Si-Free Enolate Claisen Rearrangements of Enamido Substrates

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Supporting Information

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**General Experimental Information**

Reactions were conducted in flame dried vessels using anhydrous solvents and under an inert atmosphere of nitrogen. In all cases, solvents were obtained by passing through anhydrous alumina columns using an Innovative Technology Inc. PS-400-7 solvent purification system. All reagents were purchased from commercial suppliers: Acros Organics, Alfa Aesar, Sigma Aldrich or Novabiochem and used without purification. Triethylamine and chlorotrimethylsilane (over 10 % quinoline) were freshly distilled prior to use. All distilled materials were stored under nitrogen at 4 °C or less. All reactions were monitored by thin layer chromatography (TLC) using pre-coated MN Alugram Sil G/UV<sub>254</sub> silica gel 60 aluminium backed plates. Plates were developed using UV light followed by a chemical dip, usually KMnO<sub>4</sub> and gentle heating. Flash chromatography was performed on chromatography grade, silica 60Å particle size 35-70 micron from Fisher Scientific using the solvent system as stated. Compounds purified through preparative HPLC were subjected to the ‘Waters Autopurification LC System’.

<sup>1</sup>H and <sup>13</sup>C were performed on a Brüker Avance 250 (250 MHz), Brüker Avance 300 (300 MHz), Brüker Avance 400 (400 MHz) and Brüker Avance 500 (500 MHz) as stated. Chemical shifts are reported in parts per million (ppm) relative to tetramethylsilane (TMS) (δ = 0.00). Coupling constants are reported in Hertz (Hz) and signal multiplicity is denoted as singlet (s), doublet (d), triplet (t), quartet (q), doublet of doublets (dd), doublet of triplets (dt), doublet of quartets (dq), quartet of triplets (qt), triplet of doublets (td), multiplet (m), quintet (quin) and broad (br). Mass spectroscopy was performed on a Brüker μTOF using electrospray ionisation (ESI) in either positive or negative ionisation as stated. Infra-red spectroscopy was carried out using a Perkin Elmer Spectrum RX FT-IR system with KBr plates, using a thin film.
Experimental Procedures

(E)-N-allyl-N-(3-hydroxybut-1-enyl)-4-methylbenzenesulfonamide (5e)

To a solution of Cr(VI)O₃ (10.3 g, 103 mmol, 1.5 eq.) in 20% H₂SO₄ (180 ml) at 0 °C under a nitrogen atmosphere was added a solution of 3-butyn-2-ol (5.00 g, 71.3 mmol, 1.0 eq.) in 20% H₂SO₄ (180 ml) by dropwise addition. The reaction mixture was stirred at 0 °C for 12 hours and a colour change from orange to green was noted, saturated aqueous sodium bicarbonate was added and the organics were extracted with DCM (3 x 450 mL) and dried over MgSO₄. The crude butynone was chilled to 0 °C then N-allyl-4-methylbenzenesulfonamide 15.0 g, 78.4 mmol, 1.1 eq.) and DABCO (0.80 g, 7.13 mmol, 0.1 eq.) were added. The reaction mixture was allowed to stir for 12 hours whilst slowly warming to room temperature and a colour change from a clear to a deep maroon solution was noted. The reaction mixture was washed with 5% NaOH (3 x 500 ml), brine and then the organics were dried over MgSO₄ and concentrated in vacuo to give a red oil which was subjected to flash column chromatography (25% EtOAc/Petrol 40-60°) to give the desired (E)-N-allyl-4-methyl-N-(3-oxobut-1-enyl)benzenesulfonamide 327 (10.5 g, 53%) as well as the –(Z) (0.79 g, 4%) as a brown oil in both cases.

(E) product- FTIR (film/cm⁻¹) νmax: 3082(s), 2980(s), 2879(s), 1682(s), 1586(s); ¹H NMR (250MHz, CDCl₃) δ 2.22 (s, 3H), 2.44 (s, 3H), 4.07 (dt, 2H, J = 5.24, 1.59 Hz), 5.13 (dm, 1H, J = 9.2 Hz), 5.19
(m, 1H), 5.48 (d, 1H, J = 14.3 Hz), 5.56 (ddt, 1H, J = 17.2, 10.6, 5.3 Hz), 7.34 (m, 2H), 7.71 (m, 2H), 8.03 (d, 1H, J = 14.3 Hz); 13C NMR (250MHz, CDCl3) δ: 21.7, 27.6, 48.3, 109.0, 118.9, 127.3, 129.9, 130.2, 135.3, 141.2, 145.1, 196.6; HRMS (ESI, +ve) m/z calcd. for C14H18NO3S 280.1007, found 280.0990 (M+H)+.

(Z) product- FTIR (film/cm−1) νmax: 3100(s), 2925(s), 1679(s), 1597(s); 1H NMR (250MHz, CDCl3) δ 2.03 (s, 3H), 2.33 (s, 3H), 4.41 (dt, 2H, J = 5.7, 1.3 Hz), 4.86 (dq, 1H, J = 29.0, 1.5 Hz), 4.91 (dq, 1H, J = 22.3, 1.4 Hz), 5.21 (ddq, 1H, J = 17.9, 10.3, 5.6 Hz), 5.35 (d, 1H, J = 10.3 Hz), 6.71 (d, 1H, J = 10.4 Hz), 7.23 (m, 2H), 7.62 (m, 2H); 13C NMR (250MHz, CDCl3) δ: 21.5, 30.9, 49.67, 108.5, 118.4, 127.2, 130.0, 131.3, 133.3, 135.6, 144.7, 196.2; HRMS (ESI, +ve) m/z calcd. for C14H19NNaO3S 304.0983, found 304.0978 (M+Na)+.

(E)-4-(N-Allyl-4-methylphenylsulfonamido)but-3-en-2-yl propionate (10a)

EDCI (0.54 g, 2.81 mmol) in DCM (100 mL), triethylamine (0.39 mL, 2.81 mmol), DMAP (0.02 g, 0.14 mmol), propionic acid (0.22 mL, 2.81 mmol) and (E)-N-allyl-N-(3-hydroxybut-1-enyl)-4-methylbenzenesulfonamide 5e (0.40 g, 1.41 mmol) in DCM (10 mL) were combined according to
(anti-E)-Methyl 3-(N-allyl-4-methylphenylsulfonamido)-2-methylhex-4-enoate (11a)

LiHMDS (1M in toluene, 1.34 mL, 1.34 mmol), triethylamine (1.81 mL, 13.4 mmol) and (E)-4-(N-allyl-4-methylphenylsulfonamido)but-3-en-2-yl propionate 10a (0.10 g, 0.30 mmol) in THF (1 mL) was combined according to general procedure 4 (reaction time: 75 minutes). Treatment with diazomethane and purification by flash chromatography afforded (anti-E)-methyl 3-(N-allyl-4-methylphenylsulfonamido)-2-methylhex-4-enoate 11a as a white solid (0.06 g, 55%, d.r. >25:1). M.p. 88–90 °C; FTIR (film/cm⁻¹) νmax: 2966 (m), 2916 (m), 1735 (s), 1656s (m); ¹H NMR (500 MHz, CDCl₃) δ: 1.06 (d, 3H, J = 6.9 Hz), 1.51 (dd, 3H, J = 6.4, 1.5 Hz), 2.32 (3H, s), 3.02 (ddt, 2H, J = 10.1, 7.8, 6.9 Hz), 3.69–3.85 (s, 2H), 4.27 (app. t, 1H, J = 10.1 Hz), 5.07–5.18 (m, 2H), 5.41 (ddq, 1H, J = 15.1, 10.1, 1.5 Hz), 5.55 (dq, 1H, J = 15.1, 6.4 Hz), 5.71 (ddt, 1H, J = 17.3, 10.2, 6.5 Hz), 7.26 (app. d, 2H, J = 8.2 Hz), 7.69 (app. d, 2H, J = 8.2 Hz); ¹³C NMR (125 MHz, CDCl₃) δ: 15.6, 17.7, 21.4, 43.4, 49.4, 51.7, 64.1, 117.6, 126.2, 127.7, 129.1, 132.1, 135.3, 137.8, 142.9, 175.0; HRMS (ESI, +ve) m/z calcd. for C₁₉H₂₃NO₄S 352.1582, found 352.1577 (M+H)⁺.
Methyl 2-(1-tosyl-2,5-dihydro-1H-pyrrol-2-yl)propanoate (13a)

\[
\begin{align*}
\text{Me}^+ & \quad \text{Ts}^- \\
& \quad \text{Me}^+ \\
\text{O} & \quad \text{Me}^+
\end{align*}
\]

\(13a\)

\(\textit{anti-(E)-Methyl 3-(N-\text{allyl}-4\text{-methylphenylsulfonamido)-2-methylhex-4-enoate 11a}\)} (0.02 g, 0.05 mmol), catalytic Grubbs I and DCM (5 mL) were combined according to general procedure 6 (reaction time: 6 hours). Purification was achieved by the reported procedure to yield the methyl 2-(1-tosyl-2,5-dihydro-1H-pyrrol-2-yl)propanoate \(13a\) as a white solid (0.01 g, 79%). M.p. 95–97 °C; FTIR (film/cm\(^{-1}\)) \(\nu\)\text{max}: 2960 (m), 2928 (m), 2878 (m), 1730 (s), 1597 (m); \(^1\)H NMR (500 MHz, CD\(_3\)Cl) \(\delta\): 1.12 (d, 3H, \(J = 7.1\) Hz), 2.44 (s, 3H), 3.31 (qd, 1H, \(J = 7.13, 3.96\) Hz), 3.72 (s, 3H), 4.06–4.19 (m, 2H), 4.84–4.89 (m, 1H), 5.55 (app dq, 1H, \(J = 5.5, 2.2\) Hz), 5.72 (app. dq, 1H, \(J = 5.5, 2.2\) Hz), 7.33 (app. d, 2H, \(J = 8.1\) Hz), 7.74 (app. d, 2H, \(J = 8.1\) Hz); \(^{13}\)C NMR (125 MHz, CD\(_3\)Cl) \(\delta\): 10.1, 21.5, 43.9, 51.8, 56.1, 67.9, 126.5, 126.8, 127.4, 129.8, 134.1, 143.6, 174.5; HRMS (ESI, +ve) \(m/z\) calcd. for C\(_{13}\)H\(_{20}\)NO\(_4\)S 310.113, found 310.1108 (M+H)

\((E)-4-(N-\text{Allyl}-4\text{-methylphenylsulfonamido})\text{-but-3-en-2-yl 3-methylbutanoate (10b)}\)

\[
\begin{align*}
& \quad \text{Me}^+ \\
& \quad \text{Me}^+ \\
\text{N} & \quad \text{O} \\
& \quad \text{Me}^+ \\
\text{O} & \quad \text{Me}^+ \\
& \quad \text{Me}^+
\end{align*}
\]

\(10b\)

EDCI (0.54 g, 2.81 mmol) in DCM (100 mL), triethylamine (0.39 mL, 2.81 mmol), DMAP (0.02 g, 0.14 mmol), isovaleric acid (0.31 mL, 2.81 mmol) and \((E)-N-\text{allyl-}\text{-N-(3-hydroxybut-1-enyl)-4-methylbenzenesulfonamide 5e}\) (0.40 g, 1.41 mmol) in DCM (10 mL) were combined according to general procedure 1 (reaction time: 15 hours). Purification was achieved by reported procedure to afford \((E)-4-(N-\text{allyl-4-methylphenylsulfonamido})\text{-but-3-en-2-yl 3-methylbutanoate 335} as a yellow oil (0.45 g, 87%). FTIR (film/cm\(^{-1}\)) \(\nu\)\text{max}: 2960 (m), 2931 (m), 1725 (s), 1655 (s), 1597 (m); \(^1\)H NMR (500 MHz, CD\(_2\)Cl\(_2\)) \(\delta\): 0.92–0.96 (m, 6H), 1.32 (d, 3H, \(J = 6.6\) Hz), 2.01–2.10 (m, 1H), 2.14 (d, 2H, \(J = 6.7\) Hz), 2.44 (s, 3H), 3.94–4.06 (m, 2H), 4.83 (dd, 1H, \(J = 14.1, 6.6\) Hz), 5.15 (d, 1H, \(J = 11.0\) Hz), 5.18 (d, 1H, \(J = 17.6\) Hz), 5.38 (app. quin, 1H, \(J = 6.6\) Hz), 5.64 (ddt, 1H, \(J = 17.6, 11.0, 6.3\) Hz), 7.02 (d, 1H, \(J = 14.1\) Hz), 7.35 (app. d, 2H, \(J = 7.7\) Hz), 7.69 (app. d, 2H, \(J = 7.7\) Hz); \(^{13}\)C NMR...
(125 MHz, CD$_2$Cl$_2$) $\delta$: 20.8, 21.2, 22.1, 25.7, 43.6, 47.9, 69.6, 110.2, 117.5, 126.9, 129.6, 129.8, 131.4, 136.0, 144.1, 172.0; HRMS (ESI, +ve) m/z calcd. for C$_{19}$H$_{27}$NNaO$_4$S 388.1558, found 388.1567 (M+Na)$^+$. 

\textbf{(anti-E)-Methyl 3-\textit{(N-allyl-4-methylphenylsulfonamido)-2-isopropylhex-4-enoate (11b)}}

\begin{center}
\includegraphics[width=0.4\textwidth]{structure11b}
\end{center}

LiHMDS (1M in toluene, 2.47 mL, 2.47 mmol), triethylamine (3.42 mL, 24.7 mmol) and (E)-4-(N-allyl-4-methylphenylsulfonamido)but-3-en-2-yl 3-methylbutanoate 10b (0.20 g, 0.55 mmol) in THF (2 mL) was combined according to general procedure 4 (reaction time: 75 minutes). Treatment with diazomethane and purification by flash chromatography afforded (\textit{anti-E})-methyl 3-(N-allyl-4-methylphenylsulfonamido)-2-isopropylhex-4-enoate 11b as a white solid (0.14 g, 65%, d.r. >25:1). M.p. 105–107 °C; FTIR (film/cm$^{-1}$) $\nu_{\text{max}}$: 3082 (m), 3021 (m), 2985 (m), 2958 (m), 1730 (s), 1655 (m), 1615 (m), 1597 (m), 1509 (m); $^1$H NMR (400 MHz, CD$_3$Cl) $\delta$: 0.90 (d, 3H, $J = 6.7$ Hz), 0.99 (d, 3H, $J = 6.7$ Hz), 1.67 (d, 3H, $J = 5.8$ Hz), 1.78–1.94 (1H, m), 2.43 (s, 3H), 3.08 (dd, 2H, $J = 11.3$, 2.7 Hz), 3.65 (s, 3H), 3.67–3.86 (m, 2H), 4.45 (app. t, 1H, $J = 11.3$ Hz), 5.07–5.28 (m, 1H), 5.48–5.80 (m, 1H), 7.27 (app. d, 2H, $J = 8.1$ Hz), 7.72 (app. d, 2H, $J = 8.1$ Hz); $^{13}$C NMR (125 MHz, CD$_3$Cl) $\delta$: 16.0, 17.8, 21.4, 21.9, 27.6, 51.5, 54.2, 61.9, 117.8, 126.9, 127.9, 129.1, 131.5, 135.2, 137.9, 142.9, 172.8; HRMS (ESI, +ve) m/z calcd. for C$_{20}$H$_{30}$NO$_4$S 380.1895, found 380.1900 (M+H)$^+$. 

\section*{Methyl 3-methyl-2-(1-tosyl-2,5-dihydro-1H-pyrrol-2-yl)butanoate (13b)}

\begin{center}
\includegraphics[width=0.4\textwidth]{structure13b}
\end{center}

\textit{anti-(E)-Methyl 3-(N-allyl-4-methylphenylsulfonamido)-2-isopropylhex-4-enoate 11b (0.05 g, 0.13 mmol), catalytic Grubbs I and DCM (5 mL) were combined according to general procedure 6 (reaction time: 13 hours). Purification was achieved by the reported procedure to yield the methyl 3-}


methyl-2-(1-tosyl-2,5-dihydro-1H-pyrrol-2-yl)butanoate 13b as an amorphous white solid (0.04 g, 86%). FTIR (film/cm\(^{-1}\)) \(\nu_{\text{max}}\): 2994 (m), 2956 (m), 2878 (m), 1727 (s), 1598 (m); \(^1\)H NMR (500 MHz, CD\(_3\)Cl) \(\delta\): 0.86 (d, 3H, J = 6.0 Hz), 1.10 (d, 3H, J = 6.0 Hz), 1.96–2.06 (m, 1H), 2.42 (s, 3H), 3.03 (app t, 1H, J = 6.0 Hz), 3.72 (s, 3H), 4.08–4.18 (m, 2H), 4.68–4.73 (m, 1H), 5.66 (app. dq, 1H, J = 6.4, 2.1 Hz), 5.86 (app. dq, 1H, J = 6.4, 2.1 Hz), 7.31 (app. d, 2H, J = 8.1 Hz), 7.70 (app. d, 2H, J = 8.1 Hz); \(^13\)C NMR (125 MHz, CD\(_3\)Cl) \(\delta\): 20.0, 21.5, 22.7, 26.3, 51.2, 56.0, 67.6, 125.5, 127.5, 128.5, 129.7, 134.0, 143.6, 173.9; HRMS (ESI, +ve) m/z calcd. for C\(_{17}\)H\(_{24}\)NO\(_4\)S 338.1426, found 338.1426 (M+H\(^+\)).

\[(E)-4-(N-\text{Allyl}-4\text{-methylphenylsulfonamido})\text{but-3-en-2-yl pent-4-enoate} \;10c\]

EDCi (0.54 g, 2.81 mmol) in DCM (100 mL), triethylamine (0.39 mL, 2.81 mmol), DMAP (0.02 g, 0.14 mmol), penteneoic acid (0.28 g, 2.81 mmol) and (E)-N-allyl-N-(3-hydroxybut-1-enyl)-4-methylbenzenesulfonamide 5e (0.40 g, 1.41 mmol) in DCM (20 mL) were combined according to general procedure 1 (reaction time: 15 hours). Purification was achieved by reported procedure to afford (E)-4-(N-allyl-4-methylphenylsulfonamido)but-3-en-2-yl pent-4-enoate 10c as a yellow oil (0.51 g, 99%). FTIR (film/cm\(^{-1}\)) \(\nu_{\text{max}}\): 3054 (m), 2981 (m), 2918 (m), 1718 (s), 1655 (s), 1597 (m); \(^1\)H NMR (500 MHz, (CD\(_3\))\(_2\)CO) \(\delta\): 1.28 (d, 3H, J = 6.8 Hz), 2.29–2.37 (m, 4H), 2.44 (s, 3H), 3.98–4.11 (m, 2H), 4.90 (dd, 1H, J = 14.4, 6.7 Hz), 4.94 (dd, 1H, J = 10.1, 1.2 Hz), 5.04 (dd, 1H, J = 17.1, 1.4 Hz), 5.13 (dd, 1H, J = 10.1, 1.2 Hz), 5.21 (dd, 1H, J = 17.1, 1.2 Hz), 5.35 (app. quin, 1H, J = 6.8 Hz), 5.66 (ddt, 1H, J = 17.1, 10.1, 5.4 Hz), 5.78–5.92 (m, 1H), 7.01 (d, 1H, J = 14.4 Hz), 7.44 (app. d, 2H, J = 8.2 Hz), 7.74 (app. d, 2H, J = 8.2 Hz); \(^13\)C NMR (125 MHz, (CD\(_3\))\(_2\)CO) \(\delta\): 20.4, 20.5, 33.4, 34.0, 47.6, 69.7, 110.3, 114.7, 117.1, 127.0, 129.7, 129.8, 131.8, 136.3, 137.0, 144.1, 171.4; HRMS (ESI, +ve) m/z calcd. for C\(_{19}\)H\(_{28}\)NNaO\(_4\)S 386.1402, found 386.1480 (M+Na\(^+\)).
(anti-E)-Methyl 2-allyl-3-(N-allyl-4-methylphenylsulfonamido)hex-4-enoate (11c)

LiHMDS (1M in toluene, 2.48 mL, 2.48 mmol) and triethylamine (3.43 mL, 24.80 mmol) in THF (2 mL) was combined according to general procedure 4 (reaction time: 75 minutes). Treatment with diazomethane and purification by flash chromatography afforded (anti-E)-methyl 2-allyl-3-(N-allyl-4-methylphenylsulfonamido)hex-4-enoate 11c as a yellow oil (0.15 g, 70%, d.r. 10:1). FTIR (film/cm⁻¹) ν max: 3012 (m), 2983 (m), 2934 (m), 1729 (s), 1655 (s), 1616 (s), 1596 (s), 1509 (m); ¹H NMR (400 MHz, CDCl₃) δ: 1.66 (d, 3H, J = 6.3 Hz), 2.12–2.29 (2H, m), 2.43 (s, 3H), 3.08 (td, 1H, J = 10.6, 4.5 Hz), 3.66 (s, 3H), 3.74 (dd, 1H, J = 15.8, 6.7 Hz), 3.83 (dd, 1H, J = 16.0, 6.7 Hz), 4.33 (app. t, 1H, J = 10.6 Hz), 4.98–5.22 (2H, m), 5.48 (dd, 1H, J = 15.5, 9.9 Hz), 5.60 (dq, 1H, J = 14.2, 6.3 Hz), 5.65–5.77 (m, 2H), 7.28 (app. d, 2H, J = 8.1 Hz), 7.73 (app. d, 2H, J = 8.1 Hz); ¹³C NMR (125 MHz, CDCl₃) δ: 17.8, 21.4, 34.9, 49.4, 49.5, 51.5, 63.2, 117.1, 117.8, 126.4, 127.8, 129.2, 132.4, 134.5, 135.1, 137.7, 143.0, 173.6; HRMS (ESI, +ve) m/z calcd. for C₂₉H₂₈NO₄S 378.1739, found 378.1699 (M+H)⁺.

Benzylxy-acetic acid 3-[allyl-(toluene-4-sulfonyl)-amino]-1-methyl-allyl ester (10d)

EDCi (0.54 g, 2.81 mmol) in DCM (100 mL), triethylamine (0.39 mL, 2.81 mmol), DMAP (0.02 g, 0.14 mmol), benzyloxyacetic acid (0.41 mL, 2.81 mmol) and (E)-N-allyl-N-(3-hydroxybut-1-enyl)-4-methylbenzenesulfonamide 5e (0.40 g, 1.41 mmol) in DCM (20 mL) were combined according to general procedure 1 (reaction time: 15 hours). Purification was achieved by reported procedure to afford benzylxy-acetic acid 3-[allyl-(toluene-4-sulfonyl)-amino]-1-methyl-allyl ester 10d as a yellow oil (0.54 g, 87%). FTIR (film/cm⁻¹) ν max: 3051 (m), 2971 (m), 2934 (m), 1744 (s), 1655 (s), 1616 (s), 1596 (s), 1509 (m), 1430 (s), 1362 (m), 1264 (s), 1178 (m), 1132 (s), 1063 (s), 751 (w), 699 (w), 670 (w), 634 (w), 599 (w).
1597 (m); \(^1\)H NMR (500 MHz, (CD\(_3\))\(_2\)CO) \(\delta\): 1.32 (d, 3H, \(J = 6.8 \text{ Hz}\)), 2.40 (s, 3H), 3.98–4.15 (m, 4H), 4.60 (s, 2H), 4.93 (dd, 1H, \(J = 14.3, 6.8 \text{ Hz}\)), 4.93 (dq, 1H, \(J = 10.5, 1.4 \text{ Hz}\)), 5.21 (dq, 1H, \(J = 17.2, 1.5 \text{ Hz}\)), 5.46 (app. quin, 1H, \(J = 6.8 \text{ Hz}\)), 5.65 (ddt, 1H, \(J = 17.2, 10.5, 5.2 \text{ Hz}\)), 7.08 (d, 1H, \(J = 14.3 \text{ Hz}\)), 7.28–7.43 (m, 7H), 7.74 (app. d, 2H, \(J = 8.1 \text{ Hz}\)); \(^{13}\)C NMR (125 MHz, (CD\(_3\))\(_2\)CO) \(\delta\): 20.4, 20.5, 47.6, 67.3, 70.5, 109.9, 117.1, 127.0, 127.5, 127.7, 128.2, 129.8, 130.2, 131.7, 136.3, 138.1, 144.1, 169.3; HRMS (ESI, +ve) \(m/z\) calcd. for C\(_{23}\)H\(_{27}\)NNaO\(_4\)S \(452.1508\), found 452.1543 (M+Na)

\((E)-4-(N\text{-Allyl-4-methylphenylsulfonamido})\text{but-3-en-2-yl 2-phenylacetate (10e)}\)

![Diagram](image)

EDCi (0.68 g, 3.55 mmol) in DCM (100 mL), triethylamine (0.49 mL, 3.55 mmol), DMAP (0.02 g, 0.18 mmol), phenylacetic acid (0.48 g, 3.55 mmol) and \((E)-N\text{-allyl-N-(3-hydroxybut-1-enyl)-4-methylbenzenesulfonamide 5e}\) (0.50 g, 1.78 mmol) in DCM (20 mL) were combined according to general procedure 1 (reaction time: 15 hours). Purification was achieved by reported procedure to afford \((E)-4-(N\text{-allyl-4-methylphenylsulfonamido})\text{but-3-en-2-yl 2-phenylacetate 10e}\) as a yellow oil (0.70 g, 98%). FTIR (film/cm\(^{-1}\)) \(\nu_{\text{max}}\): 3051 (m), 2977 (m), 2922 (m), 1727 (s), 1655 (s), 1597 (m); \(^1\)H NMR (250 MHz, (CD\(_3\))\(_2\)CO) \(\delta\): 1.29 (d, 3H, \(J = 6.5 \text{ Hz}\), \(\text{CH}_3\text{CH(CH}_3\text{)O-}\)), 2.40 (s, 3H, \(\text{CH}_3\text{C}_6\text{H}_4\)), 3.60 (s, 2H, \(-\text{CH}_2\text{C}_6\text{H}_5\)), 3.93–4.10 (m, 2H, \(-\text{NCH}_2\text{CHCH}_2\)), 4.88 (dd, 1H, \(J = 14.2, 6.5 \text{ Hz}\), \(-\text{NCHCH-}\)), 5.05–5.24 (m, 2H, \(-\text{NCH}_2\text{CHCH}_2\)), 5.37 (app quin, 1H, \(J = 6.5 \text{ Hz}\), \(\text{CH}_3\text{CH(CH}_3\text{)O-}\)), 5.62 (ddt, 1H, \(J = 17.3, 10.4, 5.2 \text{ Hz}\), \(-\text{NCH}_2\text{CHCH}_2\)), 7.03 (d, 1H, \(J = 14.2 \text{ Hz}\), \(-\text{NCHCH-}\)), 7.23–7.37 (m, 5H, \(\text{CH}_3\text{C}_6\text{H}_5\)), 7.39 (app. d, 2H, \(J = 8.3 \text{ Hz}\), \(\text{ArH}\)), 7.71 (app. d, 2H, \(J = 8.3 \text{ Hz}\), \(\text{ArH}\)); \(^{13}\)C NMR (100 MHz, CD\(_3\))\(_2\)Cl) \(\delta\): 20.9, 21.5, 41.7, 48.0, 70.7, 109.7, 117.9, 127.0 (x2), 128.5, 129.2, 129.8 (x2), 131.2, 134.2, 136.1, 143.9, 170.7; HRMS (ESI, +ve) \(m/z\) calcd. for C\(_{22}\)H\(_{26}\)NNaO\(_4\)S \(422.1411\), found 422.1375 (M+Na)

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**Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry**

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(anti-\(E\))-Methyl 3-(\(N\)-allyl-4-methylphenylsulfonamido)-2-phenylhex-4-enoate (11d)

![Structure](image)

LiHMDS (1 M in toluene, 0.63 mL, 0.63 mmol), TMSCl (0.19 mL, 2.91 mmol) and \((E)\)-4-(\(N\)-allyl-4-methylphenylsulfonamido)but-3-en-2-yl 2-phenylacetate 10e (0.10 g, 0.48 mmol) in THF (1 mL) was combined according to general procedure 3 (reaction time: 75 minutes). Treatment with diazomethane and purification by flash chromatography afforded (anti-\(E\))-methyl 3-(\(N\)-allyl-4-methylphenylsulfonamido)-2-phenylhex-4-enoate 11d as a white solid (0.06 g, 57%, d.r. >25:1). M.p. 103–104 °C; FTIR (film/cm\(^{-1}\)) \(\nu_{\text{max}}\): 3032 (m), 2950 (m), 2855 (m), 1734 (s), 1668 (w), 1598 (m); \(^1\)H NMR (500 MHz, CD\(_3\)Cl) \(\delta\): 1.28 (d, 3H, \(J = 4.8\) Hz, CH\(_3\)CH\(-\), 2.33 (s, 3H, CH\(_3\)C\(_6\)H\(_4\)), 3.55 (s, 3H, -CO\(_2\)CH\(_3\)), 3.62–3.87 (m, 2H, -NCH\(_2\)CH\(_2\)H), 4.19 (d, 1H, \(J = 11.2\) Hz, -CH\(_2\)CO\(_2\)CH\(_3\)), 4.68 (dd, 1H, \(J = 11.2, 7.4\) Hz, -NCH\(_2\)(CH\(_2\))CH\(_2\)), 4.99–5.30 (m, 4H, CH\(_2\)CH\(_2\)N(Ts)CH(CH\(_3\))CHCH\(_2\)CH\(_3\)), 5.63 (ddt, 1H, \(J = 17.0, 10.3, 6.5\) Hz, -NCH(\(CH\)-(CH\(_2\))CH\(-\)), 7.08–7.30 (m, 7H, ArH), 7.65 (app. d, 2H, \(J = 8.2\) Hz, ArH Ts); \(^{13}\)C NMR (125 MHz, CD\(_3\)Cl) \(\delta\): 17.6, 21.4, 50.1, 52.0, 55.7, 63.7, 118.1, 125.9, 127.7, 127.8, 128.5, 128.9, 129.2, 131.8, 134.9, 135.8, 137.8, 143.1, 172.5; HRMS (ESI, +ve) \(m/z\) calcd. for C\(_{23}\)H\(_{38}\)NO\(_4\)S 414.1739, found 414.1734 (M+H\(^+\)).

Methyl 2-phenyl-2-(1-tosyl-2,5-dihydro-1H-pyrrol-2-yl)acetate (13c)

![Structure](image)

anti-(\(E\))-Methyl 3-(\(N\)-allyl-4-methylphenylsulfonamido)-2-phenylhex-4-enoate 11d (0.10 g, 0.24 mmol), catalytic Grubbs I and DCM (10 mL) were combined according to general procedure 6 (reaction time: 13 hours). Purification was achieved by the reported procedure to yield the methyl 2-phenyl-2-(1-tosyl-2,5-dihydro-1H-pyrrol-2-yl)acetate 13c as a white solid (0.08 g, 92%). M.p. 98–100 °C. FTIR (film/cm\(^{-1}\)) \(\nu_{\text{max}}\): 3024 (m), 2950 (m), 2931 (m), 1730 (s), 1657 (m), 1615 (m), 1596
(m), 1510 (m); $^1$H NMR (500 MHz, CD$_3$Cl) $\delta$: 2.43 (s, 3H), 3.39–3.45 (m, 1H), 3.73 (s, 3H), 3.85 (app. dq, 1H, $J = 15.2, 2.1$ Hz), 4.48 (d, 1H, $J = 4.4$ Hz), 5.06–5.06 (m, 1H), 5.43 (app. dq, 1H $J = 6.4, 2.0$ Hz), 5.80 (app. dq, 1H $J = 6.4, 2.0$ Hz), 7.23–7.30 (m, 5H), 7.32 (app. d, 2H, $J = 8.2$ Hz), 7.73 (app. d, 2H, $J = 8.2$ Hz); $^{13}$C NMR (125 MHz, CD$_3$Cl) $\delta$: 21.5, 52.0, 55.5, 56.2, 68.3, 129.9, 127.3 (x2), 127.6, 127.8, 129.8, 130.0, 134.3, 143.6, 172.9; HRMS (ESI, +ve) m/z calcd. for C$_{20}$H$_{22}$NO$_4$S 372.1269, found 372.1238 (M+H)$^+$. 

$(E)$-4-(N-Allyl-4-methylphenylsulfonamido)but-3-en-2-yl 2-(2-iodophenyl)acetate (10f)

![Chemical Structure](image)

EDCi (0.54 g, 2.81 mmol) in DCM (100 mL), triethylamine (0.39 mL, 2.81 mmol), DMAP (0.02 g, 0.14 mmol), 2-Iodo phenylacetic acid (0.74 g, 2.81 mmol) and $(E)$-N-allyl-N-(3-hydroxybut-1-enyl)-4-methylbenzenesulfonamide 5e (0.40 g, 1.41 mmol) in DCM (20 mL) were combined according to general procedure 1 (reaction time: 15 hours). Purification was achieved by reported procedure to afford $(E)$-4-(N-allyl-4-methylphenylsulfonamido)but-3-en-2-yl 2-(2-iodophenyl)acetate 10f as a yellow oil (0.64 g, 86%). FTIR (film/cm$^{-1}$) $\nu_{\text{max}}$: 2978 (m), 2922 (m), 1727 (s), 1655 (s), 1596 (w); $^1$H NMR (500 MHz, (CD$_3$)$_2$CO) $\delta$: 1.31 (d, 3H, $J = 6.6$ Hz), 2.44 (s, 3H), 3.77 (app. d, 2H), 3.97–4.08 (m, 2H), 4.91 (dd, 1H, $J = 14.2, 6.6$ Hz), 5.12 (app. dq, 1H, $J = 10.4, 1.4$ Hz), 5.20 (app. dq, 1H, $J = 17.3, 1.7$ Hz), 5.39 (app. quin, 1H, $J = 6.6$ Hz), 5.65 (ddt, 1H, $J = 17.3, 10.4, 5.0$ Hz), 7.00–7.08 (m, 2H), 7.35–7.43 (m, 4H), 7.72 (app. d, 2H, $J = 8.2$ Hz), 7.88 (d, 1H, $J = 7.8$ Hz); $^{13}$C NMR (125 MHz, (CD$_3$)$_2$CO) $\delta$: 20.4, 20.5, 46.0, 47.6, 70.6, 100.6, 109.9, 117.1, 127.0, 128.4, 128.8, 129.8, 129.9, 131.0, 131.8, 136.4, 138.5, 139.2, 144.0, 169.0; HRMS (ESI, +ve) m/z calcd. for C$_{22}$H$_{24}$INaO$_4$S 548.0368, found 548.0407 (M+Na)$^+$. 

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(anti-E)-Methyl 3-(N-allyl-4-methylphenylsulfonamido)-2-(2-iodophenyl) hex-4-enoate (11e)

LiHMDS (1M in toluene, 0.34 mL, 0.34 mmol), TMSCl (0.10 mL, 1.57 mmol) and (E)-4-(N-allyl-4-methylphenylsulfonamido)but-3-en-2-yl 2-(2-iodophenyl)acetate 10f (0.07 g, 0.26 mmol) in THF (0.7 mL) was combined according to general procedure 3 (reaction time : 75 minutes). Treatment with diazomethane and purification by flash chromatography afforded (anti-E)-methyl 3-(N-allyl-4-methylphenylsulfonamido)-2-(2-iodophenyl)hex-4-enoate 11e as a white solid (0.05 g, 67%, d.r. >25:1). M.p. 97–99 °C; FTIR (film/cm⁻¹) ν_max: 3179 (w), 2953 (m), 2922 (m), 1734 (s), 1597 (m);

¹H NMR (500 MHz, CD₃Cl) δ: 1.35 (d, 3H, J = 6.5 Hz), 2.41 (s, 3H), 3.63 (s, 3H), 3.83 (app. d, 1H, J = 17.3, 6.7 Hz), 3.93 (app. d, 1H, J = 17.3, 6.7 Hz), 4.75 (d, 1H, J = 11.7 Hz), 4.91 (d, 1H, J = 11.7 Hz), 5.14–5.23 (m, 2H), 5.25–5.37 (m, 2H), 5.79 (ddt, 1H, J = 17.0, 10.8, 6.7 Hz), 6.92 (app. t, 1H, J = 7.9 Hz), 7.26 (app. d, 2H, J = 8.7 Hz), 7.27–7.33 (m, 1H), 7.51 (app. d, 1H, J = 7.9 Hz), 7.74 (app. d, 2H, J = 8.7 Hz), 7.82 (d, 1H, J = 7.9 Hz); ¹³C NMR (125 MHz, CD₃Cl) δ: 17.6, 21.4, 49.2, 52.2, 57.8, 64.2, 118.1, 124.7, 127.9, 128.5, 128.9, 129.0, 129.2, 129.3, 132.1, 135.0, 137.7, 138.9, 139.6, 143.1, 171.8; HRMS (ESI, +ve) m/z calcd. for C₂₅H₃₂NO₆S 474.1950, found 474.1948 (M+H)⁺.

Methyl 2-(2-iodophenyl)-2-(1-tosyl-2,5-dihydro-1H-pyrrol-2-yl)acetate (13d)

antí-(E)-methyl 3-(N-allyl-4-methylphenylsulfonamido)-2-(2-iodophenyl)hex-4-enoate 11e (0.09 g, 0.17 mmol), catalytic Grubbs I and toluene (5 mL) were combined according to general procedure 7 (reaction time : 5 hours). Purification was achieved by the reported procedure to yield the methyl 2-(2-iodophenyl)-2-(1-tosyl-2,5-dihydro-1H-pyrrol-2-yl)acetate 13d as a white solid (0.04 g, 51%).
M.p. 186–188 °C; FTIR (film/cm\(^{-1}\)) \(\nu_{\text{max}}\): 3026 (m), 2952 (m), 2878 (m), 1728 (s), 1597 (m); \(^1\)H NMR (500 MHz, CD\(_3\)Cl) \(\delta\): 2.42 (s, 3H), 3.66–3.75 (m, 1H), 3.75 (s, 3H), 3.97 (app. dq, 1H, \(J = 15.7, 1.9\) Hz), 4.78 (d, 1H, \(J = 5.6\) Hz), 5.19–5.24 (m, 1H), 5.50–5.59 (m, 2H), 6.95 (app. t, 1H, \(J = 7.4\) Hz), 7.24–7.34 (m, 4H), 7.73 (app. d, 2H, \(J = 8.3\) Hz), 7.89 (app. d, 1H, \(J = 7.4\) Hz); \(^{13}\)C NMR (125 MHz, CD\(_3\)Cl) \(\delta\): 21.5, 52.3, 55.5, 59.9, 68.7, 127.5, 127.6 (x2), 127.7, 129.1, 129.7, 129.9, 134.2, 136.3, 138.0, 140.2, 143.6, 172.2; HRMS (ESI, +ve) m/z calcld. for C\(_{22}\)H\(_{21}\)NO\(_4\)S\(_4\) 498.0235, found 498.0259 (M+H\(^+\)).

**anti-methyl 1-tosyl-1,2,8,8a-tetrahydroindeno[2,1-b]pyrrole-8-carboxylate 14**

To a solution of Pd(OAc)\(_2\) (3.00 mg, 0.01 mmol, 0.2 eq.), PPh\(_3\) (3.67 mg, 0.01 mmol, 0.2 eq.), Ag\(_2\)CO\(_3\) (29.1 mg, 0.11 mmol, 1.5 eq.) in MeCN was added methyl 2-(2-iodophenyl)-2-(1-tosyl-2,5-dihydro-1H-pyrrol-2-yl)acetate \(11e\) (35.0 mg, 0.07 mmol, 1.0 eq.). The reaction mixture was refluxed for 4 hours and then concentrated \(\textit{in vacuo}\) and subjected to flash column chromatography using ethyl acetate/petroleum ether 40-60 °C (20:80) to yield \textit{anti}-methyl 1-tosyl-1,2,8,8a-tetrahydroindeno[2,1-b]pyrrole-8-carboxylate \(14\) as an amorphous clear solid (22.0 mg, 84%). FTIR (film/cm\(^{-1}\)) \(\nu_{\text{max}}\): 2958 (m), 2919 (m), 2849 (m), 1734 (s), 1597 (m); \(^1\)H NMR (500 MHz, CD\(_3\)Cl) \(\delta\): 2.47 (s, 3H, -C\(_6\)H\(_4\)C\(_H\)\(\text{Ph}\)), 3.80 (s, 3H, -CO\(_2\)C\(_H\)\(\text{Me}\)), 4.92 (br. d, 1H, \(J = 9.5\) Hz, -NCH\(_2\)CH\(-\))\), 4.63 (br. s, 1H, -CHCO\(_2\)C\(_H\)\(\text{Me}\)), 4.90 (dd, 1H, \(J = 9.5, 2.0\) Hz, -NCHH\(\text{CH}\(-\)-)), 5.31 (app. dd, 1H, \(J = 4.1, 2.8\) Hz, -NCH\(\text{CH}\(-\)-CH\(-\))\), 6.36 (app. dd, 1H, \(J = 4.1, 2.8\) Hz, -NCH\(_2\)CH\(-\)-), 7.10–7.15 (m, 1H, Ar\(\text{H}\)), 7.23–7.27 (m, 2H, Ar\(\text{H}\)), 7.36 (app. d, 2H, \(J = 8.2\) Hz, Ar\(\text{H}, \text{Ts}\)), 7.45–7.51 (m, 1H, Ar\(\text{H}\)), 7.75 (app. d, 2H, \(J = 8.2\) Hz, Ar\(\text{H}, \text{Ts}\)); \(^{13}\)C NMR (125 MHz, CD\(_3\)Cl) \(\delta\): 21.6, 52.5, 54.5, 58.3, 66.1, 112.9, 125.1, 126.1, 127.8, 127.9, 128.6, 129.9, 130.5, 132.9, 137.8, 142.9, 144.2, 172.2; HRMS (ESI, +ve) m/z calcld. for C\(_{20}\)H\(_{20}\)N\(_1\)O\(_4\)S\(_1\) 370.1148, found 370.1113 (M+H\(^+\)).
(E)-4-(N-Allyl-4-methylphenylsulfonamido)but-3-en-2-yl 2-(4-methoxyphenyl)acetate (10g)

EDCi (0.54 g, 2.81 mmol) in DCM (100 mL), triethylamine (0.39 mL, 2.81 mmol), DMAP (0.02 g, 0.14 mmol), 4-methoxy phenylacetic acid (0.47 g, 2.81 mmol) and (E)-N-allyl-N-(3-hydroxybut-1-enyl)-4-methylbenzenesulfonamide 5e (0.40 g, 1.41 mmol) in DCM (20 mL) were combined according to general procedure 1 (reaction time: 15 hours). Purification was achieved by reported procedure to afford (E)-4-(N-allyl-4-methylphenylsulfonamido)but-3-en-2-yl 2-(4-methoxyphenyl)acetate 10g as a yellow oil (0.54 g, 81%). FTIR (film/cm\textsuperscript{-1}) \( \nu_{\text{max}} \): 2978 (m), 2943 (m), 1726 (s), 1655 (s), 1597 (w); \(^1\)H NMR (250 MHz, (CD\textsubscript{3})\textsubscript{2}CO) \( \delta \): 1.27 (d, 3H, \( J = 6.5 \) Hz), 2.42 (s, 3H), 3.50 (2H, s), 3.77 (s, 3H), 3.92–4.05 (m, 2H), 4.86 (dd, 1H, \( J = 14.1, 6.5 \) Hz), 5.09 (dd, 1H, \( J = 10.7, 1.5 \) Hz), 5.16 (dd, 1H, \( J = 17.1, 1.5 \) Hz), 5.37 (app. quin, 1H, \( J = 6.5 \) Hz), 5.59 (ddt, 1H, \( J = 17.1, 10.7, 5.4 \) Hz), 6.85 (d, 2H, \( J = 8.5 \) Hz), 6.99 (d, 1H, \( J = 14.1 \) Hz), 7.17 (app. d, 2H, \( J = 8.3 \) Hz), 7.37 (app. d, 2H, \( J = 8.2 \) Hz), 7.68 (d, 2H, \( J = 8.2 \) Hz); \(^{13}\)C NMR (125 MHz, (CD\textsubscript{3})\textsubscript{2}CO) \( \delta \): 21.3, 21.4, 41.0, 48.4, 55.4, 71.0, 111.0, 114.5, 118.0, 127.4, 127.8, 127.9, 130.7, 131.0, 132.6, 137.2, 144.9, 159.6, 171.3; HRMS (ESI, +ve) \( m/z \) calcd. for C\textsubscript{23}H\textsubscript{27}NNaO\textsubscript{5}S\textsubscript{4} 452.1508, found 452.1463 (M+Na)+.

(anti-E)-Methyl 3-(N-allyl-4-methylphenylsulfonamido)-2-(4-methoxyphenyl)hex-4-enoate (11f)

LiHMDS (1M in toluene, 1.16 mL, 1.16 mmol), TMSCl (0.35 mL, 5.35 mmol) and (E)-4-(N-allyl-4-methylphenylsulfonamido)but-3-en-2-yl 2-(4-methoxyphenyl)acetate 10g (0.20 g, 0.89 mmol) in THF (2 mL) was combined according to general procedure 3 (reaction time: 75 minutes). Treatment
with diazomethane and purification by flash chromatography afforded (anti-\textit{E})-methyl 3-(\textit{N}-allyl-4-methylphenylsulfonamido)-2-(4-methoxyphenyl)hex-4-enolate 11f as a white solid (0.15 g, 73\%, d.r. >25:1). M.p. 109–110 °C; FTIR (film/cm\textsuperscript{-1}) \textit{v}_{\text{max}}: 3039 (w), 2952 (m), 2919 (m), 1734 (s), 1670 (w), 1608 (m), 1598 (m), 1522 (m), 1512 (m); \textsuperscript{1}H NMR (500 MHz, CD\textsubscript{3}Cl) \delta: 1.39 (d, 3H, \textit{J} = 4.5 Hz), 2.41 (s, 3H), 3.62 (s, 3H), 3.77 (s, 3H), 3.75–3.88 (m, 2H), 4.21 (d, 1H, \textit{J} = 11.5 Hz), 4.73 (dd, 1H, \textit{J} = 11.5, 7.44 Hz), 5.12 (app. d, 1H, \textit{J} = 10.3 Hz), 5.20 (app d, 1H, \textit{J} = 17.1 Hz), 5.23–5.33 (m, 2H), 5.70 (ddt, 1H, \textit{J} = 17.1, 10.3, 6.5 Hz), 6.81 (app. d, 2H, \textit{J} = 8.7 Hz), 7.22 (app. d, 2H, \textit{J} = 8.7 Hz), 7.26 (app. d, 2H, \textit{J} = 8.4 Hz), 7.73 (app. d, 2H, \textit{J} = 8.4 Hz); \textsuperscript{13}C NMR (125 MHz, CD\textsubscript{3}Cl) \delta: 17.6, 21.4, 50.0, 51.9, 54.9, 55.1, 63.6, 113.9, 118.0, 126.0, 127.8 (x2), 129.2, 129.9, 131.7, 134.9, 137.9, 143.0, 159.0, 172.8; HRMS (ESI, +ve) \textit{m}/\textit{z} calcd. for C\textsubscript{24}H\textsubscript{30}N\textsubscript{3}O\textsubscript{5}S \textsuperscript{+} 444.1844, found 444.1857 (M+H\textsuperscript{+}).

Methyl 2-(4-methoxyphenyl)-2-(1-tosyl-2,5-dihydro-1H-pyrrol-2-yl)acetate (13e)

\textit{anti-(E)}-Methyl 3-(\textit{N}-allyl-4-methylphenylsulfonamido)-2-(4-methoxyphenyl)hex-4-enolate 11f (0.05 g, 0.11 mmol), catalytic Grubbs I and DCM (5 mL) were combined according to general procedure 6 (reaction time: 13 hours). Purification was achieved by the reported procedure to yield the methyl 2-(4-methoxyphenyl)-2-(1-tosyl-2,5-dihydro-1H-pyrrol-2-yl)acetate 13e as a clear oil (0.04 g, 89\%). FTIR (film/cm\textsuperscript{-1}) \textit{v}_{\text{max}}: 3035 (m), 2953 (m), 2884 (m), 1727 (s), 1597 (m), 1512 (m); \textsuperscript{1}H NMR (500 MHz, CD\textsubscript{3}Cl) \delta: 2.42 (s, 3H), 3.44 (ddt, 1H, \textit{J} = 15.0, 5.4, 2.0 Hz), 3.72 (s, 3H), 3.79 (s, 3H), 3.85 (app. dq, 1H, \textit{J} = 15.0, 2.0 Hz), 4.42 (d, 1H, \textit{J} = 4.3 Hz), 4.97–5.02 (m, 1H), 5.44 (app. dq, 1H \textit{J} = 6.4, 2.0 Hz), 5.80 (app. dq, 1H \textit{J} = 6.4, 2.0 Hz), 6.82 (app. d, 2H, \textit{J} = 8.6 Hz), 7.17 (app. d, 2H, \textit{J} = 8.6 Hz), 7.31 (app. d, 2H, \textit{J} = 8.6 Hz), 7.72 (app. d, 2H, \textit{J} = 8.6 Hz); \textsuperscript{13}C NMR (125 MHz, CD\textsubscript{3}Cl) \delta: 21.5, 52.0, 55.1, 55.4, 55.5, 68.4, 113.3, 126.0, 127.0, 127.3, 127.6, 129.8, 131.1, 134.4, 143.6, 158.8, 173.1; HRMS (ESI, +ve) \textit{m}/\textit{z} calcd. for C\textsubscript{21}H\textsubscript{36}NO\textsubscript{5}S \textsuperscript{+} 402.1375, found 402.1366 (M+H\textsuperscript{+}).
(E)-4-(N-Allyl-4-methylphenylsulfonamido)but-3-en-2-yl 2-(4-nitrophenyl)acetate (10h)

EDCI (0.54 g, 2.81 mmol) in DCM (100 mL), triethylamine (0.39 mL, 2.81 mmol), DMAP (0.02 g, 0.14 mmol), 4-nitrophenylacetic acid (0.51 g, 2.81 mmol) and (E)-N-allyl-N-(3-hydroxybut-1-enyl)-4-methylbenzenesulfonamide Se (0.40 g, 1.41 mmol) in DCM (20 mL) were combined according to general procedure 1 (reaction time: 15 hours). Purification was achieved by reported procedure to afford (E)-4-(N-allyl-4-methylphenylsulfonamido)but-3-en-2-yl 2-(4-nitrophenyl)acetate 10h as an orange oil (0.54 g, 86%). FTIR (film/cm⁻¹) v max: 3018 (w), 2988 (m), 2967 (m), 1727 (s), 1698 (s), 1656 (m), 1599 (w), 1522 (m); ¹H NMR (500 MHz, (CD₃)₂CO) δ: 1.29 (d, 3H, J = 6.7 Hz), 2.41 (s, 3H), 3.80 (2H, s), 3.95–4.05 (m, 2H), 4.87 (dd, 1H, J = 14.5, 6.7 Hz), 5.08 (dq, 1H, J = 10.7, 1.95 Hz), 5.15 (dq, 1H, J = 17.2, 1.3 Hz), 5.38 (app. quin, 1H, J = 6.7 Hz), 5.59 (ddt, 1H, J = 17.2, 10.7, 5.1 Hz), 7.00 (d, 1H, J = 14.5 Hz), 7.38 (app. d, 2H, J = 7.9 Hz), 7.57 (app. d, 2H, J = 8.7 Hz), 7.69 (app. d, 2H, J = 7.9 Hz), 8.18 (app. d, 2H, J = 8.7 Hz); ¹³C NMR (100 MHz, (CD₃)₂CO) δ: 20.3, 20.5, 40.6, 47.5, 70.9, 109.6, 117.1, 123.3, 126.9, 129.8, 130.1, 130.5, 131.6, 136.3, 142.5, 144.1, 147.0, 169.2; HRMS (ESI, +ve) m/z calcd. for C₄₄H₄₈N₄NaO₁₂S₂ 911.2613, found 911.2604 (2M+Na)⁺.

(anti-E)-Methyl 3-(N-allyl-4-methylphenylsulfonamido)-2-(4-nitrophenyl)hex-4-enoate (11g)

LiHMDS (1M in toluene, 1.13 mL, 1.13 mmol), TMSCl (0.34 mL, 5.22 mmol) and (E)-4-(N-allyl-4-methylphenylsulfonamido)but-3-en-2-yl 2-(4-nitrophenyl)acetate 10h (0.20 g, 0.87 mmol) in THF (2 mL) was combined according to general procedure 3 (reaction time: 75 minutes). Treatment with diazomethane and purification by flash chromatography, recrystallisation and a two subsequent recrystallisations of the mother liquor afforded (anti-E)-methyl 3-(N-allyl-4-
methylphenylsulfonamido)-2-(4-nitrophenyl)hex-4-enoate 11g as an off white solid (0.10 g, 53%, d.r. 20:1). M.p. 128–130 °C; FTIR (film/cm⁻¹) νₘₐₓ: 3018 (w), 2988 (m), 2952 (m), 2925 (m), 1736 (s), 1669 (w), 1598 (m), 1521 (s); ¹H NMR (500 MHz, CD₃Cl) δ: 1.38 (dd, 3H, J = 6.2, 1.0 Hz), 2.42 (s, 3H), 3.69 (s, 3H), 3.78 (dd, 1H, J = 16.0, 6.8 Hz), 3.86 (dd, 1H, J = 16.0, 6.8 Hz), 4.49 (d, 1H, J = 11.2 Hz), 4.69 (app. t, 1H, J = 11.2 Hz), 5.17 (app. d, 1H, J = 10.2 Hz), 5.23 (app. d, 1H, J = 17.0 Hz), 5.20–5.38 (m, 2H), 5.69 (ddt, 1H, J = 17.0, 10.2, 6.8 Hz), 7.28 (app. d, 2H, J = 8.2 Hz), 7.73 (app. d, 2H, J = 8.2 Hz), 8.16 (app. d, 2H, J = 8.2 Hz); ¹³C NMR (125 MHz, CD₃Cl) δ: 17.5, 21.4, 50.5, 52.5, 55.6, 63.8, 118.6, 123.7, 125.4, 127.8, 129.3, 129.9, 132.9, 134.5, 137.5, 143.2, 143.4, 147.4, 171.5; HRMS (ESI, +ve) m/z calcd. for C₂₃H₂₆N₂O₆S₄ 481.1409, found 481.1715 (M+Na)⁺.

Methyl 2-(4-nitrophenyl)-2-(1-tosyl-2,5-dihydro-1H-pyrrol-2-yl)acetate (13f)

![Methyl 2-(4-nitrophenyl)-2-(1-tosyl-2,5-dihydro-1H-pyrrol-2-yl)acetate (13f)](image)

anti-(E)-Methyl 3-(N-allyl-4-methylphenylsulfonamido)-2-(4-nitrophenyl)hex-4-enoate 11g (0.03 g, 0.07 mmol), catalytic Grubbs I and DCM (5 mL) were combined according to general procedure 6 (reaction time : 13 hours). Purification was achieved by the reported procedure to yield the methyl 2-(4-nitrophenyl)-2-(1-tosyl-2,5-dihydro-1H-pyrrol-2-yl)acetate 13f as an off white solid (0.03 g, 96%). M.p. 178–180 °C; FTIR (film/cm⁻¹) νₘₐₓ: 3030 (m), 2954 (m), 1732 (s), 1599 (s), 1521 (s); ¹H NMR (500 MHz, CD₃Cl) δ: 2.44 (s, 3H), 3.34–3.42 (m, 1H), 3.76 (s, 3H), 3.84 (app. d, 1H, J = 15.6 Hz), 4.69 (d, 1H, J = 4.2 Hz), 5.03–5.09 (m, 1H), 5.48–5.54 (m, 1H), 5.80–5.85 (m, 1H), 7.34 (app. d, 2H, J = 8.1 Hz), 7.45 (app. d, 2H, J = 8.4 Hz), 7.72 (app. d, 2H, J = 8.1 Hz), 8.16 (app. d, 2H, J = 8.4 Hz); ¹³C NMR (125 MHz, CD₃Cl) δ: 21.5, 52.4, 55.6, 55.7, 68.2, 122.8, 126.7, 127.4, 127.8, 129.9, 131.2, 133.7, 141.5, 144.0, 147.3, 171.6; HRMS (ESI, +ve) m/z calcd. for C₂₀H₂₁N₂O₆S 417.1120, found 417.1123 (M+H)⁺.
(E)-4-(N-Allyl-4-methylphenylsulfonamido)but-3-en-2-yl 2-(2,4-dichlorophenyl)acetate (10i)

![Chemical Structure](image)

EDCi (0.54 g, 2.81 mmol) in DCM (100 mL), triethylamine (0.39 mL, 2.81 mmol), DMAP (0.02 g, 0.14 mmol), 2,4-dichlorophenylacetic acid (0.58 g, 2.81 mmol) and (E)-N-allyl-N-(3-hydroxybut-1-enyl)-4-methylbenzenesulfonamide 5e (0.40 g, 1.41 mmol) in DCM (20 mL) were combined according to general procedure 1 (reaction time: 15 hours). Purification was achieved by reported procedure to afford (E)-4-(N-allyl-4-methylphenylsulfonamido)but-3-en-2-yl 2-(2,4-dichlorophenyl)acetate 10i as a yellow oil (0.55 g, 82%). FTIR (film/cm⁻¹) \(\nu_{\text{max}}\): 3091 (m), 2978 (m), 2937 (m), 1729 (s), 1655 (s), 1614 (s), 1591 (s), 1509 (s); \(^1\)H NMR (500 MHz, (CD₃)₂CO) \(\delta\): 1.29 (d, 3H, \(J = 6.7 \text{ Hz}\)), 2.44 (s, 3H), 3.76 (2H, s), 3.97–4.07 (m, 2H), 4.89 (dd, 1H, \(J = 14.2, 6.7 \text{ Hz}\)), 5.12 (app d, 1H, \(J = 10.3 \text{ Hz}\)), 5.19 (app d, 1H, \(J = 17.2 \text{ Hz}\)), 5.38 (app. quin, 1H, \(J = 6.7 \text{ Hz}\)), 5.63 (ddt, 1H, \(J = 17.2, 10.3, 5.1 \text{ Hz}\)), 7.01 (d, 1H, \(J = 14.2 \text{ Hz}\)), 7.32–7.47 (m, 4H), 7.50 (d, 1H, \(J = 1.9 \text{ Hz}\)), 7.71 (app. d, 2H, \(J = 8.2 \text{ Hz}\)); \(^{13}\)C NMR (125 MHz, (CD₃)₂CO) \(\delta\): 20.4, 20.5, 38.4, 47.6, 70.8, 109.7, 117.1, 126.9, 127.2, 128.7, 129.8, 129.9, 131.7, 132.2, 133.0, 133.1, 135.1, 136.4, 144.0, 168.7; HRMS (ESI, +ve) \(m/z\) calcd. for \(C_{22}H_{23}Cl_2N_1NaO_4S_1\) 490.0617, found 490.0614 (M+Na)+.

(anti-E)-Methyl 3-(N-allyl-4-methylphenylsulfonamido)-2-(2,4-dichlorophenyl)hex-4-enoate (11h)

![Chemical Structure](image)

LiHMDS (1M in toluene, 1.07 mL, 1.07 mmol), TMSCl (0.33 mL, 4.94 mmol) and (E)-4-(N-allyl-4-methylphenylsulfonamido)but-3-en-2-yl 2-(2,4-dichlorophenyl)acetate 10i (0.20 g, 0.82 mmol) in THF (2 mL) was combined according to general procedure 3 (reaction time: 75 minutes). Treatment with diazomethane and purification by flash chromatography afforded (anti-E)-methyl 3-(N-allyl-4-methylphenylsulfonamido)-2-(2,4-dichlorophenyl)hex-4-enoate 11h as a yellow oil (0.21 g, 83%). FTIR (film/cm⁻¹) \(\nu_{\text{max}}\): 3091 (m), 2978 (m), 2937 (m), 1729 (s), 1655 (s), 1614 (s), 1591 (s), 1509 (s); \(^1\)H NMR (500 MHz, (CD₃)₂CO) \(\delta\): 1.29 (d, 3H, \(J = 6.7 \text{ Hz}\)), 2.44 (s, 3H), 3.76 (2H, s), 3.97–4.07 (m, 2H), 4.89 (dd, 1H, \(J = 14.2, 6.7 \text{ Hz}\)), 5.12 (app d, 1H, \(J = 10.3 \text{ Hz}\)), 5.19 (app d, 1H, \(J = 17.2 \text{ Hz}\)), 5.38 (app. quin, 1H, \(J = 6.7 \text{ Hz}\)), 5.63 (ddt, 1H, \(J = 17.2, 10.3, 5.1 \text{ Hz}\)), 7.01 (d, 1H, \(J = 14.2 \text{ Hz}\)), 7.32–7.47 (m, 4H), 7.50 (d, 1H, \(J = 1.9 \text{ Hz}\)), 7.71 (app. d, 2H, \(J = 8.2 \text{ Hz}\)); \(^{13}\)C NMR (125 MHz, (CD₃)₂CO) \(\delta\): 20.4, 20.5, 38.4, 47.6, 70.8, 109.7, 117.1, 126.9, 127.2, 128.7, 129.8, 129.9, 131.7, 132.2, 133.0, 133.1, 135.1, 136.4, 144.0, 168.7; HRMS (ESI, +ve) \(m/z\) calcd. for \(C_{22}H_{23}Cl_2N_1NaO_4S_1\) 490.0617, found 490.0614 (M+Na)+.
methylphenylsulfonamido)-2-(2,4-dichlorophenyl)hex-4-enoate 11h as a yellow oil (0.14 g, 68%, d.r. >25:1). FTIR (film/cm\(^{-1}\) \(\nu_{\text{max}}\): 3034 (w), 2950 (m), 2919 (m), 1736 (s), 1669 (m), 1598 (m), 1512 (m), 1510 (m); \(^1\)H NMR (500 MHz, CD\(_3\)Cl) \(\delta\): 1.37 (d, 3H, \(J = 5.8\) Hz), 2.41 (s, 3H), 3.65 (s, 3H), 3.80 (dd, 1H, \(J = 15.9, 6.9\) Hz), 3.92 (dd, 1H, \(J = 15.9, 6.9\) Hz), 4.79 (dd, 1H, \(J = 11.5, 8.6\) Hz), 4.90 (d, 1H, \(J = 11.5\) Hz), 5.15 (app. d, 1H, \(J = 10.2\) Hz), 5.18–5.33 (m, 3H), 5.71 (ddt, 1H, \(J = 16.9, 10.3, 6.9\) Hz), 7.21 (d, 2H, \(J = 8.3, 2.3\) Hz), 7.26 (app. d, 2H, \(J = 8.2\) Hz), 7.36 (d, 1H, \(J = 2.3\) Hz), 7.51 (d, 1H, \(J = 8.3\) Hz), 7.72 (app. d, 2H, \(J = 8.2\) Hz); \(^{13}\)C NMR (125 MHz, CD\(_3\)Cl) \(\delta\): 17.6, 21.4, 49.5, 49.6, 52.3, 63.9, 118.2, 124.7, 127.4, 127.8, 129.2, 129.3, 130.3, 132.4, 132.5, 133.9, 134.9, 135.2, 137.6, 143.2, 171.5; HRMS (ESI, +ve) \(m/z\) calcd. for C\(_{23}\)H\(_{26}\)Cl\(_2\)NO\(_4\)S 482.0959, found 482.0971 (M+H\(^+\)).

**Methyl 2-(2,4-dichlorophenyl)-2-(1-tosyl-2,5-dihydro-1H-pyrrol-2-yl)acetate (13g)**

![Image](image_url)

anti-(E)-Methyl 3-(N-allyl-4-methylphenylsulfonamido)-2-(2,4-dichlorophenyl)hex-4-enoate 11h (0.04 g, 0.08 mmol), catalytic Grubbs I and toluene (5 mL) were combined according to general procedure 7 (reaction time : 5 hours). Purification was achieved by the reported procedure to yield the methyl 2-(2,4-dichlorophenyl)-2-(1-tosyl-2,5-dihydro-1H-pyrrol-2-yl)acetate 13g as a white solid (0.03 g, 83%). M.p. 147–148 °C; FTIR (film/cm\(^{-1}\) \(\nu_{\text{max}}\): 3039 (m), 2953 (m), 2931 (m), 2876 (m), 1734 (s), 1589 (m), 1542 (w), 1524 (w); \(^1\)H NMR (500 MHz, CD\(_3\)Cl) \(\delta\): 2.43 (s, 3H), 3.52 (ddt, 1H, \(J = 15.4, 5.2, 2.2\) Hz), 3.74 (s, 3H), 3.84 (app. dq, 1H, \(J = 15.4, 2.2\) Hz), 4.83 (d, 1H, \(J = 4.5\) Hz), 5.14–5.23 (m, 1H), 5.50 (app. dq, 1H \(J = 6.3, 2.2\) Hz), 5.79 (app. dq, 1H \(J = 6.3, 2.2\) Hz), 7.21 (d, 1H, \(J = 2.1\) Hz), 7.29–7.36 (m, 3H), 7.38 (app. d, 1H, \(J = 2.1\) Hz), 7.72 (app. d, 2H, \(J = 8.2\) Hz); \(^{13}\)C NMR (125 MHz, CD\(_3\)Cl) \(\delta\): 17.6, 21.5, 52.3, 53.2, 55.4, 68.5, 126.6, 127.0, 127.2, 127.4, 129.7, 129.8, 131.1, 133.4, 133.9, 134.0, 135.7, 143.8, 171.8; HRMS (ESI, +ve) \(m/z\) calcd. for C\(_{20}\)H\(_{20}\)Cl\(_2\)NO\(_5\)S 440.0490, found 440.0686 (M+H\(^+\)).
(E)-4-(N-Allyl-4-methylphenylsulfonamido)but-3-en-2-yl 2-(benzo[d][1,3]dioxol-5-yl)acetate (10j)

EDCI (0.54 g, 2.81 mmol) in DCM (100 mL), triethylamine (0.39 l, 2.81 mmol), DMAP (0.02 g, 0.14 mmol), 3,4-methylenedioxyphenylacetic acid (0.51 g, 2.81 mmol) and (E)-N-allyl-N-(3-hydroxybut-1-enyl)-4-methylbenzenesulfonamide 5e (0.40 g, 1.41 mmol) in DCM (20 mL) were combined according to general procedure 1 (reaction time: 15 hours). Purification was achieved by reported procedure to afford (E)-4-(N-allyl-4-methylphenylsulfonamido)but-3-en-2-yl 2-(benzo[d][1,3]dioxol-5-yl)acetate 10j as a yellow oil (0.54 g, 86%). FTIR (film/cm\(^{-1}\)) \(\nu_{\text{max}}\): 3049 (m), 2916 (m), 1729 (s), 1655 (s), 1503 (s); \(^1\)H NMR (500 MHz, CD\(_3\)Cl) \(\delta\): 1.30 (d, 3H, \(J = 6.6\) Hz), 2.41 (s, 3H), 3.46 (2H, s), 3.89–4.01 (m, 2H), 4.76 (dd, 1H, \(J = 14.3, 6.6\) Hz), 5.10 (app. d, 1H, \(J = 10.3\) Hz), 5.10 (app. d, 1H, \(J = 17.0\) Hz), 5.32 (app. quin, 1H, \(J = 6.6\) Hz), 5.50 (ddt, 1H, \(J = 17.0, 10.3, 5.3\) Hz), 5.91 (s, 2H), 6.65–6.75 (m, 3H), 6.97 (d, 1H, \(J = 14.3\) Hz), 7.26 (app. d, 2H, \(J = 7.8\) Hz), 7.63 (app. d, 2H, \(J = 7.8\) Hz); \(^{13}\)C NMR (125 MHz, CD\(_3\)Cl) \(\delta\): 20.9, 21.5, 30.9, 41.2, 47.9, 70.6, 100.9, 108.2, 109.6 (x2), 117.8, 122.2, 127.0, 127.1, 127.7, 129.7, 129.8, 131.2, 136.0, 143.9, 146.6, 147.7, 170.7; HRMS (ESI, +ve) \(m/z\) calcd. for C\(_{23}\)H\(_{24}\)NNaO\(_6\)S 466.1300, found 466.1295 (M+Na)+.

(anti-E)-Methyl 3-(N-allyl-4-methylphenylsulfonamido)-2-(benzo[d][1,3]dioxol-5-yl)hex-4-enoate (11i)

LiHMDS (1M in toluene, 0.55 mL, 0.55 mmol), TMSCl (0.17 mL, 2.53 mmol) and (E)-4-(N-allyl-4-methylphenylsulfonamido)but-3-en-2-yl 2-(benzo[d][1,3]dioxol-5-yl)acetate 10j (0.10 g, 0.42 mmol) in THF (1 mL) was combined according to general procedure 3 (reaction time: 75 minutes).
Treatment with diazomethane and purification by flash chromatography afforded (anti-\(E\))-methyl 3-(\(N\)-allyl-4-methylphenylsulfonamido)-2-(benzo[d][1,3]dioxol-5-yl)hex-4-enoate 11i as a white solid (0.06 g, 55\%, d.r. >25:1). M.p. 119–121 °C; FTIR (film/cm\(^{-1}\)) \(\nu_{\text{max}}\): 3020 (w), 2952 (m), 2928 (m), 1733 (s), 1504 (s); \(^1\)H NMR (500 MHz, CD\(_3\)Cl) \(\delta\): 1.42 (d, 3H, \(J = 4.8\) Hz), 2.41 (s, 3H), 3.17 (s, 3H), 3.77 (dd, 1H, \(J = 16.0, 6.9\) Hz), 3.84 (dd, 1H, \(J = 16.0, 6.9\) Hz), 4.19 (d, 1H, \(J = 11.3\) Hz), 4.66 (dd, 1H, \(J = 11.3\) Hz), 5.13 (app. d, 1H, \(J = 10.1\) Hz), 5.20 (app. d, 1H, \(J = 17.1\) Hz), 5.27–5.35 (m, 2H), 5.69 (ddt, 1H, \(J = 17.1, 10.1, 6.9\) Hz), 5.92–5.95 (m, 2H), 6.68–6.77 (m, 2H), 6.85 (d, 1H, \(J = 1.7\) Hz), 7.26 (app. d, 2H, \(J = 8.3\) Hz), 7.72 (app. d, 2H, \(J = 8.3\) Hz); \(^{13}\)C NMR (125 MHz, CD\(_3\)Cl) \(\delta\): 17.7, 21.4, 50.2, 52.0, 55.3, 63.6, 101.0, 108.1, 108.8, 118.1, 122.6, 125.9, 127.8, 129.2, 129.5, 131.8, 134.8, 137.8, 143.1, 147.0, 147.8, 172.6; HRMS (ESI, +ve) \(m/\text{z}\) calcd. for C\(_{24}\)H\(_{28}\)NO\(_6\)S 458.1637, found 458.1649 (M+H\(^+\)).

Methyl 2-(benzo[d][1,3]dioxol-5-yl)-2-(1-tosyl-2,5-dihydro-1H-pyrrol-2-yl)acetate 13h

\(anti-(E)\)-Methyl 3-(\(N\)-allyl-4-methylphenylsulfonamido)-2-(benzo[d][1,3]dioxol-5-yl)hex-4-enoate 11i (0.05 g, 0.11 mmol), catalytic Grubbs I and DCM (5 mL) were combined according to general procedure 6 (reaction time : 5 hours). Purification was achieved by the reported procedure to yield methyl 2-(benzo[d][1,3]dioxol-5-yl)-2-(1-tosyl-2,5-dihydro-1H-pyrrol-2-yl)acetate 13h as a white solid (0.04 g, 89\%). M.p. 134–136 °C; FTIR (film/cm\(^{-1}\)) \(\nu_{\text{max}}\): 2994 (m), 2946 (m), 2909 (m), 1728 (s), 1598 (s), 1504 (s); \(^1\)H NMR (500 MHz, CD\(_3\)Cl) \(\delta\): 2.43 (s, 3H), 3.56 (app. ddt, 1H, \(J = 15.0, 5.3, 2.0\) Hz), 3.73 (s, 3H), 3.89 (app. dq, 1H, \(J = 15.0, 2.4\) Hz), 4.38 (d, 1H, \(J = 4.4\) Hz), 4.95–4.99 (m, 1H), 5.49 (app. d, 1H, \(J = 6.3, 2.1\) Hz), 5.77 (app. dq, 1H, \(J = 6.3, 2.1\) Hz), 5.94 (app. d, 2H, \(J = 4.7\) Hz), 6.70–6.76 (m, 3H), 7.32 (app. d, 2H, \(J = 8.5\) Hz), 7.72 (app. d, 2H, \(J = 8.9\) Hz); \(^{13}\)C NMR (125 MHz, CD\(_3\)Cl) \(\delta\): 21.5, 52.1, 55.6, 55.8, 68.3, 101.0, 107.9, 110.1, 123.7, 127.0, 127.3, 127.6 (x2), 129.8, 134.2, 143.7, 146.9, 147.0, 172.9; HRMS (ESI, +ve) \(m/\text{z}\) calcd. for C\(_{21}\)H\(_{22}\)NO\(_8\)S 416.1167, found 416.1168 (M+H\(^+\)).
Chirality Transfer Study – Synthesis and Rearrangement of (S)-10e

(S)-(4-Bromobut-3-yn-2-yloxy)(tert-butyl)diphenylsilane

Part 1 - To a stirred solution of 3-butyn-2-ol (15.0 g, 214 mmol, 1.0 eq.) in THF (200 mL) was added DMAP (2.61 g, 21.4 mmol, 0.1 eq.), TEA (59.1 mL, 428 mmol, 2.0 eq.) and TBDPSCI (64.7 g, 235, 1.1 eq.). The reaction mixture was stirred for 15 hours and then poured onto saturated ammonium chloride (200 mL). The organics were extracted with heptane (3 × 200 mL), concentrated in vacuo and the crude product was subjected to flash column chromatography (0-5% EtOAc/Petrol 40-60◦) to give (but-3-yn-2-yloxy)(tert-butyl)diphenylsilane as a clear oil (66.0 g, 100%). [α]D20 = +65.0 (c 1, DCM); Other data as previously reported.

Part 2 - To a stirred solution of but-3-yn-2-yloxy)(tert-butyl)diphenylsilane (66.0 g, 214 mmol, 1.0 eq.) in acetone (200 mL) was added NBS (41.9 g, 235 mmol, 1.1 eq.) and silver nitrate (3.63 g, 21.4 mmol, 0.1 eq.). The reaction mixture was stirred for 15 hours and then poured onto saturated sodium chloride (100 mL). The organics were extracted with diethyl ether (3 × 200 mL), dried over magnesium sulphate and concentrated in vacuo to yield a yellow oil which was triturated with heptane and the insolubilities were filtered off and the mother liquor was concentrated in vacuo to yield (4-bromobut-3-yn-2-yloxy)(tert-butyl)diphenylsilane as an orange oil (65.0 g, 78%). [α]D20 = +10.3 (c 1, DCM); Other data as previously reported.

(S)-N- Allyl-N-(3-(tert-butyl)diphenylsilyloxy)but-1-ynyl)-4-methylbenzenesulfonamide

23
To a solution of N-allyl-4-methylbenzenesulphonamide (2.46 g, 11.6 mmol, 1.0 eq.) in toluene (200 mL) was added (S)-(4-bromobut-3-yn-2-yloxy)(tert-butyl)diphenylsilane (5.00 g, 12.9 mmol, 1.1 eq.), CuSO₄.5H₂O (0.58 g, 2.34 mmol, 0.2 eq.), 1,10-phenanthroline (0.84 g, 4.68 mmol, 0.4 eq.) and finely ground K₂PO₄ (4.97 g, 23.2 mmol, 2 eq.). The reaction mixture was allowed to stir at 65 °C for 48 hours, after which was concentrated in vacuo and subjected to flash column chromatography (5-10% EtOAc/Petrol 40-60°) to give (S)-N-allyl-N-(4-(tert-butyl)diphenylsilyloxy)but-1-ynyl)-4-methylbenzenesulphonamide as a colourless oil (5.05 g, 83%). [α]D²⁰ = +20.0 (c 1, DCM); FTIR (film/cm⁻¹) νmax: 3036 (m), 3105 (m), 2961 (m), 2932 (m), 1681 (m), 1647 (m), 1619 (s), 1582 (s); 1H NMR (500 MHz, CDCl₃) δ: 1.06 (s, 9H), 1.41 (d, 3H, J = 6.4 Hz), 2.44 (s, 3H), 3.79 (ddt, 1H, J = 14.6, 6.3, 1.3 Hz), 3.85 (ddt, 1H, J = 14.6, 6.3, 1.3 Hz), 4.61 (app. quin, 1H, J = 6.4 Hz), 5.11–5.17 (m, 2H), 5.62 (ddt, 1H, J = 17.3, 10.2, 6.3 Hz), 7.28–7.46 (m, 7H), 7.66–7.72 (m, 4H), 7.72–7.77 (m, 2H); 13C NMR (100 MHz, CDCl₃) δ: 19.1, 21.6, 25.3, 26.5, 26.8, 54.0, 60.1, 73.2, 119.6, 127.4, 127.6, 127.8, 129.6, 131.0, 133.7, 134.8, 135.7, 135.9, 144.4; HRMS (ESI, +ve) m/z calcd. for C₅₀H₃₅NNaO₃S₂Si 540.2005, found 540.2209 (M+Na)⁺.

**N- Allyl-N-(3-hydroxy-but-1-ynyl)-4-methyl-benzenesulphonamide**

![Chemical Structure](image)

To a solution of N-allyl-N-(3-(tert-butyldiphenylsilyloxy)but-1-ynyl)-4-methylbenzenesulphonamide (3.72 g, 7.20 mmol, 1.0 eq.) in THF (200 mL) at 0 °C was added TBAF (1M soln. in THF, 14.4 mL, 14.4 mmol, 2.0 eq.). The reaction mixture was allowed to stir for 2 hours whilst slowly warming to RT, until complete by TLC, followed by concentration in vacuo and subjection to flash column chromatography (10% EtOAc/Petrol 40-60°) to give N-allyl-N-(3-hydroxy-but-1-ynyl)-4-methylbenzenesulphonamide as a faint yellow oil (1.40 g, 70%). [α]D²⁰ = -38.0 (c 1, DCM); FTIR (film/cm⁻¹) νmax: 2978 (m), 2929 (m), 1697 (m), 1596 (w). 1H NMR (400 MHz, CDCl₃) δ: 1.47 (d, 3H, J = 6.6 Hz), 2.03 (d, 1H, J = 5.2 Hz), 2.49 (s, 3H), 3.93–4.04 (m, 2H), 4.67 (app. quin, 1H, J = 6.6 Hz), 5.22–5.31 (m, 4H), 5.71 (ddt, 1H, J = 17.1, 10.2, 6.4 Hz), 7.39 (d, 2H, J = 8.3 Hz), 7.83 (d, 2H, J = 8.3 Hz); 13C NMR (100 MHz, CDCl₃) δ: 21.6, 24.4, 26.5, 54.1, 58.5, 73.1, 120.0, 127.7, 129.7, 130.8, 134.6, 144.8; HRMS (ESI, +ve) m/z calcd. for C₁₄H₁₃NO₃S 280.1007, found 280.1004 (M+H)⁺.
(S)-(E)-N-Allyl-N-(3-hydroxybut-1-enyl)-4-methylbenzenesulfonamide

To a solution of (S)-(E)-N-allyl-4-methyl-N-(3-oxobut-1-enyl)benzenesulfonamide (0.10 g, 0.36 mmol, 1.0 eq.) in toluene (5 mL) at 0 °C was added Red-Al (0.11 µl, 0.53 mmol, 1.5 eq.) by portionwise addition. The reaction mixture was allowed to stir whilst slowly warming to RT over 4 hours and then was quenched by the addition of Na2SO4.10H2O. After the solution cleared the reaction mixture was filtered through celite and concentrated in vacuo to yield (S)-(E)-N-allyl-N-(3-hydroxybut-1-enyl)-4-methylbenzenesulfonamide as a colourless oil (0.07 g, 76%). [α]D20 = -11.0 (c 1, DCM); Other data as previously reported for racemic compound.

(S,E)-4-(N-allyl-4-methylphenylsulfonamido)but-3-en-2-yl 2-phenylacetate ((S)-10e)

EDCI (0.68 g, 3.55 mmol) in DCM (100 mL), triethylamine (0.49 mL, 3.55 mmol), DMAP (0.02 g, 0.18 mmol), phenylacetic acid (0.48 g, 3.55 mmol) and (S)-(E)-N-allyl-N-(3-hydroxybut-1-enyl)-4-methylbenzenesulfonamide (S)-5e 0.50 g, 1.78 mmol) in DCM (20 mL) were combined according to general procedure 1 (reaction time: 15 hours). Purification was achieved by reported procedure to afford (S,E)-4-(N-allyl-4-methylphenylsulfonamido)but-3-en-2-yl 2-phenylacetate (S)-10e as a yellow oil (0.53 g, 74%); [α]D20 = -8.0 (c 1, DCM). All data as previously recorded for racemic compound.
(2R,3R,E)-methyl 3-(N-allyl-4-methylphenylsulfonamido)-2-phenylhex-4-enoate ((2R,3S)-11d)

LiHMDS (1M in toluene, 0.63 ml, 0.63 mmol), TMSCl (0.19 ml, 2.91 mmol) and (S,E)-4-(N-allyl-4-methylphenylsulfonamido)but-3-en-2-yl 2-phenylacetate (S)-10e (0.10 g, 0.48 mmol) in THF (1 ml) was combined according to general procedure 3 (reaction time : 75 minutes). Treatment with diazomethane and purification by flash chromatography afforded (2R,3R,E)-methyl 3-(N-allyl-4-methylphenylsulfonamido)-2-phenylhex-4-enoate (S)-11d as a white solid (0.08 g, 71%, d.r. >25:1). M.p. 105–107 °C; [α]_D^20 = -15.0 (c 1, DCM). All other data as previously recorded for racemic compound.
## Initial optimisation Attempts

**Table 1 Propionate Diastereoselectivity Explorations**

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<td>KHMD (1.3 equiv), Me,SiCl (1.3 equiv)</td>
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<td>-</td>
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<td>MgHMDS (1.3 equiv), Me,SiCl (1.3 equiv)</td>
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<td>LDA (1.3 equiv), Me,SiCl (1.3 equiv)</td>
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<td>-</td>
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<td>Et,N (1.5 equiv), TIPSOt (1.1 equiv)</td>
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<tr>
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<td>LDA (1.5 equiv), HMPA (5 equiv),CIP(O)(OEt), (1.5 equiv)</td>
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*a/anti/syn, measured by 1H NMR analysis of crude reaction mixtures.*

**Notes:**
- Allylic alcohol 5a recovered (99%).
- Intractable mixture.
- In CH₂Cl₂ at 20 °C.
- Reaction conducted -78 °C→-10 °C and quenched with MeOH.
- Quenched with 1:1 1M HCl(aq.)/brine.
- Quenched with MeOH.
NMR Spectra

Current Data Parameters
NAME: Nov22-2007-drc
EXPNO: 70
PROCNO: 1

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Date: 20071122
Time: 18.33
INSTRUM: spect
PROBHD: 5 mm DUL 1H-13C
PULPROG: zg30
TD: 32768
SOLVENT: CDCl3
NS: 32
DS: 2
SWH: 5175.983 Hz
FIDRES: 0.157958 Hz
AQ: 3.1654389 sec
RG: 1149.4
DW: 96.600 usec
DE: 6.00 usec
TE: 300.0 K
D1: 1.00000000 sec
d11: 0.03000000 sec
DELTA: 1.89999998 sec
TD0: 1

======== CHANNEL f1 ========
NUC1: 1H
P1: 11.00 usec
PL1: 0.00 dB
SFO1: 250.1315450 MHz

F2 - Processing parameters
SI: 32768
SF: 250.1300243 MHz
WDW: EM
SSB: 0
LB: 0.30 Hz
GB: 0
PC: 1.00

Current Data Parameters
NAME: Nov23-2007-drc
EXPNO: 30
PROCNO: 1

F2 - Acquisition Parameters
Date: 20071123
Time: 15.10
INSTRUM: av300
PROBHD: 5 mm BBO BB-1H
PULPROG: zgpg30
TD: 65536
SOLVENT: CDCl3
NS: 256
DS: 2
SWH: 20325.203 Hz
FIDRES: 0.310138 Hz
AQ: 1.6122355 sec
RG: 4597.6
DW: 24.600 usec
DE: 6.00 usec
TE: 298.0 K
D1: 2.00000000 sec
d11: 0.03000000 sec
DELTA: 1.89999998 sec
TD0: 1

======== CHANNEL f1 ========
NUC1: 13C
P1: 7.50 usec
PL1: 4.00 dB

======== CHANNEL f2 ========
CPDPRG2: waltz16
NUC2: 1H
PCPD2: 80.00 usec
PL2: -1.50 dB
PL12: 19.54 dB
PL13: 22.00 dB
ADF2: 320.2220297 MHz

F2 - Processing parameters
SI: 65534
SF: 75.4903490 MHz
WDW: EM
SSB: 0
LB: 1.00 Hz
GB: 0
PC: 1.60
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**NAME** WH4-063-A1

**EXPNO** 2

**PROCNO** 1

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- *Date_*: 20081107
- *Time*: 14.20
- *INSTRUM*: spect
- *PROBHD*: 5 mm PABBO BB /
- *PULPROG*: zgpg30
- *TD*: 65536
- *SOLVENT*: CDCl3
- *NS*: 65
- *DS*: 4
- *SWH*: 29761.904 Hz
- *AQ*: 1.1010548 sec
- *RG*: 362
- *DW*: 16.800 usec
- *TE*: 298.0 K
- *D1*: 2.0000000 sec
- *d11*: 0.0300000 sec
- *DELTA*: 1.8999998 sec
- *NSU*: 0

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**F2 - Processing parameters**

- *SI*: 32768
- *SF*: 125.7578456 MHz
- *WDW*: EM
- *SSB*: 0
- *LB*: 1.00 Hz
- *GC*: 1.40
- *PC*: 1.40
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-------- CHANNEL f1 --------

| NUC1 | 13C |
| P1   | 7.50 usec |
| PL1  | 0.14 dB |
| SF   | 125.7577890 MHz |

-------- CHANNEL f2 --------

| CPURG2 | wattz16 |
| NWG    | 80.00 usec |
| F112   | 17.98 dB |
| F113   | 20.00 dB |
| F12    | 1.00 dB |
| GPUL   | 500.1300000 MHz |

F2 - Processing parameters

| SI | 32768 |
| SF | 500.1300000 MHz |

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Current Data Parameters
NAME   WH9-043-B1
EXPNO   1
PROCNO  1

F2 - Acquisition Parameters
Date_   20100820
Time    15.57
INSTRUM  spect
PROCND   5 mm PABBO BB/
FV/FRNG  zg30
TD      65536
SOLVENT CD2Cl2
NS       8
DS        0
SNM   10330.574 Hz
FIDRES  1.157632 Hz
AQ      3.1719923 sec
RG       22.6
DW     48.400 usec
SE      0.00 usec
DE       0 usec
DI      1.0000000 sec
TO1      1

======== CHANNEL f1 ========
NUC1         1H
P1            9.50 usec
PL1          -1.00 dB
SFO1       500.1330885 MHz

F2 - Processing parameters
SI       32768
SF       500.1300000 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

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34
Current Data Parameters
NAME  WH9-059-A1
EXPNO  2
PROCNO  1

F2 - Acquisition Parameters
Date_  20100826
Time  11.43
INSTRUM  spect
PROBHD  5 mm PABBO BB/
PULPROG  zgpg30
TD  65536
SOLVENT  Acetone
NS  83
DS  4
SWH  29761.904 Hz
FIDRES  0.454131 Hz
AQ  1.1010548 sec
RG  362
DW  16.800 usec
DE  0.00 usec
TE  298.0 K
D1  2.0000000 sec
d1  0.0300000 sec
DELTA  1.8999998 sec
TD0  1

======== CHANNEL f1 ========
NUC1  13C
P1  7.50 usec
PL1  0.34 dB
SFO1  125.7703643 MHz

F2 - Processing parameters
SI  32768
SF  125.7577890 MHz
WDW  EM
SSB  0
LB  1.00 Hz
PC  1.40

DELTA  1.8999998 sec
TD0  1

======== CHANNEL f2 ========
CPDPRG2  waltz16
NUC2  1H
PCPD2  80.00 usec
PL12  17.98 dB
PL13  20.00 dB
PL2  -1.00 dB
SFO2  500.1320005 MHz

F2 - Processing parameters
SI  32768
SF  500.1350000 MHz
WDW  no
SSB  0
LB  0.00 Hz
PC  1.00
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EXPNO: 1
PROCNO: 1

F2 - Acquisition Parameters
Date: 20101014
Time: 15.25
INSTANT: spcet
PROBHD: 5 mm PABBO BB/
PULPROG: zg30
TD: 65536
SOLVENT: CDCl3

SWH: 10330.578 Hz
FIDRES: 0.157632 Hz
AQ: 3.1719923 sec
RG: 362
DW: 48.400 usec
DE: 6.00 usec
TE: 298.0 K
DS: 1

======== CHANNEL f1 ========
NUC1: 1H
P1: 9.50 usec
PL1: -1.00 dB
SFO1: 500.1330885 MHz

F2 - Processing parameters
SI: 32768
SF: 500.1300000 MHz
WDW: no
SSB: 0
LB: 0.00 Hz
GB: 0
PC: 1.00

BRUKER

Current Data Parameters
NAME: WH10-HECK
EXPNO: 2
PROCNO: 1

F2 - Acquisition Parameters
Date: 20101014
Time: 15.34
INSTANT: spcet
PROBHD: 5 mm PABBO BB/
PULPROG: zg30
TD: 65536
SOLVENT: CDCl3

SWH: 29761.904 Hz
FIDRES: 0.454131 Hz
AQ: 1.1010548 sec
RG: 362
DW: 16.800 usec
DE: 6.00 usec
TE: 298.0 K
D1: 2.00000000 sec
d11: 0.03000000 sec
DELTA: 1.89000000 sec
TD0: 1

======== CHANNEL f1 ========
NUC1: 1H
P1: 7.50 usec
PL1: 0.34 dB
SFO1: 125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2: waltz16
NUC2: 1H
PCPD2: 80.00 usec
PL12: 17.98 dB
PL13: 20.00 dB
PL2: -1.00 dB
SFO2: 500.1320005 MHz

F2 - Processing parameters
SI: 32768
SF: 125.7577890 MHz
WDW: EM
SSB: 0
LB: 1.00 Hz
GB: 0
PC: 1.40
Current Data Parameters
NAME       WH9-155-3-B1
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20100916
Time              11.05
INSTRUM           spect
PROCND   5 mm PABBO BB/
PUROLROG         zg30
TD                65536
SOLVENT           CDCl3
NS                    8
DS                    0
SNR            10320.578 Hz
FIDRES         3.157632 Hz
AQ             161
SW               48.400 ussec
GR               0.00 ussec
DT               1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                1H
P1                 9.50 usec
PL1               -1.00 dB
SFO1        500.1330885 MHz

F2 - Processing parameters
SI                32768
SF          500.1300000 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

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Current Data Parameters
NAME: WH9-p-Nitro R
EXPNO: 1
PROCNO: 1

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Date: 20100919
Time: 11:07
INSTRUM: spect
SOLVENT: CDCl3
NS: 5
DS: 0
SWH: 10330.578 Hz
FIDRES: 0.157632 Hz
AQ: 3.1719923 sec
RG: 256
DW: 48.400 usec
DE: 6.00 usec
TE: 298.0 K
D1: 1.00000000 sec
TD0: 1

F2 - Processing Parameters
SI: 32768
SF: 500.1300000 MHz
WDW: EM
SSB: 0
LB: 0.00 Hz
GB: 0
PC: 1.00

======== CHANNEL f1 ========
NUC1: 1H
P1: 9.50 usec
PL1: -1.00 dB
SFO1: 500.1330885 MHz

======== CHANNEL f2 ========
CPDPRG2: waltz16
NUC2: 1H
PCPD2: 80.00 usec
PL12: 17.98 dB
PL13: 20.00 dB
PL2: -1.00 dB
SFO2: 500.1320005 MHz

Current Data Parameters
NAME: WH9-p-Nitro R
EXPNO: 2
PROCNO: 1

F2 - Acquisition Parameters
Date: 20100919
Time: 11:09
INSTRUM: spect
SOLVENT: CDCl3
NS: 139
DS: 4
SWH: 29761.904 Hz
FIDRES: 0.454131 Hz
AQ: 1.1010548 sec
RG: 362
DW: 16.800 usec
DE: 6.00 usec
TE: 298.0 K
D1: 2.00000000 sec
d11: 0.03000000 sec
DELTA: 1.8999998 sec
TD0: 1

F2 - Processing Parameters
SI: 32768
SF: 125.7577890 MHz
WDW: EM
SSB: 0
LB: 1.00 Hz
GB: 0
PC: 1.40
WH9-175-B1

Current Data Parameters
NAME      WH9-175-B1
EXPNO     1
PROCNO    1

F2 - Acquisition Parameters
Date_      20100922
Time       13.00
INSTRUM    spect
PROBHD     5 mm PABBO BB
FIDPROG    zg30
TD          65536
SOLVENT    CDCl3
NS          8
DS          0
SNV        10300.576 Hz
FIDRES     0.157632 Hz
AQ         3.1719923 sec
RG          256
DW         48.400 usec
DE         6.00 usec
TE         298.0 K
D1        1.00000000 sec
TD0          1

======== CHANNEL f1 ========
NUC1       1H
P1          9.50 usec
PL1        -1.00 dB
SFO1      500.1330885 MHz

F2 - Processing parameters
SI          32768
SF         500.1300000 MHz
WDW               no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

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WH9-175-B1

Current Data Parameters
NAME      WH9-175-B1
EXPNO     2
PROCNO    1

F2 - Acquisition Parameters
Date_      20100922
Time       13.06
INSTRUM    spect
PROBHD     5 mm PABBO BB
PULPROG    zgpg30
TD          65536
SOLVENT    CDCl3
NS         75
DS          4
SWH      29761.904 Hz
FIDRES     0.454131 Hz
AQ         1.1010548 sec
RG          812
DW         16.800 usec
DE         6.00 usec
TE         298.1 K
D1       2.00000000 sec
d11     0.03000000 sec
DELTA    1.8999998 sec
TD0          1

======== CHANNEL f1 ========
NUC1       13C
P1          7.50 usec
PL1        0.34 dB
F2 - Processing parameters
SI          32768
SF       125.7577890 MHz
WDW              EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40

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Current Data Parameters
NAME         WH9-101-B1
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PROCNO                1
F2 - Acquisition Parameters
Date_          20100906
Time              11.08
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    8
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FDIRRES         0.157632 Hz
AQ            3.1719923 sec
RG                  161
DW               48.400 usec
DE                 6.00 usec
TE                298.0 K
D1           1.00000000 sec
TD0                   1
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NUC1                1H
P1                 9.50 usec
PL1               -1.00 dB
SFO1        500.1330885 MHz
F2 - Processing parameters
SI                32768
SF          500.1300000 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00

Current Data Parameters
NAME         WH9-101-B1
EXPNO                 2
PROCNO                1
F2 - Acquisition Parameters
Date_          20100906
Time              11.14
INSTRUM           spect
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PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   99
DS                    4
SWH           29761.904 Hz
FIDRES         0.454131 Hz
AQ            1.1010548 sec
RG                  362
DW               16.800 usec
DE                 6.00 usec
TE                298.0 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                   1
======== CHANNEL f1 ========
NUC1                13C
P1                 7.50 usec
PL1                0.34 dB
SFO1        125.7703643 MHz
======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2               17.98 dB
PL13              20.00 dB
PL12              -1.00 dB
SFO2        500.1320005 MHz
F2 - Processing parameters
SI                32768
SF          125.7577890 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
HPLC Data

(anti-E)-Methyl 3-(N-allyl-4-methylphenylsulfonamido)-2-phenylhex-4-enoate (rac-11d)

\[
\begin{align*}
\text{Me} & \quad \text{CO}_2\text{Me} \\
\text{Ts}^- & \quad \text{N} \\
\end{align*}
\]

VWD: Signal A, 254 nm

Results

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(2R,3R,E)-methyl 3-(N-allyl-4-methylphenylsulfonamido)-2-phenylhex-4-enoate

(S)-(2R,3R-11d)

VWD: Signal A, 250 nm
Results

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