# Diastereoconvergent Synthesis of Anti-1,2-Amino Alcohols Bearing *N*-Containing Quaternary Stereocenters via Selenium-Catalyzed Intermolecular Direct C-H Amination

**Supporting Information**

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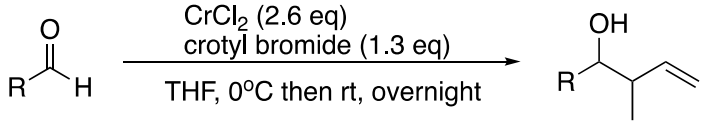
# 1 General Procedures

All reactions were performed under a nitrogen atmosphere using flame-dried glassware unless otherwise noted. Infrared spectra were measured on a Perkin Elmer Spectrum RX I spectrometer. Mass spectra were collected on a Hewlett Packard 5971A Gas Chromatograph - Mass Spectrometer or Bruker Esquire 1100 Liquid Chromatograph - Ion Trap Mass Spectrometer. Column chromatography was performed using silica gel (Whatman, 60 Å, 230-400 mesh). NMR spectra were recorded on a Bruker AV-300, AV-301, DRX-499 or AV-500 spectrometer. $^{1}H$ NMR chemical shifts ($\delta$) are reported in parts per million (ppm) and are referenced relative to TMS (0.00 ppm) or residual protonated $CHCl_3$ (7.26 ppm). $^{13}C$ NMR chemical shifts ($\delta$) are reported in parts per million (ppm) relative to the carbon resonance of $CDCl_3$ (77.16 ppm). Melting points were taken on a MEL-TEMP melting point apparatus and are uncorrected.

All commercial reagents were used as received, unless otherwise noted. All solvents were degassed and dried on solvent columns of neutral alumina. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc., stored over 4Å molecular sieves, and were used without further purification.

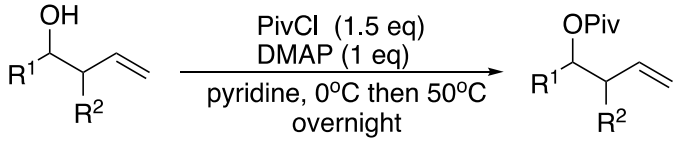
# 2 Synthesis and Characterization of Homoallylic Alcohol Pivalates

## 2.1 General Procedure A: Cr mediated crotylation of aldehydes




Anhydrous chromium (II) chloride (2.6 equiv) was suspended in THF (50 mL) at 0°C under a nitrogen atmosphere and dark brown suspension was obtained. To this suspension, aldehyde (1 equiv) and subsequently crotyl bromide (1.3 equiv) were added dropwise, and the mixture was stirred overnight at room temperature. Upon completion, the reaction was quenched by adding water. The reaction mixture was extracted with ether three times. The collected organic layers were dried over sodium sulphate and solvent was removed under reduced pressure. The crude product was purified by column chromatography.

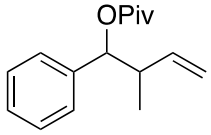
## 2.2 General Procedure B: Synthesis of Pivalates




Pivaloyl chloride (1.5 equiv) was added to a solution of alcohol (1 equiv) and DMAP (1 equiv) in pyridine at 0°C. The mixture was stirred overnight at 50°C. Upon completion, the reaction was quenched with 1 M HCl at room temperature. The aqueous phase was extracted with diethyl ether three times. The combined organic layers were washed with saturated aqueous sodium bicarbonate, brine and dried over magnesium sulphate. The solvent was removed under reduced pressure to give a crude material which was purified through column chromatography to afford pure product.

## 2.3 Characterization of Homoallylic Alcohol Pivalates

**2-methyl-1-phenylbut-3-enyl pivalate (1a)**




Prepared according to literature procedure[1] and General Procedure B. Purified through column chromatography (silica gel, ethyl acetate/hexanes = 1:20) to afford the product as a colorless oil (70% yield, d.r. 1:1).

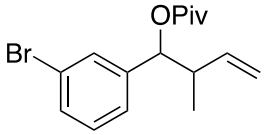
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.36 – 7.15 (m, 5 * 0.50H + m, 5 * 0.5H), 5.75 (ddd, *J* = 17.6, 9.8, 7.9 Hz, 1 * 0.5H), 5.71 – 5.60 (m, 1*0.5H, 1 * 0.5H), 5.56 (d, *J* = 7.4 Hz, 1 * 0.5H), 5.07 – 4.92 (m, 2* 0.5H, + m, 2* 0.5H), 2.73 – 2.58 (m, 1 * 0.5H, + m, 1 * 0.5H), 1.22 (s, 9 * 0.5H), 1.19 (s, 9 * 0.5H), 1.04 (d, *J* = 6.8 Hz, 3 * 0.5H), 0.91 (d, *J* = 6.9 Hz, 3 * 0.5H). (both diastereomers reported)

**$^{13}$C NMR** (75 MHz, $CDCl_3$) δ 177.25, 139.69, 139.46, 139.35, 128.11, 128.01, 127.67, 127.54, 126.94, 126.84, 115.52, 115.39, 78.61, 78.40, 43.80, 43.15, 38.92, 38.83, 27.16, 16.43, 14.97. (both diastereomers reported)

**IR** (thin film) 3067, 3033, 2974, 2933, 2872, 1732, 1480, 1456, 1281, 1154, 1031, 915, 753, 600 $cm^{-1}$.

**HRMS** (ESI, positive mode) calculated for $[M+Na]^+$ 269.1512, found 269.1515

**1-(3-bromophenyl)-2-methylbut-3-enyl pivalate(1b)**




Prepared according to General Procedure A and B. Purified through column chromatography (silica gel, ethyl acetate/hexanes = 1:25) to afford the product as a colorless oil (61% yield, d.r. 1:11).

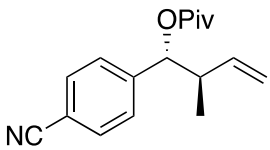
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.45 – 7.37 (m, 2H), 7.22 – 7.15 (m, 2H), 5.72 (ddd, *J* = 17.1, 10.4, 7.9 Hz, 1H), 5.51 (d, *J* = 7.3 Hz, 1H), 5.24 – 4.85 (m, 2H), 2.61 (m, 1H), 1.20 (s, 9H), 0.92 (d, *J* = 6.9 Hz, 3H). (major diastereomer reported)

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 177.26, 141.84, 139.09, 130.86, 129.90, 129.76, 125.64, 122.35, 116.06, 77.82, 43.73, 38.85, 27.13, 16.44. (major diastereomer reported)

**IR** (thin film) 2975, 2935, 2873, 1732, 1643, 1572, 1479, 1282, 1153, 997, 918, 783, 697 $cm^{-1}$.

**HRMS** (ESI, positive mode) calculated for $[C_{11}H_{12}Br]^+$ 223.0122, found 223.0117

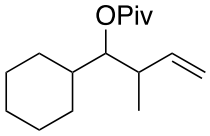
**1-(4-cyanophenyl)-2-methylbut-3-enyl pivalate (1c)**




Prepared according to General Procedure A and B. Purified through column chromatography (silica gel, ethyl acetate/hexanes = 1:5) to afford the product as a colorless oil (73% yield, anti diastereomer).

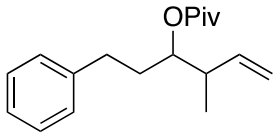
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.3 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 5.71 (ddd, *J* = 17.2, 10.3, 7.9 Hz, 1H), 5.59 (d, *J* = 6.7 Hz, 1H), 5.05 (d, *J* = 10.3 Hz, 1H), 5.00 (d, *J* = 17.1 Hz, 1H), 2.69 – 2.57 (m, 1H), 1.21 (s, 9H), 0.94 (d, *J* = 6.9 Hz, 3H).
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 177.25, 144.84, 138.45, 132.08, 127.53, 118.66, 116.51, 111.69, 77.85, 43.59, 38.89, 27.11, 16.34.
**IR** (thin film) 2970, 2936, 2874, 2229, 1732, 1642, 1612, 1480, 1460, 1397, 1367, 1281, 1154, 1033, 996, 920, 829 $cm^{-1}$.
**HRMS** (ESI, positive mode) calculated for $[M+H]^+$ 272.1650, found 272.1650

**1-cyclohexyl-2-methylbut-3-enyl pivalate (1d)**



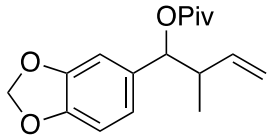

Prepared according to literature procedure[1] and General Procedure B. Purified through column chromatography (silica gel, ethyl acetate/hexanes = 1:20) to afford the product as a colorless oil (78% yield, d.r. 1:3).
**$^1$H NMR** (300 MHz, $CDCl_3$) δ 5.72 (m, 1H), 5.09 – 4.95 (m, 2H), 4.72 – 4.62 (m, 1H), 2.50 (m, 1H), 1.82 – 1.41 (m, 6H), 1.21 (s, 9H), 1.14 (m, 5H), 0.96 (d, *J* = 6.9 Hz, 3H). (major diastereomer reported)
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 178.09, 139.86, 115.16, 79.57, 39.60, 39.25, 29.60, 27.68, 27.45, 26.42, 26.12, 25.97, 17.64. (major diastereomer reported)
**IR** (thin film) 3075, 2971, 2930, 2854, 1727, 1480, 1450, 1281, 1160, 913 $cm^{-1}$.
**HRMS** (ESI, positive mode) calculated for $[M+Na]^+$ 275.1982, found 275.1984

**4-methyl-1-phenylhex-5-en-3-yl pivalate (1e)**




Prepared according to literature procedure[2] and General Procedure B. Product was isolated as a colorless oil (80% yield, d.r. 1:1). The characterization data is consistent with literature[3].

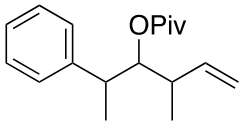
**1-(benzo[d][1,3]dioxol-5-yl)-2-methylbut-3-enyl pivalate (1f)**




Prepared according to literature procedure[1] and General Procedure B. Purified through column chromatography (silica gel, ethyl acetate/hexanes = 1:10) to afford the product as a colorless oil (65% yield, d.r. 2:3).
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 6.80 – 6.70 (m, 3H), 5.97 – 5.92 (m, 2H), 5.74 (ddd, *J* = 17.1, 10.4, 7.9 Hz, 1H * 0.40), 5.64 (ddd, *J* = 17.0, 10.6, 7.3 Hz, 1H * 0.60), 5.49 (d, *J* = 6.8 Hz, 1H * 0.60), 5.44 (d, *J* = 7.8 Hz, 1H * 0.40), 5.07 – 5.01 (m, 2H * 0.40), 5.00 – 4.93 (m, 2H * 0.60), 2.67 – 2.54 (m, 1H), 1.21 (s, 9H * 0.60), 1.18 (s, 9H * 0.40), 1.04 (d, *J* = 6.8 Hz, 3H * 0.60), 0.89 (d, *J* = 6.9 Hz, 3H * 0.40). (both diastereomers reported)
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 177.36, 177.33, 147.56, 147.45, 147.07, 146.96, 139.79, 139.21, 133.42, 133.29, 120.72, 120.57, 115.61, 115.55, 107.93, 107.86, 107.32, 107.24,

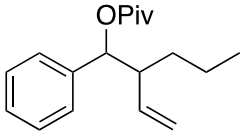
101.03, 101.00, 78.52, 78.42, 43.91, 43.21, 38.91, 38.82, 27.17, 27.15, 16.52, 15.31. (both diastereomers reported)
**IR** (thin film) 2934, 1727, 1504, 1490, 1444, 1282, 1250, 1156, 1039, 937, 808 $cm^{-1}$.
**HRMS** (ESI, positive mode) calculated for $[M+Na]^+$ 313.1410 found 313.1415

**4-methyl-2-phenylhex-5-en-3-yl pivalate (1g)**



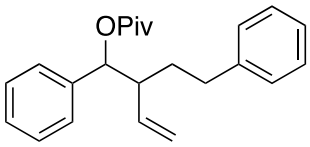

Prepared according to literature procedure[1] and General Procedure B. Purified through column chromatography (silica gel, ethyl acetate/hexanes = 1:20) to afford the product as a colorless oil (85% yield, d.r. 1:4).
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 2 * 0.2H + m, 2 * 0.8H), 7.26 – 7.18 (m, 3 * 0.2H + m, 3 * 0.8H), 5.78 (ddd, *J* = 17.3, 10.3, 8.9 Hz, 1 * 0.8H), 5.72 (ddd, *J* = 17.2, 10.6, 6.7 Hz, 1 * 0.2H), 5.17 (dd, *J* = 8.4, 4.2 Hz, 1 * 0.2H), 5.12 (dd, *J* = 9.8, 3.0 Hz, 1 * 0.8H), 5.06 (dd, *J* = 10.3, 2.0 Hz, 1 * 0.8H), 4.97 (dd, *J* = 2.1, 1.4 Hz, 1 * 0.2H), 4.95 (dt, *J* = 10.1, 1.5 Hz, 1 * 0.2H), 4.88 (dd, *J* = 17.2, 1.2 Hz, 1 * 0.8H), 3.08 – 2.93 (m, 1 * 0.2H + m, 1 * 0.8H), 2.27 – 2.12 (m, 1 * 0.2H + m, 1 * 0.8H), 1.25 (s, 9* 0.8H), 1.23 (d, *J* = 7.0 Hz, 3* 0.2H), 1.20 (s, 9* 0.2H), 1.18 (d, *J* = 7.0 Hz, 3* 0.8H), 0.97 (d, *J* = 6.8 Hz, 3* 0.2H), 0.89 (d, *J* = 7.0 Hz, 3* 0.8H). (both diastereomers reported)
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 178.14, 143.83, 138.81, 128.57, 127.88, 126.58, 116.13, 79.81, 42.24, 40.05, 39.21, 27.46, 18.37, 18.27. (major diastereomer reported)
**IR** (thin film) 3074, 3029, 1727, 1479, 1454, 1396, 1369, 1280, 1158, 1101, 999, 940, 914, 762, 702 $cm^{-1}$.
**HRMS** (ESI, positive mode) calculated for $[M+Na]^+$ 297.1825, found 297.1826

**1-phenyl-2-vinylpentyl pivalate (1h)**




Prepared according to literature procedure[4] and General Procedure B. Purified through column chromatography (silica gel, ethyl acetate/hexanes = 1:30) to afford the product as a colorless oil (64% yield, d.r. 1:3).
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.34 – 7.21 (m, 5H), 5.64 (d, *J* = 6.9 Hz, 1H), 5.58 (ddd, *J* = 17.1, 10.2, 9.2 Hz, 1H), 5.06 (dd, *J* = 10.2, 1.9 Hz, 1H), 4.97 (ddd, *J* = 17.2, 1.9, 0.6 Hz, 1H), 2.45 (tdd, *J* = 9.1, 6.9, 4.4 Hz, 1H), 1.41 – 1.29 (m, 4H), 1.19 (s, 9H), 0.81 (t, *J* = 7.2 Hz, 3H). (major diastereomer reported)
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 177.33, 139.72, 138.23, 128.12, 127.61, 126.95, 117.32, 77.62, 50.06, 38.86, 32.76, 27.18, 20.09, 13.90. (major diastereomer reported)
**IR** (thin film) 3069, 3034, 2960, 2934, 2873, 1732, 1480, 1457, 1281, 1154, 1032, 995, 969, 915, 763, 699 $cm^{-1}$.
**HRMS** (ESI, positive mode) calculated for $[M+NH_4]^+$ 292.2271, found 292.2268

**2-phenethyl-1-phenylbut-3-enyl pivalate (1i)**




Prepared according to literature procedure[4] and General Procedure B. Purified through column chromatography (silica gel, ethyl acetate/hexanes = 1:30) to afford the product as a colorless oil (61% yield, d.r. 1:2.6).

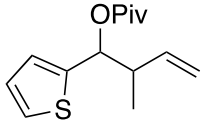
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.32 – 7.21 (m, 7H), 7.20 – 6.97 (m, 3H), 5.69 (d, *J* = 6.8 Hz, 1H), 5.64 (ddd, *J* = 17.1, 8.7, 7.7 Hz, 1H), 5.15 (dd, *J* = 10.3, 1.8 Hz, 1H), 5.02 (ddd, *J* = 17.1, 1.8, 0.6 Hz, 1H), 2.67 (ddt, *J* = 14.5, 10.0, 5.6 Hz, 1H), 2.46 (m, 2H), 1.65 (m, 2H), 1.18 (s, 9H). (major diastereomer reported)

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 177.30, 141.93, 139.33, 137.87, 128.41, 128.31, 128.17, 127.72, 126.98, 125.78, 118.08, 77.41, 49.60, 38.86, 33.11, 32.06, 27.17. (major diastereomer reported)

**IR** (thin film) 3065, 3029, 2975, 2933, 2870, 1732, 1643, 1496, 1479, 1455, 1396, 1366, 1281, 1154, 1031, 998, 917, 763, 749, 699 $cm^{-1}$.

**HRMS** (ESI, positive mode) calculated for $[M+NH_4]^+$ 354.2427, found 354.2429

**2-methyl-1-(thiophen-2-yl)but-3-enyl pivalate (1j)**




Prepared according to literature procedure[1] and General Procedure B. Purified through column chromatography (silica gel, ethyl acetate/hexanes = 1:10) to afford the product as a colorless oil (60% yield, d.r. 1:1).

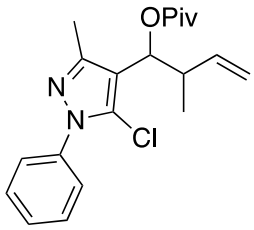
**$^1$H NMR** (300 MHz, $CDCl_3$) δ 7.27 – 7.18 (m, 1 * 0.50H + m, 1 * 0.50H), 7.02 – 6.89 (m, 2 * 0.50H + m, 2 * 0.50H), 5.92 (d, *J* = 6.8 Hz, 1 * 0.50H), 5.88 (d, *J* = 7.5 Hz, 1 * 0.50H), 5.86 – 5.64 (m, 1 * 0.50H + m, 1 * 0.50H), 5.15 – 4.97 (m, 2 * 0.50H + m, 2 * 0.50H), 2.80 – 2.63 (m, 1 * 0.50H + m, 1 * 0.50H), 1.21 (s, 9* 0.50H), 1.19 (s, 9 * 0.50H), 1.09 (d, *J* = 6.8 Hz, 3 * 0.50H), 0.97 (d, *J* = 6.8 Hz, 3 * 0.50H). (both diastereomers reported)

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 177.16, 177.13, 142.32, 142.18, 139.39, 138.82, 126.35, 126.31, 125.82, 125.66, 124.95, 124.80, 116.07, 115.98, 74.40, 74.35, 44.27, 43.44, 38.94, 38.86, 27.13, 27.11, 16.55, 15.41. (both diastereomers reported)

**IR** (thin film) 3078, 2975, 2934, 2872, 1732, 1479, 1280, 1150, 1032, 994, 966, 918, 700 $cm^{-1}$.

**HRMS** (ESI, positive mode) calculated for $[M+Na]^+$ 275.1076, found 275.1075

**1-(5-chloro-3-methyl-1-phenyl-1H-pyrazol-4-yl)-2-methylbut-3-enyl pivalate (1k)**




Prepared according to General Procedure A and B. Purified through column chromatography (silica gel, ethyl acetate/hexanes = 1:4) to afford the product as a colorless oil (62% yield, d.r. 1:4).

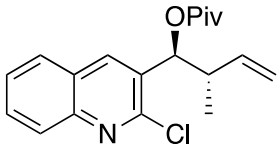
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.59 – 7.50 (m, 2H), 7.50 – 7.43 (m, 2H), 7.39 (d, *J* = 7.4 Hz, 1H), 5.78 (ddd, *J* = 17.2, 10.3, 8.0 Hz, 1H), 5.55 (d, *J* = 9.9 Hz, 1H), 5.14 (ddd, *J* = 17.1, 1.5, 1.0 Hz, 1H), 5.08 (ddd, *J* = 10.3, 1.6, 0.6 Hz, 1H), 2.93 – 2.84 (m, 1H), 2.40 (s, 3H), 1.20 (s, 9H), 0.95 (d, *J* = 6.9 Hz, 3H). (major diastereomer reported)

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 177.37, 148.48, 140.15, 138.20, 128.94, 128.07, 126.11, 124.98, 115.78, 115.55, 71.13, 42.21, 39.00, 27.23, 16.60, 13.44. (major diastereomer reported)

**IR** (thin film) 2974, 2933, 2873, 1730, 1599, 1557, 1503, 1479, 1459, 1417, 1281, 1154, 997, 920, 762, 694 $cm^{-1}$.

**HRMS** (ESI, positive mode) calculated for $[M+H]^+$ 361.1677, found 361.1686

**1-(2-chloroquinolin-3-yl)-2-methylbut-3-enyl pivalate (1l)**




Prepared according to General Procedure A and B. Purified through column chromatography (silica gel, ethyl acetate/hexanes = 1:5) to afford the product as a colorless oil (62% yield, single anti diastereomer).

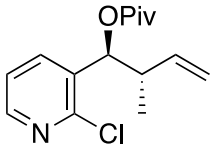
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.02 (m, 2H), 7.80 (d, *J* = 8.2 Hz, 1H), 7.72 (ddd, *J* = 8.3, 7.0, 1.3 Hz, 1H), 7.56 (ddd, *J* = 8.0, 6.8, 0.9 Hz, 1H), 6.13 (d, *J* = 5.3 Hz, 1H), 5.82 (ddd, *J* = 17.2, 10.3, 8.2 Hz, 1H), 5.03 (d, *J* = 10.4 Hz, 1H), 4.91 (d, *J* = 17.2 Hz, 1H), 2.91 – 2.80 (m, 1H), 1.27 (s, 9H), 1.15 (d, *J* = 6.9 Hz, 3H). (major diastereomer reported)

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 177.11, 149.07, 147.02, 137.84, 136.32, 132.20, 130.51, 128.38, 127.57, 127.21, 126.94, 116.96, 74.93, 42.78, 39.01, 27.18, 17.20. (major diastereomer reported)

**IR** (thin film): 2973, 1734, 1479, 1330, 1280, 1137, 1041, 995, 917, 754 $cm^{-1}$.

**HRMS** (ESI, positive mode) calculated for $[M+Na]^+$ 332.1417, found 332.1412

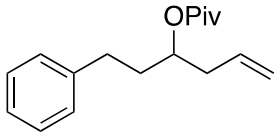
**1-(2-chloropyridin-3-yl)-2-methylbut-3-enyl pivalate(1m)**




Prepared according to General Procedure A and B. Purified through column chromatography (silica gel, ethyl acetate/hexanes = 1:4) to afford the product as a colorless oil (58% yield, single anti diastereomer).

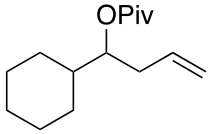
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.31 (dd, *J* = 4.7, 1.9 Hz, 1H), 7.58 (dd, *J* = 7.6, 1.9 Hz, 1H), 7.22 (dd, *J* = 7.7, 4.7 Hz, 1H), 5.99 (d, *J* = 5.4 Hz, 1H), 5.76 (ddd, *J* = 17.2, 10.3, 8.2 Hz, 1H), 5.03 (dd, *J* = 10.3, 1.0 Hz, 1H), 4.91 (d, *J* = 17.2 Hz, 1H), 2.79 – 2.65 (m, 1H), 1.23 (s, 9H), 1.10 (d, *J* = 6.9 Hz, 3H).
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 177.06, 149.53, 148.63, 137.83, 136.51, 134.59, 122.31, 116.88, 74.62, 42.62, 38.94, 27.13, 17.01.
**IR** (thin film) 2974, 2873, 1735, 1582, 1566, 1480, 1460, 1413, 1348, 1281, 1149, 1122, 1068, 996, 921, 804, 751, 726 $cm^{-1}$.
**HRMS** (ESI, positive mode) calculated for $[M+H]^+$ 282.1255, found 282.126

**1-phenylhex-5-en-3-yl pivalate (1n)**



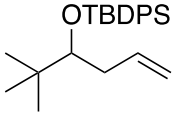

Prepared according to literature procedure[2] and General Procedure B. The characterization data is consistent with literature[3].

**1-cyclohexylbut-3-enyl pivalate (1o)**



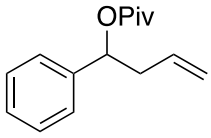

Prepared according to literature procedure[2] and General Procedure B. Purified through column chromatography (silica gel, ethyl acetate/hexanes = 1:30) to afford the product as a colorless oil (70% yield).
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 5.79 – 5.67 (m, 1H), 5.08 – 4.99 (m, 2H), 4.75 (ddd, *J* = 7.8, 6.0, 4.5 Hz, 1H), 2.38 – 2.22 (m, 2H), 1.77 – 1.71 (m, 3H), 1.70 – 1.61 (m, 2H), 1.57 – 1.48 (m, 1H), 1.27 – 1.08 (m, 12H), 1.08 – 0.95 (m, 2H).
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 178.07, 141.66, 133.59, 128.47, 128.35, 125.98, 117.79, 72.25, 38.91, 38.73, 35.59, 31.78, 27.27.
**IR** (thin film) 2975, 2929, 2854, 1727, 1480, 1450, 1283, 1163 $cm^{-1}$.
**HRMS** (ESI, positive mode) calculated for $[M+Na]^+$ 261.1825, Found 261.1822

**tert-butyl(2,2-dimethylhex-5-en-3-yloxy)diphenylsilane (1p)**



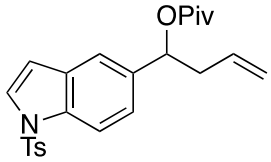

Prepared according to literature procedure[2,5] as a colorless oil (75% yield).
**$^1$H NMR** (300 MHz, $CDCl_3$) δ 7.76 – 7.66 (m, 4H), 7.47 – 7.31 (m, 6H), 5.59 – 5.39 (m, 1H), 4.72 – 4.58 (m, 2H), 3.54 – 3.41 (m, 1H), 2.39 – 2.24 (m, 1H), 2.24 – 2.11 (m, 1H), 1.04 (s, 9H), 0.90 (s, 9H).
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 137.16, 136.27, 136.15, 135.07, 133.98, 129.49, 129.34, 127.45, 127.29, 115.31, 81.55, 38.44, 36.79, 27.23, 26.73, 19.86.
**IR** (thin film) 3072, 2955, 2857, 1474, 1428, 1391, 1362, 1110, 1079, 1027, 999, 908, 821, 739, 702, 610 $cm^{-1}$.
**GC-MS** (m/z) 366.3(1)

**1-phenylbut-3-enyl pivalate (1q)**



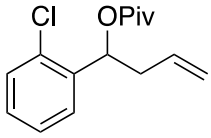

Prepared according to literature procedure[2] and General Procedure B. Purified through column chromatography (silica gel, ethyl acetate/hexanes = 1:30) to afford the product as a colorless oil (75% yield). The spectroscopic signatures were found to be consistent with literature data[6] .

**1-(1-tosyl-1H-indol-5-yl)but-3-enyl pivalate (1r)**



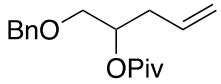

Prepared according to literature procedure[2,7] and General Procedure B. Purified through column chromatography (silica gel, ethyl acetate/hexanes = 1:3) to afford the product as a pale yellow semi solid (57% yield).
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.6 Hz, 1H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 3.7 Hz, 1H), 7.47 (s, 1H), 7.26 (d, *J* = 6.4 Hz, 2H), 7.23 (d, *J* = 8.5 Hz, 2H), 6.62 (d, *J* = 3.7 Hz, 1H), 5.82 (dd, *J* = 8.0, 5.4 Hz, 1H), 5.69 (ddt, *J* = 17.1, 10.1, 7.0 Hz, 1H), 5.04 (m, 2H), 2.63 (dt, *J* = 15.1, 7.7 Hz, 1H), 2.54 (ddd, *J* = 13.4, 6.5, 5.5 Hz, 1H), 2.35 (s, 3H), 1.19 (s, 9H).
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 177.51, 144.99, 135.82, 135.43, 134.36, 133.46, 130.72, 129.93, 126.87, 126.76, 122.92, 119.20, 117.94, 113.47, 109.00, 74.80, 41.39, 38.82, 27.17, 21.54.
**IR** (thin film) 2976, 1726, 1372, 1280, 1173, 1128, 996, 676 $cm^{-1}$.
**HRMS** (ESI, positive mode) calculated for $[M+Na]^+$ 448.1553, found 448.1543

**1-(2-chlorophenyl)but-3-enyl pivalate (1s)**



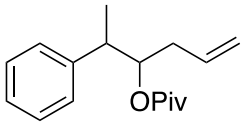

Prepared according to literature procedure[2] and General Procedure B. Purified through column chromatography (silica gel, ethyl acetate/hexanes = 1:20) to afford the product as a colorless oil (80% yield).
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.40 – 7.32 (m, 2H), 7.29 – 7.17 (m, 2H), 6.17 (dd, *J* = 8.0, 4.6 Hz, 1H), 5.77 (ddt, *J* = 17.1, 10.3, 7.0 Hz, 1H), 5.11 – 5.04 (m, 2H), 2.67 – 2.58 (m, 1H), 2.55 (dt, *J* = 14.6, 7.7 Hz, 1H), 1.23 (s, 9H).
**$^{13}$C NMR** (75 MHz, $CDCl_3$) δ 177.08, 138.44, 133.07, 132.10, 129.60, 128.66, 126.90, 126.85, 118.05, 71.44, 39.59, 38.81, 27.16.
**IR** (thin film) 3076, 2975, 2933, 2906, 2872, 1733, 1478, 1441, 1396, 1366, 1282, 1152, 1035, 986, 918, 756 $cm^{-1}$.
**HRMS** (ESI, positive mode) calculated for $[M+Na]^+$ 289.0966, found 289.0966

**1-(benzyloxy)pent-4-en-2-yl pivalate (1t)**



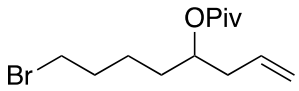

Prepared according to literature procedure[2,8] and General Procedure B. Purified through column chromatography (silica get, ethyl acetate/hexanes = 1:15) to afford the product as a colorless oil (60% yield).
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.38 – 7.26 (m, 5H), 5.74 (ddt, *J* = 17.0, 10.2, 7.1 Hz, 1H), 5.13 – 5.02 (m, 3H), 4.56 (d, *J* = 12.1 Hz, 2H), 4.51 (d, *J* = 12.1 Hz, 2H), 3.58 – 3.47 (m, 2H), 2.43 (dddt, *J* = 14.7, 6.7, 5.3, 1.3 Hz, 1H), 2.35 (dtt, *J* = 14.5, 7.3, 1.3 Hz, 1H), 1.19 (s, 9H).
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 177.98, 138.21, 133.37, 128.40, 127.65, 127.56, 117.92, 73.16, 71.35, 70.84, 38.83, 35.58, 27.21.
**IR** (thin film) 3076, 3030, 2975, 2933, 2869, 1727, 1480, 1454, 1366, 1283, 1163, 1120, 917, 737, 698 $cm^{-1}$.
**HRMS** (ESI, positive mode) calculated for $[M+Na]^+$ 299.1618, found 299.1617

**2-phenylhex-5-en-3-yl pivalate (1u)**




Prepared according to literature procedure[2] and General Procedure B. Purified through column chromatography (silica gel, ethyl acetate/hexanes = 1:30) to afford the product as a colorless oil (73% yield, d.r. 1:3).
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.34 – 7.15 (m, 5H), 5.79 – 5.62 (m, 1H), 5.18 – 5.05 (m, 1H), 5.05 – 4.86 (m, 2H), 3.04 – 2.91 (m, 1H), 2.35 (d, *J* = 14.6 Hz, 1H * 0.27), 2.27 – 2.19 (m, 1H), 2.08 (dt, *J* = 15.5, 8.3 Hz, 1H * 0.73), 1.30 – 1.21 (m, 4H), 1.20 (s, 9H * 0.73), 1.03 (s, 9H * 0.27). (both diastereomers reported)
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 177.94, 177.75, 143.45, 143.06, 133.85, 128.50, 128.18, 128.12, 127.86, 126.66, 126.45, 117.62, 117.56, 76.38, 75.87, 43.33, 43.08, 38.96, 38.78, 36.91, 36.52, 27.30, 27.05, 17.72, 17.63. (both diastereomers reported)
**IR** (thin film) 3078, 3029, 2974, 2934, 2907, 2874, 1726, 1495, 1479, 1454, 1396, 1366, 1282, 1160, 1031, 985, 915, 761, 701 $cm^{-1}$.
**HRMS** (ESI, positive mode) calculated for $[M+Na]^+$ 283.1669, found 283.1671

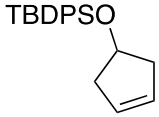
**8-bromooct-1-en-4-yl pivalate (1v)**




Prepared according to literature procedure[9,10] and General Procedure B. Purified through column chromatography (silica gel, ethyl acetate/hexanes = 1:30) to afford the product as a colorless oil (57% yield).
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 5.74 (ddt, *J* = 17.2, 10.2, 7.1 Hz, 1H), 5.11 – 5.03 (m, 2H), 4.90 (p, *J* = 6.0 Hz, 1H), 3.52 (t, *J* = 6.6 Hz, 2H), 2.38 – 2.24 (m, 2H), 1.90 – 1.70 (m, 2H), 1.68 – 1.38 (m, 2H), 1.19 (s, 9H).
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 178.06, 133.61, 117.70, 72.26, 44.74, 38.83, 38.66, 32.79, 32.24, 27.19, 22.54.
**IR** (thin film) 3078, 2957, 2870, 1725, 1643, 1480, 1460, 1284, 1162, 917, 652 $cm^{-1}$.

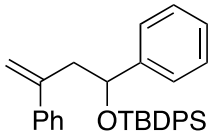
**HRMS** (ESI, positive mode) calculated for $[M+Na]^+$ 313.0774, found 313.0774

**tert-butyl(cyclopent-3-enyloxy)diphenylsilane (1w)**



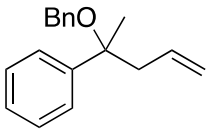

Prepared according to literature procedure[11]. Characterization data was found to be consistent with data reported therein.

**tert-butyl(1,3-diphenylbut-3-enyloxy)diphenylsilane (1x)**




Prepared according to literature procedure[1] and General Procedure B. Purified through column chromatography (silica gel, ethyl acetate/hexanes = 1:30) to afford the product as a colorless oil (67% yield).
**$^1$H NMR** (300 MHz, $CDCl_3$) δ 7.73 – 7.64 (m, 2H), 7.52 – 7.26 (m, 6H), 7.23 – 7.02 (m, 10H), 6.95 – 6.85 (m, 2H), 5.05 (d, *J* = 1.3 Hz, 1H), 4.72 – 4.61 (m, 2H), 3.07 (dd, *J* = 13.6, 5.1 Hz, 1H), 2.73 (dd, *J* = 13.5, 8.7 Hz, 1H), 1.00 (s, 9H).
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 141.43, 141.33, 137.84, 133.54, 133.42, 131.75, 131.02, 127.10, 126.85, 125.66, 125.15, 125.05, 124.81, 124.57, 124.45, 123.98, 123.52, 113.21, 72.02, 44.18, 24.46, 16.77.
**IR** (thin film): 3070, 3030, 2956, 2930, 2891, 2856, 1493, 1471, 1427, 1390, 1363, 1265, 1111, 1083, 1063, 942, 900, 848, 822, 777, 740, 700, 614 $cm^{-1}$.
**HRMS** (ESI, positive mode) calculated for $[M+Na]^+$ 485.2271, found 485.2266

**(2-(benzyloxy)pent-4-en-2-yl)benzene (1y)**




The homoallylic alcohol was prepared according to literature procedure[2], which was subjected to the following procedure for benzylation. To a flamed dried round bottom flask charged with NaH (60% suspension in mineral oil) (1.5 equiv) and THF (50 ml) at 0°C under nitrogen atmosphere was added the alcohol (1 equiv) dropwise. After 30 min, benzyl bromide (1.3 equiv) was added dropwise. The reaction mixture was refluxed overnight. The reaction was cooled to room temperature and was quenched with saturated aqueous $NH_4Cl$. The mixture was extracted with diethyl ether three times. The combined organic layers were washed with brine, dried over $Na_2SO_4$, and filtered. The solvent was removed under reduced pressure, and the crude was purified through column chromatography (silica gel, ether/hexanes = 1/20) to afford the product as a colorless oil (73% yield).
**$^1$H NMR** (300 MHz, $CDCl_3$) δ 7.57 – 7.14 (m, 10H), 5.83 – 5.58 (m, 1H), 5.09 – 4.96 (m, 2H), 4.32 (d, *J* = 11.3 Hz, 1H), 4.21 (d, *J* = 11.3 Hz, 1H), 2.68 (dd, *J* = 13.9, 7.2 Hz, 1H), 2.59 (dd, *J* = 14.0, 7.2 Hz, 1H), 1.63 (s, 3H).
**$^{13}$C NMR** (75 MHz, $CDCl_3$) δ 145.03, 139.48, 134.24, 128.26, 128.20, 127.26, 127.12, 127.03, 126.32, 117.61, 79.00, 64.63, 47.68, 23.47.

**IR** (thin film) 3063, 3029, 2978, 2933, 1494, 1447, 1381, 1288, 1219, 1171, 1091, 1067, 1028, 998, 915, 733, 699 $cm^{-1}$.
**HRMS** (ESI, positive mode) calculated for $[M+Na]^+$ 275.1406, found 275.1409

# 3 Synthesis and Characterization of 1,2-Amino Alcohols

## 3.1 General Procedure C: Allylic Amination of Homoallylic Alcohols

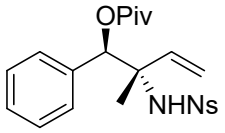
To an oven-dried 1-dram vial was added alkene (0.2 mmol, 1.0 equiv), tricyclohexylphosphine selenide (15 mol %), 4-nitrobenzenesulfonamide (0.4 mmol, 2.0 equiv), $Li_2CO_3$ (0.4 mmol, 2.0 equiv), DCM (1 mL) and (diacetoxyiodo)benzene (0.4 mmol, 2.0 equiv), in that order. The vial was capped with a Teflon-lined screw cap and the reaction was stirred at 35°C for 24 or 48 hours. Upon completion, the reaction mixture was diluted with 2 ml ethyl acetate and was pushed through a silica plug. The filtrate was collected in a vial charged with known amount of 1,3-dinitrobenzene. The solvent was then removed under reduced pressure. The NMR yield was obtained by taking a $^1H$ NMR spectrum of the crude mixture using 1,3-dinitrobenzene as internal standard. The crude product was then purified by column chromatography to afford the corresponding product and isolated yield was obtained.

## 3.2 General Procedure D: Allylic Amination of Homoallylic Alcohols

To an oven-dried 1-dram vial was added alkene (0.2 mmol, 1.0 equiv), tricyclohexylphosphine selenide (30 mol%), 4-nitrobenzenesulfonamide (0.4 mmol, 2.0 equiv), $Li_2CO_3$ (0.4 mmol, 2.0 equiv), DCE (1 mL) and (diacetoxyiodo)benzene (0.4 mmol, 2.0 equiv), in that order. The vial was capped with a Teflon-lined screw cap and the reaction was stirred at 50°C for 24 or 48 hours. Upon completion, the reaction mixture was diluted with 2 ml ethyl acetate and was pushed through a silica plug. The filtrate was collected in a vial charged with known amount of 1,3-dinitrobenzene. The solvent was then removed under reduced pressure. The NMR yield was obtained by taking a $^1H$ NMR spectrum of the crude mixture using 1,3-dinitrobenzene as internal standard. The crude product was then purified by column chromatography to afford the corresponding product and isolated yield was obtained.

## 3.3 Characterization of 1,2-Amino Alcohol Products

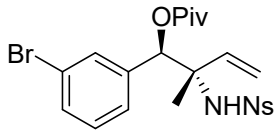
**2-methyl-2-(4-nitrophenylsulfonamido)-1-phenylbut-3-enyl pivalate (2a)**




Prepared according to General Procedure C. Purified through column chromatography (silica gel, ethyl acetate/hexanes = 1:5) as a yellow semi solid (70.3 mg, 79% yield, d.r. 1:10).
**$^1H$ NMR** (500 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.6 Hz, 2H), 7.95 (d, *J* = 8.6 Hz, 2H), 7.37 – 7.26 (m, 5H), 5.71 (s, 1H), 5.64 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.24 – 5.11 (m, 2H), 5.01 (s, 1H), 1.36 (s, 3H), 1.20 (s, 9H). Minor diastereomer: 8.24 (2H), 7.90 (2H), 7.4-7.25 (5H), 5.79 (1H), 5.25-5.11 (2H), 1.28 (3H), 1.21 (9H)
**$^{13}C$ NMR** (126 MHz, $CDCl_3$) δ 176.73, 149.83, 148.39, 136.86, 135.17, 128.82, 128.52, 128.28, 128.13, 124.06, 118.17, 79.69, 62.85, 38.95, 27.06, 20.67. (major diastereomer reported)
**IR** (thin film) 3276, 1736, 1530, 1349, 1219, 1158, 1092, 1003, 854, 772 $cm^{-1}$.

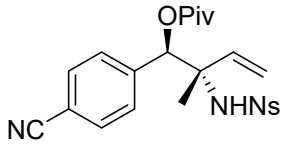
**HRMS** (ESI, positive mode) calculated for $[M+Na]^+$ 469.1404, found 469.1400

**1-(3-bromophenyl)-2-methyl-2-(4-nitrophenylsulfonamido)but-3-enyl pivalate (2b)**



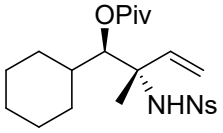

Prepared according to General Procedure D. Purified through column chromatography (silica gel, ethyl acetate/hexanes = 1:5) as a yellow waxy solid (86.2 mg, 82% yield, d.r. 1:15).
**$^1$H NMR** (500 MHz, Acetone) δ 8.40 (d, *J* = 8.8 Hz, 2H), 8.07 (d, *J* = 8.8 Hz, 2H), 7.65 (s, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.46 (d, *J* = 7.8 Hz, 2H), 7.34 (t, *J* = 7.9 Hz, 1H), 6.01 (dd, *J* = 17.4, 10.9 Hz, 1H), 5.97 (s, 1H), 5.16 (d, *J* = 10.8 Hz, 1H), 5.15 (d, *J* = 17.5 Hz, 1H), 1.37 (s, 3H), 1.21 (s, 9H). Minor diastereomer: 8.40 (2H), 8.06 (2H), 7.66 (1H), 7.53 (1H), 7.46 (1H), 7.32 (1H), 6.01 (1H), 5.85 (1H), 5.25 (1H), 5.15 (1H), 1.23 (9H). Minor diastereomer: 8.40 (2H), 8.07 (2H), 7.64 (1H), 7.53 (1H), 7.46 (1H), 7.32 (1H), 6.01 (1H), 5.85 (1H), 5.26 (1H), 1.33 (3H), 1.23 (9H).
**$^{13}$C NMR** (126 MHz, Acetone) δ 176.74, 150.70, 150.12, 140.17, 138.44, 132.24, 132.04, 130.65, 129.29, 128.30, 124.98, 122.29, 118.13, 78.88, 62.93, 39.38, 27.30, 19.89. (major diastereomer reported)
**IR** (thin film) 3276, 3105, 2976, 2934, 2873, 1738, 1532, 1479, 1350, 1309, 1279, 1165, 1093, 1035, 1006, 939, 855, 757, 736, 686, 608 $cm^{-1}$.
**HRMS** (ESI, positive mode) calculated for $[M+NH_4]^+$ 542.0954, found 542.0961

**1-(4-cyanophenyl)-2-methyl-2-(4-nitrophenylsulfonamido)but-3-enyl pivalate (2c).**




Prepared according to General Procedure D. Purified through column chromatography (silica gel, ethyl acetate/hexanes 1:5) as a yellow oil (72.6 mg, 77% yield, single diastereomer).
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.5 Hz, 2H), 8.00 (d, *J* = 8.6 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 5.87 (s, 1H), 5.77 (dd, *J* = 17.5, 10.9 Hz, 1H), 5.27 (s, 1H), 5.20 (d, *J* = 10.9 Hz, 1H), 5.09 (d, *J* = 17.4 Hz, 1H), 1.29 (s, 3H), 1.21 (s, 9H).
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 176.63, 149.97, 148.12, 140.83, 136.01, 131.93, 129.00, 128.52, 124.18, 118.72, 118.24, 112.66, 78.86, 62.48, 38.94, 27.01, 20.53.
**IR** (thin film) 3273, 3106, 2976, 2935, 2874, 2231, 1737, 1609, 1532, 1350, 1310, 1280, 1165, 1093, 1036, 1007, 855, 757, 736, 686, 617 $cm^{-1}$.
**HRMS** (ESI, positive mode) calculated for $[M+NH_4]^+$ 489.1802, found 489.1791

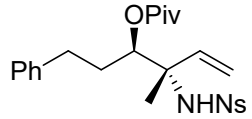
**1-cyclohexyl-2-methyl-2-(4-nitrophenylsulfonamido)but-3-enyl pivalate(2d)**




Prepared according to General Procedure C. Purified through column chromatography (silica gel, ethyl acetate/hexanes = 1:5) as a colorless solid (67.5 mg, 75% yield, d.r. 1:11).
**$^1$H NMR** (500 MHz, Acetone) δ 8.43 (d, *J* = 8.9 Hz, 2H), 8.12 (d, *J* = 8.9 Hz, 2H), 6.79 (s, 1H), 5.91 (dd, *J* = 17.5, 10.8 Hz, 1H), 5.11 (d, *J* = 17.5 Hz, 1H), 5.05 (d, *J* = 10.9 Hz, 1H), 4.84

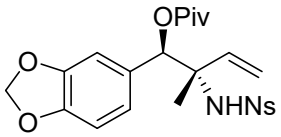
(d, *J* = 3.4 Hz, 1H), 1.97 – 1.52 (m, 6H), 1.41 (s, 3H), 1.34 – 0.95 (m, 14H). Minor diastereomer: 8.44 (2H), 8.19 (2H), 6.73 (1H), 5.93 (1H), 5.24 (1H), 5.08 (1H), 4.84 (1H), 2.0-1.0 (23 H, obscured)
**$^{13}$C NMR** (126 MHz, Acetone) δ 177.79, 150.73, 150.21, 139.74, 129.51, 124.99, 116.83, 80.76, 63.81, 39.60, 38.97, 33.92, 30.76, 29.02, 27.63, 27.24, 26.94, 20.03. (major diastereomer reported)
**IR** (thin film) 3274, 2929, 2853, 1729, 1531, 1480, 1349, 1163, 1092, 854, 749 cm$^{-1}$.
**HRMS** (ESI, positive mode) calculated for $[M+Na]^+$ 475.1873, found 475.1869

**4-methyl-4-(4-nitrophenylsulfonamido)-1-phenylhex-5-en-3-yl pivalate(2e)**



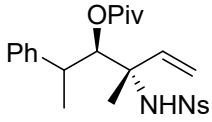

Prepared according to General Procedure C. Purified through column chromatography (silica gel, ethyl acetate/hexanes = 1:5) as a yellow oil (80.4 mg, 85% yield, d.r. 1:4.2).
**$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.9 Hz, 2H), 7.99 (d, *J* = 8.9 Hz, 2H), 7.27 (t, *J* = 7.4 Hz, 2H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.09 (d, *J* = 7.0 Hz, 2H), 5.72 (dd, *J* = 17.5, 10.8 Hz, 1H), 5.20 (d, *J* = 10.9 Hz, 1H), 5.18 (d, *J* = 17.5 Hz, 1H), 4.91 (dd, *J* = 10.4, 2.4 Hz, 1H), 2.57 (ddd, *J* = 14.2, 10.4, 5.1 Hz, 1H), 2.46 (ddd, *J* = 13.7, 10.2, 6.4 Hz, 1H), 1.92 – 1.83 (m, 1H), 1.82 – 1.73 (m, 1H), 1.33 (s, 3H), 1.22 (s, 9H). Minor diastereomer: 8.30 (2H), 7.99 (2H), 7.27 (2H), 7.19 (1H), 7.07 (2H), 5.52 (1H), 5.26 (1H), 5.20 (2H), 5.12 (1H), 4.91 (1H), 2.57 (1H), 2.46 (1H), 1.8 (2H), 1.38 (3H), 1.25 (9H).
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 178.46, 149.85, 148.47, 140.74, 136.67, 128.60, 128.56, 128.28, 126.34, 124.13, 118.07, 77.52, 63.58, 39.13, 32.15, 31.44, 27.25, 21.04. (major diastereomer reported)
**IR** (thin film) 3266, 2969, 1729, 1606, 1530, 1479, 1349, 1162, 1092, 1035, 854, 747, 685 cm$^{-1}$.
**HRMS** (ESI, positive mode) calculated for $[M+Na]^+$ 497.1717, found 497.1713

**1-(benzo[d][1,3]dioxol-5-yl)-2-methyl-2-(4-nitrophenylsulfonamido)but-3-enyl pivalate (2f)**



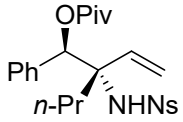

Prepared according to General Procedure C. Purified through column chromatography (silica gel, ethyl acetate/hexanes = 1:3) as a white semi solid (69.5 mg, 76% yield, d.r. 1:11).
**$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.8 Hz, 2H), 7.98 (d, *J* = 8.8 Hz, 2H), 6.8-6.7 (m, 3H), 5.97 (s, 2H), 5.64 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.60 (s, 1H), 5.20 (d, *J* = 10.8 Hz, 1H), 5.16 (d, *J* = 17.4 Hz, 1H), 4.95 (s, 1H), 1.35 (s, 3H), 1.19 (s, 9H). Minor diastereomer: 8.29 (2H), 7.97 (2H), 6.8-6.7 (3H), 5.78 (1H), 5.60 (1H), 5.21 (1H), 5.15 (1H), 1.32 (3H), 1.20 (9H)
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 176.72, 149.86, 148.37, 148.00, 147.62, 136.92, 128.80, 128.57, 124.08, 122.04, 118.18, 108.29, 108.06, 101.38, 79.55, 62.91, 38.94, 27.05, 20.64. (major diastereomer reported)
**IR** (thin film) 3281, 2974, 1734, 1530, 1490, 1444, 1349, 1249, 1159, 1093, 1036, 935, 854, 735 cm$^{-1}$.
**HRMS** (ESI, positive mode) calculated for $[M+Na]^+$ 513.1302, found 513.1299

**4-methyl-4-(4-nitrophenylsulfonamido)-2-phenylhex-5-en-3-yl pivalate (2g)**



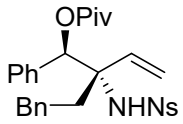

Prepared according to General Procedure C. Purified through column chromatography (silica gel, ethyl acetate/hexanes = 1:5) as a yellow oil (74 mg, 78% yield, d.r. 1:16).
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.7 Hz, 2H), 7.90 (d, *J* = 8.9 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.26 – 7.17 (m, 3H), 5.67 (dd, *J* = 17.5, 10.8 Hz, 1H), 5.20 – 5.09 (m, 3H), 4.92 – 4.83 (m, 1H), 3.12 (quin, *J* = 7.2 Hz, 1H), 1.28 (s, 3H), 1.21 (s, 9H), 1.19 (d, *J* = 7.1 Hz, 3H).
Minor diastereomer: 8.28 (2H), 7.93 (2H), 7.3-7.1 (4H), 5.62 (1H), 5.23 (1H), 5.13 (2H), 1.16 (3H)
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 177.86, 149.80, 148.47, 144.20, 137.07, 129.07, 128.59, 127.64, 127.19, 124.03, 117.73, 80.39, 64.22, 40.49, 39.22, 27.34, 21.28, 19.13. (major diastereomer reported)
**IR** (thin film) 3274, 2959, 1726, 1531, 1349, 1280, 1166, 1092, 938, 854, 738 $cm^{-1}$.
**HRMS** (ESI, positive mode) calculated for $[M+Na]^+$ 497.1717, found 497.1711

**2-(4-nitrophenylsulfonamido)-1-phenyl-2-vinylpentyl pivalate (2h)**




Prepared according to General Procedure D. Purified through column chromatography (silica gel, ethyl acetate/hexanes = 1:5) as a pale-yellow oil (68.3 mg, 72% yield, d.r. 1:7).
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.7 Hz, 2H), 7.99 (d, *J* = 8.7 Hz, 2H), 7.45 – 7.13 (m, 5H), 5.89 (s, 1H), 5.64 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.24 (d, *J* = 11.0 Hz, 1H), 5.10 (d, *J* = 17.5 Hz, 1H), 5.00 (s, 1H), 1.86 – 1.57 (m, 2H), 1.39 – 1.21 (m, 2H), 1.16 (s, 9H), 0.82 (s, 3H).
Minor diastereomer: 8.24 (2H), 7.93 (2H), 7.4-7.1 (5H), 5.91 (1H), 5.81 (1H), 5.24 (1H), 5.12 (1H), 4.78 (1H), 1.86-1.57 (2H), 1.18 (9H), 0.73 (3H)
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 176.93, 149.79, 148.50, 135.40, 135.13, 128.70, 128.49, 128.19, 128.13, 124.03, 118.58, 77.99, 66.37, 38.93, 35.80, 27.00, 16.88, 14.10. (major diastereomer reported)
**IR** (thin film) 3284, 3106, 3035, 2967, 2935, 2875, 1734, 1608, 1532, 1350, 1308, 1164, 1094, 1033, 1004, 940, 912, 856, 736, 617 $cm^{-1}$.
**HRMS** (ESI, positive mode) calculated for $[M+NH_4]^+$ 492.2162, found 492.2170

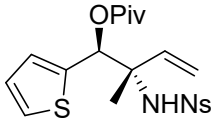
**2-(4-nitrophenylsulfonamido)-2-phenethyl-1-phenylbut-3-enyl pivalate(2i)**




Prepared according to General Procedure D. Purified through column chromatography (silica gel, ethyl acetate/hexanes = 1:7) as a pale-yellow oil (83.7 mg, 78% yield, d.r. 1:12).
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.9 Hz, 2H), 7.99 (d, *J* = 8.8 Hz, 2H), 7.32 (m, 5H), 7.28 – 6.97 (m, 5H), 5.97 (s, 1H), 5.69 (dd, *J* = 17.6, 11.0 Hz, 1H), 5.29 (d, *J* = 11.0 Hz, 1H), 5.17 (s, 1H), 5.16 (d, *J* = 17.6 Hz, 2H), 3.05 – 2.57 (m, 2H), 2.23 – 1.84 (m, 2H), 1.17 (s, 9H).
Minor diastereomer: 8.16 (2H), 7.86 (2H), 7.4-7.0 (10H), 5.98 (1H), 5.75 (1H), 5.29 (1H), 5.17 (1H), 5.02 (1H), 3.0-2.5 (2H), 2.23-1.84 (2H), 1.20 (9H).

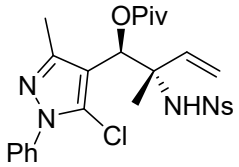
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 177.01, 149.84, 148.30, 140.87, 135.14, 134.91, 128.91, 128.57, 128.52, 128.25, 128.22, 128.17, 126.27, 124.11, 119.03, 78.24, 66.27, 38.96, 35.43, 29.78, 27.03. (major diastereomer reported)
**IR** (thin film) 3282, 2972, 1736, 1606, 1531, 1349, 1308, 1162, 1092, 855, 736, 700 $cm^{-1}$.
**HRMS** (ESI, positive mode) calculated for $[M+NH_4]^+$ 554.2319, found 554.2329

**2-methyl-2-(4-nitrophenylsulfonamido)-1-(thiophen-2-yl)but-3-enyl pivalate (2j)**



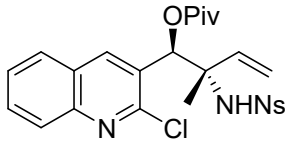

Prepared according to General Procedure C. Purified through column chromatography (silica gel, ethyl acetate/hexanes = 1:5) as a yellow oil (62.8 mg, 72% yield, d.r. 1:10).
**$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.8 Hz, 2H), 7.99 (d, *J* = 8.9 Hz, 2H), 7.29 (dd, *J* = 5.1, 0.8 Hz, 1H), 7.05 (d, *J* = 3.4 Hz, 1H), 6.98 (dd, *J* = 5.0, 3.6 Hz, 1H), 6.02 (s, 1H), 5.67 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.25 (d, *J* = 17.4 Hz, 1H), 5.23 (d, *J* = 10.8 Hz, 1H), 5.07 (s, 1H), 1.43 (s, 3H), 1.18 (s, 9H). Minor diastereomer: 8.28 (2H), 7.98 (2H), 7.05 (1H), 6.98 (1H), 6.02 (1H), 5.85 (1H), 5.26 (2H), 5.07 (1H), 1.35 (3H), 1.19 (9H).
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 176.40, 149.88, 148.22, 137.32, 136.60, 128.64, 128.20, 126.68, 126.32, 124.07, 118.83, 76.10, 62.76, 38.97, 27.00, 20.75. (major diastereomer reported)
**IR** (thin film) 3276, 2974, 1737, 1530, 1479, 1399, 1349, 1308, 1160, 1092, 1033, 1000, 854, 735, 685 $cm^{-1}$.
**HRMS** (ESI, positive mode) calculated for $[M+Na]^+$ 475.0968, found 475.0966

**1-(5-chloro-3-methyl-1-phenyl-1H-pyrazol-4-yl)-2-methyl-2-(4-nitrophenylsulfonamido) but-3-enyl pivalate (2k)**



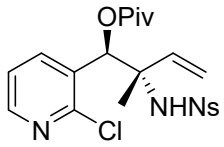

Prepared according to General Procedure D. Purified through column chromatography (silica gel, ethyl acetate/hexanes = 1:4) as a yellow oil (67.3 mg, 60% yield, d.r. 1:12).
**$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.7 Hz, 2H), 8.02 (d, *J* = 8.9 Hz, 2H), 7.61 – 7.36 (m, 5H), 5.72 (m, 1H), 5.43 – 5.21 (m, 3H), 2.34 (s, 3H), 1.25 (s, 12H). Minor diastereomer: 8.30 (2H), 8.02 (2H), 7.61 – 7.36 (5H), 5.72 (1H), 5.43 – 5.21 (3H), 2.34 (3H), 1.25 (12H)
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 176.88, 149.93, 148.29, 137.83, 136.66, 135.82, 129.09, 128.63, 128.57, 125.54, 125.13, 124.13, 118.71, 112.01, 73.68, 64.22, 39.25, 34.25, 30.35, 27.26. (major diastereomer reported)
**IR** (thin film) 3271, 3106, 2971, 2932, 2873, 1734, 1605, 1532, 1503, 1349, 1310, 1278, 1163, 1093, 1034, 1006, 941, 855, 761, 686, 609 $cm^{-1}$.
**HRMS** (ESI, positive mode) calculated for $[M+H]^+$ 561.1574, found 561.1569

**1-(2-chloroquinolin-3-yl)-2-methyl-2-(4-nitrophenylsulfonamido)but-3-enyl pivalate (2l)**



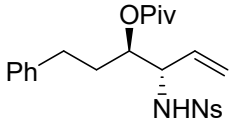

Prepared according to General Procedure D. Purified through column chromatography (silica gel, ethyl acetate/hexanes = 1:5) as a yellow oil (71.3 mg, 67% yield, d.r. 1:13).
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.5 Hz, 2H), 8.04 (s, 1H), 8.00 (d, *J* = 8.5 Hz, 1H), 7.93 (d, *J* = 8.4 Hz, 2H), 7.77 (m, 1H), 7.58 (t, *J* = 7.5 Hz, 1H), 6.28 (s, 1H), 5.82 (dd, *J* = 17.3, 10.7 Hz, 1H), 5.44 (s, 1H), 5.32 (d, *J* = 10.7 Hz, 1H), 5.21 (d, *J* = 17.4 Hz, 1H), 1.47 (s, 3H), 1.22 (s, 9H). Minor diastereomer: 8.14 (2H), 8.04 (1H), 8.00 (1H), 7.93 (2H), 7.77 (1H), 7.58 (1H), 6.28 (1H), 5.82 (1H), 5.44 (1H), 5.32 (1H), 5.21 (1H), 1.47 (3H), 1.22 (9H).
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 176.46, 149.78, 149.70, 147.90, 147.24, 137.86, 136.06, 131.48, 128.39, 128.36, 127.69, 127.53, 126.29, 124.04, 118.83, 75.31, 63.85, 38.87, 26.96, 19.74. (major diastereomer reported)
**IR** (thin film) 3273, 2976, 2933, 2873, 1738, 1531, 1350, 1165, 1136, 1092, 1050, 854, 756, 735, 686 $cm^{-1}$.
**HRMS** (ESI, positive mode) calculated for $[M+H]^+$ 532.1309, found 532.1300

**1-(2-chloropyridin-3-yl)-2-methyl-2-(4-nitrophenylsulfonamido)but-3-enyl pivalate (2m)**




Prepared according to General Procedure D. Purified through column chromatography (silica gel, ethyl acetate/hexanes = 1:3) as a yellow oil (72.3 mg, 75% yield, d.r. 1:17).
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.35 (dd, *J* = 4.6, 1.8 Hz, 1H), 8.31 (d, *J* = 8.8 Hz, 2H), 8.01 (d, *J* = 8.8 Hz, 2H), 7.64 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.22 (dd, *J* = 7.7, 4.7 Hz, 1H), 6.15 (s, 1H), 5.80 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.42 (s, 1H), 5.29 (d, *J* = 10.8 Hz, 1H), 5.14 (d, *J* = 17.4 Hz, 1H), 1.38 (s, 3H), 1.20 (s, 9H).
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 176.50, 151.13, 149.96, 149.77, 148.08, 137.92, 135.61, 130.68, 128.55, 124.21, 122.15, 119.01, 75.34, 63.64, 38.86, 26.96, 19.97. (major diastereomer reported)
**IR** (thin film) 3272, 2976, 1738, 1531, 1350, 1165, 1136, 1092, 1033, 1004, 855, 736, 686 $cm^{-1}$.
**HRMS** (ESI, positive mode) calculated for $[M+H]^+$ 482.1147, found 482.1154

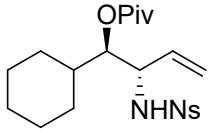
**4-(4-nitrophenylsulfonamido)-1-phenylhex-5-en-3-yl pivalate (2n)**




Prepared according to General Procedure C. Purified through column chromatography (silica gel, ethyl acetate/hexanes = 1:5) as a yellow semi solid (72.3 mg, 79% yield, d.r. 1:8).
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.8 Hz, 2H), 7.89 (d, *J* = 8.9 Hz, 2H), 7.18 (dd, *J* = 9.0, 5.7 Hz, 2H), 7.11 (t, *J* = 7.3 Hz, 1H), 6.98 (d, *J* = 7.2 Hz, 2H), 5.45 (m, 2H), 5.06 – 4.98 (m, 2H), 4.61 (dt, *J* = 9.5, 3.6 Hz, 1H), 3.99 (td, *J* = 8.3, 3.2 Hz, 1H), 2.58 (ddd, *J* = 14.3, 9.3, 5.3 Hz, 1H), 2.44 (ddd, *J* = 14.0, 8.8, 7.5 Hz, 1H), 1.90 – 1.81 (m, 1H), 1.70 (dddd, *J* = 11.2,

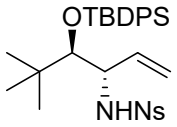
9.4, 7.2, 3.9 Hz, 1H), 1.14 (s, 9H). Minor diastereomer: 8.20 (2H), 7.91 (2H), 7.2-6.9 (5H), 5.47 (1H), 4.92 (1H), 4.88 (1H), 4.03 (1H), 2.6-1.7 (4H), 1.20 (9H)
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 178.96, 149.91, 146.82, 140.31, 132.01, 128.58, 128.26, 128.24, 126.33, 124.22, 119.25, 74.78, 59.72, 39.05, 32.77, 31.44, 27.18. (major diastereomer reported)
**IR** (thin film) 3280, 2972, 1726, 1530, 1479, 1454, 1349, 1310, 1282, 1166, 1092, 933, 854, 738, 684 $cm^{-1}$.
**HRMS** (ESI, positive mode) calculated for $[M+Na]^+$ 483.1560, found 483.1555

**1-cyclohexyl-2-(4-nitrophenylsulfonamido)but-3-enyl pivalate (2o)**



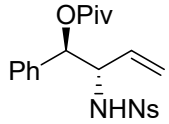

Prepared according to General Procedure C. Purified through column chromatography (silica gel, ethyl acetate/hexanes = 1:5) as a yellow oil (70 mg, 80% yield, d.r. 1:8).
**$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.9 Hz, 2H), 8.03 (d, *J* = 8.9 Hz, 2H), 5.68 (d, *J* = 8.2 Hz, 1H), 5.51 (ddd, *J* = 17.1, 10.3, 6.9 Hz, 1H), 5.13 – 5.04 (m, 2H), 4.47 (dd, *J* = 7.1, 3.4 Hz, 1H), 4.18 (ddd, *J* = 8.3, 7.1, 3.5 Hz, 1H), 1.75 – 1.68 (m, 3H), 1.68 – 1.56 (m, 4H), 1.27 – 1.03 (m, 7H), 1.01 – 0.85 (m, 11H). (major diastereomer reported)
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 179.23, 149.94, 147.12, 132.38, 128.43, 124.19, 118.89, 79.73, 57.72, 39.10, 38.86, 29.63, 27.68, 27.23, 26.03, 25.78, 25.59. (major diastereomer reported)
**IR** (thin film) 3270, 2929, 2854, 1708, 1531, 1479, 1449, 1349, 1310, 1282, 1165, 1092, 854, 738, 685 $cm^{-1}$.
**HRMS** (ESI, positive mode) calculated for $[M+Na]^+$ 461.1717, found 461.1713

**N-(4-(tert-butyldiphenylsilyloxy)-5,5-dimethylhex-1-en-3-yl)-4 nitrobenzenesulfonamide (2p)**



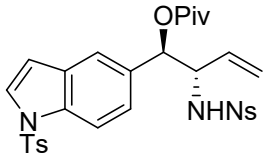

Prepared according to General Procedure C. Purified through column chromatography (silica gel, ethyl acetate/hexanes = 1:10) as a yellow solid (87.5 mg, 77% yield, single isomer).
**$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.8 Hz, 2H), 7.73 (d, *J* = 6.8 Hz, 2H), 7.67 – 7.60 (m, 4H), 7.58 – 7.51 (m, 1H), 7.51 – 7.44 (m, 3H), 7.41 (t, *J* = 7.4 Hz, 2H), 5.97 (ddd, *J* = 17.5, 10.3, 8.3 Hz, 1H), 4.98 (d, *J* = 10.4 Hz, 1H), 4.84 (d, *J* = 17.3 Hz, 1H), 4.65 (d, *J* = 9.5 Hz, 1H), 4.04 (t, *J* = 8.8 Hz, 1H), 3.58 (d, *J* = 1.3 Hz, 1H), 1.14 (s, 9H), 0.82 (s, 9H).
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 149.65, 147.29, 136.69, 136.25, 134.95, 134.00, 131.70, 130.31, 130.26, 128.20, 128.12, 127.85, 123.90, 118.82, 85.14, 59.13, 35.65, 27.55, 26.97, 20.04.
**IR** (thin film) 3319, 2957, 2859, 1531, 1474, 1427, 1349, 1311, 1166, 1107, 1032, 997, 930, 854, 822, 804, 737, 704, 685 $cm^{-1}$.
**HRMS** (ESI, positive mode) calculated for $[M+Na]^+$ 589.2163, found 589.2156

**2-(4-nitrophenylsulfonamido)-1-phenylbut-3-enyl pivalate (2q)**



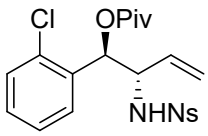

Prepared according to General Procedure C. Purified through column chromatography (silica gel, ethyl acetate/hexanes = 1:5) as a white waxy solid (78.6 mg, 86% yield, d.r. 1:11).
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.8 Hz, 2H), 7.90 (d, *J* = 8.8 Hz, 2H), 7.36 – 7.28 (m, 3H), 7.23 (dd, *J* = 6.8, 2.8 Hz, 2H), 5.71 (d, *J* = 4.5 Hz, 1H), 5.59 (ddd, *J* = 17.0, 10.4, 6.4 Hz, 1H), 5.10 (d, *J* = 10.4 Hz, 1H), 5.00 (d, *J* = 17.2 Hz, 1H), 4.94 (d, *J* = 8.7 Hz, 1H), 4.40 – 4.33 (m, 1H), 1.23 (s, 9H). Minor diastereomer: 8.20 (2H), 7.76 (2H), 7.4-7.2 (5H), 5.81 (1H), 5.65 (1H), 5.14 (2H), 4.94 (1H), 4.4 (1H), 1.23 (9H)
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 177.62, 149.91, 146.77, 135.63, 132.54, 128.70, 128.67, 128.21, 126.84, 124.23, 118.96, 76.41, 60.39, 38.99, 27.12. (major diastereomer reported)
**IR** (thin film) 3280, 2973, 1733, 1530, 1349, 1311, 1282, 1166, 1092, 1033, 991, 937, 854, 737, 684 $cm^{-1}$.
**HRMS** (ESI, positive mode) calculated for $[M+Na]^+$ 455.1247, found 455.1244

**2-(4-nitrophenylsulfonamido)-1-(1-tosyl-1*H*-indol-5-yl)but-3-enyl pivalate (2r)**




Prepared according to General Procedure C. Purified through column chromatography (silica gel, ethyl acetate/hexanes = 1:2) as a yellow oil (85.7 mg, 69% yield, d.r. 1:13).
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.8 Hz, 2H), 7.87 (d, *J* = 8.6 Hz, 1H), 7.79 (d, *J* = 8.1 Hz, 2H), 7.75 (d, *J* = 8.7 Hz, 2H), 7.56 (d, *J* = 3.7 Hz, 1H), 7.34 (s, 1H), 7.28 – 7.24 (m, 3H), 7.17 (d, *J* = 9.0 Hz, 1H), 6.54 (d, *J* = 3.6 Hz, 1H), 5.71 (d, *J* = 5.4 Hz, 1H), 5.62 (ddd, *J* = 17.0, 10.4, 6.4 Hz, 1H), 5.12 (d, *J* = 10.3 Hz, 1H), 5.06 (d, *J* = 17.1 Hz, 1H), 4.90 (d, *J* = 6.7 Hz, 1H), 4.38 – 4.30 (m, 1H), 2.36 (s, 3H), 1.21 (s, 9H). Minor diastereomer: 7.87 (2H), 7.79 (2H), 7.75 (2H), 7.56 (1H), 7.14 (1H), 6.45 (1H), 5.85 (1H), 5.71 (1H), 5.20 (2H), 4.35 (1H), 2.36 (3H), 1.21 (9H).
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 177.48, 149.75, 146.47, 145.33, 135.22, 134.51, 133.03, 130.93, 130.68, 130.07, 127.99, 127.16, 126.97, 123.93, 123.38, 119.77, 118.96, 113.49, 108.49, 76.35, 60.57, 38.92, 27.09, 21.59. (major diastereomer reported)
**IR** (thin film) 3321, 1732, 1530, 1461, 1349, 1170, 1092, 854, 737 $cm^{-1}$.
**HRMS** (ESI, positive mode) calculated for $[M+Na]^+$ 648.1445, found 648.1442

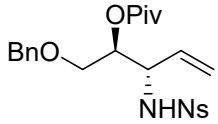
**1-(2-chlorophenyl)-2-(4-nitrophenylsulfonamido)but-3-enyl pivalate (2s)**




Prepared according to General Procedure C. Purified through column chromatography (silica gel, ethyl acetate/hexanes = 1:5) as a yellow semi solid (76.8 mg, 83% yield, d.r. 1:7.2).
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.9 Hz, 2H), 7.93 (d, *J* = 8.9 Hz, 2H), 7.29 – 7.16 (m, 4H), 6.06 (d, *J* = 5.2 Hz, 1H), 5.71 (ddd, *J* = 16.9, 10.4, 6.4 Hz, 1H), 5.33 – 5.21 (m, 1H), 5.17 (d, *J* = 10.4 Hz, 1H), 5.10 (d, *J* = 17.1 Hz, 1H), 4.35 (dt, *J* = 8.9, 6.3 Hz, 1H), 1.22 (s, 9H).

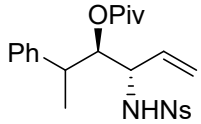
Minor diastereomer: 8.12 (2H), 7.74 (2H), 7.3-7.1 (4H), 6.2 (1H), 5.79 (1H), 5.26 (1H), 4.48 (1H), 1.23 (9H).
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 177.22, 149.94, 146.57, 134.48, 132.54, 132.13, 129.75, 129.68, 128.26, 127.71, 127.04, 124.23, 119.31, 73.11, 59.53, 38.96, 27.08. (major diastereomer reported)
**IR** (thin film) 3284, 1736, 1530, 1349, 1167, 1092, 855, 770, 738 $cm^{-1}$.
**HRMS** (ESI, positive mode) calculated for $[M+Na]^+$ 489.0858, found 489.0856

**1-(benzyloxy)-3-(4-nitrophenylsulfonamido)pent-4-en-2-yl pivalate (2t)**



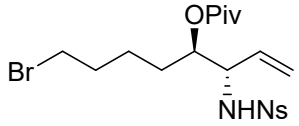

Prepared according to General Procedure C. Purified through column chromatography (silica gel, ethyl acetate/hexanes = 1:4) as a yellow oil (61 mg, 64% yield, d.r. 1:10).
**$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.9 Hz, 2H), 7.96 (d, *J* = 8.9 Hz, 2H), 7.42 – 7.27 (m, 5H), 6.10 (d, *J* = 8.4 Hz, 1H), 5.54 (ddd, *J* = 16.9, 10.3, 6.4 Hz, 1H), 5.12 (d, *J* = 17.1 Hz, 1H), 5.09 (d, *J* = 10.4 Hz, 1H), 4.76 (q, *J* = 4.1 Hz, 1H), 4.53 (d, *J* = 11.8 Hz, 1H), 4.49 (d, *J* = 11.8 Hz, 1H), 4.39 (ddd, *J* = 8.5, 6.6, 4.7 Hz, 1H), 3.67 (dd, *J* = 10.7, 3.6 Hz, 1H), 3.56 (dd, *J* = 10.7, 4.5 Hz, 1H), 1.19 (s, 9H). Minor diastereomer: 8.27 (2H), 7.98 (2H), 7.4-7.3 (5H), 5.54 (1H), 5.33 (1H), 5.10 (1H), 4.97 (1H), 4.5 (2H), 4.39 (1H), 3.56 (1H0, 3.52 (1H), 1.18 (9H).
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 178.22, 149.82, 147.39, 137.08, 132.74, 128.67, 128.22, 127.80, 124.15, 118.89, 73.80, 72.58, 68.78, 57.86, 38.92, 27.10. (major diastereomer reported)
**IR** (thin film) 3280, 2973, 1727, 1530, 1349, 1166, 854, 738 $cm^{-1}$.
**HRMS** (ESI, positive mode) calculated for $[M+Na]^+$ 499.1509, found 499.1504

**4-(4-nitrophenylsulfonamido)-2-phenylhex-5-en-3-yl pivalate (2u)**



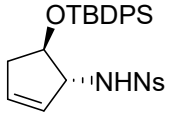

Prepared according to General Procedure C. Purified through column chromatography (silica gel, ethyl acetate/hexanes = 1:5) as a white semi solid (80.9 mg, 88% yield, d.r. 1:3). This d.r. is inherited from the d.r. of the starting material **1u**.
**$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.7 Hz, 2 * 0.27H), 8.23 (d, *J* = 8.8 Hz, 2 * 0.73H), 7.98 (d, *J* = 8.8 Hz, 2 * 0.27H), 7.75 (d, *J* = 8.9 Hz, 2 * 0.73H), 7.32 – 7.20 (m, 3H), 7.15 – 7.10 (m, 2 * 0.27H), 7.02 – 6.94 (m, 2 * 0.73H), 5.70 – 5.55 (m, 1 * 0.73H + 1 * 0.73H + 1 * 0.27H), 5.41 (ddd, *J* = 17.2, 10.2, 6.9 Hz, 1 * 0.27H), 5.25 – 5.07 (m, 2 * 0.73H + 2 * 0.27H), 4.88 (dd, *J* = 8.3, 2.3 Hz, 1 * 0.27H), 4.81 (dd, *J* = 10.2, 1.6 Hz, 1 * 0.73H), 4.29 (t, *J* = 6.9 Hz, 1 * 0.27H), 3.75 (t, *J* = 6.9 Hz, 1 * 0.73H), 3.02 – 2.88 (m, 1 * 0.27H + 1 * 0.73H), 1.25 – 1.21 (m, 9* 0.73H + 3 * 0.27H), 1.18 (d, *J* = 6.9 Hz, 3 * 0.73H), 0.93 (s, 9 * 0.27H). (both diastereomers reported)
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 179.68, 149.80, 146.39, 141.91, 131.48, 129.07, 128.27, 127.51, 127.38, 124.20, 119.74, 80.36, 57.86, 41.56, 39.27, 27.24, 18.44. (major diastereomer reported)
**IR** (thin film) 3257, 2973, 1709, 1531, 1349, 1166, 1092, 936, 854, 766, 738 $cm^{-1}$.
**HRMS** (ESI, positive mode) calculated for $[M+Na]^+$ 483.156, found 483.1554

**8-bromo-3-(4-nitrophenylsulfonamido)oct-1-en-4-yl pivalate (2v)**



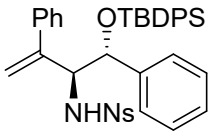

Prepared according to General Procedure C. Purified through column chromatography (silica gel, ethyl acetate/hexanes = 1:5) as a colorless oil (84.5 mg, 86% yield, d.r. 1:10).
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.5 Hz, 2H), 8.03 (d, *J* = 8.9 Hz, 2H), 5.59 – 5.42 (m, 2H), 5.07 (m, 2H), 4.74 (dt, *J* = 8.4, 4.0 Hz, 1H), 4.06 (td, *J* = 7.5, 3.5 Hz, 1H), 3.50 (t, *J* = 6.3 Hz, 2H), 1.93 – 1.32 (m, 6H), 1.19 (s, 9H). Minor diastereomer: 8.34 (2H), 8.03 (2H), 5.6-5.4 (2H), 4.95 (2H), 4.09 (1H), 3.38 (2H), 1.20 (9H)
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 178.92, 150.03, 146.89, 132.04, 128.41, 124.28, 119.35, 75.20, 59.69, 44.51, 39.02, 31.84, 30.09, 27.14, 22.56. (major diastereomer reported)
**IR** (thin film) 3274, 2959, 1726, 1531, 1349, 1280, 1166, 1092, 938, 854, 738 $cm^{-1}$.
**HRMS** (ESI, positive mode) calculated for $[M+Na]^+$ 513.0665, found 513.0660

**N-(5-(tert-butyldiphenylsilyloxy)cyclopent-2-enyl)-4-nitrobenzenesulfonamide (2w)**




Prepared according to General Procedure C. Purified through column chromatography (silica gel, ethyl acetate/hexanes = 1:10) as a yellow oil (76.4 mg, 73% yield, d.r. 1:10).
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.9 Hz, 2H), 7.92 (d, *J* = 8.9 Hz, 2H), 7.61 (dd, *J* = 8.0, 1.4 Hz, 2H), 7.56 (dd, *J* = 8.0, 1.4 Hz, 2H), 7.49 – 7.33 (m, 6H), 5.74 (ddd, *J* = 6.2, 4.1, 2.3 Hz, 1H), 5.42 (dq, *J* = 6.0, 2.0 Hz, 1H), 4.36 – 4.31 (m, 1H), 4.25 (d, *J* = 7.5 Hz, 1H), 4.14 (dt, *J* = 6.8, 4.5 Hz, 1H), 2.38 – 2.30 (m, 1H), 2.23 (dtd, *J* = 6.7, 4.1, 2.1 Hz, 1H), 0.99 (s, 9H). Minor diastereomer: 8.36 (2H), 8.01 (2H), 7.61 (2H), 7.56 (2H), 7.49-7.33 (6H), 5.79 (1H0, 5.55 (1H), 4.3-4.1 (3H), 2.3-2.2 (2H), 1.00 (9H).
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 149.89, 146.57, 135.76, 135.71, 133.40, 133.25, 133.03, 130.06, 130.00, 128.65, 128.23, 127.84, 127.76, 124.27, 79.24, 67.62, 39.85, 26.73, 19.02. (major diastereomer reported)
**IR** (thin film): 3288, 2930, 2856, 1606, 1530, 1428, 1348, 1311, 1165, 1111, 889, 854, 823, 738, 703, 686 $cm^{-1}$.
**HRMS** (ESI, positive mode) calculated for $[M+Na]^+$ 545.1537, found 545.1531

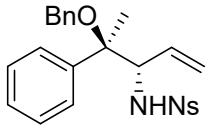
***N*-(1-(*tert*-butyldiphenylsilyloxy)-1,3-diphenylbut-3-en-2-yl)-4-nitrobenzenesulfonamide (2x)**




Prepared according to General Procedure C using I*t*BuSe catalyst. Purified through column chromatography (silica gel, ethyl acetate/hexanes = 1:10) as a pale yellow solid (82.5 mg, 64 % yield, d.r. 1:10).
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.9 Hz, 2H), 7.90 (d, *J* = 8.9 Hz, 2H), 7.70 – 7.66 (m, 2H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.41 (t, *J* = 7.4 Hz, 2H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.30 – 7.22 (m, 5H), 7.21 – 7.14 (m, 3H), 7.14 – 7.06 (m, 4H), 6.81 – 6.74 (m, 2H), 5.01 (s, 1H), 4.85 – 4.76 (m, 3H), 4.38 (d, *J* = 0.9 Hz, 1H), 0.99 (s, 9H). Minor diastereomer: 8.08 (2H), 7.69 (2H),

7.55 (2H), 7.41 (2H), 7.01 (2H), 6.87 (2H), 5.34 (1H), 5.17 (1H), 4.74 (1H), 4.53 (1H), 0.99 (9H)
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 149.70, 147.04, 144.41, 138.85, 137.51, 136.10, 135.82, 133.23, 132.50, 130.08, 129.76, 128.69, 128.16, 127.99, 127.89, 127.81, 127.56, 127.23, 126.11, 123.98, 116.34(2C overlapped), 74.52, 62.38, 26.97, 19.30. (major diastereomer reported)
**IR** (thin film) 2930, 1530, 1427, 1349, 1219, 1167, 1111, 1066, 913, 854, 772, 701 $cm^{-1}$.
**HRMS** (ESI, positive mode) calculated for $[M+Na]^+$ 685.2163, found 685.216

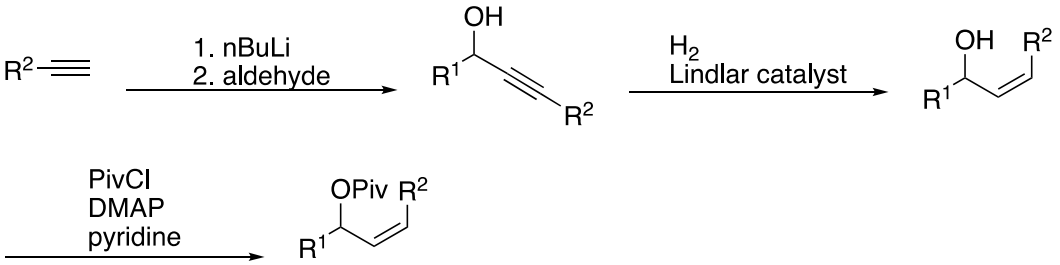
**N-(4-(benzyloxy)-4-phenylpent-1-en-3-yl)-4-nitrobenzenesulfonamide (2y)**




Prepared according to General Procedure C. Purified through column chromatography (silica gel, ethyl acetate/hexanes = 1:10) as a pale-yellow semi solid (67 mg, 74% yield, d.r. 1:2.3).
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.9 Hz, 2H), 7.87 (d, *J* = 8.9 Hz, 2H), 7.39 – 7.20 (m, 10H), 5.51 (ddd, *J* = 17.6, 10.3, 7.5 Hz, 1H), 5.16 – 5.09 (m, 1H), 4.88 (d, *J* = 10.4 Hz, 2H), 4.76 (d, *J* = 17.2 Hz, 2H), 4.41 (d, *J* = 11.3 Hz, 1H), 4.27 (d, *J* = 11.3 Hz, 1H), 3.99 (t, *J* = 8.1 Hz, 1H), 1.79 (s, 3H). (major diastereomer)
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.8 Hz, 2H), 7.72 (d, *J* = 8.9 Hz, 2H), 7.39 – 7.20 (m, 10H), 5.75 (ddd, *J* = 17.4, 10.4, 7.1 Hz, 1H), 5.20 (d, *J* = 3.8 Hz, 1H), 5.16 – 5.09 (m, 1H), 5.05 (d, *J* = 17.2 Hz, 1H), 4.32 (d, *J* = 10.9 Hz, 1H), 4.15 (d, *J* = 10.9 Hz, 1H), 3.89 (t, *J* = 7.2 Hz, 1H), 1.65 (s, 3H). (minor diastereomer)
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 149.68, 146.83, 140.30, 138.19, 133.69, 128.49, 128.38, 128.29, 127.64, 127.53, 127.16, 126.84, 123.94, 118.59, 81.36, 66.47, 64.86, 21.57. (major diastereomer reported)
**IR** (thin film) 1528, 1348, 1219, 1166, 854, 772, 737 $cm^{-1}$.
**HRMS** (ESI, positive mode) calculated for $[M+Na]^+$ 475.1298, found 475.1294

# 4 Synthesis and Characterization of cis-Allyl Pivalates

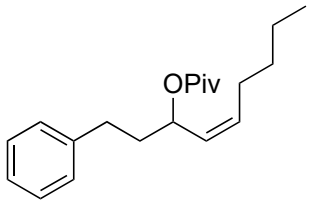
## 4.1 General Procedure E: Synthesis of cis-Allyl Pivalates




The cis allylic alcohols were prepared according to literature procedure[12]. The alcohols were subjected to General Procedure B to afford pivalates.

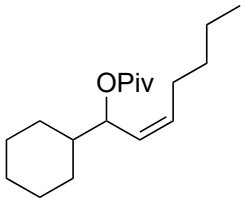
## 4.2 Characterization of cis-Allyl Pivalates

**(*Z*)-1-phenylnon-4-en-3-yl pivalate (3a)**



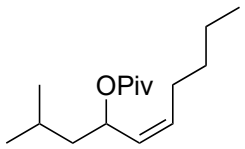

Purified through column chromatography (silica gel, ethyl acetate/hexanes = 1:25) as a colorless oil (70% yield).
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.31 – 7.24 (m, 2H), 7.22 – 7.14 (m, 3H), 5.59 – 5.49 (m, 2H), 5.33 (ddt, *J* = 10.8, 9.0, 1.6 Hz, 1H), 2.70 – 2.56 (m, 2H), 2.11 (m, 2H), 2.06 – 1.95 (m, 1H), 1.86 – 1.76 (m, 1H), 1.38 – 1.24 (m, 4H), 1.20 (s, 9H), 0.88 (t, *J* = 7.1 Hz, 3H).
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 177.71, 141.59, 134.26, 128.44, 128.34, 127.98, 125.95, 69.74, 38.78, 36.66, 31.73, 31.52, 27.66, 27.20, 22.34, 13.95.
**IR** (thin film) 3026, 2957, 2930, 2870, 1726, 1479, 1456, 1281, 1030, 748, 699 $cm^{-1}$.
**HRMS** (ESI, positive mode) calculated for $[M+Na]^+$ 325.2138, found 325.2140

**(*Z*)-1-cyclohexylhept-2-enyl pivalate (3b)**




Purified through column chromatography (silica gel, ethyl acetate/hexanes = 1:30) as a colorless oil (77% yield).
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 5.55 (dt, *J* = 10.1, 7.4 Hz, 1H), 5.32 – 5.21 (m, 2H), 2.25 – 1.98 (m, 1H), 1.81 – 1.59 (m, 5H), 1.55 – 1.47 (m, 1H), 1.39 – 1.29 (m, 4H), 1.18 (m, 12H), 1.05 – 0.93 (m, 2H), 0.90 (t, *J* = 7.1 Hz, 3H).
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 177.66, 134.57, 126.74, 73.87, 42.07, 38.84, 31.79, 28.59, 28.53, 27.77, 27.21, 26.47, 26.08, 25.96, 22.41, 13.99.
**IR** (thin film) 2927, 2854, 1726, 1479, 1451, 1395, 1365, 1281, 1161, 1030, 972, 937, 880, 769, 739 $cm^{-1}$.
**HRMS** (ESI, positive mode) calculated for $[M+Na]^+$ 303.2295, found 303.2297

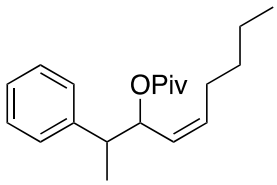
**(*Z*)-2-methyldec-5-en-4-yl pivalate (3c)**




Purified through column chromatography (silica gel, ethyl acetate/hexanes = 1:30) as a colorless oil (81% yield).
**$^1$H NMR (500 MHz, $CDCl_3$)** δ 5.57 (q, *J* = 7.5 Hz, 1H), 5.49 (dt, *J* = 11.0, 7.5 Hz, 1H), 5.26 (dd, *J* = 11.1, 9.0 Hz, 1H), 2.22 – 2.12 (m, 2H), 1.66 – 1.55 (m, 2H), 1.41 – 1.26 (m, 5H), 1.17 (s, 9H), 0.98 – 0.85 (m, 9H).

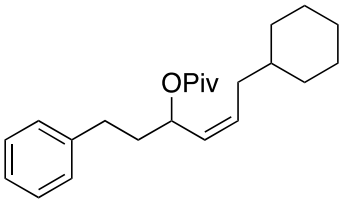
**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 177.74, 133.59, 128.66, 68.73, 43.91, 38.68, 31.76, 27.59, 27.14, 24.52, 22.95, 22.43, 22.34, 13.96.
**IR** (thin film) 2958, 2931, 2872, 1727, 1480, 1466, 1396, 1367, 1282, 1159, 1033, 963, 935, 770, 751 $cm^{-1}$.
**HRMS** (ESI, positive mode) calculated for $[M+Na]^+$ 277.2138, found 277.2138

**(*Z*)-1-phenyloct-3-en-2-yl pivalate (3d)**




Purified through column chromatography (silica gel, ethyl acetate/hexanes = 1:25) as a colorless oil (64% yield, d.r. 1:8).
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.48 – 7.23 (m, 2H), 7.22 – 7.15 (m, 3H), 5.59 (t, *J* = 8.0 Hz, H), 5.41 (dt, *J* = 10.9, 7.5 Hz, 1H), 5.15 (t, *J* = 10.2 Hz, 1H), 3.00 (quin, *J* = 6.8 Hz, 1H), 2.05 (dq, *J* = 14.5, 7.2 Hz, 1H), 1.90 (dt, *J* = 14.5, 7.4 Hz, 1H), 1.32 (d, *J* = 7.1 Hz, 3H), 1.29 – 1.11 (m, 13H), 0.83 (t, *J* = 7.1 Hz, 3H).
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 177.58, 142.74, 134.77, 128.29, 128.11, 126.55, 126.27, 73.92, 44.19, 38.86, 31.47, 27.66, 26.94, 22.37, 16.88, 13.96.
**IR** (thin film) 3028, 2960, 2930, 2871, 1727, 1479, 1454, 1280, 1156, 1031, 957, 761, 700 $cm^{-1}$.
**HRMS** (ESI, positive mode) calculated for $[M+Na]^+$ 325.2138, found 325.2140

**(*Z*)-6-cyclohexyl-1-phenylhex-4-en-3-yl pivalate (3e)**




Purified through column chromatography (silica gel, ethyl acetate/hexanes = 1:25) as a colorless oil (78% yield).
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.32 – 7.26 (m, 2H), 7.22 – 7.14 (m, 3H), 5.60 – 5.49 (m, 2H), 5.42 – 5.34 (m, 1H), 2.70 – 2.55 (m, 2H), 2.05 – 1.94 (m, 3H), 1.86 – 1.75 (m, 1H), 1.70 – 1.59 (m, 5H), 1.30 – 1.06 (m, 13H), 0.93 – 0.79 (m, 2H).
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 177.72, 141.63, 132.93, 128.58, 128.44, 128.37, 125.95, 69.69, 38.79, 38.08, 36.68, 35.60, 33.13, 33.03, 31.53, 27.21, 26.49, 26.36.
**IR** (thin film) 3025, 2923, 2851, 1726, 1496, 1479, 1450, 1395, 1365, 1281, 1157, 1030, 748, 699 $cm^{-1}$.
**HRMS** (ESI, positive mode) calculated for $[M+Na]^+$ 365.2451, found 365.2455

# 5 Synthesis and Characterization of 1,4-aminoalcohols

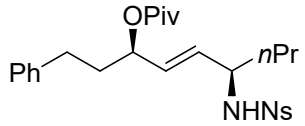
## 5.1 General Procedure F: Allylic Amination of Internal Allylic Alcohols

To an oven-dried 1-dram vial was added alkene (0.2 mmol, 1.0 equiv), phosphine selenide (15 mol%), 4-nitrobenzenesulfonamide (0.4 mmol, 2.0 equiv), DCM (1 mL) and (diacetoxyiodo)benzene (0.4 mmol, 2.0 equiv), in that order. The vial was capped with a

Teflon-lined screw cap and the reaction was stirred at room temperature for 48 hours. Upon completion, the reaction mixture was diluted with 2 ml ethyl acetate and was pushed through a silica plug. The filtrate was collected in a vial charged with known amount of 1,3-dinitrobenzene. The solvent was then removed under reduced pressure. The NMR yield was obtained by taking a $^1$H NMR spectrum of the crude mixture using 1,3-dinitrobenzene as internal standard. The crude product was then purified by column chromatography to afford the corresponding product and isolated yield was obtained.

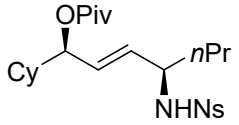
## 5.2 Characterization of 1,4-Amino Alcohol Products

**(E)-6-(4-nitrophenylsulfonamido)-1-phenylnon-4-en-3-yl pivalate (4a)**



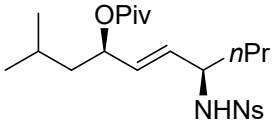

Purified through column chromatography (silica gel, ethyl acetate/hexanes = 1:8) as a yellow oil (78.4 mg, 78% yield, d.r. 1:4.9).
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.8 Hz, 2H), 8.02 (d, *J* = 8.9 Hz, 2H), 7.28 (t, *J* = 7.5 Hz, 2H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.10 (d, *J* = 7.1 Hz, 2H), 5.47 (dd, *J* = 15.7, 6.0 Hz, 1H), 5.38 (dd, *J* = 15.7, 6.9 Hz, 1H), 5.14 – 5.03 (m, 1H), 4.76 (d, *J* = 7.6 Hz, 1H), 3.89 (quin, *J* = 6.8 Hz, 1H), 2.62 – 2.44 (m, 2H), 1.88 – 1.76 (m, 1H), 1.76 – 1.66 (m, 1H), 1.51 – 1.38 (m, 2H), 1.31 – 1.20 (m, 2H), 1.18 (s, 9H), 0.85 (t, *J* = 7.2 Hz, 3H). Minor diastereomer: 8.31 (2H), 8.00 (2H), 7.28 (2H), 7.20 (1H), 7.10 (2H), 5.47 (2H), 5.38 (1H), 4.76 (1H), 2.55 (2H), 1.75 (2H), 1.16 (9H), 0.85 (3H).
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 177.50, 149.91, 147.17, 140.99, 131.34, 130.92, 128.55, 128.24, 128.22, 126.15, 124.28, 72.26, 55.62, 38.82, 37.91, 36.18, 31.40, 27.12, 18.61, 13.56. (major diastereomer reported)
**IR** (thin film) 3276, 2964, 1726, 1530, 1348, 1164 cm$^{-1}$.
**HRMS** (ESI, positive mode) calculated for $[M+Na]^+$ 525.2030, found 525.2028

**(E)-1-cyclohexyl-4-(4-nitrophenylsulfonamido)hept-2-enyl pivalate (4b)**



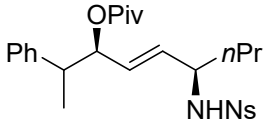

Prepared according to General Procedure C. Purified through column chromatography (silica gel, ethyl acetate/hexanes = 1:10) as a yellow oil (84.6 mg, 88% yield, d.r. 1:3).
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.35 (d, *J* = 8.8 Hz, 2H), 8.04 (d, *J* = 8.9 Hz, 2H), 5.55 – 5.29 (m, 2H), 4.94 – 4.77 (m, 2H), 4.02 – 3.80 (m, 2H), 1.79 – 0.43 (m, 27H). Minor diastereomer: 8.35 (2H), 8.03 (2H), 5.5-5.3 (2H), 4.77 (2H0, 3.9 (1H), 1.14 (9H), 0.86 (3H).
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 177.51, 149.91, 147.27, 132.06, 129.64, 128.21, 124.32, 76.90, 55.64, 41.81, 38.92, 38.23, 30.34, 28.79, 28.17, 27.17, 26.29, 25.89, 25.83, 18.61, 13.60. (major diastereomer reported)
**IR** (thin film) 2930, 1726, 1531, 1348, 1165 cm$^{-1}$.
**HRMS** (ESI, positive mode) calculated for $[M+Na]^+$ 503.2186, found 503.2179

**(E)-2-methyl-7-(4-nitrophenylsulfonamido)dec-5-en-4-yl pivalate (4c)**



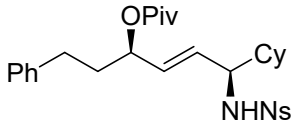

Prepared according to General Procedure C. Purified through column chromatography (silica gel, ethyl acetate/hexanes = 1:10) as a yellow semi solid (79 mg, 87% yield, d.r. 1:3.5).
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.35 (d, *J* = 8.7 Hz, 2H), 8.03 (d, *J* = 8.7 Hz, 2H), 5.50 – 5.27 (m, 2H), 5.12 (dt, *J* = 10.5, 5.4 Hz, 1H), 4.68 (s, 1H), 3.94 – 3.84 (m, 1H), 1.55 – 1.35 (m, 3H), 1.35 – 1.17 (m, 4H), 1.15 (s, 9H), 0.93 – 0.75 (m, 9H). Minor diastereomer: 8.35 (2H), 8.03 (2H), 5.5-5.25 (2H), 5.10 (1H), 4.68 (1H), 3.84 (1H), 1.13 (9H), 0.89 (9H).
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 177.57, 149.95, 147.25, 131.56, 130.81, 128.31, 124.31, 71.22, 55.66, 43.42, 38.76, 38.06, 27.10, 24.44, 22.89, 22.00, 18.60, 13.58. (major diastereomer reported)
**IR** (thin film) 3276, 2959, 1726, 1531, 1349, 1165, 856, 737 $cm^{-1}$.
**HRMS** (ESI, positive mode) calculated for $[M+Na]^+$ 477.2030, found 477.2025

**(*E*)-6-(4-nitrophenylsulfonamido)-2-phenylnon-4-en-3-yl pivalate (4d)**




Prepared according to General Procedure C. Purified through column chromatography (silica gel, ethyl acetate/hexanes = 1:10) as a yellow semi solid (78 mg, 75% yield, d.r. 1:3).
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.9 Hz, 1H), 7.94 (d, *J* = 8.8 Hz, 1H), 7.33 – 7.18 (m, 3H), 7.16 – 7.06 (m, 2H), 5.32 – 5.14 (m, 3H), 4.66 (br s, 1H), 3.72 (quin, *J* = 7.1 Hz, 1H), 2.90 (quin, *J* = 6.7 Hz, 1H), 1.40 – 1.20 (m, 6H), 1.17 (s, 9H), 1.10 – 0.98 (m, 1H), 0.75 (t, *J* = 7.3 Hz, 3H). Minor diastereomer: 8.30 (2H), 7.92 (2H), 5.25 (3H), 4.66 (1H), 3.72 (1H), 2.90 (1H), 1.15 (9H), 0.80 (3H).
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 177.44, 149.89, 147.08, 142.30, 132.32, 129.69, 128.41, 128.15, 128.09, 126.86, 124.32, 77.15, 55.57, 44.21, 38.92, 37.89, 27.16, 18.35, 17.28, 13.57. (major diastereomer reported)
**IR** (thin film) 3276, 2964, 1726, 1530, 1348, 1164, 1093, 967, 855, 737, 701 $cm^{-1}$.
**HRMS** (ESI, positive mode) calculated for $[M+Na]^+$ 525.2030, found 525.2021

**(*E*)-6-cyclohexyl-6-(4-nitrophenylsulfonamido)-1-phenylhex-4-en-3-yl pivalate (4e)**

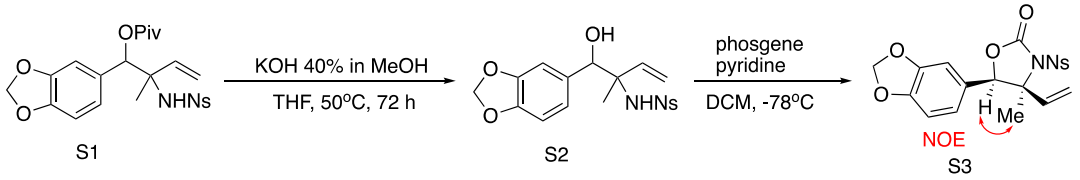



Prepared according to General Procedure C. Purified through column chromatography (silica gel, ethyl acetate/hexanes = 1:10) as a yellow semi solid (61.9 mg, 57% yield, d.r. 1:3.5).
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.6 Hz, 2H), 8.01 (d, *J* = 8.7 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.20 (t, *J* = 7.3 Hz, 1H), 7.09 (d, *J* = 7.3 Hz, 2H), 5.41 – 5.30 (m, 2H), 5.14 – 5.00 (m, 1H), 4.84 – 4.72 (m, 1H), 3.71 (dt, *J* = 8.3, 4.0 Hz, 1H), 2.60 – 2.44 (m, 2H), 1.85 – 1.74 (m, 1H), 1.75 – 1.59 (m, 5H), 1.55 (m, 1H), 1.42 – 1.33 (m, 1H), 1.16 (m, 12H), 0.96 – 0.81 (m, 2H). Minor diastereomer: 8.30 (2H), 7.99 (2H), 7.28 (2H), 7.20 (1H), 7.10 (2H), 5.45 (2H), 5.11 (2H), 4.80 (1H), 3.68 (1H), 2.5 (2H), 1.15 (9H).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 177.45, 149.90, 147.16, 140.98, 131.57, 129.99, 128.60, 128.27, 128.22, 126.20, 124.27, 72.27, 60.70, 42.76, 38.84, 36.26, 31.45, 28.95, 28.78, 27.15, 26.11, 25.89, 25.86. (major diastereomer reported)
**IR** (thin film) 3276, 2926, 1726, 1531, 1348, 1163, 1092, 855, 737 $cm^{-1}$.
**HRMS** (ESI, positive mode) calculated for $[M+Na]^+$ 565.2343, found 565.2337

# 6 Stereochemistry Determination

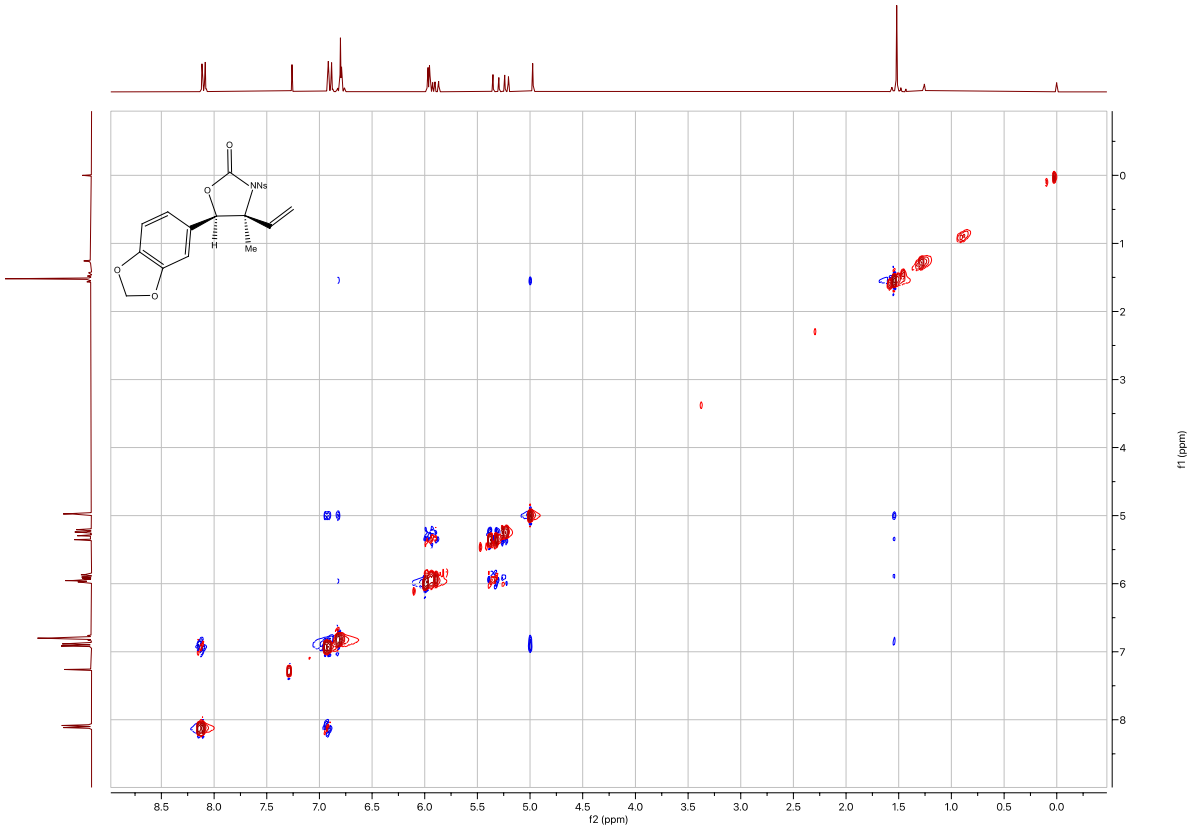
## 6.1 Procedures for Probing Stereochemistry for Anti-1,2-Amino Alcohols with Allylic Substitution



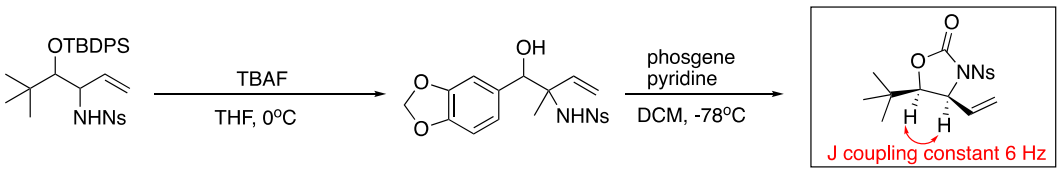

**Deprotections of S1:** In a round-bottom flask charged with S1 (1 equiv) was added THF. A solution of KOH (40% in MeOH, excess) was added. The reaction was heated at 50 °C for 72 hours. The reaction mixture was diluted with water and extracted with ethyl acetate three times. The organic layer was then washed with water and brine, dried over sodium sulphate, and removed under reduced pressure. The crude product was then purified on column to afford S2 as a colorless oil which was used in next step.

**Cyclisation of S2:** In a flame dried round bottom flask was added S2 (1 equiv), pyridine (20 equiv) and DCM at -78°C. A solution of phosgene (15 wt% in toluene, 1.5 equiv) was added dropwise. The reaction was allowed to stir at the same temperature for 2 hours. The reaction was quenched with water and diluted with ether. The reaction was extracted with ether, washed with 1 M HCl and brine. The solvent was dried over sodium sulphate and removed under reduced pressure. The crude product was purified on column to afford S3 as a colorless oil.

The pure product of S3 was subject to NOESY experiment to confirm the stereochemistry. An NOE was observed between the benzylic proton and allylic methyl group.




## 6.2 Procedures for Probing Stereochemistry for Anti-1,2-Amino Alcohols without Allylic Substitution



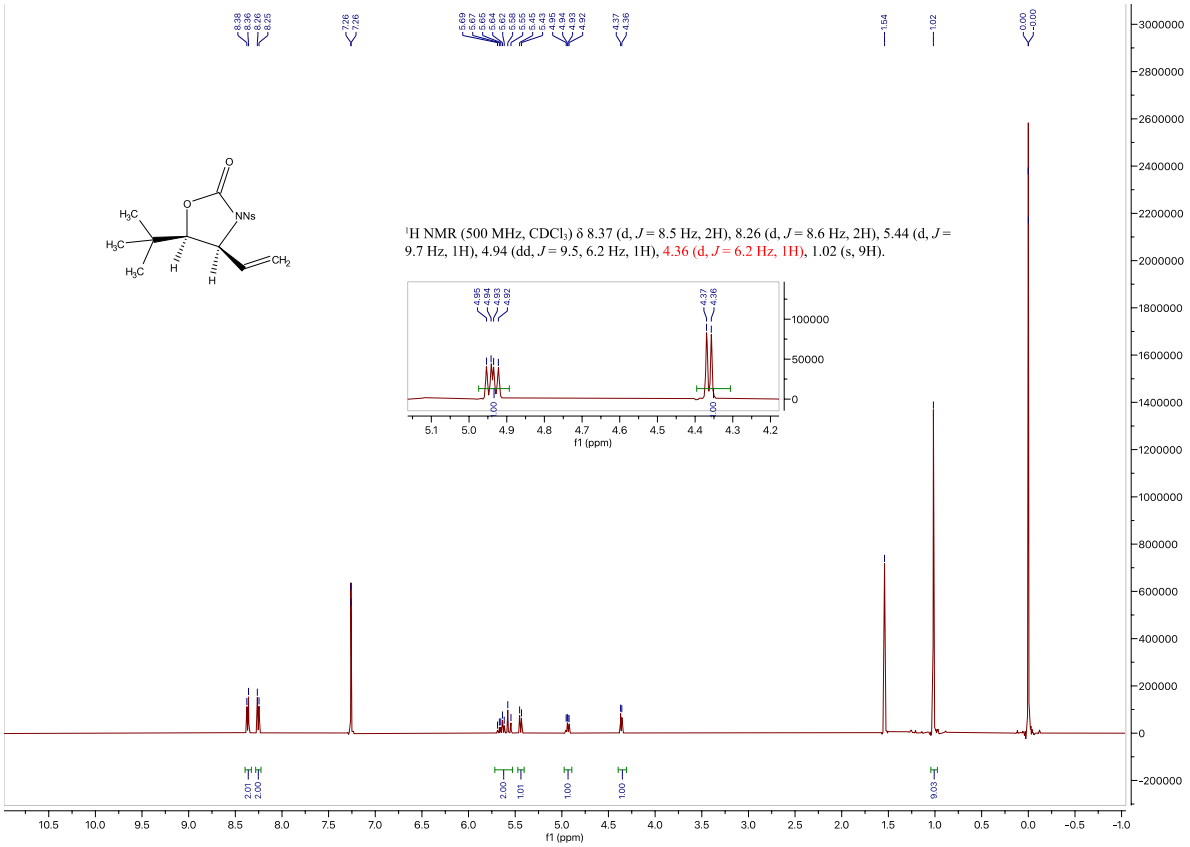

S4 S5 S6

**Deprotections of S4:** S4 (1 equiv) was dissolved in 10 mL of dry tetrahydrofuran. To the solution was added TBAF (3 equiv). The resulting solution was stirred at room temperature for 4 h and then quenched by addition of a saturated aqueous solution of $NH_4Cl$ (10 mL). The reaction mixture was was extracted with EtOAc three times. The organic layers were combined, washed with brine (20 mL), dried with $Na_2SO_4$, and concentrated in vacuo. The crude product was purified on column to afford S5.

**Cyclisation of S5:** S5 was subjected to the same cyclization procedure for S2 to give S6.

An NMR was taken for S6 to confirm the stereochemistry. A *J*-coupling constant of 6 Hz is typical for cis protons in oxazolidines like S6 according to literature precedent[13].

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.37 (d, $J$ = 8.5 Hz, 2H), 8.26 (d, $J$ = 8.6 Hz, 2H), 5.44 (d, $J$ = 9.7 Hz, 1H), 4.94 (dd, $J$ = 9.5, 6.2 Hz, 1H), 4.36 (d, $J$ = 6.2 Hz, 1H), 1.02 (s, 9H).

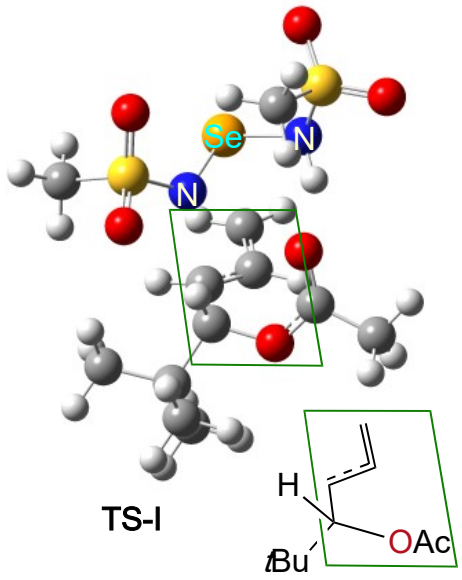



# 7 Computational Study

DFT calculations were performed using the Gaussian-16 software package. Structures were optimized at the ωB97-XD/6-311++G(d,p) level of theory, using the PCM model with $CH_2Cl_2$ as solvent. Frequency calculations were performed on all structures and enthalpies and free energies were calculated using the harmonic approximation at standard state (1 M concentration). Free energies have also been adjusted and recorded for 0.04 M concentration to better reflect the experimental conditions. All structures had zero negative frequencies, and the transition state had one negative frequency whose motions corresponded to the expected reaction coordinate.

## 7.1 Computational Study for Anti-1,2-Amino Alcohols

### *7.1.1 Anti-conformation for [2,3]-sigmatropic rearrangement transition state*



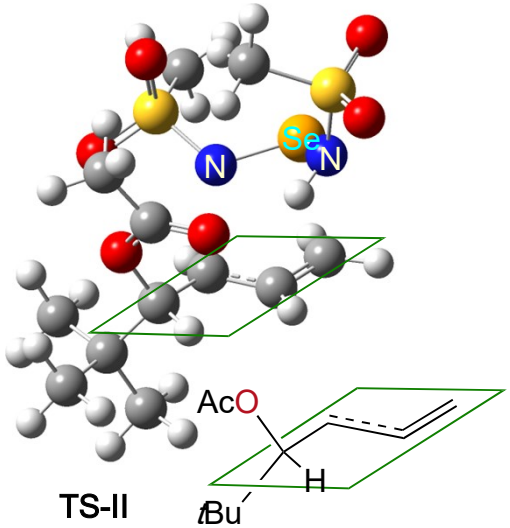

TS-I

C -0.13250400 -0.03918600 2.94582000
C -0.93916600 0.59820300 2.03008700
C -1.57681000 -0.15821200 1.05419300
H -0.84556000 1.67049500 1.90816900
C -2.32943200 0.44620800 -0.09911600
H -1.84336600 -1.17658100 1.29998400
C -3.82894500 0.05187700 -0.13663100
C -3.95020800 -1.47484600 -0.25816700
H -3.32155100 -1.85987700 -1.06521000
H -4.98871700 -1.73697100 -0.47585700
H -3.68144500 -1.98904200 0.66885600
C -4.45598100 0.69120300 -1.38304000
H -3.95260200 0.34738700 -2.29193200
H -4.39706600 1.78059600 -1.34646100
H -5.51014100 0.40979800 -1.45309700
C -4.55341600 0.53655400 1.12430800
H -4.12531700 0.09220500 2.02824500
H -5.60796400 0.25079700 1.07918000
H -4.49908300 1.62337900 1.21954600
O -2.28345600 1.88658000 -0.05477100
H -1.85738800 0.10909000 -1.02377800
C -1.21053500 2.53122000 -0.51721500
C -1.42220000 4.01452100 -0.50745600
H -1.72203500 4.33987300 0.49035100
H -2.23135100 4.26787200 -1.19575900
H -0.50746200 4.51929700 -0.80886700
O -0.20112800 1.97147900 -0.88126300
Se 1.61597300 -0.83950900 1.24624800
H -0.29477000 -1.08432800 3.18710900
H 0.47567100 0.52284500 3.64500200

N 0.22270100 -1.02740700 0.17819600
N 2.15225600 0.88136900 0.75790200
S 0.13644200 -2.18530900 -0.96562700
S 3.32437900 1.10445700 -0.41902200
H 1.33491200 1.45779700 0.54841800
O -0.92190100 -1.77132200 -1.88520200
O 1.44542600 -2.48658800 -1.54516400
O 3.54442100 2.54121000 -0.46434100
O 4.42555900 0.22102000 -0.07346200
C 2.62352900 0.59228800 -1.96936500
H 2.44200900 -0.48195800 -1.93288600
H 3.35677900 0.84035200 -2.73655800
H 1.69673000 1.14677000 -2.11139400
C -0.43831700 -3.66396400 -0.14626500
H -0.55434100 -4.43356400 -0.90864400
H 0.30244700 -3.96610300 0.59296000
H -1.39678300 -3.44514100 0.32259800

Imaginary frequencies = 1 at -288 $cm^{-1}$
Energy = -4230.3534
Enthalpy = -4229.9513
Free Energy (1 M) = -4230.0383
Free Energy (0.04 M) = -4230.0353

### *7.1.2 Syn-conformation for [2,3]-sigmatropic rearrangement transition state*



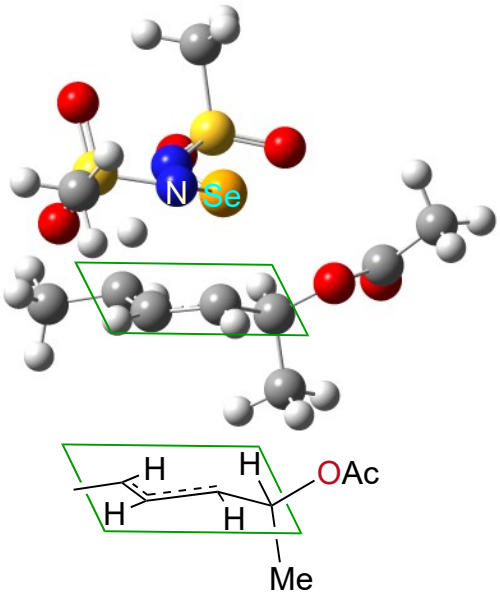

C 0.15417200 0.66752000 2.99261800
C 0.96239500 -0.20861800 2.30438600
C 1.65256500 0.21359700 1.17181800
H 0.81648100 -1.27469600 2.44971300
C 2.40409700 -0.85096200 0.38852700
H 2.01009800 1.23288800 1.10516500
C 3.93226800 -0.63171200 0.34341600
C 4.44852500 -0.52666400 1.78527000
H 4.06658700 0.36277200 2.29364800
H 5.53989200 -0.46396600 1.78002600

H 4.16314700 -1.40340800 2.37534900
C 4.30527700 0.62983000 -0.44200400
H 3.92082400 1.53671100 0.03046500
H 3.90988900 0.59352600 -1.45797000
H 5.39453800 0.71647400 -0.49202100
C 4.56638900 -1.85889200 -0.32634700
H 4.31096500 -2.77796700 0.21074600
H 5.65533700 -1.76041600 -0.32681400
H 4.23421100 -1.96128600 -1.36157800
O 1.94481100 -0.97702400 -0.96400700
H 2.21368900 -1.80784800 0.88138200
C 0.85344400 -1.69942700 -1.19588200
O 0.19880300 -2.23400600 -0.32385900
C 0.53937000 -1.74862600 -2.65954400
H 0.00190400 -0.83150200 -2.91930700
H 1.45406800 -1.78326500 -3.25012200
H -0.08843600 -2.61096100 -2.87684600
Se -1.48259800 0.97884800 1.09499600
H 0.34291300 1.73556600 2.95093600
H -0.48315000 0.32714600 3.80057200
N -0.04724800 0.88701700 0.06327600
N -2.06471400 -0.79015300 1.02394000
S 0.08062800 1.87594000 -1.24288100
S -3.37536400 -1.17578300 0.05793100
H -1.28053000 -1.43254800 0.87797100
O -4.34797100 -0.11521700 0.26529900
O -3.72165800 -2.54568100 0.39424500
O -0.83375600 1.44624000 -2.30394600
O 1.49847700 1.93785900 -1.57004800
C -0.42166700 3.52041900 -0.74952500
H -0.22952500 4.16890700 -1.60369900
H 0.18335200 3.82349300 0.10387500
H -1.48414900 3.52027200 -0.51020600
C -2.81492700 -1.13392600 -1.62773500
H -3.69091300 -1.30122500 -2.25396700
H -2.36107600 -0.16310300 -1.83345900
H -2.09335200 -1.93955100 -1.74648900

Imaginary frequencies = 1 at -255 $cm^{-1}$
Energy = -4230.3507
Enthalpy = -4229.9486
Free Energy (1 M) = -4230.0340
Free Energy (0.04 M) = -4230.0310

## 7.2 Computational Study for Syn-1,4-Amino Alcohols

### *7.2.1 Syn-conformation for ene transition state*



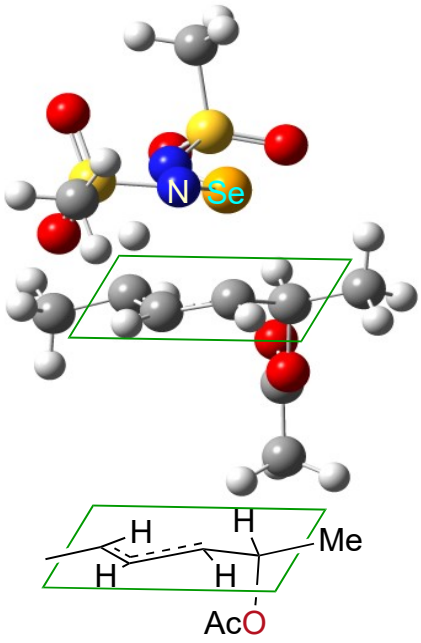

**TS-III**

C -1.98080800 -1.52682800 0.39753100
C -0.49938900 -1.79852900 0.20459800
C 0.39079100 -1.76991500 1.29563600
C 0.26916700 -0.89238300 2.39825200
C 1.25766300 -0.98220500 3.54117700
H 0.52958500 0.07506900 1.69919900
H -0.74630700 -0.62902100 2.69557200
H 2.26328800 -1.17334500 3.16483600
H 0.97558700 -1.78493700 4.22693300
H 1.26980900 -0.04819700 4.10421700
H -0.29045500 -2.55788400 -0.54721300
H 1.34309800 -2.27343200 1.16310600
Se 0.26474800 -0.01192500 -0.94953000
N 1.83169400 -0.48872200 -1.49910300
N 0.48372900 1.06240200 0.43542400
S 3.20211700 -0.25568100 -0.63736500
S -0.71401800 2.18991800 0.66573900
O 3.08976700 -0.80036600 0.72152300
O 3.68045700 1.12176700 -0.73804300
C 4.31116100 -1.29274900 -1.56498400
H 5.28835300 -1.19602900 -1.09251900
H 3.95363900 -2.31893500 -1.51384500
H 4.34298100 -0.93447600 -2.59192600
O -0.90056600 2.31506500 2.10337900
C 0.01786500 3.69108600 0.05463200
H -0.70476600 4.48775500 0.22939300
H 0.93900700 3.86867300 0.60585900
H 0.21240100 3.56863000 -1.00943900
O -1.88586400 1.87487000 -0.15364900

H -2.15362200 -0.65782300 1.03590000
O -2.49354200 -1.21612500 -0.90747400
C -3.65568200 -0.53297400 -0.97365800
C -3.94525800 -0.10955300 -2.37998300
H -3.75815300 -0.92712200 -3.07665800
H -4.97486000 0.23215200 -2.45817900
H -3.27017100 0.71236100 -2.63173000
O -4.33410800 -0.29773800 -0.00783300
C -2.66489800 -2.75491600 0.98277100
H -2.51359000 -3.61954600 0.33250500
H -2.24501300 -2.97836600 1.96586300
H -3.73263000 -2.56959000 1.09483800

Imaginary frequencies = 1 at 465 $cm^{-1}$
Energy = -4151.6949
Enthalpy = -4151.3558
Free Energy (1 M) = -4151.4385
Free Energy (0.04 M) = -4151.4355

### *7.2.2 Anti-conformation for ene transition state*



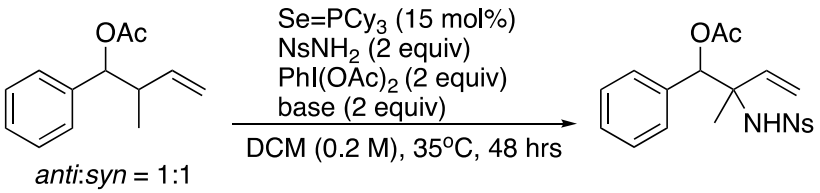

**TS-IV**

C -2.29337600 -0.11902300 -2.53800800
C -2.11514600 -0.45389100 -1.07015100
H -3.25883200 0.36686800 -2.68498800
H -1.52060900 0.57427000 -2.87537700
H -2.25357700 -1.02256900 -3.15065400
C -0.84827700 -1.24494500 -0.76607300
C -0.54282100 -1.61714600 0.55983000
C -0.85539800 -0.83380500 1.69477200
C -0.54961100 -1.36181200 3.08030400
H -0.02978100 0.00044800 1.38051900
H -1.75891600 -0.22608300 1.62489900

H 0.40204000 -1.89477000 3.08835100
H -1.33967600 -2.04020500 3.41137600
H -0.49262500 -0.53887800 3.79357100
H -0.57966700 -1.97854900 -1.52459700
H 0.16870600 -2.42624700 0.69234800
Se 0.82934500 0.22321400 -1.13904000
N 2.25566200 -0.74877700 -1.16901000
N 0.77046700 1.04463300 0.42168400
S 3.12863300 -1.09216400 0.17395900
S -0.03156200 2.50006600 0.43580600
O 2.28912800 -1.66615300 1.23273700
O 3.98420800 0.02505900 0.56700300
C 4.16762600 -2.38108300 -0.47738800
H 4.83016800 -2.67943000 0.33479100
H 3.53821500 -3.21087000 -0.79158400
H 4.73845800 -1.97764500 -1.31125000
O -0.67876900 2.60477400 1.73364400
C 1.28096400 3.69797400 0.35905100
H 0.81412400 4.68031200 0.42561500
H 1.94806500 3.52283800 1.20056100
H 1.80215400 3.57890900 -0.58918800
O -0.86301400 2.63960700 -0.76257500
H -2.16478400 0.45808400 -0.47435100
O -3.20476300 -1.31436000 -0.66797300
C -4.14686600 -0.81713300 0.15599200
C -5.21416000 -1.83535900 0.41971200
H -4.76560700 -2.73729000 0.84022600
H -5.94931000 -1.42686700 1.10902500
H -5.69651400 -2.11081800 -0.52009700
O -4.10971700 0.29846300 0.61153200

Imaginary frequencies = 1 at -379 $cm^{-1}$
Energy = -4151.6920
Enthalpy = -4151.3528
Free Energy (1 M) = -4151.4378
Free Energy (0.04 M) = -4151.4348

## 8 Reaction Optimization – Base Screen




*anti*:*syn* = 1:1

| entry | base | substrate (%)[a] | yield (%)[a] |
|---|---|---|---|
| 1 | BaO | 62 | 0 |
| 2 | $Cs_2CO_3$ | 42 | 0 |
| 3 | $Li_2CO_3$ | 0 | 70 (6:1) |
| 4 | $K_2CO_3$ | 71 | 0 |
| 5 | $Na_2CO_3$ | 75 | 0 |
| 6 | $K_3PO_4$ | 82 | 0 |
| 7 | $K_2HPO_4$ | 50 | 0 |
| 8 | $KH_2PO_4$ | 8 | 17 |

[a] Yields and d.r. determined by $^1$H NMR using 1,3-dinitrobenzene as internal standard.

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