H), 5.76 (s; 1H), 5.70 (s; 1H), 3.64 (d, J = 18.8 Hz; 1H), 2.66 (d, J = 18.8 Hz; 1H), 2.10 (s; 3H), 1.77 (s; 3H), 1.30 (s; 9H); ¹³C-NMR (100 MHz, CDCl₃): δ 203.40, 197.36, 170.99, 168.27, 147.80, 137.47, 134.29, 132.29, 129.86, 128.13, 126.96, 82.49, 63.28, 46.79, 27.67, 17.03, 8.34; HRMS (ESI⁺): Calculated for C₂₁H₂₄O₄Na ([M + Na]⁺): 363.1572, found: 363.1573; [α]D²² +83.4 (c 0.50, CHCl₃) for an enantiomerically enriched sample with 90:10 er. Enantiomeric ratio was determined by HPLC analysis (Phenomenex C1 column, 254 nm, n-Hexane/IPA = 95:5, 1.0 mL min⁻¹, t_major = 5.50 min, t_minor = 6.40 min). Absolute stereochemistry of 4ma is assigned in analogy with 4ba.

H. Less selective alkenylation products and unreactive substrates

Similar procedure as described for the preparation of 4aa was followed for the preparation S6-S8.
**tert-Butyl (S)-5-methoxy-1-oxo-2-(3-oxo-3-phenylprop-1-en-2-yl)-2,3-dihydro-1H-indene-2-carboxylate S6:** Purification by silica gel (100-200 mesh) column chromatography (10% EtOAc in petroleum ether) afforded pure S6 as a colorless oil (31 mg, 0.079 mmol; 79% yield). *R* = 0.25 (10% EtOAc in petroleum ether). **FT-IR (neat):** ν 2976 (w), 1728 (s), 1705 (s), 1658 (m), 1598 (s), 1257 (s), 1152 (s), 1026 (m) cm⁻¹; **¹H-NMR (400 MHz, CDCl₃):** δ 7.84-7.87 (m; 2H), 7.76 (d, *J* = 8.2 Hz; 1H), 7.53-7.58 (m; 1H), 7.43-7.47 (m; 2H), 5.88 (s; 1H), 5.75 (s; 1H), 4.24 (d, *J* = 17.7 Hz; 1H), 3.90 (s; 3H), 3.26 (d, *J* = 17.7 Hz; 1H), 1.31 (s; 9H); **¹³C-NMR (100 MHz, CDCl₃):** δ 199.03, 197.35, 168.27, 166.23, 157.04, 147.83, 137.44, 132.33, 129.88, 128.49, 128.44, 128.15, 127.35, 126.45, 116.12, 109.21, 82.65, 55.73, 41.38, 27.65; **HRMS (ESI+):** Calculated for C₂₄H₂₄O₅Na ([M + Na]⁺): 415.1521, found: 415.1525; [α]₂²D +161.3 (c 1.00, CHCl₃) for an enantiomerically enriched sample with 87:13 er. Enantiomeric ratio was determined by HPLC analysis (Daicel Chiralpak AS-H column, 254 nm, *n*-Hexane/EtOH = 95:5, 1.0 mL min⁻¹, *τ*minor = 7.65 min, *τ*major = 8.29 min). Absolute stereochemistry of S6 is assigned in analogy with 4ba.

**tert-Butyl (S)-1-oxo-2-(3-oxo-3-phenylprop-1-en-2-yl)-2,3-dihydro-1H-cyclopenta[a]naphthalene-2-carboxylate S7:** Purification by silica gel (100-200 mesh) column chromatography (8% EtOAc in petroleum ether) afforded pure S7 as a colorless oil (33 mg, 0.080 mmol; 80% yield). *R* = 0.30 (10% EtOAc in petroleum ether). **FT-IR (neat):** ν 2976 (w), 1711 (s), 1655 (m), 1602 (w), 1256 (m), 1152 (s), 1029 (m) cm⁻¹; **¹H-NMR (400 MHz, CDCl₃):** δ 9.17 (d, *J* = 8.1 Hz; 1H), 8.11 (d, *J* = 8.4 Hz; 1H), 7.87-7.93 (m; 3H), 7.69-7.73 (m; 1H), 7.55-7.61 (m; 3H), 7.35-7.49 (m; 2H), 5.93 (s; 1H), 5.77 (s; 1H), 4.39 (d, *J* = 18.1 Hz; 1H), 3.44 (d, *J* = 18.1 Hz; 1H), 1.34 (s; 9H); **¹³C-NMR (100 MHz, CDCl₃):** δ 201.32, 197.38, 168.16, 157.72, 148.13, 137.45, 136.96, 132.88, 132.37, 129.90, 129.58, 129.31, 129.19, 128.35, 128.18, 127.31, 126.81, 123.93, 123.76, 82.73, 65.86, 41.60, 27.70; **HRMS (ESI+):** Calculated for C₂₇H₂₄O₄Na ([M + Na]⁺): 412.1675, found: 412.1675; [α]₂²D +161.3 (c 1.00, CHCl₃) for an enantiomerically enriched sample with 83:16.5 er. Enantiomeric ratio was determined by HPLC analysis (Daicel Chiralpak IC column, 254 nm, *n*-Hexane/IPA = 95:5, 1.0 mL min⁻¹, *τ*minor = 10.99 min, *τ*major = 12.44 min). Absolute stereochemistry of S7 is assigned in analogy with 4ba.
tert-Butyl  

(S)-2-(4,4-dimethyl-3-oxopent-1-en-2-yl)-1-oxo-2,3-dihydro-1H-indene-2-carboxylate S8: Purification by silica gel (100-200 mesh) column chromatography (8% EtOAc in petroleum ether) afforded pure S8 as a colorless oil (19 mg, 0.055 mmol; 55% yield). Rf = 0.25 (10% EtOAc in petroleum ether). **FT-IR (neat):** ν 2968 (m), 2924 (m), 1722 (s), 1614 (m), 1152 (s), 1013 (w) cm⁻¹; **1H-NMR (400 MHz, CDCl₃):** δ 7.78 (d, J = 7.7 Hz; 1H), 7.50 (d, J = 7.7 Hz; 1H), 7.39-7.43 (m; 1H), 7.14 (d, J = 15.6 Hz; 1H), 6.74 (d, J = 15.6 Hz; 1H), 3.87 (d, J = 17.1 Hz; 1H), 3.30 (d, J = 17.1 Hz; 1H), 1.13 (s; 9H); **13C-NMR (100 MHz, CDCl₃):** δ 203.68, 198.88, 167.94, 152.10, 142.10, 135.53, 134.49, 127.98, 126.27, 125.28, 125.13, 82.99, 63.49, 43.21, 38.42, 27.78, 26.06; **HRMS (ESI+):** Calculated for C₂₁H₂₆O₄Na ([M + Na]+): 365.1729, found: 365.1730; Enantiomeric ratio was determined by HPLC analysis (Phenomenex C-1 column, 254 nm, n-Hexane/EtOH = 95:5, 1.0 mL min⁻¹, τminor = 5.01 min, τminor = 5.50 min). Absolute stereochemistry of S8 is assigned in analogy with 4ba.

I. Large scale reaction: procedure for umpolung alkenylation of the cyclic β-ketoester 1a with β-nitroenone 2a

In an oven-dried reaction tube equipped with an argon inlet, β-ketoester 1a (232.3 mg, 1.0 mmol, 1.0 equiv.) and the catalyst VII (23.3 mg, 0.05 mmol, 0.05 equiv.) was taken, put in vacuum, purged with argon. 2-MeTHF (5.0 mL) was added and the resulting solution was cooled to –60 °C. After 10 min, β-nitroenone 2a (212.6 mg, 1.20 mmol, 1.2 equiv.) in 5.0 mL 2-MeTHF was added dropwise and the resulting solution was stirred at –60 °C for 48 h. The reaction mixture was allowed to come to 25 °C and solvent was evaporated in vacuo to obtain a red oil. THF (5.0 mL) was added to it and the resulting solution was cooled to 0 °C. DBU (304 mg, 2.0 mmol, 2.0 equiv.) in 5.0 mL THF was added dropwise and the resulting reddish solution was stirred at 25 °C for 8 h. The reaction mixture was quenched by the addition of 3 (M) aqueous HCl solution and extracted with CHCl₃. The combined organic layer was dried over anh. Na₂SO₄, concentrated in vacuo to obtain a yellow crude oil which was purified by silica gel (100-200 mesh) column chromatography using 7% EtOAc in petroleum ether as eluent to obtain pure 4aa as a colorless oil (359 mg, 0.991 mmol; 99% yield). The aqueous layer was basified with NH₃ solution until pH = 9 and then extracted with CHCl₃. The combined organic layer was washed with brine, dried over anh. Na₂SO₄, concentrated in vacuo to obtain a brown solid which
was purified by silica gel (230-400 mesh) column chromatography using CH₂Cl₂/MeOH/NEt₃ (100:3:1) as eluent to obtain pure VII as an off-white solid (18 mg, 0.039 mmol; 77% yield).

J. Hydrogenation of umpolung alkenylation product 4aa

In an oven-dried 10 mL 2-neck round-bottom flask, the umpolung alkenylation product 4aa (50.0 mg, 0.138 mmol, 1.0 equiv.) was taken in 1.4 mL abs. MeOH along with 10% Pd/C (15.0 mg, 0.014 mmol, 0.1 equiv.) and hydrogenated at 25 °C under atmospheric H₂ pressure for 24 h. The reaction mixture was then filtered through a celite bed and washed with MeOH. The filtrate was dried over anh. Na₂SO₄, concentrated in vacuo to obtain a yellow oil which was purified by silica gel (100-200 mesh) column chromatography using 6% EtOAc in petroleum ether as eluent to obtain 5 as a colorless oil (34 mg, 0.093 mmol; 68% yield). R_f = 0.40 (10% EtOAc in petroleum ether). Diastereoselectivity of the product 5 was determined by 1H-NMR of the crude reaction mixture and found to be >20:1. FT-IR (neat): ν 1715 (s), 1658 (m), 1591 (m), 1255 (m) cm⁻¹; ¹H-NMR (400 MHz, CDCl₃): δ 8.04-8.06 (m; 2H), 7.80 (d, J = 7.7 Hz; 1H), 7.62-7.66 (m; 2H), 7.56-7.60 (m; 2H), 7.39 (t, J = 7.0 Hz; 1H), 4.68 (q, J = 7.5 Hz; 1H), 4.00 (d, J = 18.1 Hz; 1H), 3.55 (d, J = 18.1 Hz; 1H), 1.21 (s; 9H), 0.98 (d, J = 7.5 Hz; 3H); ¹³C-NMR (100 MHz, CDCl₃): δ 202.95, 202.76, 168.90, 155.85, 136.11, 135.48, 135.37, 133.05, 128.72, 128.53, 128.36, 124.57, 82.23, 44.25, 34.45, 27.53, 13.16; HRMS (ESI+): Calculated for C₂₃H₂₄O₄Na ([M + Na]⁺): 387.1572, found: 387.1573; [α]D²² +20.36 (c 1.00, CHCl₃) for an enantiomerically enriched sample with 97.5:2.5 er. Enantiomeric ratio was determined by HPLC analysis (Daicel Chiralpak AD-H column, 254 nm, n-Hexane/IPA = 90:10, 1.0 mL min⁻¹, τ_minor = 8.04 min, τ_major = 9.45 min).

K. Chemoselective reduction of umpolung alkenylation product 4aa

In an oven-dried reaction tube equipped with an argon inlet, the umpolung alkenylation product 4aa (50.0 mg, 0.138 mmol, 1.0 equiv.) was taken in 1.4 mL toluene and cooled to −40 °C. To this solution, 1 (M) DIBAL-H solution in cyclohexane (0.42 mL, 0.42 mmol, 3.0 equiv.) was added dropwise and the resulting solution was stirred at −40 °C for 12 h. The reaction mixture was quenched with 2 drops of EtOAc and 2 drops of 10% aqueous NaOH solution,
brought to 25 °C and filtered through a whatmann filter paper. The filtrate was dried over anh. Na₂SO₄, concentrated in vacuo to obtain colorless oil which was purified by silica gel (100-200 mesh) column chromatography using 10% EtOAc in petroleum ether as eluent to obtain 6 as a white solid (31 mg, 0.085 mmol; 62% yield). Rₚ = 0.35 (20% EtOAc in petroleum ether). M.P. = 65-67 °C. Diastereoselectivity of the product 6 was determined by ¹H-NMR of the crude reaction mixture and found to be >20:1. FT-IR (neat): ν 2976 (w), 1655 (m), 1591 (m), 1151 (s) cm⁻¹; ¹H-NMR (400 MHz, CDCl₃): δ 7.81-7.84 (m; 2H), 7.54-7.58 (m; 1H), 7.43-7.47 (m; 3H), 7.26-7.28 (m; 2H), 7.22-7.24 (m; 1H), 5.85 (s; 1H), 5.60 (s; 1H), 5.45 (d, J = 6.6 Hz; 1H), 3.83 (d, J = 16.1 Hz; 1H), 3.72 (d, J = 7.2 Hz; 1H), 3.25 (d, J = 16.1 Hz; 1H), 1.27 (s; 9H); ¹³C-NMR (100 MHz, CDCl₃): δ 198.15, 171.82, 148.77, 142.64, 140.54, 137.58, 132.59, 130.02, 128.68, 128.18, 127.15, 124.90, 124.48, 124.22, 82.21, 81.70, 62.75, 40.18, 27.73; HRMS (ESI+): Calculated for C₂₃H₂₄O₄Na ([M + Na]⁺): 387.1572, found: 387.1572; [α]D²² +157.2 (c 1.00, CHCl₃) for an enantiomerically enriched sample with 97.5:2.5 er. Enantiomeric ratio was determined by HPLC analysis (Daicel Chiralpak AD-H column, 254 nm, n-Hexane/EtOH = 95:5, 1.0 mL min⁻¹, τ_minor = 11.54 min, τ_major = 13.79 min).

L. Cu(I)-mediated 1,4-addition reaction of Meli to the umpolung alkenylation product 4aa

In an oven-dried 10 mL round-bottom flask, copper (I) cyanide (8.5 mg, 0.1 mmol, 1.0 equiv.) was taken in 1.0 mL Et₂O and cooled to 0 °C. To this solution, 3 (M) methyl lithium solution in diethoxymethane (66 µL, 0.2 mmol, 2.0 equiv.) was added and the resulting solution was stirred at 0 °C for 15 min. The umpolung alkenylation product 4aa (36.2 mg, 0.1 mmol, 1.0 equiv.) in 1 mL Et₂O was added and the resulting solution was brought to 25 °C and stirred at 25 °C for 24 h. The reaction mixture was quenched with water and extracted with EtOAc. The combined organic layer was dried over anh. Na₂SO₄, concentrated in vacuo to obtain colorless oil which was purified by silica gel (100-200 mesh) column chromatography using 5% EtOAc in petroleum ether as eluent to obtain 7a as a colorless oil (36 mg, 0.095 mmol, 95% yield). Rₚ = 0.38 (10% EtOAc in petroleum ether). Diastereoselectivity of the product 7a was determined by ¹H-NMR of the crude reaction mixture and found to be 15:1. FT-IR (neat): ν 2976 (w), 1715 (s), 1658 (m), 1591 (m), 1255 (m), 1151 (s) cm⁻¹; ¹H-NMR (400 MHz, CDCl₃): δ 7.91 (d, J = 8.4 Hz; 2H), 7.51-7.59 (m; 4H), 7.40-7.44 (m; 2H), 7.26-7.30 (m; 1H), 4.76 (dd, J = 5.9, 8.0 Hz; 1H), 3.84 (d, J = 16.6 Hz; 1H), 3.66 (d, J = 16.6 Hz; 1H), 1.88-1.96 (m; 1H), 1.75-1.81 (m; 1H), 1.38 (s; 9H), 0.94 (t, J = 7.5 Hz; 3H); ¹³C-NMR (100 MHz, CDCl₃): δ 203.72, 201.69, 168.60, 154.61, 138.10, 135.00, 134.91, 133.05, 128.56, 128.42, 127.05, 126.07, 124.33, 82.33, 65.77,
49.27, 33.44, 27.62, 24.24, 12.88; **HRMS (ESI+):** Calculated for C_{24}H_{26}O_{4}Na ([M + Na]^+): 401.1729, found: 401.1730; \([\alpha]_D^{22} +144.7\) (c 1.00, CHCl\(_3\)) for an enantiomerically enriched sample with 97.5:2.5 er. Enantiomeric ratio was determined by HPLC analysis (Daicel Chiralpak AD-H column, 254 nm, \(n\)-Hexane/EtOH = 95:5, 1.0 mL min\(^{-1}\), \(\tau_{\text{minor}} = 9.28\) min, \(\tau_{\text{major}} = 11.00\) min).

**Compound 7b:** Similar procedure as described for the preparation of 7a was followed. Purified by silica gel (100-200 mesh) column chromatography using 6% EtOAc in petroleum ether as eluent to obtain 7b as a colorless oil (53 mg, 0.095 mmol, 95% yield). \(R_f = 0.40\) (10% EtOAc in petroleum ether). Diastereoselectivity of the product 7b was determined by \(^1\)H-NMR of the crude reaction mixture and found to be >20:1. **FT-IR (neat):** \(\nu\) 1718 (s), 1658 (m), 1589 (m), 1255 (m), 1151 (s), 1024 (m) cm\(^{-1}\); \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.57-7.61 (m; 3H), 7.50-7.54 (m; 2H), 7.36-7.40 (m; 1H), 7.28 (d, J = 7.3 Hz; 1H), 7.06-7.25 (m; 7H), 5.08 (dd, J = 5.2, 8.9 Hz; 1H), 3.96 (d, J = 16.6 Hz; 1H), 3.72 (d, J = 16.6 Hz; 1H), 3.11-3.13 (m; 2H), 1.38 (s; 9H); \(^{13}\)C-NMR (100 MHz, CDCl\(_3\)): \(\delta\) 203.12, 201.38, 168.30, 154.58, 138.49, 138.01, 135.15, 134.82, 132.75, 129.15, 128.40, 128.32, 128.03, 127.14, 126.45, 126.12, 124.38, 82.51, 65.65, 50.09, 36.76, 33.45, 27.64; **HRMS (ESI+):** Calculated for C_{29}H_{28}O_{4}Na ([M + Na]^+): 463.1885, found: 463.1885; \([\alpha]_D^{22} +211.3\) (c 1.00, CHCl\(_3\)) for an enantiomerically enriched sample with 97.5:2.5 er. Enantiomeric ratio was determined by HPLC analysis (Daicel Chiralpak AD-H column, 254 nm, \(n\)-Hexane/IPA = 90:10, 1.0 mL min\(^{-1}\), \(\tau_{\text{minor}} = 10.23\) min, \(\tau_{\text{major}} = 12.27\) min).

**M. Single crystal X-ray diffraction analysis of 4ba**

A single crystal of 4ba (recrystallized from EtOH/CHCl\(_3\) 1:1 at 25 °C) was mounted and the diffraction data were collected at 150 K on a Bruker D8 Quest CMOS diffractometer using SMART/SAINT software. Intensity data were collected using graphite-monochromatized Mo-K\(_a\) radiation (0.71073 Å) at 110 K. The structures were solved by direct methods using the SHELX-97 and refined by full-matrix least squares on \(F^2\). Empirical absorption corrections were applied with SADABS. All Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included in geometric positions. Structure was drawn using Ortep. The crystallographic refinement parameters are given below:

**Table 1. Crystal data and structure refinement for 4ba:**

<table>
<thead>
<tr>
<th>Identification code</th>
<th>4ba</th>
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<tbody>
<tr>
<td>Empirical formula</td>
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<tr>
<td>Formula weight</td>
<td>441.31</td>
</tr>
<tr>
<td>Temperature</td>
<td>150(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
</tbody>
</table>
Crystal system: monoclinic
Space group: P 2₁
Unit cell dimensions:
- \(a = 8.473(5) \text{ Å}\)
- \(b = 10.542(5) \text{ Å}\)
- \(c = 11.891(5) \text{ Å}\)
- \(\alpha = 90°\)
- \(\beta = 106.339°\)
- \(\gamma = 90°\)
Volume: \(1019.2(9) \text{ Å}^3\)

Z: 2
Density (calculated): 1.438 Mg/mm³
Absorption coefficient: 2.042 mm⁻¹

F(000): 452.0

2Θ range for data collection: 6.328 to 55.19°
Index ranges:
- \(-11 \leq h \leq 10\)
- \(-13 \leq k \leq 13\)
- \(-15 \leq l \leq 15\)

Reflections collected: 36769
Independent reflections: 4681 [\(R_{int} = 0.0398\)]

Refinement method: Full-matrix least-squares on \(F^2\)

Data / restraints / parameters: 4681 / 1 / 338

Goodness-of-fit on \(F^2\): 1.042

Final R indices [\(I > 2\sigma (I)\)]:
- \(R_1 = 0.0323\)
- \(\omega R_2 = 0.0767\)

R indices (all data):
- \(R_1 = 0.0368\)
- \(\omega R_2 = 0.0785\)

Absolute structure parameter: 0.001(8)

Largest diff. peak and hole: 0.39 and -0.22 e.Å⁻³

**Table 2. Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for 4ba.** \(U_{eq}\) is defined as 1/3 of of the trace of the orthogonalised \(U_{ii}\) tensor.

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<th>Atom</th>
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<th>y</th>
<th>z</th>
<th>(U_{eq})</th>
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<td>O002</td>
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<tr>
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<td>8065.8(19)</td>
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<tr>
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<td>C007</td>
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<td>87(4)</td>
<td>-13309(4)</td>
<td>8972(3)</td>
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Table 3. Anisotropic Displacement Parameters (Å²×10³) for 4ba. The Anisotropic displacement factor exponent takes the form: \(-2\pi^2[h^2a^*2U_{11}+2hkab^*U_{12}+...]\)

<table>
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<th>Atom</th>
<th>(U_{11})</th>
<th>(U_{22})</th>
<th>(U_{33})</th>
<th>(U_{23})</th>
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<td>C007</td>
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## Table 4. Bond Lengths for 4ba

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<th>Length/Å</th>
<th>Atom</th>
<th>Atom</th>
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<td>C009</td>
<td>C027</td>
<td>1.523(6)</td>
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<td>C010</td>
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<td>1.406(5)</td>
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ORTEP representation of the X-ray structure of (S)-4ba (thermal ellipsoids at 30% probability)