Supporting Information

for

Enantioselective [3 + 2] annulation of \( \alpha \)-substituted allenoates with \( \beta,\gamma \)-unsaturated \( N \)-sulfonylimines catalyzed by a bifunctional dipeptide phosphine

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A. General Information

Unless otherwise specified, all reactions were carried out under a nitrogen atmosphere in anhydrous conditions. All the solvents were purified according to the standard procedures. All chemicals which are commercially available were used without further purification unless otherwise noted. Thin-layer chromatography (TLC) was performed on silica gel plates (60F-254) using UV-light (254 and 365 nm). Flash chromatography was conducted on silica gel (300–400 mesh). $^1$H and $^{13}$C NMR spectra were recorded at ambient temperature in CDCl$_3$ on a Bruker AMX500 (500 MHz) spectrometer. Chemical shifts were reported in parts per million (ppm). All high resolution mass spectra were obtained on a Finnigan/MAT 95XL-T spectrometer. Optical rotations were measured using a Jasco DIP-1000 polarimeter. Enantiomeric excesses were determined by HPLC analysis on a chiral stationary phase.

Catalysts 3 & 4 were prepared by following our previously reported procedures [1]. The $\alpha$-substituted alleoates were synthesized according to the reported procedures [2]. The $\beta,\gamma$-unsaturated $N$-sulfonylimines were prepared according the literature procedure from respective ketones [3].

B. Synthesis of dipeptide phosphine 4b

![Chemical structure of 4b](image)

To a stirred solution of 4-1 [4] (1.17 g, 2 mmol) in anhydrous CH$_2$Cl$_2$ (20 mL) at room temperature was added TFA (4 mL). The resulting mixture was stirred for 2 h and then
quenched with saturated aqueous NaHCO₃ (100 mL). The product was extracted with CH₂Cl₂ several times (3 × 100 mL). The combined organic extracts were washed by brine (150 mL), dried over Na₂SO₄, filtered and concentrated. The residue was dissolved in anhydrous CH₂Cl₂ (20 mL) at 0 °C, Et₃N (5.6 mL, 4 mmol) was added, followed by 3,5-bis(trifluoromethyl)benzoyl chloride (550 mg, 2 mmol). After stirring at 0 °C for 1 h, solvent was removed and the residue was purified directly by flash column chromatography (hexane/ethyl acetate = 20 : 1) to afford 4b as a white solid (871 mg, 60% yield).

¹H NMR (500 MHz, CDCl₃) δ 8.32 (s, 2H), 8.01 (s, 1H), 7.77 (d, J = 5.2 Hz, 1H), 7.52–7.41 (m, 4H), 7.41–7.29 (m, 6H), 7.10 (d, J = 9.1 Hz, 1H), 4.61–4.56 (m, 1H), 4.53–4.47 (m, 1H), 3.96 (qt, J = 9.1 Hz, 4.8 Hz, 1H), 2.35 (ddd, J = 13.9 Hz, 4.8 Hz, 1.7 Hz, 1H), 2.15 (ddd, J = 13.8 Hz, 9.3 Hz, 2.5 Hz, 1H), 2.04–1.96 (m, 1H), 1.31 (d, J = 6.3 Hz, 3H), 0.99 (s, 9H), 0.88 (dd, J = 6.7 Hz, 4.9 Hz, 6H), 0.29 (s, 3H), 0.21 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 168.54, 164.25, 138.73, 138.63, 138.29, 138.18, 136.25, 133.26, 133.10, 132.77, 132.71, 132.56, 132.50, 132.23, 131.96, 129.09, 128.75, 128.73, 128.69, 128.67, 128.62, 127.65, 127.63, 126.31, 125.30, 125.27, 125.24, 124.14, 121.97, 119.80, 68.13, 58.23, 52.69, 52.57, 32.57, 32.50, 32.44, 25.98, 19.09, 18.07, 18.01, 17.96, 17.28, -4.71, -4.80; ³¹P NMR (202 MHz, CDCl₃) δ -22.68. HRMS (ESI) m/z calcd for C₃₆H₄₆F₆N₂O₃PSi [M+H]+ = 727.2914, found = 727.2923.

C. Representative procedure

\[
\begin{align*}
\text{CO}_2R^1 & + \text{CO}_2R^2 \\
\text{1} & \rightleftharpoons \text{CO}_2R^3 & \text{NTs} \\
\text{2} & \rightarrow \text{TsHNCO}_2R^4 & \text{4b (20 mol%)} \\
\text{toluene, rt, 24 h} & \rightarrow \text{5} \\
\end{align*}
\]
To a dried round bottle flask with a magnetic stirring bar under N\textsubscript{2} at room temperature were added allenoate 1 (0.15 mmol) and β,γ-unsaturated N-sulfonylimine 2 (0.1 mmol), followed by the addition of anhydrous toluene (0.5 mL). Catalyst 4b (0.02 mmol, 14.5 mg) was then introduced, and the reaction mixture was stirred for 24 h. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel to afford annulation adducts 5.

D. Analytical data of allenoates

**tert-Butyl 2-(4-chlorobenzyl)buta-2,3-dienoate 1d**

![tert-Butyl 2-(4-chlorobenzyl)buta-2,3-dienoate 1d](image)

White solid; \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\) 7.26 (d, \(J = 8.3\) Hz, 2H), 7.17 (d, \(J = 8.3\) Hz, 2H), 5.06 (d, \(J = 2.6\) Hz, 2H), 3.50 (s, 2H), 1.45 (s, 9H); \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}) \(\delta\) 214.21, 165.84, 137.83, 132.02, 130.17, 128.32, 101.29, 81.23, 78.97, 34.33, 28.03; HRMS (EI) m/z calcd for C\textsubscript{15}H\textsubscript{17}O\textsubscript{2}Cl [M\textsuperscript{+}] = 264.09171, found = 264.09105.

**tert-Butyl 2-(3-chlorobenzyl)buta-2,3-dienoate 1e**

![tert-Butyl 2-(3-chlorobenzyl)buta-2,3-dienoate 1e](image)

Colorless oil; \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\) 7.27–7.17 (m, 3H), 7.14 (d, \(J = 7.0\) Hz, 1H), 5.10 (t, \(J = 2.5\) Hz, 2H), 3.52 (t, \(J = 2.5\) Hz, 2H), 1.47 (s, 9H); \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}) \(\delta\) 214.27, 165.75, 141.40, 133.96, 129.44, 128.91, 127.02, 126.45, 101.04, 81.28, 79.02, 34.65, 28.02; HRMS (EI) m/z calcd for C\textsubscript{15}H\textsubscript{17}O\textsubscript{2}Cl [M\textsuperscript{+}] = 264.09171, found = 264.09235.

**tert-Butyl 2-(2-chlorobenzyl)buta-2,3-dienoate 1f**

S4
Colorless oil; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.36 (d, $J = 7.5$ Hz, 1H), 7.30 – 7.27 (m, 1H), 7.23–7.14 (m, 2H), 5.01 (t, $J = 3.1$ Hz, 2H), 3.68 (t, $J = 3.0$ Hz, 2H), 1.49 (s, 9H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 214.17, 165.90, 136.73, 134.43, 130.84, 129.32, 127.73, 126.53, 100.29, 81.17, 79.17, 32.55, 28.05; HRMS (EI) m/z calcd for C$_{15}$H$_{17}$O$_2$Cl [M]$^+$ = 264.09171, found = 264.09212.

tert-Butyl 2-(naphthalen-1-ylmethyl)buta-2,3-dienoate 1g

Colorless oil; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.09 – 8.00 (m, 1H), 7.85 (dd, $J = 6.7$ Hz, 2.7 Hz, 1H), 7.73 (dd, $J = 6.2$ Hz, 3.1 Hz, 1H), 7.56–7.37 (m, 4H), 4.83 (t, $J = 3.1$ Hz, 2H), 4.01 (t, $J = 3.1$ Hz, 2H), 1.49 (s, 9H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 214.24, 166.11, 135.05, 133.73, 132.09, 128.51, 127.06, 126.93, 125.67, 125.32, 125.27, 124.21, 101.41, 81.07, 79.13, 31.84, 28.01; HRMS (EI) m/z calcd for C$_{19}$H$_{20}$O$_2$ [M]$^+$ = 280.14633, found = 280.14743.

tert-Butyl 2-(4-methylbenzyl)buta-2,3-dienoate 1h

Colorless oil; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.15 (d, $J = 7.9$ Hz, 2H), 7.11 (d, $J = 7.9$ Hz, 2H), 5.06 (t, $J = 2.5$ Hz, 2H), 3.52 (s, 2H), 2.34 (s, 3H), 1.47 (s, 9H); $^{13}$C NMR (125 MHz,
CDCl$_3$ δ 214.32, 166.13, 136.28, 135.66, 128.90, 128.70, 101.78, 81.00, 78.70, 34.49, 28.06, 21.06; HRMS (EI) m/z calcd for C$_{16}$H$_{20}$O$_2$ [M]$^+$ = 244.14633, found = 244.14693.

tert-Butyl 2-(4-nitrobenzyl)buta-2,3-dienoate 1i

![tert-Butyl 2-(4-nitrobenzyl)buta-2,3-dienoate 1i](image)

Colorless oil; $^1$H NMR (500 MHz, CDCl$_3$) δ 8.13 (dd, $J = 8.8$ Hz, 2.2 Hz, 2H), 7.39 (d, $J = 8.7$ Hz, 2H), 5.10 (t, $J = 2.1$ Hz, 2H), 3.66–3.55 (m, 2H), 1.43 (s, 9H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 214.22, 165.49, 147.21, 146.64, 129.61, 123.50, 100.37, 81.52, 79.34, 34.88, 27.98; HRMS (EI) m/z calcd for C$_{15}$H$_{17}$O$_4$N [M]$^+$ = 275.11576, found = 275.11545.

E. Analytical data and HPLC chromatogram of the products

Methyl (1S,5S,E)-1-benzyl-4-(2-methoxy-1-((4-methylphenyl)sulfonamido)-2-oxoethyldene)-5-phenylcyclopent-2-ene-1-carboxylate 5a

![Methyl (1S,5S,E)-1-benzyl-4-(2-methoxy-1-((4-methylphenyl)sulfonamido)-2-oxoethyldene)-5-phenylcyclopent-2-ene-1-carboxylate 5a](image)

White solid; $[\alpha]^D_{25} = +237.1$ (c 1.0, CHCl$_3$); $^1$H NMR (500 MHz, CDCl$_3$) δ 7.54 (d, $J = 8.1$ Hz, 2H), 7.41–7.18 (m, 9H), 7.11 (d, $J = 8.1$ Hz, 2H), 6.98 (d, $J = 7.5$ Hz, 2H), 6.59 (d, $J = 5.7$ Hz, 1H), 6.14 (s, 1H), 5.06 (s, 1H), 3.62 (s, 3H), 3.07 (s, 3H), 2.71 (d, $J = 13.5$ Hz, 1H), 2.35 (s, 3H), 2.24 (d, $J = 13.5$ Hz, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 175.13, 164.32, 163.56, 146.94, 143.63, 140.19, 137.15, 135.95, 134.28, 129.62, 129.23, 128.23, 128.06, 127.56, 126.91, 126.71, 126.48, 115.45, 65.15, 56.24, 52.21, 51.34, 42.00, 21.45; HRMS (ESI) m/z calcd for C$_{30}$H$_{29}$NNaO$_6$S [M+Na]$^+$ = 554.1608, found = 554.1616; The ee value
was 76%, $t_R$ (major) = 24.993 min, $t_R$ (minor) = 29.252 min (Chiralpak ID, $\lambda = 254$ nm, 40% $i$-PrOH/hexane, flow rate = 1.0 mL/min).

**Racemic 5a**

**Enantiomerically enriched 5a**

*tert*-Butyl (1S,5S,E)-1-benzyl-4-(2-methoxy-1-((4-methylphenyl)sulfonamido)-2-oxoethylidene)-5-phenylcyclopent-2-ene-1-carboxylate 5b
White solid; [\alpha]^{25}_D = +170.7 (c 1.0, CHCl_3); ¹H NMR (500 MHz, CDCl₃) δ 7.53 (d, J = 8.2 Hz, 2H), 7.33 (t, J = 7.3 Hz, 3H), 7.28–7.16 (m, 6H), 7.11 (d, J = 8.2 Hz, 2H), 7.03 (d, J = 6.7 Hz, 2H), 6.58 (d, J = 5.7 Hz, 1H), 6.07 (s, 1H), 5.03 (s, 1H), 3.07 (s, 3H), 2.68 (d, J = 13.7 Hz, 1H), 2.34 (s, 3H), 2.30 (dd, J = 17.8 Hz, 4.0 Hz, 2H), 1.37 (s, 9H); ¹³C NMR (125 MHz, CDCl₃) δ 173.60, 164.79, 163.65, 148.08, 143.57, 140.34, 137.42, 136.01, 133.82, 129.98, 129.20, 128.04, 127.94, 127.59, 126.76, 126.48, 115.18, 81.87, 65.51, 56.40, 51.29, 41.40, 27.90, 21.45; HRMS (ESI) m/z calcd for C₃₃H₃₅NNaO₆S [M+Na]^+ = 596.2077, found = 596.2083; The ee value was 84%, tᵣ (minor) = 16.840 min, tᵣ (major) = 26.629 min (Chiralpak IC, λ = 254 nm, 20% i-PrOH/hexane, flow rate = 1.0 mL/min).

Racemic 5b
Enantiomerically enriched 5b

Benzyl (1S,5S,E)-1-benzyl-4-(2-methoxy-1-((4-methylphenyl)sulfonamido)-2-oxoethylidene)-5-phenylcyclopent-2-ene-1-carboxylate 5c

White solid; [α]_D^{25} = +135.3 (c 1.0, CHCl₃); ^1H NMR (500 MHz, CDCl₃) δ 7.52 (d, J = 8.1 Hz, 2H), 7.36 (t, J = 7.4 Hz, 2H), 7.32 (dd, J = 6.0 Hz, 3.6 Hz, 3H), 7.28 (t, J = 7.4 Hz, 2H), 7.20–7.13 (m, 5H), 7.09 (d, J = 8.2 Hz, 2H), 6.95 (dd, J = 6.2 Hz, 2.7 Hz, 2H), 6.61 (d, J = 5.8 Hz, 1H), 6.09 (s, 1H), 5.10–5.01 (m, 3H), 3.07 (s, 1H), 2.73 (d, J = 13.5 Hz, 1H), 2.34 (s, 1H), 2.28 (d, J = 13.5 Hz, 1H); ^13C NMR (125 MHz, CDCl₃) δ 174.48, 163.59, 146.87, 140.14, 137.07, 134.40, 129.71, 129.23, 128.50, 128.26, 128.22, 128.09, 127.56, 126.92, 126.66, 66.99, 65.17, 56.34, 51.34, 41.86, 21.45; HRMS (ESI) m/z calcd for C₃₆H₃₃NaO₆S [M+Na]^+ = 630.1921 , found = 630.1924; The ee value was 78%, t_R (minor) = 27.893 min, t_R (major) = 31.025 min (Chiralpak ID, λ = 254 nm, 40% i-PrOH/hexane, flow rate = 1.0 mL/min).
Racemic 5c

Enantiomerically enriched 5c

tert-Butyl \((1S,5S,E)-1-(4\text{-chlorobenzyl})-4-(2\text{-methoxy}-1\text{-((4\text{-methylphenyl)sulfonamido})-2-oxoethylidene})-5\text{-phenylcyclopent-2-ene-1-carboxylate 5d}\)
White solid; \([\alpha]^2_{D} = +165.2 \text{ (c 1.0, CHCl}_3)\); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.52 (d, \(J = 8.2\) Hz, 2H), 7.38–7.24 (m, 6H), 7.19 (d, \(J = 8.3\) Hz, 2H), 7.10 (d, \(J = 8.2\) Hz, 2H), 6.95 (d, \(J = 8.3\) Hz, 2H), 6.50 (d, \(J = 5.7\) Hz, 1H), 6.06 (s, 1H), 5.01 (s, 1H), 3.07 (s, 3H), 2.66 (d, \(J = 13.8\) Hz, 1H), 2.34 (s, 3H), 2.30 (d, \(J = 13.8\) Hz, 1H), 1.39 (s, 9H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 173.37, 164.46, 163.56, 147.39, 143.60, 140.14, 135.98, 134.24, 132.40, 131.27, 129.21, 128.16, 127.57, 126.86, 115.36, 82.09, 77.27, 77.02, 76.77, 65.38, 56.28, 51.31, 40.53, 27.93, 21.45; HRMS (ESI) m/z calcd for C\(_{33}\)H\(_{34}\)ClNNaO\(_6\)S \([\text{M+Na}]^+\) = 630.1688, found = 630.1692; The ee value was 86%, \(t_R\) (minor) = 15.961 min, \(t_R\) (major) = 25.349 min (Chiralpak IC, \(\lambda = 254\) nm, 20% \(i\)-PrOH/hexane, flow rate = 1.0 mL/min).

Racemic 5d
Enantiomerically enriched 5d

tert-Butyl (1S,5S,E)-1-(3-chlorobenzyl)-4-(2-methoxy-1-((4-methylphenyl)sulfonamido)-2-oxoethylidene)-5-phenylcyclopent-2-ene-1-carboxylate 5e

White solid; $[\alpha]^{25}_{D} = +155.5$ (c 1.0, CHCl$_3$); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.52 (d, $J = 8.2$ Hz, 2H), 7.30 (dd, $J = 25.2$ Hz, 9.9 Hz, 6H), 7.16 (d, $J = 7.2$ Hz, 2H), 7.11 (d, $J = 8.2$ Hz, 2H), 7.01 (s, 1H), 6.90 (d, $J = 6.7$ Hz, 1H), 6.52 (d, $J = 5.7$ Hz, 1H), 6.08 (s, 1H), 5.03 (s, 1H), 3.07 (s, 3H), 2.66 (d, $J = 13.8$ Hz, 1H), 2.35 (s, 3H), 2.31 (d, $J = 13.7$ Hz, 1H), 1.41 (s, 9H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 173.30, 164.38, 163.56, 147.32, 143.61, 140.10, 139.52, 135.99, 134.23, 133.86, 130.04, 129.27, 129.21, 128.08, 127.57, 126.90, 126.69, 115.41, 82.24, 65.35, 56.23, 51.32, 40.88, 27.92, 21.45; HRMS (ESI) m/z calcd for C$_{33}$H$_{34}$ClNNaO$_6$S [$M+Na]^+$ = 630.1688, found = 630.1690; The ee value was 89%, $t_R$ (minor) = 15.478 min, $t_R$ (major) = 25.954 min (Chiralpak IC, $\lambda = 254$ nm, 20% i-PrOH/hexane, flow rate = 1.0 mL/min).
S13

Racemic 5e

Enantiomerically enriched 5e

tert-Butyl (1S,5S,E)-1-(2-chlorobenzyl)-4-(2-methoxy-1-((4-methylphenyl)sulfonamido)-2-oxoethylidene)-5-phenycyclopent-2-ene-1-carboxylate 5f
White solid; [α]$_D^{25}$ = +123.3 (c 1.0, CHCl$_3$); $^1$H NMR (500 MHz, CDCl$_3$) δ 7.50 (d, $J$ = 8.1 Hz, 2H), 7.33 – 7.21 (m, 8H), 7.17–7.12 (m, 2H), 7.09 (d, $J$ = 8.0 Hz, 2H), 6.51 (d, $J$ = 5.6 Hz, 1H), 6.06 (s, 1H), 5.14 (s, 1H), 3.09 (s, 3H), 2.72 (q, $J$ = 14.4 Hz, 2H), 2.34 (s, 3H), 1.36 (s, 9H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 173.48, 164.55, 163.67, 148.23, 143.54, 140.20, 135.92, 135.85, 134.81, 133.76, 131.21, 129.53, 129.18, 127.86, 127.61, 126.88, 126.38, 115.07, 82.04, 65.59, 56.45, 51.31, 37.23, 27.83, 21.45; HRMS (ESI) m/z calcd for C$_{33}$H$_{34}$ClNNaO$_6$S [M+Na]$^+$ = 630.1688, found = 630.1691; The ee value was 94%, $t_R$ (minor) = 15.619 min, $t_R$ (major) = 26.266 min (Chiralpak IC, $\lambda$ = 254 nm, 20% $i$-PrOH/hexane, flow rate = 1.0 mL/min).

Racemic 5f
Enantiomerically enriched 5f

tert-Butyl \((1S,5S,E)-4-(2\text{-methoxy}-1-((4\text{-methylphenyl})\text{sulfonamido})-2\text{-oxoethylidene})-1-(\text{naphthalen-1-ylmethyl})-5\text{-phenylcyclopent-2-ene-1-carboxylate} 5g

White solid; \([\alpha]^{25}_D = +180.1\) (c 0.5, CHCl3); \(^1\)H NMR (500 MHz, CDCl3) \(\delta\) 7.82 (d, \(J = 7.6\) Hz, 1H), 7.73 (t, \(J = 9.0\) Hz, 2H), 7.55 (d, \(J = 8.2\) Hz, 2H), 7.52–7.31 (m, 8H), 7.24 (dd, \(J = 17.5\) Hz, 6.1 Hz, 2H), 7.12 (d, \(J = 8.1\) Hz, 2H), 6.38 (d, \(J = 5.7\) Hz, 1H), 6.07 (s, 1H), 5.18 (s, 1H), 3.10 (s, 3H), 3.05 (d, \(J = 14.4\) Hz, 1H), 2.87 (d, \(J = 14.4\) Hz, 1H), 2.35 (s, 3H), 1.24 (s, 9H); \(^{13}\)C NMR (125 MHz, CDCl3) \(\delta\) 173.94, 164.62, 163.71, 148.83, 143.59, 140.74, 136.01, 133.92, 133.82, 133.44, 132.57, 129.22, 128.61, 127.81, 127.60, 127.38, 126.88, 125.94, 125.45, 125.05, 124.27, 115.15, 81.88, 66.11, 56.79, 51.33, 37.02, 27.76, 21.46; HRMS (ESI) m/z calcd for C\(_{37}\)H\(_{37}\)NNaO\(_6\)S [M+Na]\(^+\) = 646.2234, found = 646.2238; The ee value was
93%, $t_R$ (minor) = 15.433 min, $t_R$ (major) = 25.707 min (Chiralpak IC, $\lambda = 254$ nm, 20% $i$-PrOH/hexane, flow rate = 1.0 mL/min).

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**Racemic 5g**

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**Enantiomerically enriched 5g**

**tert-Butyl (1S,5S,E)-4-(2-methoxy-1-((4-methylphenyl)sulfonamido)-2-oxoethylidene)-1-(4-methylbenzyl)-5-phenylcyclopent-2-ene-1-carboxylate 5h**
White solid; $[\alpha]^{25}_D = +152.3$ (c 1.0, CHCl₃); $^1$H NMR (500 MHz, CDCl₃) δ 7.53 (d, $J = 8.2$ Hz, 2H), 7.33 (t, $J = 7.5$ Hz, 3H), 7.25 (t, $J = 7.2$ Hz, 3H), 7.11 (d, $J = 8.2$ Hz, 2H), 7.02 (d, $J = 7.9$ Hz, 2H), 6.91 (d, $J = 7.9$ Hz, 2H), 6.56 (d, $J = 5.7$ Hz, 1H), 6.06 (s, 1H), 4.99 (s, 1H), 3.06 (s, 3H), 2.64 (d, $J = 13.7$ Hz, 1H), 2.34 (s, 3H), 2.30 (s, 3H), 2.24 (d, $J = 13.8$ Hz, 1H), 1.39 (s, 9H); $^{13}$C NMR (125 MHz, CDCl₃) δ 173.69, 164.93, 163.66, 148.29, 143.55, 140.37, 136.03, 135.95, 134.22, 133.74, 129.85, 129.20, 128.71, 127.93, 127.59, 126.72, 115.10, 81.79, 65.57, 56.45, 51.27, 40.97, 27.94, 21.45, 20.99; HRMS (ESI) m/z calcd for C$_{34}$H$_{37}$NNaO$_6$S [M+Na]$^+$ = 610.2234, found = 610.2237; The ee value was 86%, $t_R$ (minor) = 16.601 min, $t_R$ (major) = 24.594 min (Chiralpak IC, $\lambda = 254$ nm, 20% $i$-PrOH/hexane, flow rate = 1.0 mL/min).

Racemic 5h
EnantiomERICALLY enriched 5h

tert-Butyl (1S,5S,E)-4-(2-methoxy-1-((4-methylphenyl)sulfonamido)-2-oxoethylidene)-1-(4-nitrobenzyl)-5-phenylcyclopent-2-ene-1-carboxylate 5i

White solid; [α]$_D^{25}$ = +150.4 (c 1.0, CHCl$_3$); $^1$H NMR (500 MHz, CDCl$_3$) δ 8.07 (d, $J$ = 8.6 Hz, 2H), 7.49 (d, $J$ = 8.2 Hz, 2H), 7.32 (d, $J$ = 5.7 Hz, 6H), 7.16 (d, $J$ = 8.6 Hz, 2H), 7.10 (d, $J$ = 8.1 Hz, 2H), 6.45 (d, $J$ = 5.7 Hz, 1H), 6.10 (s, 1H), 5.07 (s, 1H), 3.07 (s, 3H), 2.81 (d, $J$ = 13.9 Hz, 1H), 2.52 (d, $J$ = 13.9 Hz, 1H), 2.34 (s, 3H), 1.39 (s, 9H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 172.93, 163.93, 163.43, 146.75, 146.37, 145.59, 143.68, 139.84, 135.92, 134.90, 130.66, 129.23, 127.53, 127.08, 123.18, 115.72, 82.52, 65.23, 56.06, 51.37, 40.71, 27.92, 21.45; HRMS (ESI) m/z calcd for C$_{33}$H$_{34}$N$_2$NaO$_8$S [M+Na]$^+$ = 641.1928, found = 641.1935; The ee value was 92%, t$_R$ (minor) = 22.363 min, t$_R$ (major) = 37.610 min (Chiralpak IC, λ = 254 nm, 40% i-PrOH/hexane, flow rate = 1.0 mL/min).
Racemic 5i

Enantiomerically enriched 5i

Benzyl (1S,5S,E)-4-(2-methoxy-1-((4-methylphenyl)sulfonamido)-2-oxoethylidene)-1-(2-methoxy-2-oxoethyl)-5-phenylcyclopent-2-ene-1-carboxylate 5j

\[
\text{TsHN} \quad \text{CO}_2\text{Me} \\
\text{CO}_2\text{Me} \quad \text{Ph} \\
\text{CO}_2\text{Bn}
\]
White solid; $[\alpha]^{25}_D = +38.1$ (c 1, CHCl$_3$); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.44 (d, $J = 8.2$ Hz, 2H), 7.39 (d, $J = 5.6$ Hz, 1H), 7.31 (dt, $J = 27.5$ Hz, 5.7 Hz, 9H), 7.18 (s, 1H), 7.03 (d, $J = 8.1$ Hz, 2H), 6.53 (d, $J = 5.6$ Hz, 1H), 6.09 (s, 1H), 5.26 (s, 1H), 5.19 (s, 2H), 3.45 (s, 3H), 3.10 (s, 3H), 2.72 (d, $J = 17.4$ Hz, 1H), 2.34–2.26 (m, 4H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 172.73, 171.28, 163.84, 163.53, 145.91, 143.59, 139.77, 136.62, 135.67, 129.18, 128.52, 128.23, 128.01, 127.60, 127.21, 116.10, 67.41, 62.39, 54.74, 51.53, 51.42, 37.61, 29.70, 21.43; HRMS (ESI) m/z calcd for C$_{32}$H$_{31}$NNaO$_8$S [M+Na]$^+$ = 612.1663, found = 612.1667; The ee value was 82%, $t_R$ (major) = 38.160 min, $t_R$ (minor) = 47.679 min (Chiralpak IC, $\lambda = 254$ nm, 40% $i$-PrOH/hexane, flow rate = 1.0 mL/min).
Enantiomerically enriched 5j

tert-Butyl (1S,5S,E)-1-benzyl-4-(2-ethoxy-1-((4-methylphenyl)sulfonamido)-2-oxoethylidene)-5-phenylcyclopent-2-ene-1-carboxylate 5k

![Molecular structure image]

White solid; [$\alpha$]$^{{25}}$D = +201.9 (c 1.0, CHCl$_3$); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.56 (d, $J = 8.1$ Hz, 2H), 7.38–7.16 (m, 9H), 7.11 (d, $J = 8.2$ Hz, 2H), 7.05 (d, $J = 7.1$ Hz, 2H), 6.56 (d, $J = 5.7$ Hz, 1H), 6.15 (s, 1H), 5.04 (s, 1H), 3.59 (ddd, $J = 47.2$ Hz, 10.8 Hz, 7.1 Hz, 2H), 2.70 (d, $J = 13.7$ Hz, 1H), 2.34 (s, 3H), 2.27 (d, $J = 13.7$ Hz, 1H), 1.39 (s, 9H), 0.75 (t, $J = 7.1$ Hz, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 173.65, 164.12, 163.33, 147.67, 143.54, 140.51, 137.46, 136.11, 134.00, 130.00, 129.23, 128.04, 127.63, 126.73, 126.48, 115.44, 81.80, 65.45, 60.79, 56.44, 41.47, 27.91, 21.41, 13.65; HRMS (ESI) m/z calcd for C$_{34}$H$_{37}$NNaO$_6$S [M+Na]$^+$ =610.2234, found = 610.2240; The ee value was 85%, $t_R$ (minor) = 15.748 min, $t_R$ (major) = 19.359 min (Chiralpak IC, $\lambda = 254$ nm, 20% i-PrOH/hexane, flow rate = 1.0 mL/min).
Racemic 5k

Enantiomerically enriched 5k

tert-Butyl (1S,5S,E)-1-benzyl-4-(2-ethoxy-1-((4-methylphenyl)sulfonamido)-2-oxoethylidene)-5-(4-fluorophenyl)cyclopent-2-ene-1-carboxylate 5l

S22
White solid; \( (\alpha)_2^{25} D = +200.0 \) (c 1.0, CHCl\(_3\)); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 7.53 (d, \( J = 8.2 \) Hz, 2H), 7.24 (ddd, \( J = 17.6 \) Hz, 15.5 Hz, 6.1 Hz, 6H), 7.14 (d, \( J = 8.2 \) Hz, 2H), 7.03 (d, \( J = 6.5 \) Hz, 4H), 6.56 (d, \( J = 5.7 \) Hz, 1H), 6.13 (s, 1H), 5.05 (s, 1H), 3.74–3.43 (m, 2H), 2.67 (d, \( J = 13.7 \) Hz, 1H), 2.36 (s, 2H), 2.30 (d, \( J = 13.7 \) Hz, 1H), 1.38 (s, 9H), 0.77 (t, \( J = 7.1 \) Hz, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \( \delta \) 173.49, 164.19, 163.10, 147.71, 143.70, 137.23, 136.33, 136.16, 133.89, 129.88, 129.29, 128.09, 127.52, 126.56, 115.45, 114.79, 114.62, 81.95, 77.27, 77.02, 76.76, 65.43, 60.84, 55.47, 41.48, 27.89, 21.42, 13.68; HRMS (ESI) m/z caled for C\(_{34}\)H\(_{36}\)FNNaO\(_6\)S \([\text{M+Na}]^+\) =628.2140 , found = 628.2143; The ee value was 86%, \( t_R \) (minor) = 11.744 min, \( t_R \) (major) = 15.561 min (Chiralpak IC, \( \lambda = 254 \) nm, 20% \( \nu \)-PrOH/hexane, flow rate = 1.0 mL/min).

**Racemic 5l**

---

### Peak Table

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Enantiomerically enriched 5l

**tert-Butyl (1S,5S,E)-1-benzyl-5-(4-chlorophenyl)-4-(2-ethoxy-1-((4-methylphenyl)sulfonamido)-2-oxoethylidene)cyclopent-2-ene-1-carboxylate 5m**

White solid; \([\alpha]^{25}_D = +176.3\) (c 0.5, CHCl₃); \(^1\)H NMR (500 MHz, CDCl₃) \(\delta\) 7.52 (d, \(J = 8.2\) Hz, 2H), 7.30 (s, 3H), 7.27 (d, \(J = 5.7\) Hz, 1H), 7.21 (dd, \(J = 10.0\) Hz, 7.1 Hz, 4H), 7.14 (d, \(J = 8.2\) Hz, 2H), 7.06–6.98 (m, 2H), 6.55 (d, \(J = 5.7\) Hz, 1H), 6.12 (s, 1H), 5.03 (s, 1H), 3.59 (ddq, \(J = 56.7\) Hz, 10.8 Hz, 7.1 Hz, 2H), 2.67 (d, \(J = 13.7\) Hz, 1H), 2.36 (s, 3H), 2.29 (d, \(J = 13.7\) Hz, 1H), 1.37 (s, 9H), 0.78 (t, \(J = 7.1\) Hz, 3H); \(^{13}\)C NMR (125 MHz, CDCl₃) \(\delta\) 173.40, 163.88, 163.04, 147.72, 143.75, 139.06, 137.13, 136.14, 133.89, 132.49, 129.88, 129.32, 128.10, 127.52, 126.59, 115.51, 82.01, 65.38, 60.88, 55.58, 41.51, 27.88, 21.44, 13.69; HRMS (ESI) m/z calcd for C₃₄H₃₆ClNNaO₆S [M+Na]^+ = 644.1844, found = 644.1854; The ee value was 82%, \(t_R\) (minor) = 11.271 min, \(t_R\) (major) = 16.788 min (Chiralpak IC, \(\lambda = 254\) nm, 20% i-PrOH/hexane, flow rate = 1.0 mL/min).
Racemic 5m

Enantiomerically enriched 5m

tert-Butyl (1S,5S,E)-1-benzyl-4-(2-ethoxy-1-((4-methylphenyl)sulfonamido)-2-oxoethylidene)-5-(4-methoxyphenyl)cyclopent-2-ene-1-carboxylate 5n

\[
\begin{array}{cccccc}
\text{TsHN} & \text{CO}_2\text{Et} & \text{OMe} \\
\text{Bn} & \text{CO}_2\text{tBu}
\end{array}
\]
Yellow solid; $[\alpha]_{D}^{25} = +194.6$ (c 1.0, CHCl$_3$); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.55 (d, $J = 8.2$ Hz, 2H), 7.27 (d, $J = 5.8$ Hz, 2H), 7.24 – 7.14 (m, 4H), 7.12 (d, $J = 8.1$ Hz, 2H), 7.04 (d, $J = 6.9$ Hz, 2H), 6.87 (d, $J = 8.4$ Hz, 2H), 6.53 (d, $J = 5.7$ Hz, 1H), 6.13 (s, 1H), 4.99 (s, 1H), 3.83 (s, 3H), 3.68–3.49 (m, 2H), 2.70 (d, $J = 13.7$ Hz, 1H), 2.34 (s, 3H), 2.26 (d, $J = 13.8$ Hz, 1H), 1.37 (s, 9H), 0.78 (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 173.69, 164.52, 163.34, 158.37, 147.68, 143.54, 137.58, 136.19, 133.95, 132.77, 129.98, 129.24, 128.02, 127.62, 126.45, 115.27, 113.30, 81.71, 65.60, 60.79, 55.74, 55.29, 41.39, 27.90, 21.43, 13.72; HRMS (ESI) m/z calcd for C$_{35}$H$_{39}$NNaO$_7$S [M+Na]$^+$ = 640.2339, found = 640.2337; The ee value was 90%, $t_R$ (minor) = 19.172 min, $t_R$ (major) = 34.647 min (Chiralpak IC, $\lambda = 254$ nm, 20% i-PrOH/hexane, flow rate = 1.0 mL/min).

Racemic 5n
Enantiomerically enriched 5n

\textit{tert}-Butyl (1S,5S,E)-1-benzyl-4-(2-ethoxy-1-((4-methylphenyl)sulfonamido)-2-oxoethylidene)-5-(thiophen-2-yl)cyclopent-2-ene-1-carboxylate 5o

\[
\text{TsHN} \xrightarrow{\text{CO}_2\text{Et}} \text{CO}_2\text{Bu} \\
\text{CO}_2\text{Et} \xrightarrow{\text{Bn}} \text{CO}_2\text{Bu}
\]

White solid; \([\alpha]^{25}_D = +87.9 \text{ (c 1.0, CHCl}_3\); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta 7.55 \text{ (d, } J = 8.2 \text{ Hz, 2H), 7.26 – 7.17 \text{ (m, 5H), 7.15 \text{ (d, } J = 8.2 \text{ Hz, 2H), 7.08 \text{ (d, } J = 6.8 \text{ Hz, 2H), 6.96 \text{ (d, } J = 3.3 \text{ Hz, 2H), 6.51 \text{ (d, } J = 5.8 \text{ Hz, 1H), 6.11 \text{ (s, 1H), 5.40 \text{ (s, 1H), 3.80–3.48 \text{ (m, 2H), 2.95 \text{ (d, } J = 13.9 \text{ Hz, 1H), 2.59 \text{ (d, } J = 13.9 \text{ Hz, 1H), 2.36 \text{ (s, 3H), 1.36 \text{ (s, 9H), 0.86 \text{ (t, } J = 7.1 \text{ Hz, 3H); 13C NMR (125 MHz, CDCl}_3\) \(\delta 172.91, 163.43, 162.69, 144.96, 143.59, 142.43, 137.43, 136.10, 133.39, 129.89, 129.28, 128.06, 127.68, 126.49, 126.16, 123.71, 115.67, 81.94, 65.75, 61.03, 51.42, 39.92, 27.85, 21.45, 13.76; HRMS (ESI) m/z calcd for C\(_{32}\)H\(_{35}\)NNaO\(_6\)S\(_2\) [M+Na]^+ = 616.1798, found = 616.1802; The ee value was 86%, t\(_R\) (minor) = 17.527 min, t\(_R\) (major) = 26.310 min (Chiralpak IC, \(\lambda = 254 \text{ nm, 20\% i-PrOH/hexane, flow rate = 1.0 mL/min). }

S27
Racemic 5o

Enantiomerically enriched 5o

F. X-Ray crystallographic analysis and determination of the absolute configurations of the products

X-Ray crystallographic analysis of 5a
Figure 1. X-ray structure of 5a

Table 1. Crystal data and structure refinement for f562.

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Data / restraints / parameters 5317 / 1 / 350
Goodness-of-fit on F^2 1.083
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R indices (all data) R1 = 0.0545, wR2 = 0.1398
Absolute structure parameter 0.106(9)
Extinction coefficient n/a
Largest diff. peak and hole 0.477 and -0.632 e.Å^-3

G. References


H. NMR spectra of the products

TsHN\text{CO}_{2}\text{Me} \quad \text{Ph} \quad \text{Bn} \quad \text{CO}_{2}\text{Me}