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

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SUPPORTING INFORMATION: PART A

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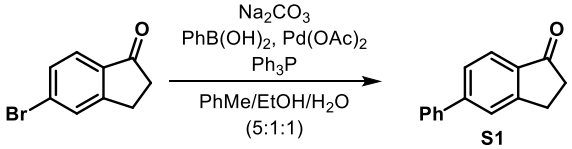
General information: Unless stated otherwise, all reactions were carried out with distilled and dried solvents under an atmosphere of N_2 or argon, oven (120 °C) dried glassware with standard vacuum line techniques were used. Organic solvents used for carrying out reactions were dried using standard methods. All work up and purification were carried out with reagent grade solvents in air. Organometallic reagents were titrated using standard procedure[1] to determine their concentration. Thin-layer chromatography was performed using Merck silica gel 60 F_{254} 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 (^{1}H) and 100 MHz (^{13}C). Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as internal standard ($CDCl_3$: δ 7.26 for ^{1}H-NMR and $CDCl_3$: δ 77.0 for ^{13}C NMR). For ^{1}H 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]



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/H_2O (5:1:1) and degassed for 15 min. Palladium(II) acetate (4.5 mg, 0.02 mmol,

[1] J. Leonard, B. Lygo and G. Procter, *Advanced Practical Organic Chemistry*, 3rd ed.; CRC Press, 2010.

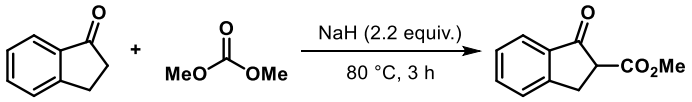
[2] A. Ray Choudhury and S. Mukherjee, *Chem. Sci.* 2016, **7**, 6940-6945.

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_2SO_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). $\mathbf{R_f}$ = 0.25 (20% EtOAc in petroleum ether). **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 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, $CDCl_3$):** δ 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.[3]

B. Preparation of cyclic β-ketoesters:

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

Methyl 1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (**S2**) was prepared following a modified literature procedure.[4]



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_2SO_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). $\mathbf{R_f}$ = 0.55 (20% EtOAc in petroleum ether). **FT-IR (neat):** ν 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. Signals corresponding to the keto tautomer: δ 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;

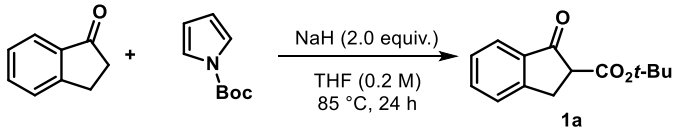
[3] H. Wang, L. Li, X.-F. Bai, W.-H. Deng, Z.-J. Zheng, K.-F. Yang and L.-W. Xu, *Green Chem.*, 2013, **15**, 2349-2355.

[4] A. M. R. Smith, D. Billen and K. K. Hii, *Chem. Commun.* 2009, 3925-3927.

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); **^{13}C-NMR (100 MHz, CDCl$_3$):** 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 $C_{11}H_{10}O_3Na$ ([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-1*H*-indene-2-carboxylate (1a)

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

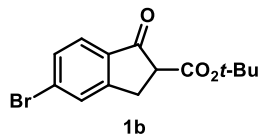


In an oven-dried 100 mL 2-neck round-bottom flask equipped with a reflux condenser, 60% sodium hydride in mineral oil (605 mg, 15.13 mmol, 2.0 equiv.) was taken in 30 mL THF under positive argon pressure. To this suspension, 1-indanone (1.0 g, 7.56 mmol, 1.0 equiv.) in 7.5 mL THF was added at 25 °C. 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 reluxing. 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 Et_2O. The combined organic layer was dried over anh. Na_2SO_4, 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). **R_f** = 0.45 (5% EtOAc in petroleum ether). **FT-IR (neat):** ν 2978 (m), 1712 (s), 1643 (w), 1150 (s) cm^{-1}; **^{1}H-NMR (400 MHz, CDCl$_3$):** 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), 3.50 (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); **^{13}C-NMR (100 MHz, CDCl$_3$):** 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 $C_{14}H_{16}O_3Na$ ([M + Na]$^+$): 255.0997, found: 255.0997.

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

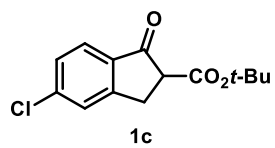
[5] T. A. Moss, D. R. Fenwick and D. J. Dixon, *J. Am. Chem. Soc.* 2008, **130**, 10076-10077.

***tert*-Butyl 5-bromo-1-oxo-2,3-dihydro-1*H*-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). **R_f** = 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), 7.50-7.52 (m; 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 $C_{14}H_{15}BrO_3Na$ ($[M + Na]^+$): 333.0102, found: 333.0101.



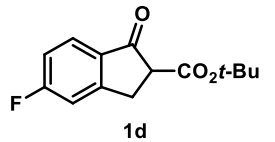
1b

***tert*-Butyl 5-chloro-1-oxo-2,3-dihydro-1*H*-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. **R_f** = 0.45 (5% EtOAc in petroleum ether). **M.P.** = 69-70 °C; **FT-IR (neat):** ν 2978 (m), 1715 (s), 1649 (m), 1154 (s) 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, 126.67, 125.56, 82.23, 54.38, 29.98, 28.40, 27.94; **HRMS (ESI+):** Calculated for $C_{14}H_{15}ClO_3Na$ ($[M + Na]^+$): 289.0607, found: 289.0607.



1c

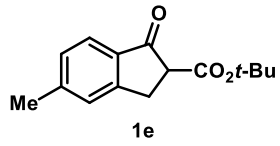
***tert*-Butyl 5-fluoro-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate 1d:** Purification by silica gel (100-200 mesh) column chromatography (1% EtOAc in petroleum ether) afforded pure **1d** as a light brown solid (325 mg, 1.299 mmol; 65% yield). **R_f** = 0.45 (5% EtOAc in petroleum ether). **M.P.** = 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,



1d

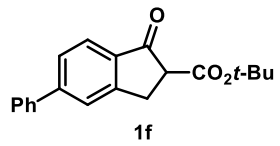
167.95, 167.33 (d, *J* = 257.6 Hz), 156.57 (d, *J* = 10.6 Hz), 131.80, 126.80 (d, *J* = 10.6 Hz), 116.02 (d, *J* = 23.8 Hz), 113.13 (d, *J* = 22.5 Hz), 82.17, 54.51, 30.12, 28.41, 27.94; **HRMS (ESI+):** Calculated for $C_{14}H_{15}FO_3Na$ ($[M + Na]^+$): 273.0903, found: 273.0900.

***tert*-Butyl 5-methyl-1-oxo-2,3-dihydro-1*H*-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). $\mathbf{R_f}$ = 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 $C_{15}H_{18}O_3Na$ ($[M + Na]^+$): 269.1154, found: 269.1162.



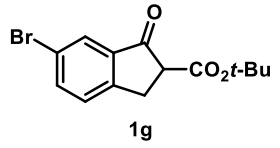
1e

***tert*-Butyl 1-oxo-5-phenyl-2,3-dihydro-1*H*-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). $\mathbf{R_f}$ = 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 199.48, 168.39, 154.36, 148.38, 140.08, 134.37, 128.99, 128.46, 127.52, 127.17, 124.97, 124.92, 82.08, 54.69, 30.38, 28.05; **HRMS (ESI+):** Calculated for $C_{20}H_{20}O_3Na$ ($[M + Na]^+$): 331.1310, found: 331.1313.



1f

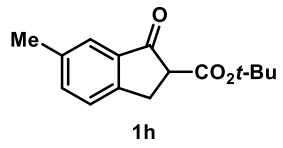
***tert*-Butyl 6-bromo-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate 1g:** Purification by silica gel (100-200 mesh) column chromatography (1% EtOAc in petroleum ether) afforded pure **1g** as an off-white solid (275 mg, 0.884 mmol; 44% yield). $\mathbf{R_f}$ = 0.35 (5% EtOAc in petroleum ether). **M.P.** = 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



1g

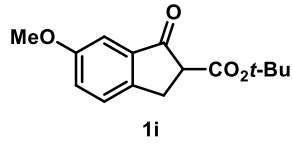
Hz; 1H), 3.26 (dd, *J* = 8.2, 17.2 Hz; 1H), 1.48 (s; 9H); Representative signals corresponding to the enol tautomer: δ 7.73 (d, *J* = 1.6 Hz; 1H), 7.49 (dd, *J* = 1.9, 8.1 Hz; 1H), 7.29 (d, *J* = 8.0 Hz; 1H), 3.41 (s; 2H), 1.56 (s; 9H); **^{13}C-NMR (100 MHz, $CDCl_3$):** Signals corresponding to both 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 $C_{14}H_{15}BrO_3Na$ ([M + Na]$^+$): 333.0102, found: 333.0103.

***tert*-Butyl 6-methyl-1-oxo-2,3-dihydro-1*H*-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). **R_f** = 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}; **^{1}H-NMR (400 MHz, $CDCl_3$):** 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), 7.35 (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); **^{13}C-NMR (100 MHz, $CDCl_3$):** 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 $C_{15}H_{18}O_3Na$ ([M + Na]$^+$): 269.1154, found: 269.1155.



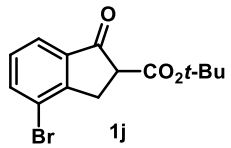
1h

***tert*-Butyl 6-methoxy-1-oxo-2,3-dihydro-1*H*-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). **R_f** = 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}; **^{1}H-NMR (400 MHz, $CDCl_3$):** The compound exists as a 10.0:1 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; 2H), 1.56 (s; 9H); **^{13}C-NMR (100 MHz, $CDCl_3$):** Signals corresponding to both tautomers: δ 199.97, 168.37, 159.60, 146.56, 136.63, 127.14, 124.67, 105.57, 81.97, 55.58, 55.01, 29.66, 27.99; **HRMS (ESI+):** Calculated for $C_{15}H_{18}O_4Na$ ([M + Na]$^+$): 285.1103, found: 285.1104.



1i

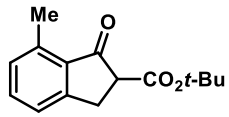
***tert*-Butyl 4-bromo-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate 1j:** Purification by silica gel (100-200 mesh) column chromatography (1% EtOAc in petroleum ether) afforded pure **1j** as a colorless oil (565 mg, 1.816 mmol; 91% yield) which gradually solidified. **R_f** = 0.45 (5% EtOAc in petroleum ether). **M.P.** =



1j

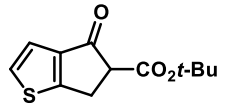
75-77 °C; **FT-IR (neat):** ν 2977 (m), 1718 (s), 1649 (s), 1370 (s), 1248 (s), 1159 (s) cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** The compound exists as a 2.5:1 mixture of keto/enol tautomer. Signals corresponding to the keto tautomer: δ 7.76 (d, *J* = 7.7 Hz; 1H), 7.69 (d, *J* = 7.6 Hz; 1H), 7.24-7.30 (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); **^{13}C-NMR (100 MHz, $CDCl_3$):** 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 $C_{14}H_{15}BrO_3Na$ ($[M + Na]^+$): 333.0102, found: 333.0103.

***tert*-Butyl 7-methyl-1-oxo-2,3-dihydro-1*H*-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). **R_f** = 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}; **^{1}H-NMR (400 MHz, $CDCl_3$):** 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); **^{13}C-NMR (100 MHz, $CDCl_3$):** 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 $C_{15}H_{18}O_3Na$ ($[M + Na]^+$): 269.1154, found: 269.1154.



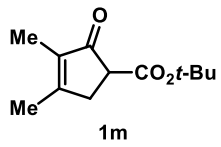
1k

***tert*-Butyl 4-oxo-5,6-dihydro-4*H*-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). **R_f** = 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}; **^{1}H-NMR (400 MHz, $CDCl_3$):** 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); **^{13}C-NMR (100 MHz, $CDCl_3$):** 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 $C_{12}H_{14}O_3SNa$ ($[M + Na]^+$): 261.0561, found: 261.0564.



1l

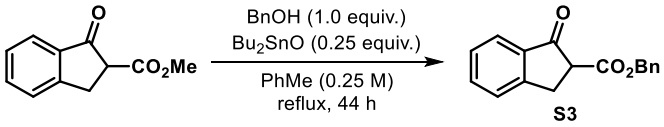
***tert*-Butyl 3,4-dimethyl-2-oxocyclopent-3-ene-1-carboxylate 1m:** Purification by silica gel (100-200 mesh) column chromatography (6% EtOAc in petroleum ether) afforded pure **1m** as a brown oil (165 mg, 0.785 mmol; 62% yield). $\mathbf{R_f}$ = 0.25 (10% EtOAc in petroleum ether). **FT-IR (neat):** ν 2977 (m), 1713 (s), 1649 (m), 1371 (m), 1267 (s), 1152 (s) cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** 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); **^{13}C-NMR (100 MHz, $CDCl_3$):** 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; **HRMS (ESI+):** Calculated for $C_{12}H_{18}O_3Na$ ($[M + Na]^+$): 233.1154, found: 233.1154.



1m

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

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



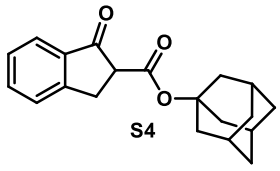
S3

In an oven-dried 50 mL round-bottom flask equipped with a reflux condenser and an argon inlet, methyl 1-oxo-2,3-dihydro-1*H*-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. Na_2SO_4, 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. $\mathbf{R_f}$ = 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}; **^{1}H-NMR (400 MHz, $CDCl_3$):** 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); **^{13}C-NMR (100 MHz, $CDCl_3$):** 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,

[6] A. M. R. Smith, H. S. Rzepa, A. J. P. White, D. Billen and K. K. Hii, *J. Org. Chem.* 2010, **75**, 3085-3096.

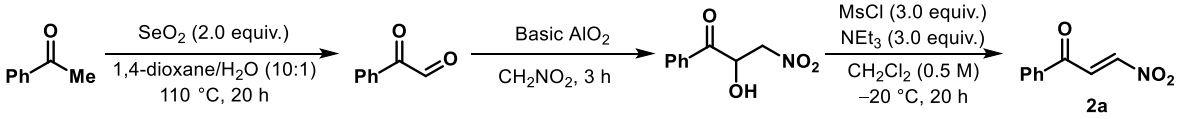
126.52, 124.68, 120.76, 67.29, 53.26, 30.25; **HRMS (ESI+):** Calculated for $C_{17}H_{14}O_3Na$ ([M + Na]$^+$): 289.0841, found: 289.0843.

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 (1*S*, 3*S*)-adamantan-1-yl 1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate **S4** as a white solid (500 mg, 1.687 mmol; 34% yield). $\mathbf{R_f}$ = 0.55 (10% EtOAc in petroleum ether). **M.P.** = 100-102 °C; **FT-IR (neat):** ν 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: 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), 3.61 (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: δ 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: δ 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 $C_{20}H_{22}O_3Na$ ([M + Na]$^+$): 333.1467, found: 133.1467.

C. Preparation of β-nitroenone: Representative procedure for the synthesis of (*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_2O (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_2SO_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.

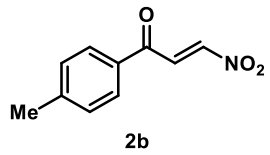
In an oven-dried 250 mL round-bottom flask, 2-oxo-2-phenylacetaldehyde (5.74 g, 42.79 mmol, 1.0 equiv.) was taken in 85 mL nitromethane along with basic alumina (10.7 g). The resulting mixture was stirred vigorously at 25 °C for 3 h. The reaction mixture was then filtered through a pad of celite and 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, 22.032 mmol, 1.0 equiv.) was taken in 44 mL CH_2Cl_2 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 $CHCl_3$. The combined organic layer was dried over anh. Na_2SO_4, 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). $\mathbf{R_f}$ = 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}; **^{1}H-NMR (400 MHz, $CDCl_3$):** 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); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 186.99, 148.09, 135.85, 134.82, 129.62, 129.20, 128.91. Spectral data are in agreement with the literature.[7]

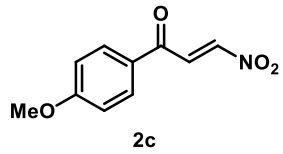
The same procedure as above was followed for the synthesis of **2b-p**.

(*E*)-3-Nitro-1-(p-tolyl)prop-2-en-1-one 2b: Purification by silica gel (230-400 mesh) column chromatography (2% Et_2O in petroleum ether) afforded pure **2b** as a yellow oil (125 mg, 0.654 mmol; 18% yield). $\mathbf{R_f}$ = 0.35 (5% EtOAc in petroleum ether). **FT-IR (neat):** ν 3104 (m), 1677 (s), 1595 (m), 1532 (s), 1353 (s) cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.11 (d, *J* = 13.3 Hz; 1H), 7.90 (d, *J* = 8.2 Hz; 2H), 7.68 (d, *J* = 13.3 Hz; 1H), 7.35 (d, *J* = 8.2 Hz; 2H), 2.46 (s; 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 186.42, 147.92, 146.26, 133.49, 129.92, 129.81, 129.08, 21.86; **HRMS (ESI+):** Calculated for $C_{10}H_9NO_3Na$ ($[M + Na]^+$): 214.0480, found: 214.0479.



2b

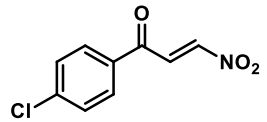
(*E*)-1-(4-Methoxyphenyl)-3-nitroprop-2-en-1-one 2c: Purification by silica gel (230-400 mesh) column chromatography (3% EtOAc in petroleum ether) afforded pure **2c** as a yellow solid (612 mg, 2.718 mmol; 34% yield). $\mathbf{R_f}$ = 0.50 (10% EtOAc in petroleum ether). **M.P.** = 76-78 °C; **FT-IR (neat):** ν 3103 (w), 1677 (s), 1589 (m), 1533 (s), 1354 (m) cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.12 (d, *J* = 13.3 Hz; 1H), 7.98-8.00 (m; 2H), 7.68 (d, *J* = 13.3 Hz; 1H), 7.00-7.03 (m; 2H), 3.92 (s; 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 184.99, 165.03, 147.71, 131.50, 129.87, 129.05, 114.49, 55.70.



2c

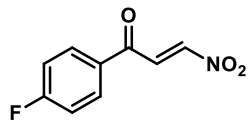
[7] K. Xu, Z. Zhang, P. Qian, Z. Zha and Z. Wang, *Chem. Commun.*, 2015, **51**, 11108-11111.

(*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). $\mathbf{R_f}$ = 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}; **^{1}H-NMR (400 MHz, $CDCl_3$):** 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); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 185.76, 148.41, 141.66, 134.17, 130.24, 129.62, 129.05.



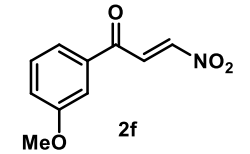
2d

(*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). $\mathbf{R_f}$ = 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}; **^{1}H-NMR (400 MHz, $CDCl_3$):** 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); **^{13}C-NMR (100 MHz, $CDCl_3$):** 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).



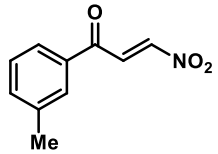
2e

(*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. $\mathbf{R_f}$ = 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}; **^{1}H-NMR (400 MHz, $CDCl_3$):** 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); **^{13}C-NMR (100 MHz, $CDCl_3$):** 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 $C_{10}H_9NO_4Na$ ($[M + Na]^+$): 230.0429, found: 230.0430.



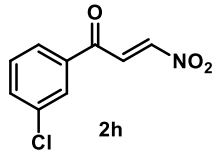
2f

(*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). $\mathbf{R_f}$ = 0.35 (5% EtOAc in petroleum ether). **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); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 187.10, 147.95, 139.24, 135.89, 135.65, 129.82, 129.32, 129.04, 126.19, 21.27.



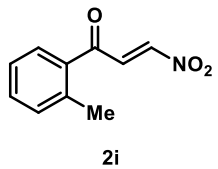
2g

(*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). $\mathbf{R_f}$ = 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); **^{13}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.



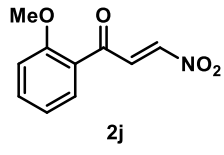
2h

(*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). $\mathbf{R_f}$ = 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); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 187.10, 147.95, 139.24, 135.89, 135.65, 129.82, 129.32, 129.04, 126.19, 21.27.



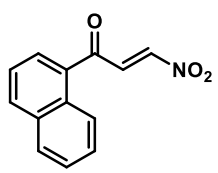
2i

(*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). $\mathbf{R_f}$ = 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); **^{13}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.



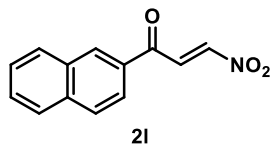
2j

(*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). $\mathbf{R_f}$ = 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); **^{13}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.



2k

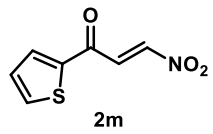
(*E*)-1-(Naphthalen-2-yl)-3-nitroprop-2-en-1-one 2l: Similar procedure as described for the preparation of **2a** was followed. Purification by silica gel (230-400 mesh) column chromatography (2% EtOAc in petroleum ether) afforded pure **2l** as a yellow solid (470 mg, 2.068 mmol; 23% yield). $\mathbf{R_f}$ = 0.30 (5%



2l

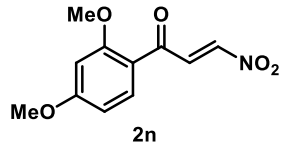
EtOAc in petroleum ether). **M.P.** = 70-72 °C; **FT-IR (neat):** ν 1669 (s), 1609, 1524 (s), 1353 (s) cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.49 (s; 1H), 8.27 (d, *J* = 13.2 Hz; 1H), 8.00-8.05 (m; 2H), 7.96 (d, *J* = 8.7 Hz; 1H), 7.91 (d, *J* = 8.1 Hz; 1H), 7.74 (d, *J* = 13.2 Hz; 1H), 7.66-7.70 (m; 1H), 7.60-7.64 (m; 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** 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). **R_f** = 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}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.98 (d, *J* = 13.2 Hz; 1H), 7.90-7.91 (m; 1H), 7.87-7.88 (m; 1H), 7.73 (d, *J* = 13.2 Hz; 1H), 7.25-7.27 (m; 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 178.54, 147.78, 143.57, 137.23, 134.42, 129.36, 128.96.



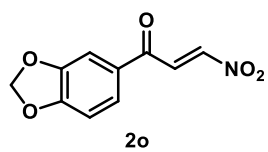
2m

(*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). **R_f** = 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}; **^{1}H-NMR (400 MHz, $CDCl_3$):** 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); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 185.65, 166.33, 161.75, 145.37, 135.41, 133.48, 119.67, 106.38, 98.30, 55.86, 55.73.



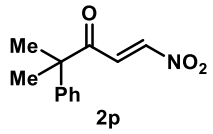
2n

(*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). **R_f** = 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}; **^{1}H-NMR (400 MHz, $CDCl_3$):** 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); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 184.61, 153.55, 149.00, 147.79, 130.95, 129.71, 126.30, 108.29, 108.07, 102.40.



2o

(*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). **R_f** = 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}; **^{1}H-NMR (400 MHz, $CDCl_3$):** 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),

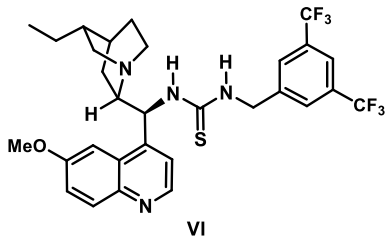


2p

1.57 (s; 6H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 198.61, 147.34, 141.09, 129.44, 129.40, 127.95, 126.33, 52.23, 24.32.

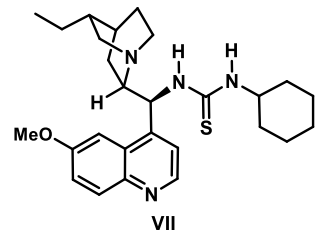
D. Preparation of bifunctional (thio)urea catalysts

The bifunctional (thio)urea catalysts were prepared following reported literature procedure.[8]



VI

Purified by silica gel (100-200 mesh) column chromatography using 100:3:1 CH_2Cl_2/MeOH/Et_3N 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)**: ν 2932 (m), 1509 (m), 1384 (s), 1278 (s) cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 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_3OD):** δ 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 $C_{30}H_{32}F_6N_4OSH$ ($[M+H]^+$): 611.2279, Found: 611.2279; **$[\alpha]_D^{24}$** –67.5 (*c* 1.0, $CHCl_3$).



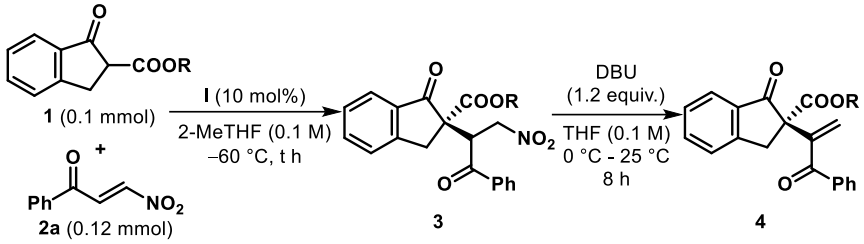
VII

Purified by silica gel (100-200 mesh) column chromatography using 100:3:1 CH_2Cl_2/MeOH/Et_3N 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)**: ν 3257 (br m), 2931 (s), 1621 (m), 1508 (m), 1230 (s), 1029 (m) cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 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), 5.16 (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_3OD):** δ 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 $C_{27}H_{38}N_4OSH$ ($[M+H]^+$): 467.2845, Found: 467.2845; **$[\alpha]_D^{24}$** –120.9 (*c* 1.0, $CHCl_3$).

[8] (a) C. B. Tripathi and S. Mukherjee, *Org. Lett.* 2015, **17**, 4424-4427; (b) M. S. Manna and S. Mukherjee, *J. Am. Chem. Soc.* 2015, **137**, 130-133; (c) C. B. Tripathi and S. Mukherjee, *Angew. Chem., Int. Ed.* 2013, **52**, 8450-8453; (d) M. S. Manna, V. Kumar and S. Mukherjee, *Chem. Commun.* 2012, **48**, 5193-5195.

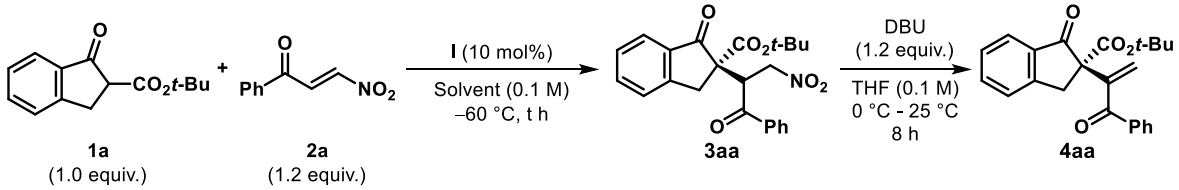
E. Reaction conditions optimization

Optimization of ester substituents of β-ketoesters



Entry	R	*t* [h]	dr of 3	yield [%] of 3	yield [%] of 4	er of 4
1	Me	10	2:1	99	80	80:20
2	*t*-Bu	48	>20:1	88	85	94.5:5.5
3	1-Adamantyl	60	>20:1	92	70	80.5:19.5
4	Bn	44	1:1	94	67	52:48

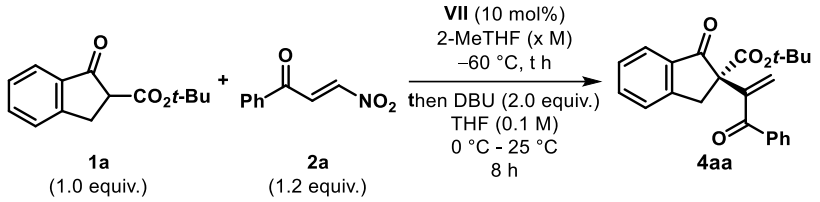
Solvent optimization[a]



Entry	Catalyst	Solvent	*t* [h]	dr of 3aa[b]	Yield [%] of 3aa[c]	Yield [%] of 4aa[c]	er of 4aa[d]
1	**I**	2-MeTHF	48	>20:1	88	85	94.5:5.5
2	**I**	PhMe	48	>20:1	90	89	88.5:11.5
3	**I**	THF	48	>20:1	88	86	89:11
4	**I**	Et_2O	40	>20:1	>99	77	92.5:7.5
5	**I**	CH_2Cl_2	48	>20:1	88	85	94.5:5.5
6	**I**	TBME	72	>20:1	78	81	88:12
7	**I**	EtOAc	40	>20:1	81	75	92:8

[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.

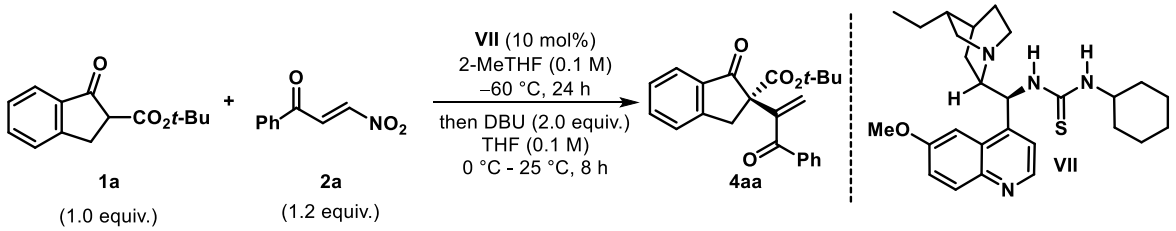
Additive and concentration optimization[a]



Entry	Conc. (x M)	*t* [h]	Yield [%] of 4aa[b]	er of 4aa[c]
1	0.1	24	91	97.5:2.5
2[d]	0.1	24	88	97:3
3	0.2	24	90	96.5:3.5
4	0.05	48	90	97:3

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

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

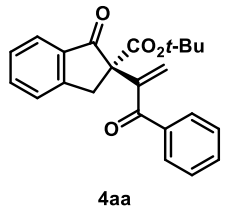


In an oven-dried reaction tube equipped with an argon inlet, β-ketoester **1a** (23.2 mg, 0.1 mmol, 1.0 equiv.) and the catalyst **VII** (4.7 mg, 0.01 mmol, 0.1 equiv.) was taken, put in vacuum, purged with argon. 2-MeTHF (0.5 mL) was added and the resulting solution was cooled to –60 °C. After 10 min, 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 $CHCl_3$. The combined organic layer was dried over anh. Na_2SO_4, 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

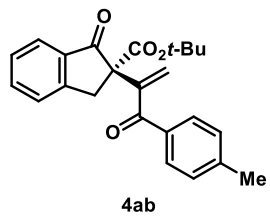
***tert*-Butyl (*S*)-1-oxo-2-(3-oxo-3-phenylprop-1-en-2-yl)-2,3-dihydro-1*H*-indene-2-carboxylate**



4aa

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). $\mathbf{R_f}$ = 0.35 (10% EtOAc in petroleum ether). **FT-IR (neat):** ν 2978 (m), 1711 (s), 1659 (s), 1602 (s), 1256 (s), 1152 (s), 1029 (m) cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 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, $CDCl_3$):** δ 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 $C_{23}H_{22}O_4Na$ ($[M + Na]^+$): 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}, τ_{minor} = 7.13 min, τ_{major} = 8.28 min). Absolute stereochemistry of **4aa** is assigned in analogy with **4ba**.

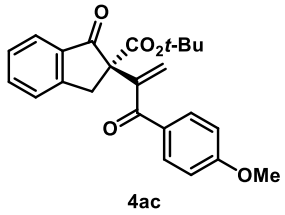
***tert*-Butyl (*S*)-1-oxo-2-(3-oxo-3-(p-tolyl)prop-1-en-2-yl)-2,3-dihydro-1*H*-indene-2-carboxylate**



4ab

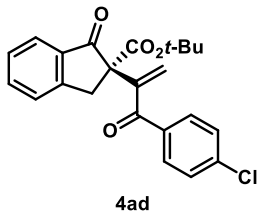
4ab: Purification by silica gel (100-200 mesh) column chromatography (6% EtOAc in petroleum ether) afforded pure **4ab** as a colorless oil (34 mg, 0.090 mmol; 90% yield). $\mathbf{R_f}$ = 0.35 (10% EtOAc in petroleum ether). **FT-IR (neat):** ν 2976 (w), 1712 (s), 1655 (m), 1606 (m), 1257 (m), 1151 (s), 1027 (m) cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 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, $CDCl_3$):** δ 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, 41.36, 27.64, 21.59; **HRMS (ESI+):** Calculated for $C_{24}H_{24}O_4Na$ ($[M + Na]^+$): 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}, τ_{minor} = 5.00 min, τ_{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-1*H*-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). $\mathbf{R_f}$ = 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^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** 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); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 201.26, 195.85, 167.99, 163.23, 153.92, 147.76, 135.67, 135.27, 132.35, 129.92, 127.59, 126.49, 125.75, 124.66, 113.44, 82.70, 65.86, 55.44, 41.49, 27.63; **HRMS (ESI+):** Calculated for $C_{24}H_{24}O_5Na$ ($[M + Na]^+$): 415.1521, found: 415.1520; **$[\alpha]_D^{22}$** +196.5 (*c* 1.00, $CHCl_3$) 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^{-1}, τ_{major} = 18.69 min, τ_{minor} = 21.57 min). Absolute stereochemistry of **4ac** is assigned in analogy with **4ba**.

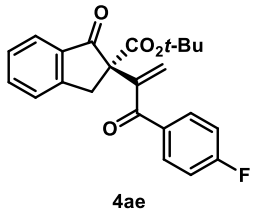


4ac

***tert*-Butyl (*S*)-2-(3-(4-chlorophenyl)-3-oxoprop-1-en-2-yl)-1-oxo-2,3-dihydro-1*H*-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). $\mathbf{R_f}$ = 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^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** 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; 1H), 1.31 (s; 9H); **^{13}C-NMR (100 MHz, $CDCl_3$):** 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 $C_{23}H_{21}ClO_4Na$ ($[M + Na]^+$): 419.1026, found: 419.1026; **$[\alpha]_D^{22}$** +230.4 (*c* 1.00, $CHCl_3$) 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/IPA = 90:10, 1.0 mL min^{-1}, τ_{minor} = 5.47 min, τ_{major} = 6.45 min). Absolute stereochemistry of **4ad** is assigned in analogy with **4ba**.

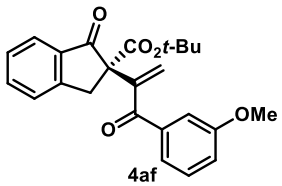


4ad

***tert*-Butyl (*S*)-2-(3-(4-fluorophenyl)-3-oxoprop-1-en-2-yl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate 4ae:** 

4ae

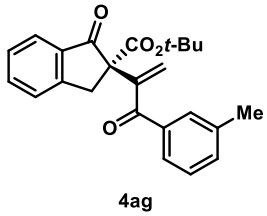
Purification by silica gel (100-200 mesh) column chromatography (8% EtOAc in petroleum ether) afforded pure **4ae** as a colorless oil (33 mg, 0.087 mmol; 87% yield). $\mathbf{R_f}$ = 0.40 (10% EtOAc in petroleum ether). **FT-IR (neat):** ν 2978 (w), 1712 (s), 1659 (m), 1598 (m), 1253 (m), 1152 (s), 1027 (m) cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 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, $CDCl_3$):** δ 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 $C_{23}H_{21}FO_4Na$ ($[M + Na]^+$): 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}, τ_{minor} = 5.20 min, τ_{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-1*H*-indene-2-carboxylate 4af:** 

4af

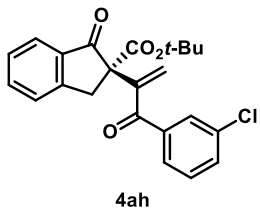
Purification by silica gel (100-200 mesh) column chromatography (10% EtOAc in petroleum ether) afforded pure **4af** as a colorless oil (34 mg, 0.087 mmol; 87% yield). $\mathbf{R_f}$ = 0.30 (10% EtOAc in petroleum ether). **FT-IR (neat):** ν 2975 (m), 2927 (m), 1712 (s), 1651 (m), 1600 (s), 1257 (s), 1157 (s), 1028 (m) cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 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, $CDCl_3$):** δ 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 $C_{24}H_{24}O_5Na$ ($[M + Na]^+$): 415.1521, found: 415.1520; **$[\alpha]_D^{22}$** +253.1 (*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}, τ_{minor} = 5.76 min, τ_{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-1*H*-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). $\mathbf{R_f}$ = 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}; **^{1}H-NMR (400 MHz, $CDCl_3$):** 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); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 201.20, 197.37, 167.96, 153.87, 147.71, 138.01, 137.46, 135.71, 135.26, 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 $C_{24}H_{24}O_4Na$ ($[M + Na]^+$): 399.1574, found: 399.1574; $\mathbf{[\alpha]_D^{22}}$ +325.7 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample with 97:3 er. Enantiomeric ratio was determined by HPLC analysis (Daicel Chiralpak IG column, 254 nm, *n*-Hexane/EtOH = 95:5, 1.0 mL min^{-1}, τ_{major} = 21.56 min, τ_{minor} = 23.07 min). Absolute stereochemistry of **4ag** is assigned in analogy with **4ba**.



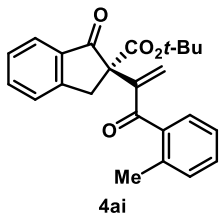
4ag

***tert*-Butyl (*S*)-2-(3-(3-chlorophenyl)-3-oxoprop-1-en-2-yl)-1-oxo-2,3-dihydro-1*H*-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). $\mathbf{R_f}$ = 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}; **^{1}H-NMR (400 MHz, $CDCl_3$):** 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); **^{13}C-NMR (100 MHz, $CDCl_3$):** 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, 127.97, 127.74, 127.73, 126.49, 124.76, 82.96, 65.52, 41.22, 27.66; **HRMS (ESI+):** Calculated for $C_{23}H_{21}ClO_4Na$ ($[M + Na]^+$): 419.1026, found: 419.1026; $\mathbf{[\alpha]_D^{22}}$ +179.1 (*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 IG column, 254 nm, *n*-Hexane/IPA = 90:10, 1.0 mL min^{-1}, τ_{minor} = 7.23 min, τ_{major} = 8.31 min). Absolute stereochemistry of **4ah** is assigned in analogy with **4ba**.



4ah

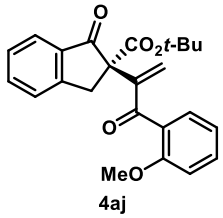
***tert*-Butyl (*S*)-1-oxo-2-(3-oxo-3-(o-tolyl)prop-1-en-2-yl)-2,3-dihydro-1*H*-indene-2-carboxylate 4ai:** Purification by silica gel (100-200 mesh) column chromatography (7% EtOAc in petroleum ether) afforded pure **4ai** as a colorless oil (30 mg, 0.080 mmol; 80% yield). $\mathbf{R_f}$ = 0.45 (10% EtOAc in petroleum ether). **FT-IR (neat):** ν 2977 (w), 1711 (s), 1662 (m), 1605 (w), 1254 (m), 1152 (s), 1028 (m) cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** 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),



4ai

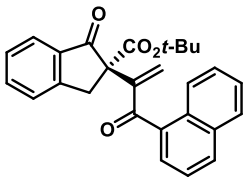
7.19-7.25 (m; 2H), 5.99 (s; 1H), 5.75 (s; 1H), 4.35 (d, *J* = 17.8 Hz; 1H), 3.19 (d, *J* = 17.8 Hz; 1H), 2.37 (s; 3H), 1.41 (s; 9H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 200.99, 198.93, 167.79, 153.57, 148.85, 137.83, 136.74, 135.71, 135.22, 130.86, 130.31, 130.18, 128.63, 127.64, 126.46, 124.98, 124.68, 82.55, 64.76, 40.70, 27.71, 19.62; **HRMS (ESI+):** Calculated for $C_{24}H_{24}O_4Na$ ([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}, τ_{minor} = 6.61 min, τ_{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-1*H*-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). **R_f** = 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 $C_{24}H_{24}O_5Na$ ([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}, τ_{minor} = 6.13 min, τ_{major} = 6.58 min). Absolute stereochemistry of **4aj** is assigned in analogy with **4ba**.



4aj

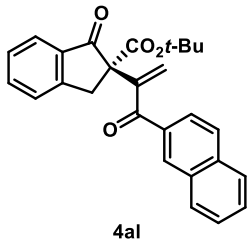
***tert*-Butyl (*S*)-2-(3-(naphthalen-1-yl)-3-oxoprop-1-en-2-yl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate 4ak:** Purification by silica gel (100-200 mesh) column chromatography (7% EtOAc in petroleum ether) afforded pure **4ak** as a colorless oil (32 mg, 0.078 mmol; 78% yield). **R_f** = 0.35 (10% 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 $C_{27}H_{24}O_4Na$ ([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



4ak

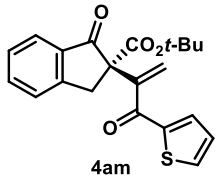
min^{-1}, τ_{minor} = 5.72 min, τ_{major} = 6.60 min). Absolute stereochemistry of **4ak** is assigned in analogy with **4ba**.

***tert*-Butyl (*S*)-2-(3-(naphthalen-2-yl)-3-oxoprop-1-en-2-yl)-1-oxo-2,3-dihydro-1*H*-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). $\mathbf{R_f}$ = 0.35 (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}; **^{1}H-NMR (400 MHz, $CDCl_3$):** 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); **^{13}C-NMR (100 MHz, $CDCl_3$):** 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 $C_{27}H_{24}O_4Na$ ($[M + Na]^+$): 435.1572, found: 435.1576; **$[\alpha]_D^{22}$** +193.9 (*c* 1.00, $CHCl_3$) 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}, τ_{major} = 9.91 min, τ_{minor} = 11.60 min). Absolute stereochemistry of **4al** is assigned in analogy with **4ba**.



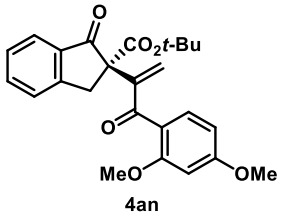
4al

***tert*-Butyl (*S*)-1-oxo-2-(3-oxo-3-(thiophen-2-yl)prop-1-en-2-yl)-2,3-dihydro-1*H*-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). $\mathbf{R_f}$ = 0.30 (10% EtOAc in petroleum ether). **FT-IR (neat):** ν 2976 (w), 1711 (s), 1634 (m), 1256 (m), 1151 (s), 1022 (w) cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** 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); **^{13}C-NMR (100 MHz, $CDCl_3$):** 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 $C_{21}H_{20}O_4Na$ ($[M + Na]^+$): 391.0980, found: 391.0979; **$[\alpha]_D^{22}$** +248.0 (*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 AD-H column, 254 nm, *n*-Hexane/EtOH = 95:5, 1.0 mL min^{-1}, τ_{minor} = 10.32 min, τ_{major} = 13.13 min). Absolute stereochemistry of **4am** is assigned in analogy with **4ba**.



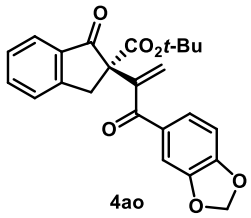
4am

***tert*-Butyl (*S*)-2-(3-(2,4-dimethoxyphenyl)-3-oxoprop-1-en-2-yl)-1-oxo-2,3-dihydro-1*H*-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). $\mathbf{R_f}$ = 0.20 (20% EtOAc in petroleum ether). **FT-IR (neat):** ν 2974 (w), 1710 (s), 1659 (m), 1605 (m), 1263 (m), 1156 (s), 1028 (m) cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 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), 3.84 (s; 3H), 3.77 (s; 3H), 3.27 (d, *J* = 17.7 Hz; 1H), 1.38 (s; 9H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 201.31, 195.55, 167.93, 163.12, 159.71, 153.91, 149.07, 135.55, 135.32, 132.47, 127.99, 127.48, 126.43, 124.61, 120.61, 103.83, 98.95, 82.33, 65.08, 55.65, 55.46, 40.77, 27.70; **HRMS (ESI+):** Calculated for $C_{25}H_{26}O_6Na$ ([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}, τ_{minor} = 9.55 min, τ_{major} = 13.18 min). Absolute stereochemistry of **4an** is assigned in analogy with **4ba**.



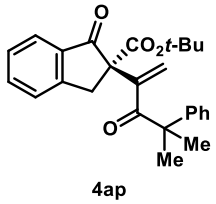
4an

***tert*-Butyl (*S*)-2-(3-(benzo[d][1,3]dioxol-5-yl)-3-oxoprop-1-en-2-yl)-1-oxo-2,3-dihydro-1*H*-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). $\mathbf{R_f}$ = 0.30 (10% EtOAc in petroleum ether). **FT-IR (neat):** ν 2923 (w), 1712 (s), 1651 (m), 1606 (m), 1251 (s), 1153 (s), 1034 (m) cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.83 (d, *J* = 7.7 Hz; 1H), 7.63-7.66 (m; 1H), 7.49-7.53 (m; 2H), 7.39-7.43 (m; 1H), 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, $CDCl_3$):** δ 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 $C_{24}H_{22}O_6Na$ ([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}, τ_{minor} = 11.49 min, τ_{major} = 13.72 min). Absolute stereochemistry of **4ao** is assigned in analogy with **4ba**.



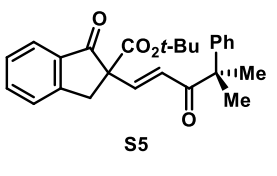
4ao

***tert*-Butyl (*S*)-2-(4-methyl-3-oxo-4-phenylpent-1-en-2-yl)-1-oxo-2,3-dihydro-1*H*-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). $\mathbf{R_f}$ = 0.35 (10% EtOAc in petroleum ether). **FT-IR (neat):** ν 2968 (m), 2924 (m), 1722 (s), 1614 (m), 1152 (s), 1013 (w) cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 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; 9H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 203.32, 201.00, 168.02, 153.40, 145.99, 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 $C_{26}H_{28}O_4Na$ ($[M + Na]^+$): 427.4958, found: 427.4957; **$[\alpha]_D^{22}$** +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/EtOH = 95:5, 1.0 mL min^{-1}, τ_{minor} = 7.56 min, τ_{major} = 8.29 min). Absolute stereochemistry of **4ap** is assigned in analogy with **4ba**.



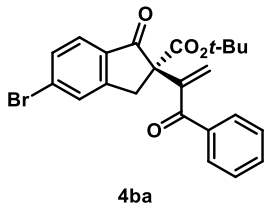
4ap

***tert*-butyl (*E*)-2-(4-methyl-3-oxo-4-phenylpent-1-en-1-yl)-1-oxo-2,3-dihydro-1*H*-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). $\mathbf{R_f}$ = 0.30 (10% EtOAc in petroleum ether). **FT-IR (neat):** ν 2970 (m), 2924 (m), 1724 (s), 1614 (m), 1150 (s), 1013 (w) cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.69 (d, *J* = 7.7 Hz; 1H), 7.58 (t, *J* = 7.5 Hz; 1H), 7.27-7.41 (m; 4H), 7.12-7.20 (m; 4H), 6.15 (d, *J* = 15.6 Hz; 1H), 3.74 (d, *J* = 17.7 Hz; 1H), 3.07 (d, *J* = 17.7 Hz; 1H), 1.47 (s; 3H), 1.44 (s; 3H), 1.32 (s; 9H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 200.79, 198.42, 167.62, 152.02, 143.54, 141.91, 135.41, 134.12, 128.72, 127.86, 126.83, 126.62, 126.27, 126.12, 125.09, 82.93, 63.70, 51.27, 37.71, 27.65, 25.15, 25.06; **HRMS (ESI+):** Calculated for $C_{26}H_{28}O_4Na$ ($[M + Na]^+$): 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}, τ_{minor} = 16.88 min, τ_{major} = 18.33 min) and found to be 52:48.



S5

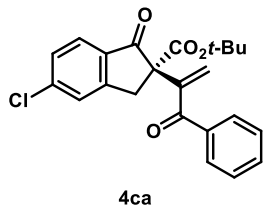
***tert*-Butyl (*S*)-5-bromo-1-oxo-2-(3-oxo-3-phenylprop-1-en-2-yl)-2,3-dihydro-1*H*-indene-2-carboxylate 4ba:** Purification by silica gel (100-200 mesh) column chromatography (6% EtOAc in petroleum ether) afforded pure **4ba** as a colorless oil (41 mg, 0.093 mmol; 93% yield). $\mathbf{R_f}$ = 0.30 (10% EtOAc in petroleum ether). **M.P.** = 97-98 °C. **FT-IR (neat):** ν 2977 (w), 2927 (w), 1716 (s), 1658 (m), 1594 (w), 1250 (m), 1151 (s) cm^{-1}; **^{1}H-NMR (400**



4ba

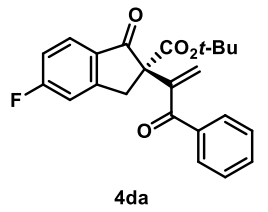
MHz, $CDCl_3$): δ 7.82-7.85 (m; 2H), 7.68-7.70 (m; 2H), 7.54-7.58 (m; 2H), 7.44-7.48 (m; 2H), 5.88 (s; 1H), 5.79 (s; 1H), 4.25 (d, *J* = 18.1 Hz; 1H), 3.31 (d, *J* = 18.1 Hz; 1H), 1.32 (s; 9H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 199.88, 197.03, 167.56, 155.31, 147.30, 137.24, 134.09, 132.48, 131.38, 131.30, 129.85, 129.76, 128.22, 127.63, 125.82, 83.06, 65.68, 40.88, 27.63; **$[\alpha]_D^{22}$** +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}, τ_{minor} = 12.14 min, τ_{major} = 14.55 min). Absolute stereochemistry of **4ba** was assigned by single crystal X-ray diffraction analysis.

***tert*-Butyl (*S*)-5-chloro-1-oxo-2-(3-oxo-3-phenylprop-1-en-2-yl)-2,3-dihydro-1*H*-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), 1658 (m), 1597 (m), 1256 (m), 1152 (m), 1024 (w) cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.83-7.85 (m; 2H), 7.76 (d, *J* = 8.4 Hz; 1H), 7.54-7.58 (m; 1H), 7.50 (s; 1H), 7.44-7.47 (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* = 17.8 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 $C_{23}H_{21}ClO_4Na$ ($[M + Na]^+$): 419.1026, found: 419.1027; **$[\alpha]_D^{22}$** +236.6 (*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 AS-H column, 254 nm, *n*-Hexane/EtOH = 95:5, 1.0 mL min^{-1}, τ_{minor} = 5.13 min, τ_{major} = 6.16 min). Absolute stereochemistry of **4ca** is assigned in analogy with **4ba**.



4ca

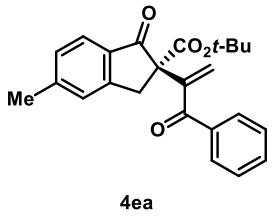
***tert*-Butyl (*S*)-5-fluoro-1-oxo-2-(3-oxo-3-phenylprop-1-en-2-yl)-2,3-dihydro-1*H*-indene-2-carboxylate 4da:** Purification by silica gel (100-200 mesh) column chromatography (6% EtOAc in petroleum ether) afforded pure **4da** as a colorless oil (36 mg, 0.095 mmol; 95% yield). **R_f** = 0.35 (10% 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; 3H), 7.54-7.58 (m; 1H), 7.44-7.47 (m; 2H), 7.08-7.17 (m; 2H), 5.89 (s; 1H), 5.78 (s; 1H), 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* = 258.2 Hz), 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 $C_{23}H_{21}FO_4Na$ ($[M + Na]^+$): 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



4da

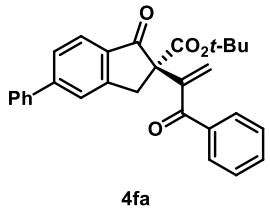
min^{-1}, τ_{minor} = 5.13 min, τ_{major} = 8.52 min). Absolute stereochemistry of **4da** is assigned in analogy with **4ba**.

***tert*-Butyl (*S*)-5-methyl-1-oxo-2-(3-oxo-3-phenylprop-1-en-2-yl)-2,3-dihydro-1*H*-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). $\mathbf{R_f}$ = 0.30 (10% EtOAc in petroleum ether). **FT-IR (neat):** ν 2977 (w), 1731 (s), 1710 (s), 1659 (m), 1607 (m), 1256 (m), 1153 (s), 1026 (m) cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.84-7.86 (m; 2H), 7.72 (d, *J* = 7.9 Hz; 1H), 7.53-7.57 (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), 4.23 (d, *J* = 17.5 Hz; 1H), 3.28 (d, *J* = 17.5 Hz; 1H), 2.45 (s; 3H), 1.31 (s; 9H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 200.49, 197.26, 168.12, 154.35, 147.83, 147.20, 137.46, 133.03, 132.33, 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 $C_{24}H_{24}O_4Na$ ($[M + Na]^+$): 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}, τ_{major} = 9.83 min, τ_{minor} = 10.79 min). Absolute stereochemistry of **4ea** is assigned in analogy with **4ba**.



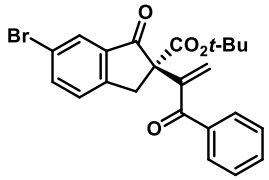
4ea

***tert*-Butyl (*S*)-1-oxo-2-(3-oxo-3-phenylprop-1-en-2-yl)-5-phenyl-2,3-dihydro-1*H*-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). $\mathbf{R_f}$ = 0.35 (10% EtOAc in petroleum ether). **FT-IR (neat):** ν 2925 (w), 1709 (s), 1658 (m), 1604 (m), 1254 (m), 1151 (m), 1024 (w) cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.86-7.91 (m; 3H), 7.68-7.69 (m; 1H), 7.63-7.66 (m; 3H), 7.55-7.59 (m; 1H), 7.40-7.50 (m; 5H), 5.92 (s; 1H), 5.79 (s; 1H), 4.34 (d, *J* = 17.8 Hz; 1H), 3.39 (d, *J* = 17.8 Hz; 1H), 1.34 (s; 9H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 200.62, 197.21, 168.02, 154.51, 148.90, 147.73, 140.01, 137.39, 134.10, 132.38, 129.88, 128.96, 128.49, 128.18, 127.51, 127.45, 127.16, 125.07, 124.87, 82.81, 65.91, 41.35, 27.66; **HRMS (ESI+):** Calculated for $C_{29}H_{26}O_4Na$ ($[M + Na]^+$): 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}, τ_{major} = 6.69 min, τ_{minor} = 12.06 min). Absolute stereochemistry of **4fa** is assigned in analogy with **4ba**.



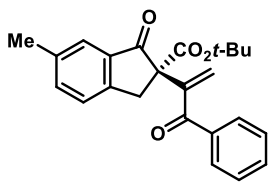
4fa

***tert*-Butyl (*S*)-6-bromo-1-oxo-2-(3-oxo-3-phenylprop-1-en-2-yl)-2,3-dihydro-1*H*-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). $\mathbf{R_f}$ = 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}; **^{1}H-NMR (400 MHz, $CDCl_3$):** 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); **^{13}C-NMR (100 MHz, $CDCl_3$):** 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 $C_{23}H_{21}BrO_4Na$ ($[M + Na]^+$): 463.0521, found: 463.0520; **$[\alpha]_D^{22}$** +206.9 (*c* 2.00, $CHCl_3$) for an enantiomerically enriched sample with 99:1 er. Enantiomeric ratio was determined by HPLC analysis (Daicel Chiralpak IE column, 254 nm, *n*-Hexane/IPA = 90:10, 1.0 mL min^{-1}, τ_{minor} = 11.41 min, τ_{major} = 18.12 min). Absolute stereochemistry of **4ga** is assigned in analogy with **4ba**.



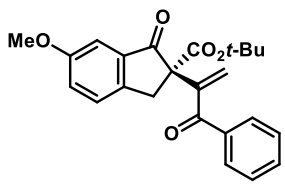
4ga

***tert*-Butyl (*S*)-6-methyl-1-oxo-2-(3-oxo-3-phenylprop-1-en-2-yl)-2,3-dihydro-1*H*-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). $\mathbf{R_f}$ = 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}; **^{1}H-NMR (400 MHz, $CDCl_3$):** 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); **^{13}C-NMR (100 MHz, $CDCl_3$):** 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 $C_{24}H_{24}O_4Na$ ($[M + Na]^+$): 399.1572, found: 399.1570; **$[\alpha]_D^{22}$** +280.3 (*c* 2.00, $CHCl_3$) 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}, τ_{minor} = 4.90 min, τ_{major} = 5.26 min). Absolute stereochemistry of **4ha** is assigned in analogy with **4ba**.



4ha

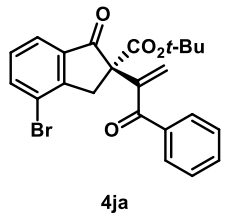
***tert*-Butyl (*S*)-6-methoxy-1-oxo-2-(3-oxo-3-phenylprop-1-en-2-yl)-2,3-dihydro-1*H*-indene-2-carboxylate 4ia:** Purification by silica gel (100-200 mesh) column chromatography (7% EtOAc in petroleum ether) afforded pure **4ia** as a colorless oil (36 mg, 0.092 mmol; 92% yield). $\mathbf{R_f}$ = 0.25 (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}; **^{1}H-NMR (400 MHz, $CDCl_3$):** 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-



4ia

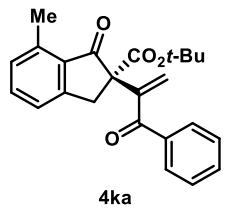
7.27 (m; 2H), 5.88 (s; 1H), 5.76 (s; 1H), 4.19 (d, *J* = 17.5 Hz; 1H), 3.86 (s; 3H), 3.26 (d, *J* = 17.5 Hz; 1H), 1.33 (s; 9H); **^{13}C-NMR (100 MHz, CDCl$_3$):** δ 201.05, 197.14, 167.98, 159.62, 147.72, 146.84, 137.42, 136.35, 132.34, 129.85, 128.16, 127.26, 127.18, 125.33, 105.60, 82.71, 66.39, 55.60, 40.61, 27.65; **HRMS (ESI+):** Calculated for $C_{24}H_{24}O_5Na$ ([M + Na]$^+$): 415.1521, found: 415.1521; **[α]$_D^{22}$** +239.4 (*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}, τ_{minor} = 5.67 min, τ_{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-1*H*-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$_f$** = 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}; **^{1}H-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); **^{13}C-NMR (100 MHz, CDCl$_3$):** δ 200.44, 196.88, 167.46, 153.42, 147.28, 138.47, 137.24, 137.09, 132.45, 129.83, 129.40, 128.22, 127.76, 123.47, 121.97, 83.10, 65.66, 42.25, 27.62; **HRMS (ESI+):** Calculated for $C_{23}H_{21}BrO_4Na$ ([M + Na]$^+$): 463.0521, found: 463.0520; **[α]$_D^{22}$** +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}, τ_{minor} = 4.99 min, τ_{major} = 5.78 min). Absolute stereochemistry of **4ja** is assigned in analogy with **4ba**.



4ja

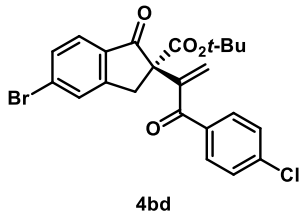
***tert*-Butyl (*S*)-7-methyl-1-oxo-2-(3-oxo-3-phenylprop-1-en-2-yl)-2,3-dihydro-1*H*-indene-2-carboxylate 4ka:** Purification by silica gel (100-200 mesh) column chromatography (7% EtOAc in petroleum ether) afforded pure **4ka** as a colorless oil (34 mg, 0.090 mmol; 90% yield). **R$_f$** = 0.35 (10% EtOAc in petroleum ether). **FT-IR (neat):** ν 2973 (w), 1715 (s), 1658 (m), 1590 (m), 1255 (m), 1151 (s), 1024 (m) cm^{-1}; **^{1}H-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 $C_{24}H_{24}O_4Na$ ([M + Na]$^+$): 399.1572, found: 399.1569; **[α]$_D^{22}$** +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



4ka

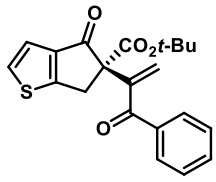
nm, *n*-Hexane/EtOH = 98:2, 1.0 mL min^{-1}, τ_{minor} = 5.99 min, τ_{major} = 8.99 min). Absolute stereochemistry of **4ka** is assigned in analogy with **4ba**.

***tert*-Butyl (*S*)-5-bromo-2-(3-(4-chlorophenyl)-3-oxoprop-1-en-2-yl)-1-oxo-2,3-dihydro-1*H*-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). $\mathbf{R_f}$ = 0.50 (10% EtOAc in petroleum ether). **FT-IR (neat):** ν 2976 (w), 1715 (s), 1658 (m), 1591 (m), 1255 (m), 1151 (s), 1024 (m) cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** 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* = 8.6 Hz; 2H), 5.85 (s; 1H), 5.74 (s; 1H), 4.22 (d, *J* = 17.9 Hz; 1H), 3.31 (d, *J* = 17.9 Hz; 1H), 1.30 (s; 9H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 199.78, 195.89, 167.51, 155.26, 147.15, 139.04, 135.49, 134.02, 131.45, 131.41, 131.32, 129.76, 128.61, 127.35, 125.85, 83.21, 65.69, 40.90, 27.63; **HRMS (ESI+):** Calculated for $C_{23}H_{20}BrClO_4Na$ ($[M + Na]^+$): 497.0131, found: 497.0134; **$[\alpha]_D^{22}$** +173.6 (*c* 1.00, $CHCl_3$) 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**.

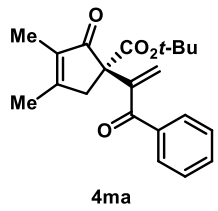


4bd

***tert*-Butyl (*S*)-4-oxo-5-(3-oxo-3-phenylprop-1-en-2-yl)-5,6-dihydro-4*H*-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). $\mathbf{R_f}$ = 0.40 (10% EtOAc in petroleum ether). **FT-IR (neat):** ν 2976 (w), 1715 (s), 1658 (m), 1591 (m), 1255 (m), 1151 (s), 1024 (m) cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** 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); **^{13}C-NMR (100 MHz, $CDCl_3$):** 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 $C_{21}H_{20}O_4SNa$ ($[M + Na]^+$): 391.0980, found: 391.0980; **$[\alpha]_D^{22}$** +123.1 (*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 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**.



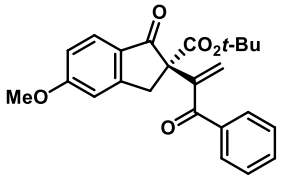
4la



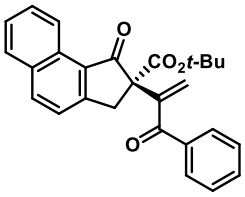
4ma

***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). **R_f** = 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}; **^{1}H-NMR (400 MHz, $CDCl_3$):** 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); **^{13}C-NMR (100 MHz, $CDCl_3$):** 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 $C_{21}H_{24}O_4Na$ ($[M + Na]^+$): 363.1572, found: 363.1573; **$[\alpha]_D^{22}$** +83.4 (*c* 0.50, $CHCl_3$) 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}, τ_{major} = 5.50 min, τ_{minor} = 6.40 min). Absolute stereochemistry of **4ma** is assigned in analogy with **4ba**.

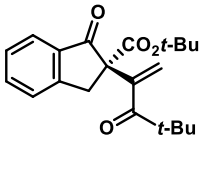
H. Less selective alkenylation products and unreactive substrates



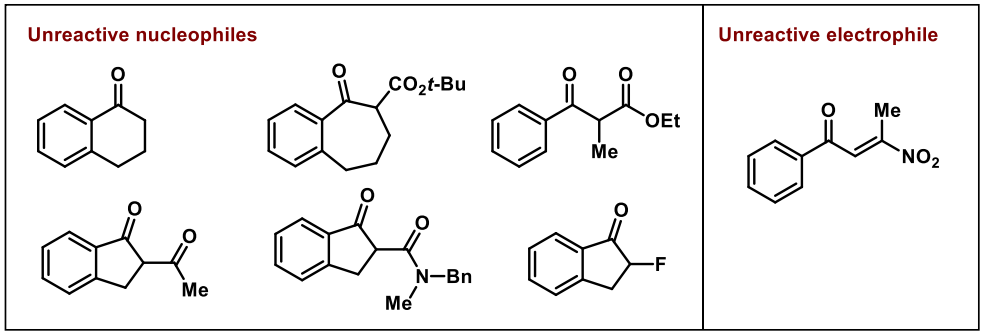
S6
48 h, 79% yield
87:13 er



S7
30 h, 80% yield
83.5:16.5 er

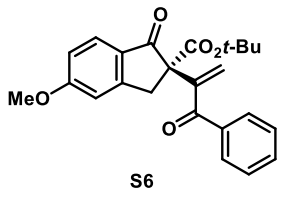


S8
48 h, 55% yield
50:50 er



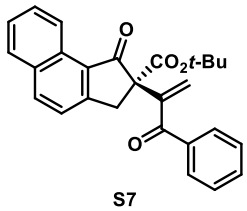
Similar procedure as described for the preparation of **4aa** was followed for the preparation **S6-8**.

***tert*-Butyl (*S*)-5-methoxy-1-oxo-2-(3-oxo-3-phenylprop-1-en-2-yl)-2,3-dihydro-1*H*-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). $\mathbf{R_f}$ = 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}; **^{1}H-NMR (400 MHz, $CDCl_3$):** 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), 6.91-6.95 (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); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 199.03, 197.35, 168.27, 166.23, 157.04, 147.83, 137.44, 132.33, 130.14, 129.88, 128.49, 128.44, 128.15, 127.35, 126.45, 116.12, 109.21, 82.65, 65.79, 55.73, 41.38, 27.65; **HRMS (ESI+):** Calculated for $C_{24}H_{24}O_5Na$ ([M + Na]$^+$): 415.1521, found: 415.1525; **$[\alpha]_D^{22}$** +161.3 (*c* 1.00, $CHCl_3$) 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**.

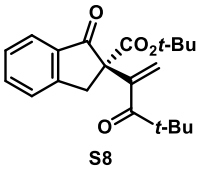


S6

***tert*-butyl (*S*)-1-oxo-2-(3-oxo-3-phenylprop-1-en-2-yl)-2,3-dihydro-1*H*-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). $\mathbf{R_f}$ = 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}; **^{1}H-NMR (400 MHz, $CDCl_3$):** 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); **^{13}C-NMR (100 MHz, $CDCl_3$):** 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 $C_{27}H_{24}O_4Na$ ([M + Na]$^+$): 412.1675, found: 412.1675; **$[\alpha]_D^{22}$** +129.3 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample with 83.5:16.5 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**.



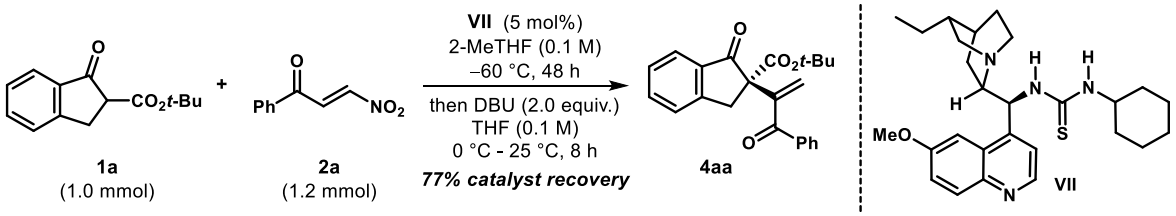
S7



S8

***tert*-Butyl (*S*)-2-(4,4-dimethyl-3-oxopent-1-en-2-yl)-1-oxo-2,3-dihydro-1*H*-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). $\mathbf{R_f}$ = 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}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.78 (d, *J* = 7.7 Hz; 1H), 7.62-7.66 (m; 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); **^{13}C-NMR (100 MHz, $CDCl_3$):** 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 $C_{21}H_{26}O_4Na$ ($[M + Na]^+$): 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}, τ_{minor} = 5.01 min, τ_{minor} = 5.50 min). Absolute stereochemistry of **S8** is assigned in analogy with **4ba**.

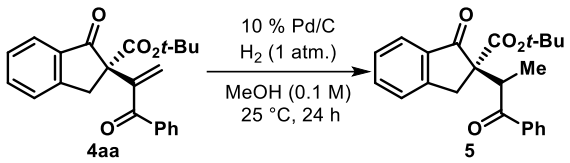
I. Large scale reaction: procedure for umpolung alkenylation of the cyclic β-ketoester 1a with β-nitroenone 2a



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 $CHCl_3$. The combined organic layer was dried over anh. Na_2SO_4, 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 NH_3 solution until pH = 9 and then extracted with $CHCl_3$. The combined organic layer was washed with brine, dried over anh. Na_2SO_4, concentrated in vacuo to obtain a brown solid which

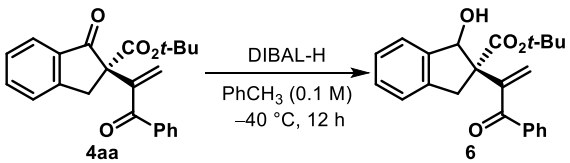
was purified by silica gel (230-400 mesh) column chromatography using CH_2Cl_2/MeOH/NEt_3 (100:3:1) as eluent to obtain pure **VII** as an off-white solid (18 mg, 0.039 mmol; 77% yield).

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 H_2 pressure for 24 h. The reaction mixture was then filtered through a celite bed and washed with MeOH. The filtrate was dried over anh. Na_2SO_4, 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). $\mathbf{R_f}$ = 0.40 (10% EtOAc in petroleum ether). Diastereoselectivity of the product **5** was determined by ^{1}H-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}; **^{1}H-NMR (400 MHz, $CDCl_3$):** 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); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 202.95, 202.76, 168.90, 155.85, 136.11, 135.48, 135.37, 133.05, 128.72, 128.53, 128.36, 127.43, 124.57, 82.23, 64.50, 44.25, 34.45, 27.53, 13.16; **HRMS (ESI+):** Calculated for $C_{23}H_{24}O_4Na$ ([M + Na]$^+$): 387.1572, found: 387.1573; $\mathbf{[\alpha]_D^{22}}$ +203.6 (*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}, τ_{minor} = 8.04 min, τ_{major} = 9.45 min).

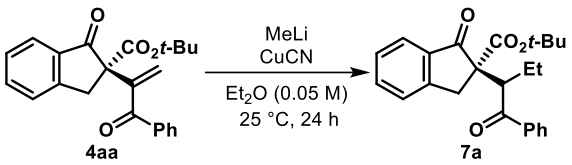
K. Chemoselective reduction of umpolung alkenylation product 4aa



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. Na_2SO_4, 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). $\mathbf{R_f}$ = 0.35 (20% EtOAc in petroleum ether). **M.P.** = 65-67 °C. Diastereoselectivity of the product **6** was determined by ^{1}H-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}; **^{1}H-NMR (400 MHz, $CDCl_3$):** 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); **^{13}C-NMR (100 MHz, $CDCl_3$):** 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 $C_{23}H_{24}O_4Na$ ([M + Na]$^+$): 387.1572, found: 387.1572; $\mathbf{[\alpha]_D^{22}}$ +157.2 (*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}, τ_{minor} = 11.54 min, τ_{major} = 13.79 min).

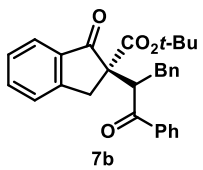
L. Cu(I)-mediated 1,4-addition reaction of MeLi to the umpolung alkenylation product 4aa



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 Et_2O 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 Et_2O 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. Na_2SO_4, 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). $\mathbf{R_f}$ = 0.38 (10% EtOAc in petroleum ether). Diastereoselectivity of the product **7a** was determined by ^{1}H-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}; **^{1}H-NMR (400 MHz, $CDCl_3$):** 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); **^{13}C-NMR (100 MHz, $CDCl_3$):** 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 $C_{24}H_{26}O_4Na$ ([M + Na]$^+$): 401.1729, found: 401.1730; **[α]$_D^{22}$** +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}, τ_{minor} = 9.28 min, τ_{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):** ν 1718 (s), 1658 (m), 1589 (m), 1255 (m), 1151 (s), 1024 (m) cm^{-1}; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 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, $CDCl_3$):** δ 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 $C_{29}H_{28}O_4Na$ ([M + Na]$^+$): 463.1885, found: 463.1885; **[α]$_D^{22}$** +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}, τ_{minor} = 10.23 min, τ_{major} = 12.27 min).



7b

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-Ka 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:

Identification code	**4ba**
Empirical formula	$C_{23}H_{21}BrO_4$
Formula weight	441.31
Temperature	150(2) K
Wavelength	0.71073 Å

Crystal system	monoclinic	
Space group	P 2_1	
Unit cell dimensions	a = 8.473(5) Å	α = 90°
	b = 10.542(5) Å	β = 106.339°
	c = 11.891(5) Å	γ = 90°
Volume	1019.2(9) $Å^3$	
Z	2	
Density (calculated)	1.438 Mg/mm^3	
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 > 2σ (I)]	R_1 = 0.0323, ωR_2 = 0.0767	
R indices (all data)	R_1 = 0.0368, ωR_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 (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 4ba. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor

Atom	*x*	*y*	*z*	U(eq)
Br01	6102.9(4)	-7175.5(3)	6316.0(3)	36.47(12)
O002	2634(3)	-11623(2)	8853(2)	29.8(5)
O003	980(3)	-13270(2)	8065.8(19)	24.3(5)
O004	366(3)	-12065(3)	5555(2)	32.0(5)
O005	4647(4)	-14400(3)	8660(2)	41.7(7)
C006	2677(4)	-10642(3)	5995(3)	20.9(6)
C007	1431(5)	-16558(3)	7258(3)	26.0(7)
C008	4271(4)	-10714(3)	6732(3)	22.4(6)
C009	87(4)	-13309(4)	8972(3)	29.7(7)

C010	3995(5)	-17011(5)	8696(3)	31.4(10)
C011	1763(4)	-11800(3)	6091(3)	22.3(7)
C012	4730(4)	-8631(3)	6159(3)	25.5(7)
C013	2895(4)	-12627(3)	7089(3)	21.5(6)
C014	2908(4)	-14025(3)	6787(3)	21.9(6)
C015	4598(4)	-11981(3)	7345(3)	26.9(7)
C016	3155(4)	-8554(3)	5396(3)	27.0(7)
C017	3591(4)	-14853(3)	7839(3)	24.8(6)
C018	2107(4)	-9582(3)	5310(3)	24.9(7)
C019	-1145(5)	-14363(5)	8544(4)	41.7(10)
C020	3466(5)	-18221(4)	8808(3)	36.6(9)
C021	2181(4)	-12436(3)	8129(3)	21.3(6)
C022	5330(4)	-9691(3)	6828(3)	25.0(6)
C023	900(5)	-17778(4)	7389(3)	32.9(8)
C024	2528(5)	-14487(4)	5709(3)	29.4(7)
C025	-783(6)	-12056(6)	8996(4)	44.7(10)
C026	2984(4)	-16159(3)	7902(3)	23.5(6)
C027	1301(6)	-13636(5)	10147(4)	40.4(9)
C028	1926(5)	-18609(4)	8157(3)	35.2(8)

Table 3. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 4ba. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br01	36.17(19)	23.37(16)	57.6(2)	0.14(18)	25.80(15)	-6.81(17)
O002	35.8(13)	23.5(11)	28.6(12)	-3.3(10)	6.6(10)	-4.4(10)
O003	23.6(11)	23.7(11)	26.4(11)	-2.2(9)	8.3(9)	-3.8(9)
O004	24.1(10)	29.2(12)	34.1(11)	5.3(12)	-5.6(8)	-3.6(11)
O005	42.8(16)	31.8(14)	36.4(14)	1.0(11)	-11.8(12)	-1.6(12)
C006	24.1(16)	19.7(16)	20.1(15)	-2.5(12)	8.2(12)	2.1(12)
C007	32.5(18)	21.1(16)	22.2(15)	3.4(13)	4.1(14)	5.5(14)
C008	22.4(15)	21.8(15)	24.5(15)	-0.5(12)	9.2(12)	1.5(12)
C009	29.4(17)	30.3(18)	34.3(18)	-3.2(15)	16.8(15)	-1.3(14)
C010	33.7(17)	36(3)	23.3(14)	5.5(14)	5.2(13)	12.1(16)

C011	22.7(15)	21.9(15)	21.5(14)	0.5(11)	5.1(12)	1.5(11)
C012	29.0(16)	20.1(15)	33.9(17)	-1.4(13)	19.6(14)	-2.3(12)
C013	20.2(14)	19.6(13)	22.7(14)	1.9(11)	2.7(11)	-0.5(11)
C014	19.9(14)	19.5(14)	26.5(16)	2.9(12)	6.7(12)	1.0(11)
C015	18.8(14)	27(2)	32.3(17)	3.5(13)	2.3(12)	-3.2(12)
C016	34.2(17)	19.7(15)	30.4(17)	4.6(13)	14.6(14)	3.1(13)
C017	23.5(15)	23.2(15)	24.9(15)	-0.5(13)	2.0(13)	5.8(12)
C018	27.8(18)	23.3(16)	24.4(15)	0.0(13)	8.4(13)	3.0(13)
C019	36(2)	42(2)	53(3)	-4.4(19)	23(2)	-11.5(17)
C020	54(2)	31(2)	28.9(18)	14.0(15)	19.0(17)	20.4(18)
C021	21.0(13)	17.7(17)	22.3(14)	2.7(10)	1.1(11)	1.4(10)
C022	20.7(15)	24.3(16)	31.2(16)	-0.9(13)	9.3(13)	-1.2(12)
C023	42(2)	25.7(17)	32.9(19)	-1.4(15)	12.9(17)	-0.7(16)
C024	37(2)	25.7(18)	26.6(17)	3.0(15)	10.3(14)	0.9(15)
C025	40(2)	41(3)	59(2)	-3(2)	23.0(19)	11(2)
C026	28.7(16)	22.3(15)	20.3(15)	3.0(12)	8.1(12)	7.1(13)
C027	44(2)	47(2)	32.3(19)	5.0(17)	15.3(17)	-4(2)
C028	57(2)	21.8(17)	36.2(19)	7.2(14)	27.9(18)	7.6(16)

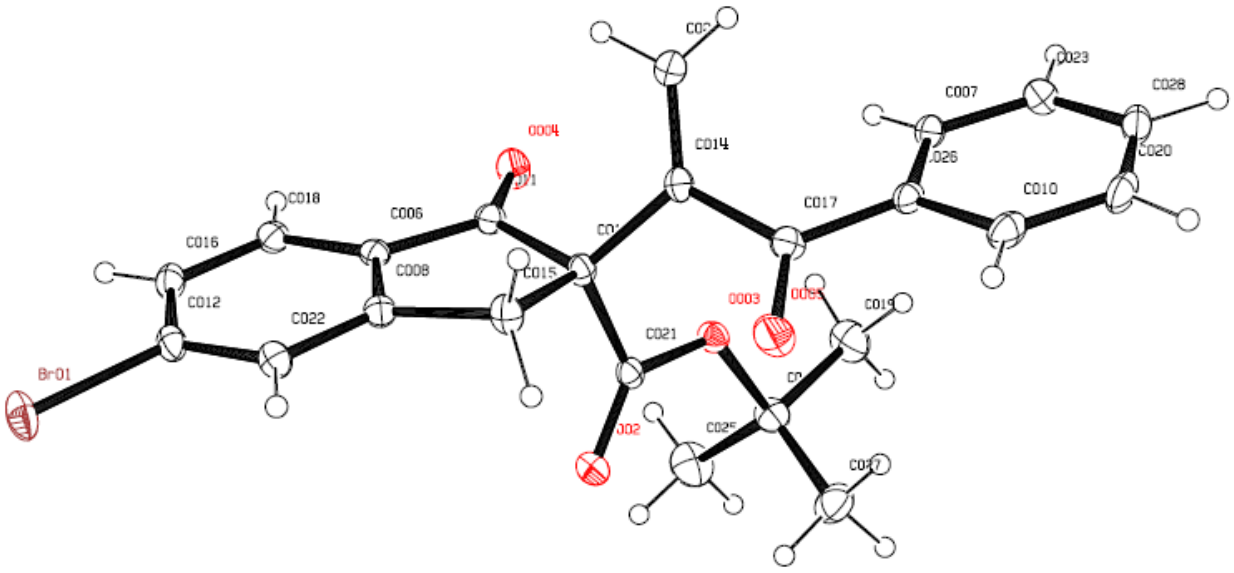
Table 4. Bond Lengths for 4ba

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br01	C012	1.902(3)	C009	C027	1.523(6)
O002	C021	1.198(4)	C010	C020	1.370(7)
O003	C009	1.481(4)	C010	C026	1.406(5)
O003	C021	1.330(4)	C011	C013	1.565(4)
O004	C011	1.208(4)	C012	C016	1.389(5)
O005	C017	1.221(4)	C012	C022	1.383(5)
C006	C008	1.390(5)	C013	C014	1.518(4)
C006	C011	1.466(4)	C013	C015	1.546(4)
C006	C018	1.387(5)	C013	C021	1.536(4)
C007	C023	1.386(5)	C014	C017	1.501(5)
C007	C026	1.389(5)	C014	C024	1.323(5)
C008	C015	1.510(5)	C016	C018	1.387(5)

C008	C022	1.387(5)	C017	C026	1.479(5)
C009	C019	1.511(6)	C020	C028	1.379(6)
C009	C025	1.517(7)	C023	C028	1.382(6)

Table 5. Bond Angles for 4ba

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C021	O003	C009	121.1(3)	C014	C013	C021	110.4(3)
C008	C006	C011	110.3(3)	C015	C013	C011	104.1(3)
C018	C006	C008	122.0(3)	C021	C013	C011	104.0(2)
C018	C006	C011	127.7(3)	C021	C013	C015	109.9(3)
C023	C007	C026	120.4(3)	C017	C014	C013	113.2(3)
C006	C008	C015	111.5(3)	C024	C014	C013	124.8(3)
C022	C008	C006	120.1(3)	C024	C014	C017	121.6(3)
C022	C008	C015	128.4(3)	C008	C015	C013	105.1(3)
O003	C009	C019	102.8(3)	C018	C016	C012	118.7(3)
O003	C009	C025	109.8(3)	O005	C017	C014	117.6(3)
O003	C009	C027	108.8(3)	O005	C017	C026	120.7(3)
C019	C009	C025	110.7(4)	C026	C017	C014	121.7(3)
C019	C009	C027	111.5(4)	C016	C018	C006	118.5(3)
C025	C009	C027	112.7(4)	C010	C020	C028	120.4(3)
C020	C010	C026	120.4(4)	O002	C021	O003	126.8(3)
O004	C011	C006	127.7(3)	O002	C021	C013	123.6(3)
O004	C011	C013	124.8(3)	O003	C021	C013	109.6(2)
C006	C011	C013	107.3(3)	C012	C022	C008	117.2(3)
C016	C012	Br01	117.7(3)	C028	C023	C007	119.9(4)
C022	C012	Br01	118.7(3)	C007	C026	C010	118.7(3)
C022	C012	C016	123.6(3)	C007	C026	C017	122.9(3)
C014	C013	C011	113.9(3)	C010	C026	C017	118.3(3)
C014	C013	C015	114.0(3)	C020	C028	C023	120.2(4)



ORTEP representation of the X-ray structure of (*S*)-4ba (thermal ellipsoids at 30% probability)