Stereoretentive and Regioselective Selenium-catalyzed Intermolecular Propargylic C-H Amination of Alkynes

Supporting Information

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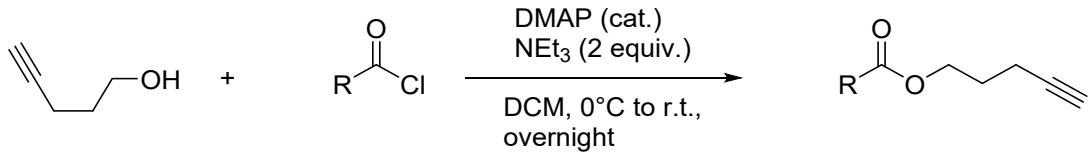
General Experimental and Materials:

All reactions were performed under a nitrogen atmosphere using oven-dried or flame-dried glassware unless otherwise indicated. Dichloromethane (CH2Cl2) and tetrahydrofuran (THF) were degassed and dried by passing through a column of activated neutral alumina. Deuterated solvents ($CDCl_3$, acetone-d_6) were obtained from Cambridge Isotope Laboratories, Inc. and stored over activated 3A molecular sieves. Ethyl acetate (EtOAc), hexanes, and diethylether (Et_2O) were obtained from Fisher Scientific or Sigma Aldrich and used without further purification. All other reagents were purchased from Sigma Aldrich, Tokyo Chemical Industry, Fisher Scientific, Alfa Aesar, and Oakwood Chemical and used without further purification unless otherwise indicated. Infrared spectra were acquired using a Perkin Elmer Spectrum RX I spectrometer. Mass spectra were acquired using a 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. 1H NMR chemical shifts (δ) are reported in parts per million (ppm) and are referenced relative to Me_4Si (0.00 ppm), $CHCl_3$ (7.26 ppm) or acetone-d_5 (2.06 ppm). ^{13}C NMR chemical shifts (δ) are reported in parts per million (ppm) relative to the carbon resonance of $CDCl_3$ (77.26 ppm) or acetone-d_6 (29.92 ppm). Melting points were taken on a MEL-TEMP melting point apparatus and are uncorrected. HPLC spectra were obtained on a Shimadzu LC-6AD with a SPD-20A UV/Vis-detector.

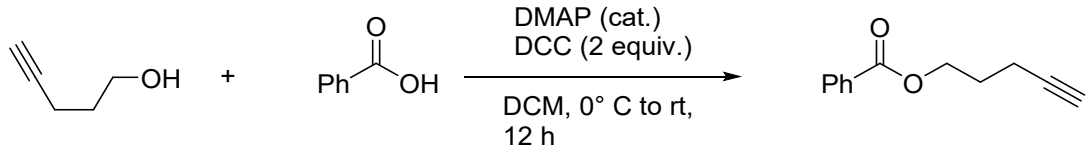
Preparation of Alkyne Substrates:

General Procedure A for alcohol protection:



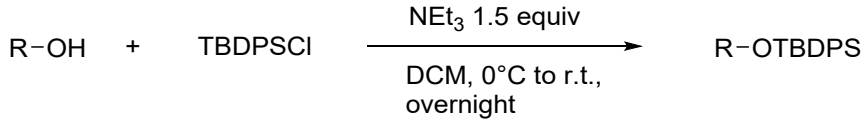
A flame-dried round-bottomed flask equipped with a magnetic stir bar was charged with 4-pentyn-1-ol (5 mmol, 1 equiv.) and 4-dimethylaminopyridine (0.1 mmol, 0.02 equiv.). Dry dichloromethane (10 mL, 0.5 M) was added and the reaction mixture was stirred and cooled to 0° C. Benzoyl chloride (5.5 mmol, 1.1 equiv.) was added to the reaction mixture followed by triethylamine (10 mmol, 2 equiv.). The mixture was then allowed to warm to room temperature and stir overnight. The reaction was quenched with water (20 mL) and diluted with ether (30 mL). The organic layer was then washed with saturated sodium bicarbonate (2 x 20 mL) and brine (1 x 20 mL) and dried over sodium sulfate. The solvent was then removed under reduced pressure and the crude products were purified by silica gel chromatography.

General Procedure B for alcohol protection:

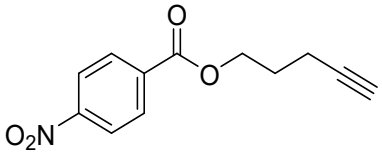


In a 200 ml round bottom flask, mixture of benzoic acid (5.5 mmol), 4-pentyn-1-ol (0.466 mL, 5.0 mmol), DCC (2.67 g, 11.00 mmol) dissolved in dry dichloromethane (50 mL), was stirred at 0 °C under an nitrogen atmosphere for 30 min. Then, a solution of 4-dimethylaminopyridine (0.49 g, 4.0 mmol) in dry dichloromethane (20 mL) was added and the mixture was stirred at 0 °C for 1 h and allowed to warm to room temperature and stirred 12 h. The mixture was filtered and the filtrate was washed with 0.5M HCl (2 x 50 mL), $NaHCO_3$ (2 x 50 mL), and brine (1 x 50 mL). The solvent was removed under reduced pressure and the crude product was purified by chromatography on a silica gel column.

General Procedure C for alcohol protection:



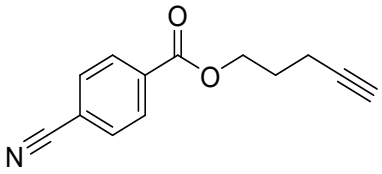
A flame-dried round-bottomed flask equipped with a magnetic stir bar was charged with a mixture of alcohol (1 equiv) and triethylamine (1.5 equiv) dissolved in dry dichloromethane (0.25 M), then was stirred at 0 °C under an nitrogen atmosphere for 10 min. TBDPSCl (1.2 equiv) was added dropwise? and the mixture was stirred at 0 °C for 1 h then allowed to warm to room temperature. The reaction was monitored by TLC until starting alcohol was consumed. After that, the mixture was washed with 0.5M HCl (2 x 25 mL), $NaHCO_3$ (2 x 25 mL), and brine (1 x 25 mL). The solvent was removed under reduced pressure and the crude product was purified by chromatography on a silica gel column.



Pent-4-ynyl 4-nitrobenzoate (**1e**): Prepared according to general procedure A using 5 mmol of 4-pentyn-1-ol. Purified by silica gel chromatography (80:20, hexanes/ethyl acetate) to afford the product as a clear liquid (1.000 g, 85%).

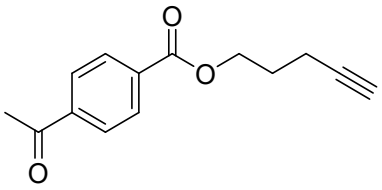
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (d, *J* = 9.0 Hz, 2H), 8.22 (d, *J* = 9.0 Hz, 2H), 4.49 (t, *J* = 6.0 Hz, 2H), 2.40 (td, *J* = 6.5, 3.0 Hz, 2H), 2.03 (quin, *J* = 6.5 Hz, 2H) 2.00 (t. *J* = 2.5 Hz, 1H)

^{13}C NMR (126 MHz, $CDCl_3$) δ 164.69, 150.65, 135.67, 130.83, 123.61, 82.81, 69.43, 64.56, 27.57, 15.44.
IR (thin film): 3263, 1719, 1598, 1517, 1344, 1274, 1121, 1022, 877, 852, 825, 784, 717 cm^{-1}
MS (ESI positive mode): m/z 256.1 $[M+Na]^+$



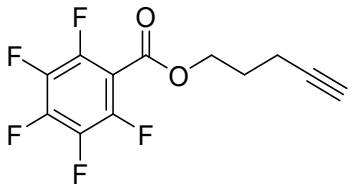
Pent-4-ynyl 4-cyanobenzoate (**1f**): Prepared according to general procedure B using 5.5 mmol of 4-pentyn-1-ol. Purified by silica gel chromatography (80:20, hexanes/ethyl acetate) to afford the product as a white solid (823 mg, 77%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.0 Hz, 2H), 7.75 (d, *J* = 8.0 Hz, 2H), 4.47 (t, 6.5 Hz, 2H), 2.38 (td, *J* = 7.0, 3.0 Hz, 2H), 2.01 (quin, *J* = 7.0 Hz, 2H), 1.99 (t, *J* = 2.0 Hz, 1H)
^{13}C NMR (126 MHz, $CDCl_3$) δ 164.84, 134.02, 132.21, 130.01, 117.97, 116.43, 82.77, 69.37, 64.33, 27.50, 15.35.
IR (thin film): 3284, 3061, 2962, 2853, 2118, 1718, 1687, 1573, 1502, 1406, 1358, 1275, 1178, 1121, 1017, 959, 860, 769, 696 cm^{-1}
MS (ESI positive mode): m/z 236.4 $[M+Na]^+$



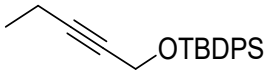
Pent-4-ynyl 4-acetylbenzoate (**1i**): Prepared according to general procedure B using 5.0 mmol of 4-pentyn-1-ol. Purified by silica gel chromatography (80:20, hexanes/ethyl acetate) to afford the product as a white solid (937 mg, 81%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 9.0 Hz, 2H), 7.89 (d, *J* = 9.0 Hz, 2H), 4.34 (t, *J* = 6.0 Hz, 2H), 2.53 (s, 3H), 2.28 (td, *J* = 7.0, 2.5 Hz, 2H), 1.94 (t, *J* = 3.0 Hz, 1H), 1.91 (quin, *J* = 7.0 Hz, 2H)
^{13}C NMR (126 MHz, $CDCl_3$) δ 197.21, 165.38, 140.10, 133.79, 129.64, 128.05, 82.80, 69.25, 63.83, 27.46, 26.68, 15.21.
IR (thin film): 3260, 2967, 1956, 1714, 1683, 1574, 1501, 1405, 1358, 1277, 1123, 1018, 958, 856, 768, 743, 694, 612 cm^{-1}.
MS (ESI positive mode): m/z 253.2 $[M+Na]^+$



Pent-4-ynyl 2,3,4,5,6-pentafluorobenzoate (**1n**): Prepared according to general procedure A using 5 mmol of the 4-pentyn-1-ol. Purified by silica gel chromatography (80:20, hexanes/ethyl acetate) to afford the product as a clear liquid (1.187 g, 85%).

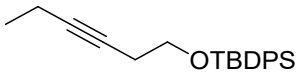
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.46 (t, *J* = 6.0 Hz, 2H), 2.33 (td, *J* = 7.0, 2.5 Hz, 2H), 1.95 (t, *J* = 3.0 Hz, 1H), 1.95 (quint, *J* = 7.0 Hz, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 158.85, 145.38 (d, *J* = 263 Hz), 143.25 (d, *J* = 272 Hz), 137.69 (d, *J* = 255 Hz)108.17, 82.34, 77.02, 69.20, 65.13, 27.24, 14.95.
IR (thin film): 3307, 2966, 2120, 1741, 1652, 1525, 1422, 1388, 1328, 1230, 1107, 1003, 953, 813, 763, 644 cm^{-1}.
MS (ESI positive mode): m/z 301.4 $[M+Na]^+$



t-Butyl(pent-2-ynyloxy)diphenylsilane (**5c**): Prepared according to general procedure C for alcohol protection using 6.5 mmol of 2-penytn-1-ol. Purified by silica gel chromatography (95:5, hexanes/ethyl acetate) to afford the product as a clear liquid (1.61 g, 76%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (m, 4H), 7.47 (m, 6H), 4.42 (m, 2H), 2.25 (q, *J* = 7.5, 2.0 Hz, 2H), 1.18 (m, 12H)

^{13}C NMR (126 MHz, $CDCl_3$) δ 135.66, 133.47, 129.68, 127.62, 87.17, 77.83, 53.04, 26.81, 19.23, 13.78, 12.52.
IR (thin film): 3070, 3048, 2958, 2931, 2857, 2234, 1589, 1461, 1373, 1318, 1261, 1188, 1110, 1075, 998, 822, 702, 611cm^{-1}.
MS (ESI positive mode): m/z 345.3 $[M+Na]^+$:



t-Butyl(hex-3-ynyloxy)diphenylsilane (**5d**): Prepared according to general procedure for alcohol protection using 6.0 mmol of 3-hexyn-1-ol. Purified by silica gel chromatography (95:5, hexanes/ethyl acetate) to afford the product as a clear liquid (1.510 g, 74%).

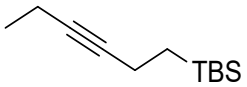
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (m, 4H), 7.41 (m, 6H), 3.78 (t, *J* = 7.0 Hz, 2H), 2.46 (tt, *J* = 7.0, 2.5 Hz, 2H), 2.17 (qt, *J* = 7.5, 2.5 Hz, 2H), 1.13 (t, 3H), 1.09 (s, 9H)

^{13}C NMR (126 MHz, $CDCl_3$) δ 135.76, 134.02, 129.79, 127.81, 83.07, 76.50, 63.18, 27.02, 23.15, 19.46, 14.41, 12.64.
IR (thin film): 3069, 2931, 2856, 1959, 1889, 1825, 1589, 1462, 1427, 1387, 1360, 1263, 1188, 1109, 998, 917, 823, 738, 702, 613, 506 cm^{-1}.
MS (ESI positive mode): m/z 359.3 $[M+Na]^+$

t-Butyl(hept-4-ynyloxy)diphenylsilane (**5e**): Silyl ether intermediate was prepared by general procedure for alcohol protection using 5.0 mmol of the 4-pentyn-1-ol. Purified by silica gel chromatography (95:5, hexanes/ethyl acetate) to afford the product as a clear liquid (1.001 g, 72%). This protected alcohol was added to a flame-dried round-bottomed flask equipped with a magnetic stir bar, which was then charged with HMPA (1 equiv) dissolved in dry THF (0.25 M) and was cooled at -78 °C under a nitrogen atmosphere. *n*-BuLi (2.1 ml, 2.5 M) was added dropwise and the reaction was allowed to warm to room temperature and then stirred for 20 minutes. The mixture was cooled to -78 °C and bromoethane was added dropwise. The reaction was allowed to warm to room temperature and stirred overnight. The reaction was quenched slowly with water and extracted with CH_2Cl_2, then washed with water (2 x 25 ml), and brine (1 x 25 ml). The solution was dried over Na_2SO_4 and the solvent removed under reduced pressure to give the crude alkyne. This was purified by silica gel chromatography (95:5, hexanes/ethyl acetate) to afford the product as a clear liquid (1.260 g, 72%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (m, 4H), 7.43 (m, 6H), 3.78 (t, *J* = 7.0 Hz, 2H), 2.46 (tt, *J* = 7.0, 2.0 Hz, 2H), 2.17 (qt, *J* = 7.5, 2.0 Hz, 2H), 1.13 (t, 3H), 1.09 (s, 9H)

^{13}C NMR (126 MHz, $CDCl_3$) δ 135.76, 134.02, 129.79, 127.81, 83.07, 76.50, 63.18, 27.02, 23.15, 19.46, 14.41, 12.64.
IR (thin film): 3071, 2932, 2858, 1969, 1889, 1823, 1678, 1589, 1472, 1428, 1389, 1361, 1322, 1189, 1109, 979, 823, 739, 702, 613 cm^{-1}.
MS (ESI positive mode): m/z 373.4 $[M+Na]^+$

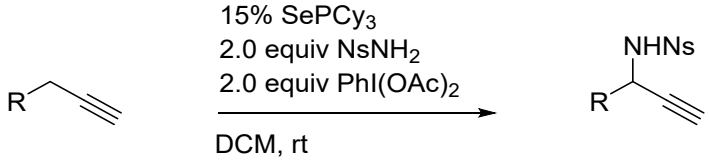


t-Butyl(4-hexyn-1-yl)dimethylsilane (**5l**): 1-Iodo-3-hexyne (832 mg, 4.0 mmol) was dissolved in dry ether (20 mL) and was cooled at -78 °C under an nitrogen atmosphere. *t*-BuLi (5.2 mL, 1.7 M, 2.2 equiv) was added dropwise and the reaction was allowed to warm to room temperature and stirred for 30 min. The mixture was cooled back down to -78 °C and TBSCl (2.4 g, 16 mmol, 4 equiv) in 10ml of ether was added dropwise. The mixture was allowed to warm to room temperature and stirred overnight. The reaction was quenched slowly with water and extracted with 2 times with ether. The organic extracts were

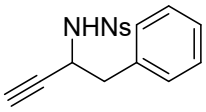
then washed with water (2x) and brine (1x), dried over Na_2SO_4 and the solvent was removed under reduced pressure to give the crude product. This was purified by silica gel chromatography (95:5, hexanes/ethyl acetate) to afford the product as a clear liquid (255 mg, 65%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 2.20 (m, 4H), 1.09 (t, *J* = 7.5 Hz, 3H), 0.85 (s, 9H), 0.78 (m, 2H), -0.05 (s, 6H)
^{13}C NMR (126 MHz, $CDCl_3$) δ 81.75, 80.91, 26.46, 16.46, 14.28, 13.59, 12.56, 12.41, -6.37.
IR (thin film): 2954, 2884, 2857, 1905, 1711, 1594, 1469, 1362, 1254, 1169, 1051, 1006, 937 834cm^{-1}.
MS (ESI positive mode): m/z 219.2 $[M+Na]^+$

<u>General Procedure for Propargyl Amination</u>:

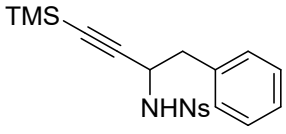


A flame-dried borosilicate glass vial equipped with a magnetic stir bar was charged with $SePCy_3$ (0.03 mmol, 0.15 equiv.), amine (0.4 mmol, 2 equiv.), and alkyne (0.2 mmol, 1.0 equiv.). The vial was thoroughly flushed with nitrogen and capped with a Teflon-lined screw cap. Dry dioxane (1 mL, 0.2 M) was added, followed by iodobenzene diacetate (0.4 mmol, 2 equiv.). The solution was stirred at the specified temperature and the reaction was monitored by TLC. Upon completion, an equal volume of ethyl acetate was added to the reaction and the mixture was flushed through a silica gel plug with ethyl acetate. The eluent was then concentrated on a rotary evaporator to afford the crude reaction product, which was then purified by column chromatography.



4a: Prepared according to standard amination conditions. Purified by silica gel chromatography (85:15 hexanes/ethyl acetate) to afford the product as a white solid (54.9 mg, 83%)

^{1}H NMR (500 MHz, DMSO-d_6) δ 8.71 (d, *J* = 8.5 Hz, 1H), 8.32 (d, *J* = 9.0 Hz, 2H), 7.94 (d, *J* = 9.0 Hz, 2H), 7.24–7.16 (m, 5H), 4.21 (dq, *J* = 2.0, 8.0 Hz, 1H), 3.06 (d, *J* = 2.5 Hz, 1H), 2.91–2.84 (m, 2H).
^{13}C NMR (126 MHz, DMSO-d_6) δ 149.4, 146.6, 136.4, 129.4, 128.2, 128.1, 126.6, 124.2, 81.8, 75.6, 46.3, 41.5.
IR (thin film) 3430, 2916, 2857, 1636, 1527, 1347, 1162, 1090, 1053, 853, 738 cm^{-1}
MS (ESI positive mode): m/z 353.5 $[M+Na]^+$
MP: 164-165 ˚C

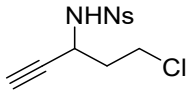


4b: Prepared according to standard amination conditions. Purified by silica gel chromatography (85:15 hexanes/ethyl acetate) to afford the product as a white solid (74.3 mg, 92%)

^{1}H NMR (300 MHz, DMSO-d_6) δ 8.65 (d, J = 9.0 Hz, 1H), 8.37 (d, J = 8.7 Hz, 2H), 7.99 (d, J = 8.7 Hz, 2H), 7.31–7.11 (m, 5H), 4.21 (q, J = 9.0 Hz, 1H), 2.98–2.72 (m, 2H), -0.13 (s, 9H).
^{13}C NMR (126 MHz, DMSO-d_6) δ 149.4, 146.7, 136.3, 129.5, 128.4, 127.9, 126.6, 124.2, 103.7, 88.8, 47.0, 41.5, -0.7.
IR (thin film): 3434, 3103, 2960, 2172, 1607, 1531, 1349, 1312, 1250, 1167, 1092, 844, 738 cm^{-1}

MS (ESI positive mode): m/z 425.5 $[M+Na]^+$

MP: 117-118 ˚C

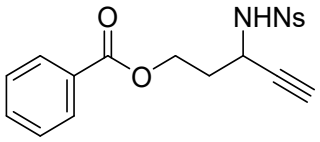


4c: Prepared according to standard amination conditions. Purified by silica gel chromatography (85:15 hexanes/ethyl acetate) to afford the product as a white solid (52.2 mg, 86%)

^{1}H NMR (500 MHz, DMSO-d_6) δ 8.72 (d, J = 9.0 Hz, 1H), 8.42 (d, J = 9.0 Hz, 2H), 8.07 (d, J = 8.5 Hz, 2H), 4.21 (qd, J = 7.0, 2.0 Hz, 1H), 3.69 – 3.61 (m, 2H), 3.13 (d, J = 2.0 Hz, 1H) 2.05 – 1.97 (m, 2H).
^{13}C NMR (126 MHz, DMSO-d_6) δ 149.6, 146.4, 128.4, 124.3, 80.5, 76.0, 42.4, 41.0, 38.1.
IR (Thin film) 3433, 2916, 2853, 1634, 1528, 1441, 1420, 1349, 1311, 1164, 1093, 1067, 968, 855, 739, 621, 553 cm^{-1}

MS (ESI positive mode): $[M+Na]^+$ 325.6

MP: 155-156 ˚C

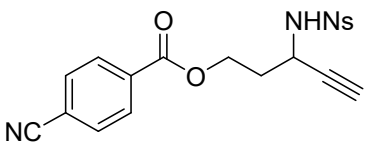


4d: Prepared according to standard amination conditions. Purified by silica gel chromatography (80:20 hexanes/ethyl acetate) to afford the product as a white solid (58.1 mg, 74%)

^{1}H NMR (500 MHz, DMSO-d_6) δ 8.76 (d, J = 8.5 Hz, 1H), 8.35 (d, J = 8.5 Hz, 2H), 8.05 (d, J = 8.5 Hz, 2H), 7.93 (d, J = 7.0 Hz, 2H), 7.66 (t, J = 7.5 Hz, 1H), 7.52 (t, J = 8.0 Hz, 2H), 4.29 – 4.21 (m, 3H), 3.14 (d, J = 2.0 Hz, 1H), 2.06 – 2.02 (m, 2H).
^{13}C NMR (126 MHz, DMSO-d_6) δ 165.5, 149.5, 146.4, 133.4, 129.4, 129.1, 128.7, 128.4, 124.3, 81.4, 75.5, 60.8, 42.0, 34.5.
IR (thin film) 3422, 3279, 2926, 2853, 1705, 1633, 1607, 1530, 1451, 1349, 1313, 1278, 1166, 1119, 1092, 855, 739, 714, 683, 619, 559 cm^{-1}

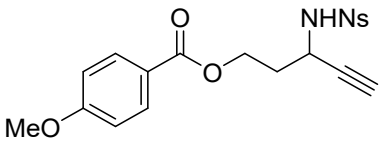
MS (ESI positive mode): 411.5 $[M+Na]^+$

mp: 183-185 ˚C



4e: Prepared according to standard amination conditions with CH_2Cl_2 as solvent. Purified by silica gel chromatography (85:15, hexanes/ethyl acetate) to afford the product as a clear liquid (46 mg, 68%).

^{1}H NMR (500 MHz, DMSO-d_6) δ 8.76 (d, J = 8.5 Hz, 1H), 8.34 (d, J = 9.0 Hz, 2H), 8.06 (m, 4H), 8.05 (d, J = 9.0 Hz, 2H), 4.32 (m, 2H), 4.25 (m, 1H), 3.14 (d, J = 2.5 Hz, 1H), 2.06 (m, 2H)
^{13}C NMR (126 MHz, DMSO-d_6) δ 164.26, 149.46, 146.40, 133.34, 132.75, 129.83, 128.36, 124.30, 118.03, 115.51, 81.48, 75.41, 61.45, 41.96, 34.29.
IR (thin film): 3273, 3103, 2859, 1724, 1608, 1530, 1404, 1350, 1312, 1277, 1167, 1120, 1092, 1019, 856, 768, 738, 685, 663, 617 cm^{-1}.
MS (ESI positive mode): m/z 436.0 $[M+Na]^+$
mp: 137-140 °C

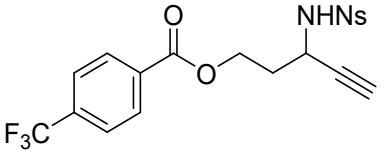


4f: Prepared according to standard amination conditions. Purified by silica gel chromatography (85:15 hexanes/ethyl acetate) to afford the product as a white solid (60.8 mg, 73%)

^{1}H NMR (500 MHz, DMSO-d_6) δ 8.75 (d, J = 8.5 Hz, 1H), 8.35 (d, J = 9.0 Hz, 2H), 8.05 (d, J = 9.0 Hz, 2H), 7.86 (d, J = 9.0 Hz, 2H), 7.04 (d, J = 9.0 Hz, 2H), 4.25 – 4.20 (m, 3H), 3.84 (s, 3H), 3.14 (d, J = 2.0 Hz, 1H), 2.04 – 1.98 (m, 2H).
^{13}C NMR (126 MHz, DMSO-d_6) δ 165.1, 163.2, 149.5, 146.4, 131.2, 128.3, 124.3, 121.6, 114.0, 81.4, 75.4, 60.4, 55.5, 42.0, 34.5.
IR (thin film) 3434. 2947, 2916, 2843, 1705, 1638, 1606, 1528, 1461, 1347, 1316, 1254, 1166, 1109, 1025, 849, 761, 735, 678, 610, 553 cm^{-1}

MS (ESI positive mode): 441.0 $[M+Na]^+$

mp: 168-169 ˚C

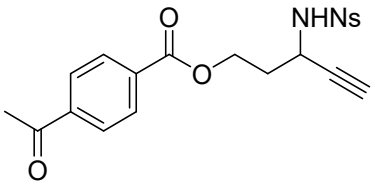


4g: Prepared according to standard amination conditions. Purified by silica gel chromatography (85:15 hexanes/ethyl acetate) to afford the product as a white solid (64.7 mg, 71%)

^{1}H NMR (500 MHz, DMSO-d_6) δ 8.78 (d, J = 8.8 Hz, 1H),8.36 (d, J = 8.9 Hz, 2H), 8.13 (d, J = 8.1 Hz, 2H), 8.07 (d, J = 8.9 Hz, 2H), 7.92 (d, J = 8.3 Hz, 2H), 4.35 (t, J = 6.0 Hz, 2H), 4.27 (td, J = 8.7, 2.2 Hz, 1H), 3.17 (d, J = 2.3 Hz, 1H), 2.15 – 2.02 (m, 2H).
^{13}C NMR (126 MHz, DMSO-d_6) δ 165.1, 150.2, 147.1, 133.9, 133.6 (q, $^2J_{CF}$ = 31.9 Hz), 130.7, 129.1, 126.4, 125.0, 124.4 (q, $^1J_{CF}$ = 272.9 Hz), 82.2, 76.2, 62.1, 42.7, 35.0.
IR (thin film) 3434 2957, 2916, 1721, 1635, 1531, 1347, 1326, 1277, 1165, 1128, 854, 771, 739, 683, 621, 564 cm^{-1}

MS (ESI positive mode): 479.4 $[M+Na]^+$

mp: 153-154 ˚C

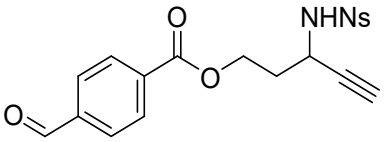


4h: Prepared according to standard amination conditions. Purified by silica gel chromatography (98:2 CH_2Cl_2/MeOH) to afford the product as a white solid (56 mg, 65%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (d, *J* = 9.0 Hz, 2H), 8.10 (d, *J* = 8.5 Hz, 2H), 8.07 (d, *J* = 8.5 Hz, 2H), 8.02 (d, *J* = 8.5 Hz, 2H), 5.25 (d, *J* = 9.0 Hz, 1H), 4.56 (dt, *J* = 11.5, 6.0 Hz, 1H), 4.49 (dt, *J* = 11.5, 6.0 Hz, 1H), 4.42 (m, 1H), 2.65 (s, 3H), 2.24 (q, *J* = 6.1 Hz, 2H), 2.11 (d, *J* = 2.5 Hz, 1H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 197.63, 165.76, 150.36, 146.01, 140.69, 133.57, 130.03, 128.81, 128.48, 124.40, 80.33, 74.18, 61.15, 43.37, 35.62, 27.04.
IR (thin film) 3261, 1718, 1686, 1530, 1349, 1268, 1166, 1091, 1015, 912, 855, 737, 615 cm^{-1}

MS (ESI positive mode): m/z 453.2 $[M+Na]^+$

mp: 155-157 °C

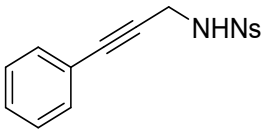


4i: Prepared according to standard amination conditions in DCM . Purified by alumina chromatography (80:20 DCM/Hexanes to 1:99 MeOH/DCM) to afford the product as a white solid (117 mg, 70%)

^{1}H NMR (500 MHz, DMSO-d_6) δ 10.12 (s, 1H), 8.76 (d, *J* = 9.0 Hz, 1H), 8.34 (d, *J* = 9.0 Hz, 2H), 8.12 (d, *J* = 8.0 Hz, 2H), 8.06-8.03 (m, 4H), 4.32 (t, *J* = 6.0 Hz, 2H), 4.32 (q, *J* = 8.0 Hz, 1H), 3.15 (d, *J* = 2.0 Hz, 1H), 2.10 – 2.04 (m, 2H).
^{13}C NMR (126 MHz, DMSO-d_6) δ 193.0, 164.8, 149.5, 146.4, 139.2, 134.1, 129.9, 129.6, 128.4, 124.3, 81.5, 75.5, 61.3, 42.0, 34.4.
IR (Thin film) 3431, 2917, 2850, 1702, 1635, 1529, 1456, 1348, 1165, 1091 cm^{-1}

MS (ESI positive mode): m/z 439.6 $[M+Na]^+$

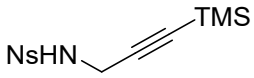
mp: 147-148 ˚C



4j: Prepared according to amination conditions with 2.0 equiv. of benzoic acid, in toluene at 35 °C. Purified by silica gel chromatography (90:10 hexanes/ethyl acetate) to afford the product as a solid (84 mg, 79%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (d, *J* = 9 Hz, 2H), 8.12 (d, *J* = 9 Hz, 2H), 7.29 (t, *J* = 7 Hz, 1H), 7.22 (t, *J* = 7 Hz, 2H), 7.05 (d, *J* = 7 Hz, 2H), 4.97 (t, *J* = 6.5 Hz, 1H), 4.18 (d, *J* = 6.0 Hz, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 146.16, 131.46, 129.18, 128.93, 128.52, 124.58, 124.37, 121.52, 85.70, 82.64, 34.05.
IR (thin film): 3290, 3105, 1711, 1607, 1530, 1349, 1165, 1091, 855, 737, 684, 616 cm^{-1}.
MS (ESI positive mode): m/z 317.1 $[M+H]^+$

mp: 125-127 °C

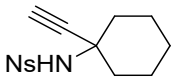


4k: Prepared according to standard amination conditions. Purified by silica gel chromatography (85:15 hexanes/ethyl acetate) to afford the product as a white solid (47.6 mg, 73%)

^{1}H NMR (500 MHz, DMSO-d_6) δ 8.56 (s, 1H), 8.45 (d, J = 8.3 Hz, 2H), 8.09 (d, J = 8.4 Hz, 2H), 3.89 (s, 2H), -0.07 (s, 9H).
^{13}C NMR (126 MHz, DMSO-d_6) δ 149.6, 146.6, 128.5, 124.4, 101.0, 88.3, 32.7, -0.6.
IR (thin film**)** 3450.0, 2957.5, 2905.7, 1636.5, 1531.3, 1345.8, 1306.1, 1249.1, 1162.1, 1077.8 cm^{-1}

MS (ESI positive mode): 335.3 $[M+Na]^+$

mp: 141-143 ˚C



4l: Prepared according to standard amination conditions. Purified by silica gel chromatography (85:15 hexanes/ethyl acetate) to afford the product as a white solid (51.9 mg, 84%)

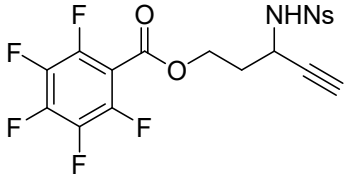
^{1}H NMR (500 MHz, DMSO-d_6) δ 8.38 (d, J = 9.0 Hz, 2H), 8.27 (s, 1H), 8.07 (d, J = 9.0 Hz, 2H), 2.97 (s, 1H), 1.76 (m, 2H), 1.64 – 1.54 (m, 4H), 1.45 – 1.36 (m, 3H), 1.23 – 1.17 (m, 1H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 149.2, 148.2, 128.5, 124.0, 83.4, 76.5, 53.3, 38.0, 24.3, 21.7.

IR (thin film): 3256, 2944, 2857, 1531, 1421, 1351, 1335, 1306, 1167, 1094, 1002, 855, 740 cm^{-1}

MS (ESI positive mode): m/z 331.5 $[M+Na]^+$

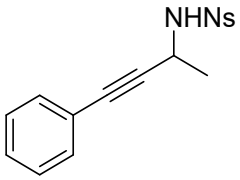
mp: 155-156 ˚C



4m: Prepared according to standard amination conditions. Purified by silica gel chromatography (85:15 hexanes/ethyl acetate) to afford the product as a clear liquid (67 mg, 70%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37 (d, J = 8.5 Hz, 2H), 8.10 (d, J = 9.0 Hz, 2H), 5.24 (d, J = 9.5 Hz, 1H), 4.55 (m, 2H), 4.38 (m, 1H), 2.19 (m, 2H), 2.15 (d, J = 2.5 Hz, 1H)

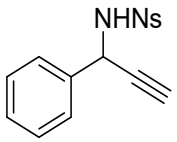
^{13}C NMR (126 MHz, $CDCl_3$) δ 158.89, 150.42, 145.86, 128.86, 124.42, 79.76, 74.49, 62.54, 43.20, 35.21.
IR (thin film): 3291, 3106, 1750, 1530, 1350, 1194, 1165, 1093, 934, 854, 738 cm^{-1}.
MS (ESI positive mode): m/z 501.1 $[M+Na]^+$



4n: Prepared according to standard amination conditions in toluene. Purified by silica gel chromatography (85:15 hexanes/ethyl acetate) to afford the product as a white solid (54.6 mg, 83%).
^{1}H NMR (500 MHz, DMSO-d_6) δ 8.66 (d, J = 9.0 Hz, 1H), 8.32 (d, J = 8.5 Hz, 2H), 8.10 (d, J = 8.5 Hz, 2H), 7.29 (t, J = 7.5 Hz, 1H), 7.22 (t, J = 7.5 Hz, 2H), 6.98 (d, J = 7 Hz, 2H), 4.39 (dq, J = 4.0, 7.0 Hz, 1H), 1.41 (d, J = 7.5 Hz, 3H).
^{13}C NMR (126 MHz, DMSO-d_6) δ 149.3, 146.7, 130.9, 128.6, 128.5, 128.3, 124.3, 121.3, 88.8, 83.0, 41.1, 22.4.
IR (thin film): 3270, 2991, 2939, 2865, 1605, 1529, 1490, 1424, 1348, 1311, 1167, 1123, 1090, 974, 853 cm^{-1}

MS (ESI positive mode): m/z 353.5 $[M+Na]^+$

mp: 132-133 ˚C

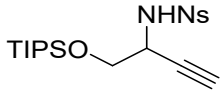


4o: Prepared according to standard amination conditions in toluene at 35˚C with the addition of CaO (0.4 mmol). Purified by silica gel chromatography (85:15 hexanes/ethyl acetate) to afford the product as a pale yellow solid (46.8 mg, 74%)

^{1}H NMR (300 MHz, DMSO-d_6) δ 9.11 (d, J = 9.2 Hz, 1H), 8.36 (d, J = 8.8 Hz, 2H), 8.03 (d, J = 8.8 Hz, 2H), 7.31 (m, 5H), 5.32 (dd, J = 9.1, 2.2 Hz, 1H), 3.34 (d, J = 2.4 Hz, 1H).
^{13}C NMR (126 MHz, DMSO-d_6) δ 149.4, 146.6, 137.6, 128.4, 128.3, 128.0, 127.0, 124.1, 80.7, 77.0, 48.2.
IR (Thin film**)** 3273 2916, 2849, 1524, 1427, 1338, 1311, 1089, 1048, 964, 858 cm^{-1}

MS (ESI positive mode): m/z 339.2 $[M+Na]^+$

mp: 172-173 ˚C

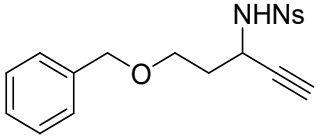


4p: Prepared according to standard amination conditions at 35˚C. Purified by silica gel chromatography (85:15 hexanes/ethyl acetate) to afford the product as a pale yellow solid (54.8 mg, 64%)

^{1}H NMR (300 MHz, DMSO-d_6) δ 8.64 (d, J = 8.9 Hz, 1H), 8.40 (d, J = 8.8 Hz, 2H), 8.07 (d, J = 8.9 Hz, 2H), 4.04 (qd, J = 6.3, 2.1 Hz, 1H), 3.65 (d, J = 6.4 Hz, 2H), 3.08 (d, J = 2.2 Hz, 1H), 1.08–0.90 (m, 21H).
^{13}C NMR (126 MHz, DMSO-d_6) δ 149.5, 146.8, 128.3, 124.2, 80.0, 75.6, 65.5, 47.3, 17.6, 11.3.
IR (Thin film) 3426, 2946, 2849, 1643, 1530, 1344, 1165, 1053cm^{-1}

MS (ESI positive mode): $[M+Na]^+$ 449.3

mp: 67-68 ˚C

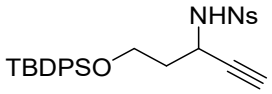


4q: Prepared according to standard amination conditions with the addition of 4-nitrobenzoic acid (0.4 mmol). Purified by silica gel chromatography (85:15 hexanes/ethyl acetate) to afford the product as a pale yellow solid (43.9 mg, 59%)

^{1}H NMR (500 MHz, DMSO-d_6) δ 8.65 (d, J = 8.9 Hz, 1H), 8.42 (d, J = 9.0 Hz, 2H), 8.08 (d, J = 9.0 Hz, 2H), 7.38 – 7.27 (m, 5H), 4.42 (s, 2H), 4.18 (qd, J = 7.5, 2.1 Hz, 1H), 3.49 (t, J = 6.0 Hz, 2H), 3.06 (d, J = 2.3 Hz, 1H), 1.94 – 1.78 (m, 2H).
^{13}C NMR (126 MHz, DMSO-d_6) δ 150.2, 147.4, 139.0, 129.1, 128.9, 128.0, 125.0, 82.2, 76.0, 72.7, 66.1, 42.8, 36.5.
IR (thin film**)** 3439, 2954, 2916, 2857, 1644, 1529, 1348, 1311, 1164, 1090, 852 cm^{-1}

MS (ESI positive mode): 397.4 $[M+Na]^+$

mp: 99-101 ˚C

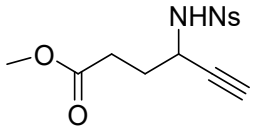


4r: Prepared according to standard amination conditions. Purified by silica gel chromatography (85:15 hexanes/ethyl acetate) to afford the product as a white solid (90.1 mg, 86%)

^{1}H NMR (500 MHz, DMSO-d_6) δ 8.66 (d, J = 8.8 Hz, 1H), 8.42 (d, J = 8.9 Hz, 2H), 8.08 (d, J = 8.9 Hz, 2H), 7.63 – 7.55 (m, 4H), 7.51 – 7.40 (m, 6H), 4.33 (td, J = 9.2, 2.0 Hz, 1H), 3.76 – 3.65 (m, 2H), 3.08 (d, J = 2.2 Hz, 1H), 1.91 – 1.77 (m, 2H), 0.97 (s, 9H).
^{13}C NMR (126 MHz, DMSO-d_6) δ 149.5, 146.7, 134.9, 132.8, 129.8, 129.0, 128.4, 127.8, 124.3, 81.5, 75.3, 59.3, 41.7, 38.3, 26.5, 18.7.
IR (thin film) 3280. 2929, 2855, 1530, 1427, 1348, 1311, 1167, 1110, 1090, 999 cm^{-1}

MS (ESI positive mode): 545.3 $[M+Na]^+$

mp: 107-108 ˚C

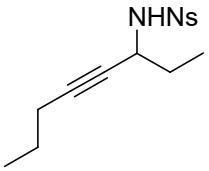


4s: Prepared according to standard amination conditions with the addition of 4-nitrobenzoic acid (0.4 mmol). For purification and analysis, the free carboxylic acid was methylated using the following procedure: methylnitronitrosoguanidine (2.0 mmol) was added to a mixture of aqueous KOH (1 M, 8 mL) and 8 mL of diethyl ether at 0 ˚C. After stirring for 10 minutes, the ether layer was slowly added to the crude amination reaction mixture and stirred for 30 minutes at 0 ˚C. Excess glacial acetic acid was added dropwise until gas evolution ceased. Purified by silica gel chromatography (85:15 hexanes/ethyl acetate) to afford the product as a white solid (45.1 mg, 70%)

^{1}H NMR (500 MHz, DMSO-d_6) δ 8.62 (d, J = 9.0 Hz, 1H), 8.42 (d, J = 8.5 Hz, 2H), 8.05 (d, J = 9.0 Hz, 2H), 4.11 (qd, J = 7.5, 2.0 Hz, 1H), 3.57 (s, 3H), 3.08 (d, J = 2.5 Hz, 1H), 2.42 (td, J = 7.2, 1.6 Hz, 2H), 1.84 (q, J = 7.3 Hz, 2H).
^{13}C NMR (126 MHz, DMSO-d_6) δ 172.9, 150.1, 147.0, 128.9, 124.8, 81.7, 76.1, 51.9, 44.5, 31.2, 29.8.
IR (thin film**)** 3265, 2922, 2851, 1712, 1528, 1461, 1347, 1162, 1075, 853, 731 cm^{-1}

MS (ESI positive mode): m/z 349.0 $[M+Na]^+$

mp: 112-114 ˚C



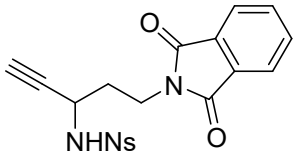
4t: Prepared according to standard amination conditions. Purified by silica gel chromatography (85:15, hexanes/ethyl acetate) to afford the product as a white solid (33 mg, 54%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (d, *J* = 9.0 Hz, 2H), 8.08 (d, *J* = 9.0 Hz, 2H), 4.90 (d, *J* = 9.5 Hz, 1H), 4.05 (m, 1H), 1.83 (dt, *J* = 2.0, 7.0 Hz, 2H), 1.69 (m, 2H), 1.23 (sextet, *J* = 7.0 Hz, 2H), 0.98 (t, *J* = 7.5 Hz, 3H), 0.77 (t, *J* = 7.5 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 150.18, 146.61, 128.85, 124.16, 85.87, 77.64, 47.86, 30.46, 21.87, 20.40, 13.39, 9.98.

IR (thin film) 3280, 3106, 2967, 2936, 2875, 1607, 1531, 1428, 1350, 1311, 1168, 1091, 996, 854, 738, 685, 619, 560 cm^{-1}

MS (ESI positive mode): m/z 333.1 $[M+Na]^+$

mp: 101-104 °C



4u: Prepared according to standard amination conditions. Purified by silica gel chromatography (85:15 hexanes/ethyl acetate) to afford the product as a white solid (71.8 mg, 87%)

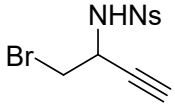
^{1}H NMR (500 MHz, DMSO) δ 8.75 (s, 1H), 8.41 (d, *J* = 8.9 Hz, 3H), 8.07 (d, *J* = 8.9 Hz, 2H), 7.89 – 7.83 (m, 5H), 4.15 (t, *J* = 6.6 Hz, 1H), 3.69 (t, *J* = 7.5 Hz, 2H), 3.08 (d, *J* = 2.3 Hz, 1H), 2.00 – 1.89 (m, 2H).

^{13}C NMR (126 MHz, DMSO) δ 167.8, 134.3, 131.7, 128.5, 124.3, 123.0, 81.0, 75.7, 63.6, 43.0, 34.2.

IR (thin film): 3433, 1707, 1635, 1530, 1402, 1349, 1167, 1093 cm^{-1}

MS (ESI positive mode): m/z 436.4 $[M+Na]^+$

mp: 199-201˚C

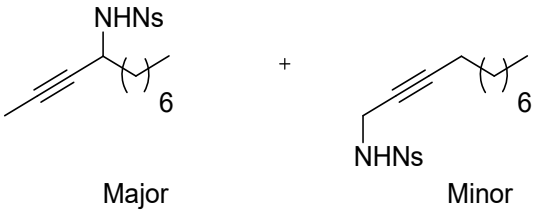


4v: Prepared according to standard amination conditions in CH_2Cl_2. Purified by silica gel chromatography (85:15 hexanes/ethyl acetate) to afford the product as a white solid (49.1 mg, 74%)

^{1}H NMR (500 MHz, DMSO-d_6) δ 8.93 (d, *J* = 9.0 Hz, 1H), 8.42 (d, *J* = 8.5 Hz, 2H), 8.01 (d, *J* = 9.0 Hz, 2H), 4.38 (m, 1H), 3.57 (dd, *J* = 10.5, 6.0 Hz, 1H), 3.52 (dd, *J* = 10.0, 6.5 Hz, 1H), 3.26 (d, *J* = 2.5 Hz, 1H).
^{13}C NMR (126 MHz, DMSO-d_6) δ 149.6, 146.3, 128.4, 124.3, 79.3, 76.7, 46.1, 35.3.
IR (thin film) 3442, 924, 2857, 1644, 1529, 1420, 1349, 1313, 1164, 1091 cm^{-1}

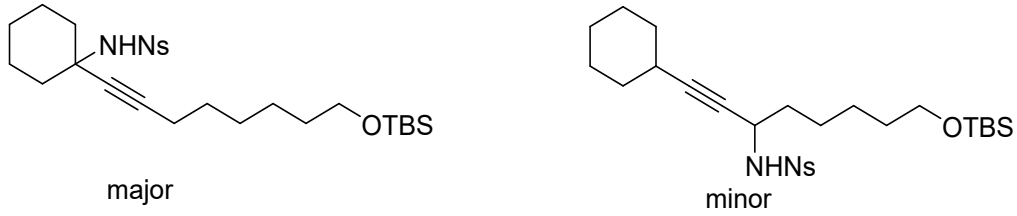
MS (ESI positive mode): m/z 354.4 $[M+Na]^+$

mp: 147-148 ˚C



6a/7a: Prepared according to standard amination conditions. Purified by silica gel chromatography (80:20, hexanes/ethyl acetate) to afford a 4:1 mixture of regioisomeric products as a liquid (50mg, 71%).

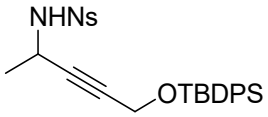
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (d, *J* = 9 Hz, 2H) (major + minor), 8.10 (d, *J* = 9 Hz, 2H) (major + minor), 5.20 (t, *J* = 6 Hz, 1H) (minor), 5.13 (d, *J* = 9.5 Hz, 1H) (major), 4.05 (qt, *J* = 7, 2.5 Hz, 1H) (major), 3.89 (td, *J* = 4.5, 2.5 Hz, 2H) (minor), 1.9-1.8 (m, 2H) (minor), 1.7-1.5 (m, 2H) (major), 1.45 (d, *J* = 2 Hz, 3H) (major), 1.4-1.3 (m, 2H) (major), 1.3-1.1 (m, 10H) (major + minor), 1.0-0.8 (m, 3H) (major + minor).
^{13}C NMR (126 MHz, $CDCl_3$) δ 150.18, 150.06, 146.53, 146.16, 129.14, 128.89, 124.19, 124.00, 86.28, 81.27, 77.41, 73.61, 46.41, 36.80, 33.54, 31.84, 31.75, 29.17, 29.13, 29.03, 28.92, 28.85, 28.37, 25.44, 22.67, 22.64, 18.45, 14.13, 14.10, 3.19.
IR (thin film): 3280, 3106, 2927, 2857, 1607, 1531, 1428, 1349, 1311, 1166, 1092, 1054, 855, 738, 685, 619 cm^{-1}.
MS (ESI positive mode): m/z 375.1 $[M+Na]^+$



6b/7b: Prepared according to standard amination conditions. Purified by silica gel chromatography (90:10, hexanes/ethyl acetate) to afford the major product **7b** as a liquid (62 mg, 58%) and the minor product **6b** as a liquid (29.8 mg, 29%).

6b (major): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (d, *J* = 9 Hz, 2H), 8.11 (d, *J* = 9 Hz, 2H), 4.85 (s, 1H), 3.60 (t, *J* = 6.5 Hz, 2H), 2.04 – 1.97 (m, 2H), 1.84 – 1.79 (m, 2H), 1.69 – 1.44 (m, 10H), 1.30 – 1.21 (m, 10H), 0.91 (s, 9H), 0.06 (s, 6H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 149.8, 148.1, 128.9, 123.7, 87.4, 78.4, 63.1, 55.3, 39.6, 32.7, 28.6, 28.4, 26.0, 25.3, 24.9, 22.5, 18.5, 18.4, -5.3.

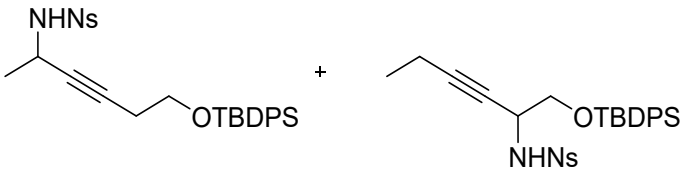
7b (minor): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.36 (d, *J* = 8 Hz, 2H), 8.11 (d, *J* = 8 Hz, 2H), 4.77 (d, *J* = 9 Hz, 1H), 4.14 (s, 1H), 3.61 (t, *J* = 6 Hz, 2H), 2.05 (s, 1H), 1.74–1.00 (m, 25H), 0.91 (s, 9H), 0.06 (s, 6H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 170.2, 150.1, 146.5, 128.7, 124.1, 89.8, 77.5, 63.0, 46.4, 37.2, 32.6, 32.3, 28.6, 26.0, 25.6, 25.3, 25.2, 24.6, 18.4, -5.3.
IR (thin film): 3276, 2931, 2857, 1606, 1532, 1348, 1160, 1095 cm^{-1}
MS (ESI positive mode): m/z 545.8 $[M+Na]^+$



6c: Prepared according to standard amination conditions. Purified by silica gel chromatography (85:15 hexanes/ethyl acetate) to afford a single isomer of the product as a clear liquid (83 mg, 80%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (d, *J* = 9 Hz, 2H), 7.98 (d, *J* = 9 Hz, 2H), 7.63 (m, 4H), 7.46 (m, 2H), 7.40 (m, 4H), 4.59 (d, *J* = 8.5 Hz, 1H), 4.17 (m, 1H), 4.08 (dd, *J* = 16, 1.5 Hz 1H), 4.02 (dd, *J* = 16, 1.5 Hz 1H), 1.32 (d, *J* = 7.0 Hz, 3H), 1.00 (s, 9H).

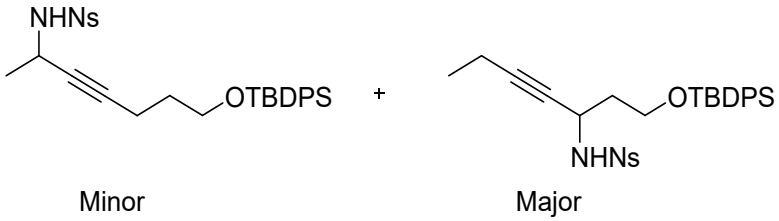
^{13}C NMR (126 MHz, $CDCl_3$) δ 150.23, 146.38, 135.86, 135.81, 133.24, 133.22, 130.25, 130.21, 128.81, 127.99, 127.97, 124.27, 83.61, 83.05, 52.41, 41.98, 26.83, 23.50, 19.29.
IR (thin film): 3280, 3104, 3071, 2931, 2859, 2255, 1961, 1892, 1826, 1710, 1606, 1530, 1471, 1427, 1348, 1311, 1158, 1109, 1071, 1011, 955, 909, 853, 823, 736, 703, 618, 571 cm^{-1}.
MS (ESI positive mode): m/z 545.0 $[M+Na]^+$



6d/7d: Prepared according to standard amination conditions. Purified by silica gel chromatography (85:15, hexanes/ethyl acetate) to afford a 12:1 mixture of products as a liquid (84 mg, 79%).

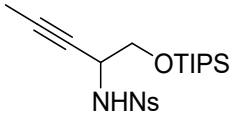
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (d, *J* = 9 Hz, 2H) (minor), 8.26 (d, *J* = 9 Hz, 2H) (major), 8.09 (d, *J* = 9 Hz, 2H) (minor), 8.02 (d, *J* = 9 Hz, 2H) (major), 7.63 (d, *J* = 8 Hz, 4H) (major + minor), 7.45 (t, *J* = 7.5 Hz, 2H) (major + minor), 7.40 (t, *J* = 8 Hz, 4H) (major + minor), 5.18 (d, *J* = 8.5 Hz, 1H) (minor), 4.82 (d, *J* = 8.5 Hz, 1H) (major), 4.25-4.20 (m, 1H) (major + minor), 4.16 (dd, *J* = 11, 4.5 Hz, 2H) (minor), 3.87 (m, 2H) (major+minor), 2.20 (tt, *J* = 7, 2 Hz, 2H) (major), 2.06 (s, 3H) (minor), 2.02 (s, 3H) (major), 1.91 (qd, *J* = 7.5, 2 Hz, 2H) (minor), 1.42 (d, *J* = 8 Hz, 3H) (major), 0.87 (t, *J* = 7.5 Hz, 3H) (minor)

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.83, 150.25, 146.50, 128.81, 124.21, 80.61, 80.38, 65.72, 61.81, 45.71, 41.96, 23.69, 20.88, 18.99, 13.37, 12.12
IR (thin film): 3279, 3070, 2931, 2857, 2247, 1606, 1530, 1471, 1427, 1348, 1311, 1160, 1111, 1012, 965, 911, 853, 823 737, 703, 614 cm^{-1}.
MS (ESI positive mode): $[M+H]^+$ 537.4



6e/7e: Prepared according to standard amination conditions. Purified by silica gel chromatography (85:15 hexanes/ethyl acetate) to afford a 1.2:1 mixture of regioisomeric products as a liquid (92 mg, 82%).

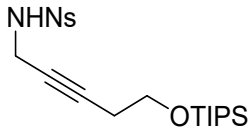
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (d, *J* = 9.0 Hz, 2H, major), 8.26 (d, *J* = 9.0 Hz, 2H, minor) 8.01 (m, 4H, major + minor), 7.64 (m, 8H, major + minor), 7.41 (m, 12H, major + minor), 6.14 (d, *J* = 8.5 Hz, 1H, major), 4.74 (d, *J* = 8.5 Hz, 1H, minor), 4.55 (m, 1H, major), 4.20 (m, 1H, minor), 4.02 (dt, *J* = 9.0, 2.5 Hz, 2H, major), 3.76 (dt, *J* = 9.0, 2.5 Hz, 2H, major), 3.54 (m, 2H, minor), 2.03 (m, 3H, major + minor), 1.83 (m, 3H, major + minor), 1.50 (sextet, *J* = 6.0 Hz, 2H, minor), 1.38 (d, *J* = 7.0 Hz, 3H, minor), 1.09 (s, 9H, major), 1.03 (s, 9H, minor), 1.09 (t, *J* = 7.5 Hz, 3H, major)
^{13}C NMR (126 MHz, $CDCl_3$) δ 150.12, 150.00, 147.11, 146.47, 135.69, 135.66, 135.58, 133.82, 133.78, 133.00, 132.63, 130.14, 130.09, 129.84, 128.90, 128.77, 127.99, 127.98, 127.82, 124.10, 123.94, 87.91, 84.65, 78.82, 76.16, 62.18, 61.31, 45.18, 42.09, 37.38, 31.20, 26.96, 26.92, 24.02, 19.31, 19.23, 14.92, 13.58, 12.16.
IR (thin film): 3284, 3071, 2932, 2858, 1607, 1531, 1472, 1428, 1349, 1312, 1166, 1110, 1010, 966, 910, 854, 823, 737, 704, 616 cm^{-1}.
MS (ESI positive mode): m/z 573.3 $[M+Na]^+$



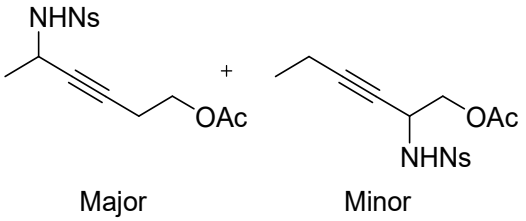
6f/7f: Prepared according to standard amination conditions. Purification by silica gel chromatography (85:15 hexanes/ethyl acetate) allowed separation of the 2:1 mixture of regioisomers to afford product **7f** as a white solid (25 mg, 28%) and **6f** as a white solid (37 mg, 41%).

6f: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (d, *J* = 9.0 Hz, 2H), 8.10 (d, *J* = 9.0 Hz, 2H), 5.13 (d, *J* = 7.5 Hz, 1H), 4.17 (m, 1H), 3.84 (dd, *J* = 9.5, 4.0 Hz, 1H), 3.75 (d, *J* = 9.5, 4.0 Hz, 1H), 1.50 (d, *J* = 2.0 Hz, 3H), 1.06 (m, 21H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.15, 146.69, 128.96, 124.02, 82.00, 74.97, 66.2148.07, 18.08, 17.96, 12.00, 3.32.
IR (thin film): 3280, 3104, 3071, 2931, 2859, 2255, 1961, 1892, 1826, 1710, 1606, 1530, 1471, 1427, 1348, 1311, 1158, 1109, 1071, 1011, 955, 909, 853, 823, 736, 703, 618, 571 cm^{-1}.
MS (ESI positive mode): m/z 463.1 $[M+Na]^+$
mp: 70-72 °C



7f: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (d, *J* = 9.0 Hz, 2H), 8.08 (d, *J* = 9.0 Hz, 2H), 4.92 (t, *J* = 6.0 Hz, 1H), 3.90 (dt, *J* = 5.5, 2.5 Hz, 1H), 3.58 (t, *J* = 7.0 Hz, 2H), 2.17 (tt, *J* = 7.0, 2.5 Hz, 2H), 1.03 (m, 21H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 150.28, 146.10, 128.83, 124.28, 83.51, 74.76, 61.74, 33.61, 23.05, 18.01, 12.04.
IR (thin film): 3280, 3104, 3071, 2931, 2859, 2255, 1961, 1892, 1826, 1710, 1606, 1530, 1471, 1427, 1348, 1311, 1158, 1109, 1071, 1011, 955, 909, 853, 823, 736, 703, 618, 571 cm^{-1}.
MS (ESI positive mode): m/z 463.1 $[M+Na]^+$
mp: 62-63 °C

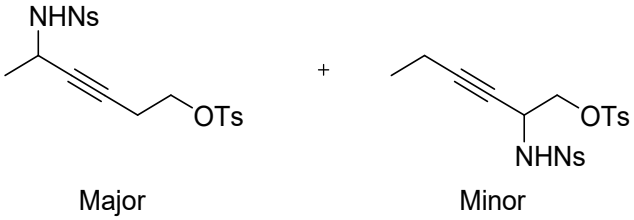


6g/7g: Prepared according to standard amination conditions with CH_2Cl_2 as solvent. Purified by silica gel chromatography (85:15 hexanes/ethyl acetate) to afford a 9:1 mixture of regioisomeric products as a clear liquid (46 mg, 68%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.36 (d, *J* = 9.0 Hz, 2H, major + minor), 8.10 (d, *J* = 9.0 Hz, 2H, major + minor), 5.31 (d, *J* = 9.0 Hz, 1H, minor), 5.11 (d, *J* = 9.0 Hz, 1H, major), 4.5-4.4 (m, 1H, minor), 4.3-4.2 (m, 1H, major + minor), 4.16 (dd, *J* = 11.0, 4.5 Hz, 2H, minor), 3.9-3.8 (m, 2H, major), 2.20 (tt, *J* = 7.0, 2.0 Hz, 2H, major), 2.06 (s, 3H, minor), 2.02 (s, 3H, major), 1.91 (qd, *J* = 7.5, 2.0 Hz, 2H, minor), 1.42 (d, *J* = 8.0 Hz, 3H, major), 0.87 (t, *J* = 7.5 Hz, 3H, minor)

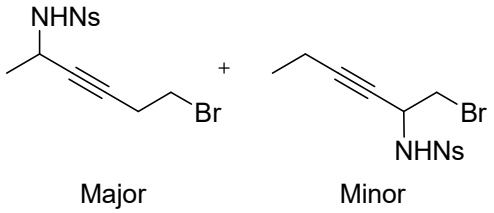
^{13}C NMR (126 MHz, $CDCl_3$) δ 170.83, 150.25, 146.50, 128.81, 124.21, 80.61, 80.38, 65.72, 61.81, 45.71, 41.96, 23.69, 20.88, 18.99, 13.37, 12.12

IR (thin film): 3270, 2984, 1739, 1531, 1350, 1241, 1160, 1089, 1043, 854, 738, 685, 618 cm^{-1}.
MS (ESI positive mode): m/z 573.3 $[M+Na]^+$



6h: Prepared according to standard amination conditions. Purified by silica gel chromatography (80:20 hexanes/ethyl acetate) to afford a 19:1 mixture of regioisomeric products as a solid (49 mg, 62%).

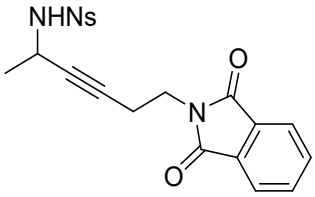
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (d, *J* = 9 Hz, 2H, major + minor), 8.07 (d, *J* = 9 Hz, 2H, major + minor), 7.76 (d, *J* = 8 Hz, 2H, major + minor), 7.36 (d, *J* = 8 Hz, 2H, major + minor), 5.03 (d, *J* = 8.5 Hz, 1H, major), 4.4-4.3 (m, 1H, minor), 4.2-4.1 (m, 1H, major), 4.1-4.0 (m, 2H, minor), 3.9-3.8 (m, 2H, major), 2.46 (s, 3H, major + minor), 2.3-2.2 (m, 2H, major), 1.90 (qd, *J* = 7.5, 2.0 Hz, 2H minor), 1.41 (d, *J* = 7 Hz, 3H, major), 0.88 (t, *J* = 7.5 Hz, 3H, minor)
^{13}C NMR (126 MHz, $CDCl_3$) δ 150.35, 146.49, 145.46, 133.08, 130.23, 128.93, 128.06, 124.39, 81.36, 79.60, 67.53, 42.05, 23.85, 21.90, 19.81, 0.23.
IR (thin film): 3279, 3070, 2931, 2857, 2247, 1606, 1530, 1471, 1427, 1348, 1311, 1160, 1111, 1012, 965, 911, 853, 823 737, 703, 614 cm^{-1}.
MS (ESI positive mode): m/z 475.0 $[M+Na]^+$
mp: 154-157 °C



6i/7i: Prepared according to standard amination conditions with CH_2Cl_2 as solvent. Purified by silica gel chromatography (85:15 hexanes/ethyl acetate) to afford a 5:1 mixture of regioisomeric products as a clear liquid (44 mg, 61%).

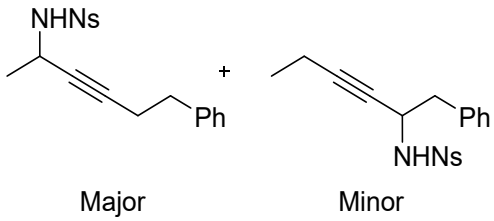
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.36 (d, *J* = 9.0 Hz, 2H, major + minor), 8.11 (d, *J* = 9.0 Hz, 2H, major + minor), 5.38 (d, *J* = 9.0 Hz, 1H, minor), 5.14 (d, *J* = 9.0 Hz, 1H, major), 4.5-4.4 (m, 1H, minor), 4.3-4.2 (m, 1H, major), 3.54 (dd, *J* = 10.5, 5.0 Hz, 1H, minor), 3.50 (dd, *J* = 10.5, 5.0 Hz, 1H, minor), 3.17 (t, *J* = 7.0 Hz, 2H, major), 2.64 (m, 2H, major), 1.92 (qd, *J* = 7.5, 2.0 Hz, 2H, minor), 1.44 (d, *J* = 7 Hz, 3H, major), 0.89 (t, *J* = 7.5 Hz, 3H, minor)

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.21, 146.36, 146.06, 128.82, 124.28, 88.94, 81.74, 80.80, 74.35, 46.89, 41.95, 36.61, 29.38, 23.73, 22.85, 13.31, 12.14.
IR (thin film): 3282, 3106, 2983, 2935, 2872, 1607, 1530, 1421, 1350, 1312, 1161, 1089, 958, 911, 854, 738, 685, 617, 551 cm^{-1}.
MS (ESI positive mode): m/z 383.0 $[M+Na]^+$
mp: 107-109 °C



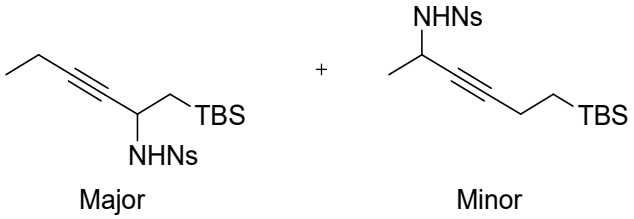
6j/7j: Prepared according to standard amination conditions. Crude mixture was obtained in a 6:1 ratio of isomers in 62% yield. Purified by silica gel chromatography (40:40:20 hexanes/toluene/ethyl acetate) to afford pure isomer **7j** as a white solid (45 mg, 53%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (d, *J* = 9.0 Hz, 2H), 8.06 (d, *J* = 9.0 Hz, 2H), 7.9-7.8 (m, 2H), 7.8-7.7 (m, 2H), 5.00 (d, *J* = 7.5 Hz, 1H), 4.2-4.1 (m, 1H), 3.7-3.6 (m, 2H), 2.4-2.3 (m, 1H), 2.2-2.1 (m, 1H), 1.34 (d, *J* = 7.0 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 168.26, 150.23, 146.45, 134.44, 131.93, 128.81, 124.19, 123.58, 81.52, 80.77, 42.06, 36.64, 23.83, 18.74.
IR (thin film): 3266, 2935, 1772.1, 1710, 1608, 1530, 1432, 1397, 1349, 1160, 1114, 1087, 1001, 913, 854, 738, 720 cm^{-1}.
MS (ESI positive mode): m/z 450.1 $[M+Na]^+$
mp: 184-187 °C



6k/7k: Prepared according to amination conditions with toluene as the solvent. Purified by silica gel chromatography (85:15 hexanes/ethyl acetate) to afford a 2.5:1 mixture of regioisomeric products as a liquid (48 mg, 64%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 (d, *J* = 9.0 Hz, 2H, minor), 8.25 (d, *J* = 9.0 Hz, 2H, major), 7.98 (d, *J* = 9.0 Hz, 2H, major + minor), 7.3-7.2 (m, 3H, major + minor), 7.1-7.0 (m, 2H, major) 4.7-4.6 (m, 1H, major + minor), 4.4-4.3 (m, 1H, minor), 4.3-4.2 (m, 1H, major), 2.98 (dd, *J* = 6.5, 2.0 Hz, 2H, minor), 2.57 (t, *J* = 7.0 Hz, 2H, major), 2.20 (tt, *J* = 7.0, 2.0 Hz, 2H, major), 1.91 (qd, *J* = 7.5, 2.0 Hz, 2H, minor), 1.42 (d, *J* = 7.0 Hz, 3H, major), 0.87 (t, *J* = 7.5 Hz, 3H, minor)
^{13}C NMR (126 MHz, $CDCl_3$) δ 150.13, 146.36, 140.22, 135.47, 130.03, 128.80, 128.62, 128.56, 128.53, 127.44, 126.67, 124.14, 124.11, 84.46, 79.67, 47.22, 42.96, 42.14, 34.65, 23.98, 20.66, 13.50, 12.16.
IR (thin film): 3282, 2935, 1606, 1530, 1427, 1349, 1312, 1162, 1089, 1014, 960, 854, 738, 700, 618 cm^{-1}
MS (ESI positive mode): m/z 359.2 $[M+H]^+$

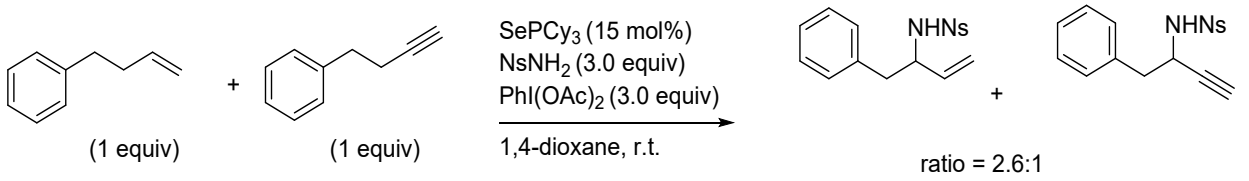


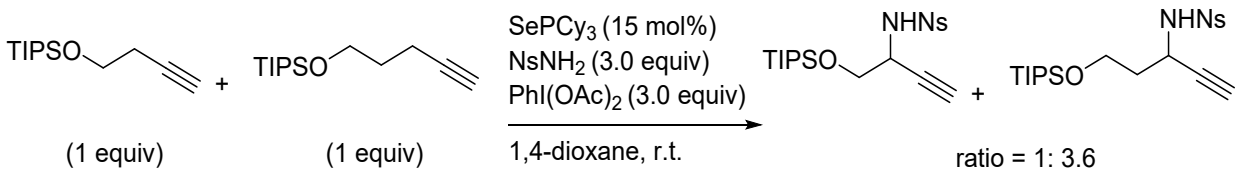
6l/7l: Prepared according to standard amination conditions. Purified by silica gel chromatography (90:10 hexanes/ethyl acetate) to afford a 9:1 mixture of regioisomeric products as a liquid (49 mg, 62%).

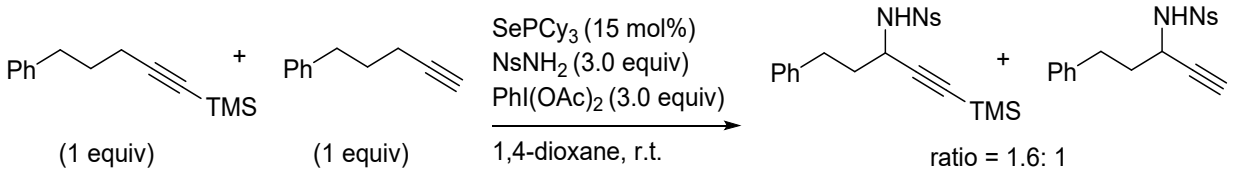
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 (d, *J* = 9 Hz, 2H, major + minor), 8.10 (d, *J* = 9 Hz, 2H, major + minor), 4.79 (m, 1H, major + minor), 4.21 (m, 1H, major + minor), 1.9-1.8 (m, 2H, minor), 1.80 (dq, *J* = 7.5, 2Hz, 2H, major), 1.43 (d, 3H, minor), 1.2-1.0 (m, 2H, major), 0.83 (m, 9H, major + minor), 0.6-0.5 (m, 2H, minor), 0.04 (m, 6H, major), -0.13 (s, 6H, minor)

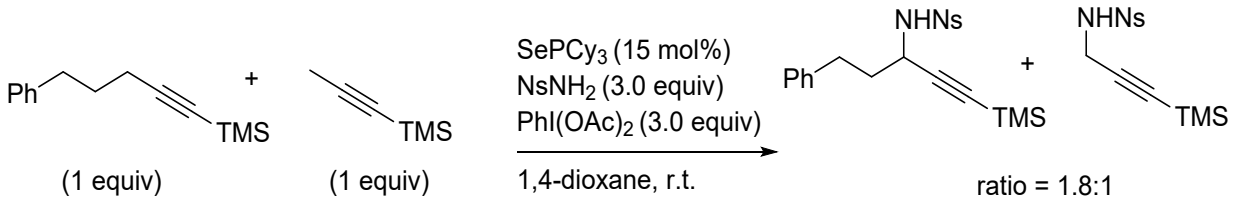
^{13}C NMR (126 MHz, $CDCl_3$) δ 150.24, 146.90, 129.07, 129.01, 87.08, 78.87, 44.41, 42.32, 26.59, 26.49, 24.06, 22.81, 16.64, 13.46, 12.20, 12.07, -5.27, -5.78, -6.24
IR (thin film): 2988, 2361, 2341, 1756, 1725, 1600, 1463, 1348, 1174, 749, 668 cm^{-1}.
MS (ESI positive mode): m/z 419.1 $[M+Na]^+$

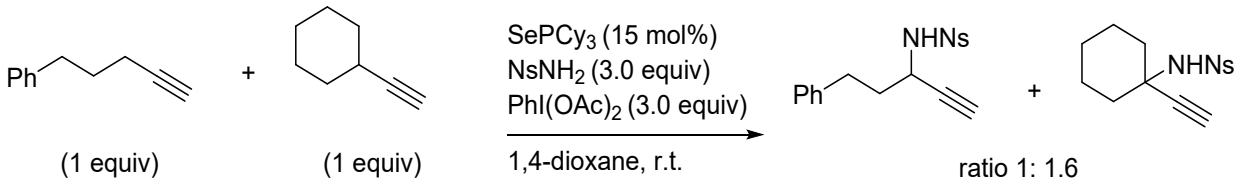
Intermolecular competition experiments: A 1:1 mixture of starting alkynes was subjected to the standard propargyl amination conditions. After 10 hours, the reaction mixture was diluted with DCM and pushed through a silica plug. The aminated product ratio was determined by ^{1}H NMR spectroscopy.



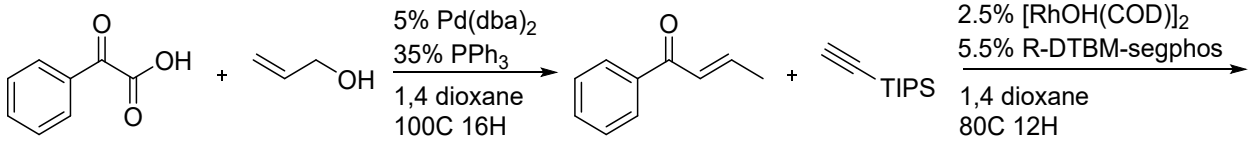


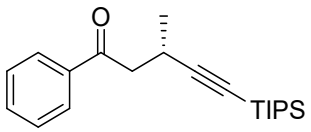






Stereochemistry Retention:



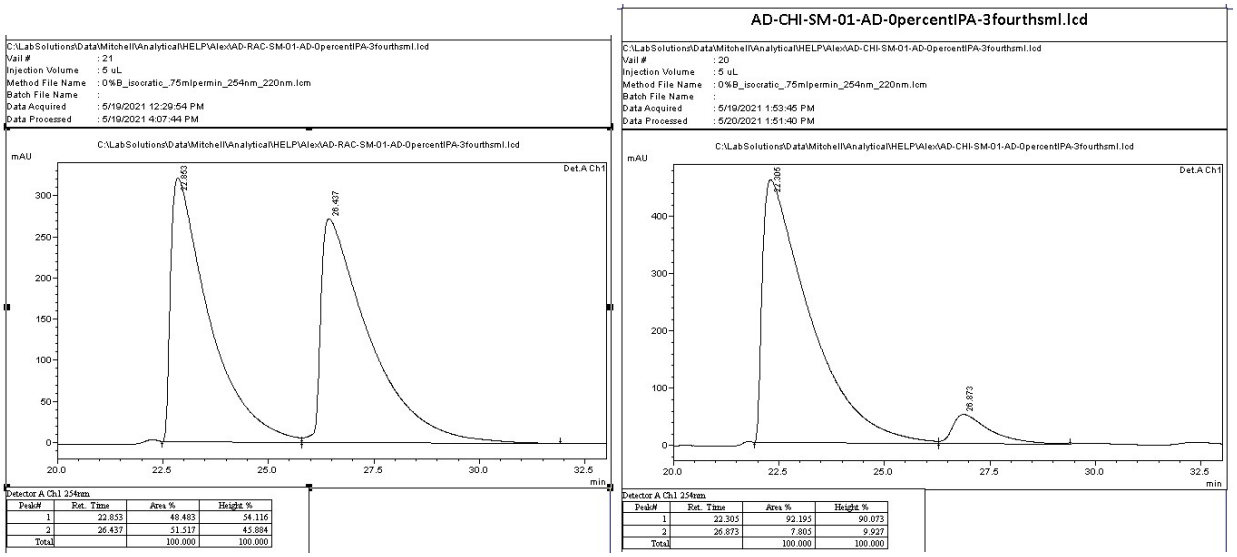


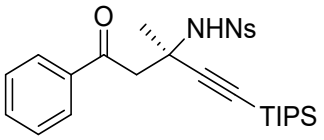
8: A 25 ml flame dried round-bottomed flask was charged with bis(dibenzylideneacetone)palladium(0) (28.8 mg, 0.05 mmol) and triphenylphosphine (91.8 mg, 0.35 mmol). A solution of the carboxylic acid (1.0 mmol) in 1,4-dioxane (8 mL) and allyl alcohol (104 µL, 1.5 mmol) were added via syringe. The reaction mixture was stirred at 100 °C for 16 h and was then cooled to room temperature. The solvent was

removed and the remaining residue was further purified by flash chromatography (90:10 hexane/ethyl acetate), giving (*E*)-1-phenylbut-2-en-1-one in 89% yield (130 mg)[ref]

A mixture of $[Rh(OH)(COD)]_2$ (10 mg, 0.022 mmol) and (*R*)-DTBM-Segphos (58.5 mg, 0.05 mmol) in 1,4-dioxane (2.0 mL) was stirred at room temperature for 5 min. Triisopropylsilylacetylene (328.5 mg, 01.8 mmol) and enone (0.89 mmol) were then added, and the mixture was stirred at 80 °C for 12 h. After cooling, the mixture was passed through a short column of silica gel with ethyl acetate and concentrated under vacuum. The resulting residue was subjected to column chromatography (95:5 hexane/ethyl acetate) to give compound in 74% yield (216 mg). The NMR spectrum was consistent with literature values.[2]

HPLC (Chiralcel AD, 100% hexanes, 0.75 ml/min): 22.3 and 26.9 min, 84% ee.

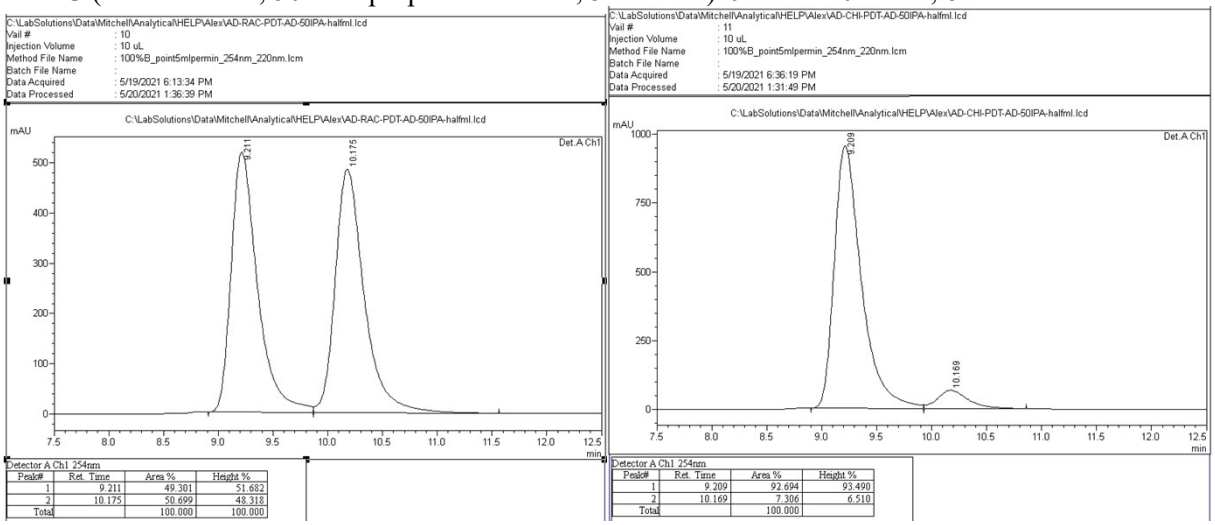




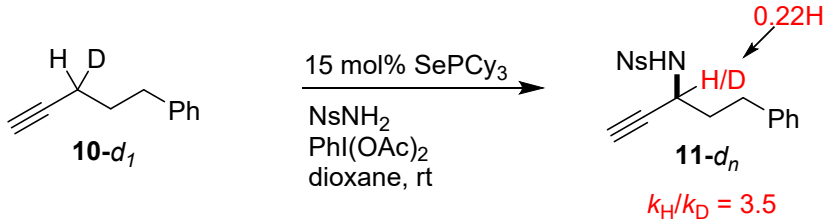
9: Prepared according to amination conditions with 2 equiv. benzoic acid in toluene at 35 °C. Purified by silica gel chromatography (90:10 hexanes/ethyl acetate) to afford the product as a liquid (84 mg, 79%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.9 Hz, 2H), 8.14 (d, *J* = 8.8 Hz, 2H), 7.93–7.87 (m, 2H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 2H), 6.94 (s, 1H), 3.65 (d, *J* = 17.0 Hz, 1H), 3.26 (d, *J* = 17.0 Hz, 1H), 0.9-0.8 (m, 18H), 0.80–0.71 (m, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 198.63, 149.94, 147.85, 136.67, 134.21, 128.93, 128.71, 128.35, 124.19, 106.74, 86.52, 52.38, 49.78, 29.29, 18.45, 11.06.
IR (thin film): 3289, 2943, 2865, 1678, 1597, 1531, 1449, 1349, 1226, 1166, 1094, 998, 882, 854, 736, 685, 610 cm^{-1}.
MS (ESI positive mode): m/z 529.4 $[M+H]^+$

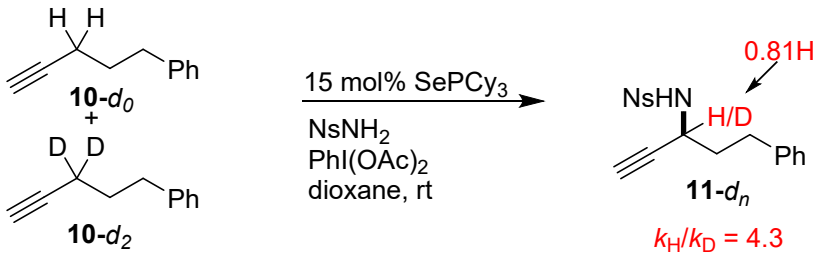
HPLC (Chiralcel AD, 50% isopropanol/hexanes, 5 mL/min): 9.2 and 10.2 min, 84% ee.



<u>Intramolecular competition KIE:</u> 3-deuterio-5-phenyl-1-pentyne was subjected to the standard propargyl amination conditions. Upon consumption of the starting material the product was purified by silica gel chromatography (85:15 hexanes/ethyl acetate). The KIE was determined by product ratio using ^{1}H NMR spectroscopy.



<u>One-pot Intermolecular competition KIE:</u> A 1:1 mixture of 5-phenyl-1-pentyne and 3,3-dideuterio-5-phenyl-1-pentyne was subjected to the standard propargyl amination conditions. After 15% conversion the product was purified by silica gel chromatography (85:15 hexanes/ethyl acetate). The KIE was determined by product ratio using ^{1}H NMR spectroscopy.



DFT Calculations:

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 and adjusted from 1 atm to 1 M concentration (by adding RT ln(24.46) = 1.9 kcal/mol for each species). All minimum structures had zero negative frequencies, and all transition states had one negative frequency whose motions corresponded to the expected reaction coordinate.

Summary Table

alkyne	ΔG‡ (kcal/mol)	ΔG_{rxn} (kcal/mol)	NBO Δq on internal C
HCCC**H**$_3$	+16.5	-16.5	0.25
HCCC**H**$_2$CH$_3$	+14.4	-21.2	0.27
HCCC**H**(CH$_3$)$_2$	+12.2	-25.0	0.27
HCCC**H**$_2$CH$_2$OAc	+16.5	-17.2	0.27
HCCC**H**$_2$CH$_2$CH$_2$OAc	+15.2	-20.4	0.26
HCCC**H**$_2$CH$_2$Si(CH$_3$)$_3$	+11.9	-24.0	0.26
CH$_3$CH$_2$CCC**H**$_2$CH$_3$	+13.5	-19.0	0.26
CH$_3$C**H**$_2$CCCH$_2$OAc	+15.9	-20.9	0.23
CH$_3$CH$_2$CCC**H**$_2$OAc	+18.5	-15.8	0.21
CH$_3$C**H**$_2$CCCH$_2$CH$_2$OAc	+15.1	-17.9	0.26
CH$_3$CH$_2$CCC**H**$_2$CH$_2$OAc	+17.2	-14.5	0.26

Bond lengths for ene reaction of propyne with selenium bis(imide):
Starting alkyne: C1-C2: 1.201, C2-C3: 1.458
Transition state: C1-C2: 1.248, C2-C3: 1.376
Product: C1-C2: 1.297, C2-C3 1.298
% of total bond distance change in TS: C1-C2: 49%, C2-C3: 51%

Calculated structures and energies

Se(NSO2Me)2

1	Se	-0.0000010	-0.2310520	-0.2476140
2	N	-1.3033390	0.3996440	0.6405580
3	N	1.3033400	0.3996520	0.6405490
4	S	-2.8301700	-0.0717300	0.0941810
5	C	-3.5650560	1.5084880	-0.2412960
6	O	-3.5020400	-0.6890570	1.2200750

7	O	-2.7134770	-0.8315000	-1.1470280
8	S	2.8301680	-0.0717310	0.0941770
9	C	3.5650730	1.5084870	-0.2412640
10	O	2.7134770	-0.8314780	-1.1470460
11	O	3.5020240	-0.6890860	1.2200650
12	H	4.5925080	1.3071310	-0.5444550
13	H	3.5380790	2.0988860	0.6721990
14	H	3.0087570	1.9855690	-1.0455650
15	H	-4.5924820	1.3071350	-0.5445200
16	H	-3.0087120	1.9855610	-1.0455830
17	H	-3.5380880	2.0988950	0.6721630

Energy = -3687.9672

Enthalpy = -3687.8486

Free Energy (1 M) = -3687.9035

# of imaginary frequencies: 0

Propyne

1	C	0.2185030	-0.0000190	-0.0001530
2	C	-1.2398510	0.0000030	0.0000260
3	H	-1.6252880	-0.7018130	-0.7426250
4	H	-1.6249880	-0.2923100	0.9792580
5	H	-1.6250880	0.9941930	-0.2363100
6	C	1.4197980	0.0000010	0.0000670
7	H	2.4846610	0.0000170	0.0000410

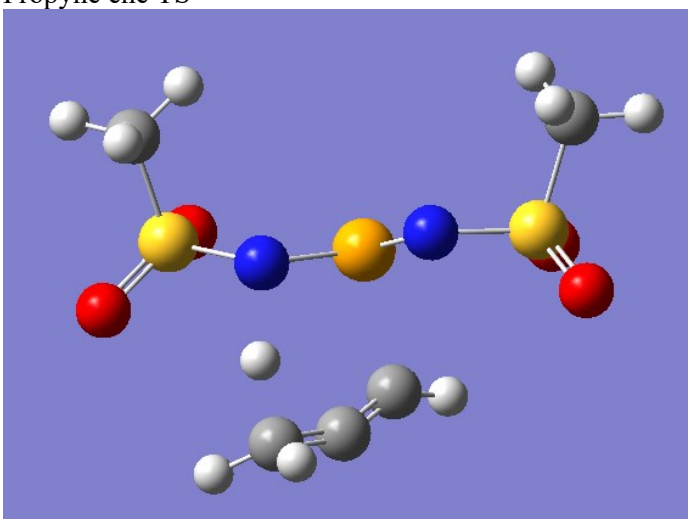
Energy = -116.6457

Enthalpy = -116.5858

Free Energy (1 M) = -116.6139

# of imaginary frequencies: 0

Propyne ene TS



1	Se	0.1054620	-0.1530230	0.4561650
2	N	-1.2613940	-0.0673260	-0.6492590
3	N	1.3353270	-0.3019500	-0.7760130

4	S	-2.7460210	-0.5029740	-0.0017750
5	C	-3.0341590	-2.0999180	-0.7277710
6	O	-3.7155980	0.4343570	-0.5440550
7	O	-2.6550930	-0.6512460	1.4480830
8	S	2.8565490	-0.2180280	-0.1652440
9	C	3.5376130	-1.8299660	-0.4912760
10	O	2.8011600	-0.0219300	1.2950150
11	O	3.6280790	0.7511850	-0.9322940
12	H	4.5741060	-1.8121680	-0.1556290
13	H	3.4822720	-2.0119420	-1.5630210
14	H	2.9603260	-2.5672210	0.0633540
15	H	-4.0212740	-2.4184200	-0.3935270
16	H	-2.2661130	-2.7862250	-0.3764880
17	H	-3.0046100	-1.9913200	-1.8099950
18	C	0.2954940	1.9754230	0.9816150
19	C	-0.3706940	2.5475700	0.0948440
20	C	-1.2121820	2.6364910	-0.9904510
21	H	0.9623420	2.0950890	1.8150820
22	H	-1.3381190	1.3858290	-1.0422630
23	H	-0.7668210	2.9494550	-1.9321770
24	H	-2.2186210	3.0041330	-0.8015180

Energy = -3804.6050

Enthalpy = -3804.4279

Free Energy (1 M) = -4910

# of imaginary frequencies: 1

Propyne ene product

1	Se	-0.1806180	0.7302140	-0.5644850
2	N	0.8274570	-0.3710750	0.5543680
3	N	-1.6537920	0.9613960	0.3595770
4	S	2.1410420	-1.2294280	-0.0243960
5	C	1.5216720	-2.8897280	-0.1400810
6	O	3.1682410	-1.1757590	0.9974990
7	O	2.4078220	-0.7337320	-1.3638900
8	S	-2.7891710	-0.1935060	0.0890820
9	C	-2.6184730	-1.3126750	1.4676630
10	O	-2.5039660	-0.9598990	-1.1325520
11	O	-4.0946660	0.4452510	0.1967000
12	H	-3.3800820	-2.0840030	1.3572000
13	H	-2.7682820	-0.7483400	2.3861740
14	H	-1.6190250	-1.7452290	1.4330310
15	H	2.3369720	-3.5068500	-0.5164140
16	H	0.6810940	-2.8924280	-0.8319010
17	H	1.2186390	-3.2089100	0.8553160

18	C	0.5899690	2.4270860	-0.0812670
19	C	1.8137220	2.4831130	0.3458850
20	C	3.0343490	2.4896480	0.7876870
21	H	-0.0750780	3.2645030	-0.2516260
22	H	0.9228250	-0.0511110	1.5144650
23	H	3.2402850	2.4233180	1.8505280
24	H	3.8711940	2.5649300	0.1017420

Energy = -3804.6607

Enthalpy = -3804.4779

Free Energy (1 M) = -3804.5437

# of imaginary frequencies: 0

Butyne

1	C	-1.9565610	-0.2616900	-0.0001020
2	C	-0.8305030	0.1588640	-0.0001110
3	C	0.5478490	0.6478450	0.0000540
4	H	-2.9557990	-0.6299600	0.0006740
5	H	0.6929380	1.2859310	0.8768820
6	C	1.5802580	-0.4852960	0.0000030
7	H	1.4666760	-1.1147510	-0.8851290
8	H	2.5904100	-0.0706510	0.0002190
9	H	1.4664220	-1.1150660	0.8848780
10	H	0.6930960	1.2861570	-0.8765850

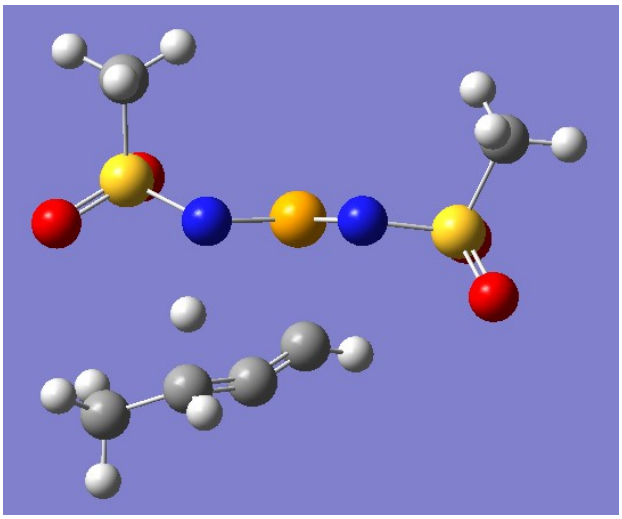
Energy = -155.9573

Enthalpy = -155.8663

Free Energy (1 M) = -155.8990

# of imaginary frequencies: 0

Butyne ene TS



1	Se	0.2847740	-0.2908800	0.4573160
2	N	-1.1024270	-0.3113810	-0.6237260
3	N	1.5094600	-0.2362450	-0.7893110
4	S	-2.4844290	-1.0236290	-0.0100070
5	C	-2.4006230	-2.6929190	-0.6210170
6	O	-3.5947600	-0.3510910	-0.6635770
7	O	-2.4523170	-1.0578210	1.4506320
8	S	3.0193020	-0.0023970	-0.1924900
9	C	3.8801610	-1.5066000	-0.5997370
10	O	2.9679460	0.1219860	1.2760880
11	O	3.6613700	1.0831230	-0.9227240
12	H	4.9125120	-1.3809440	-0.2743510
13	H	3.8299040	-1.6455720	-1.6781610
14	H	3.4035400	-2.3319490	-0.0744240
15	H	-3.3279690	-3.1793900	-0.3192740
16	H	-1.5422490	-3.1898200	-0.1725970
17	H	-2.3155820	-2.6545000	-1.7049840
18	C	0.2552290	1.8092490	1.0731390
19	C	-0.5416060	2.3586560	0.2843330
20	C	-1.4910190	2.4381930	-0.7170040
21	H	0.9876120	1.9702550	1.8430260
22	H	-1.4278470	1.2092470	-0.8631460
23	C	-2.9233660	2.8237310	-0.3764470
24	H	-3.0035170	3.9087300	-0.2900690
25	H	-3.5883490	2.4825920	-1.1685170
26	H	-3.2397390	2.3673730	0.5615830
27	H	-1.1084020	2.8322330	-1.6595790

Energy = -3843.9202
Enthalpy = -3843.7125
Free Energy (1 M) = -3843.7795
# of imaginary frequencies: 1

Butyne ene product

1	Se	0.3509840	-0.6079530	-0.5966700
2	N	-0.5197240	0.5933920	0.5443170
3	N	1.7599870	-1.0543470	0.3489300
4	S	-1.8062020	1.5087070	-0.0193290
5	C	-1.0987560	3.1269650	-0.1962850
6	O	-2.8030900	1.5360170	1.0338300
7	O	-2.1457910	1.0013800	-1.3385980
8	S	3.0621400	-0.0844110	0.1077360
9	C	3.0614540	1.0128520	1.5144740
10	O	2.9102940	0.7460590	-1.0956130
11	O	4.2526550	-0.9205230	0.2033880
12	H	3.9385250	1.6534620	1.4277510
13	H	3.1109790	0.4085510	2.4183490
14	H	2.1457730	1.6023120	1.4881300
15	H	-1.8876920	3.7759320	-0.5752230
16	H	-0.2749680	3.0629590	-0.9050990
17	H	-0.7563640	3.4581660	0.7821020
18	C	-0.6632820	-2.1978430	-0.1847990
19	C	-1.8428340	-2.0875100	0.3431230
20	C	-3.0124050	-1.8943350	0.8811610
21	H	-0.1585960	-3.1084480	-0.4836300
22	H	-0.6666810	0.2371900	1.4858810
23	C	-4.2770030	-1.6615330	0.1097910
24	H	-5.0321350	-2.3980520	0.3946300
25	H	-4.6670030	-0.6702110	0.3552300
26	H	-4.1073050	-1.7167110	-0.9650030
27	H	-3.0704120	-1.8918530	1.9675880

Energy = -3843.9798
Enthalpy = -3843.7668
Free Energy (1 M) = -3843.8363
# of imaginary frequencies: 0

Isopropylacetylene

1	C	2.2244490	0.0000840	0.1191510
2	C	1.0471290	0.0000410	-0.1249140
3	C	-0.3936810	0.0000340	-0.4016770
4	H	3.2681860	0.0000730	0.3306360
5	H	-0.5127670	0.0000240	-1.4910400
6	C	-1.0556120	-1.2687390	0.1535770
7	H	-0.9593750	-1.3057570	1.2421350
8	H	-2.1191470	-1.2728220	-0.0979010
9	H	-0.5981900	-2.1683240	-0.2632530
10	C	-1.0558110	1.2686290	0.1535940
11	H	-0.5988300	2.1683210	-0.2634950
12	H	-2.1194190	1.2723300	-0.0975870
13	H	-0.9593050	1.3058620	1.2421190

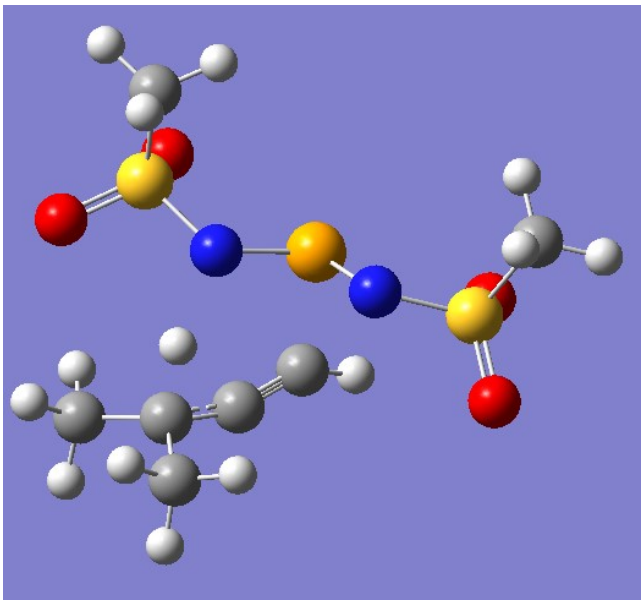
Energy = -195.2708

Enthalpy = -195.1504

Free Energy (1 M) = -195.1863

# of imaginary frequencies: 0

Isopropylacetylene ene TS



1	Se	0.3547310	-0.5343550	0.4598120
2	N	-1.0486930	-0.4175680	-0.5863340
3	N	1.5498720	-0.1818660	-0.7648540
4	S	-2.3898640	-1.2770720	-0.0870420
5	C	-2.2874310	-2.7867340	-1.0245110
6	O	-3.5415170	-0.5242680	-0.5567410

7	O	-2.3066640	-1.6037490	1.3356340
8	S	3.0603850	0.0083970	-0.1547330
9	C	3.9752900	-1.3528420	-0.8472580
10	O	3.0383450	-0.1441650	1.3115330
11	O	3.6367060	1.2396810	-0.6799790
12	H	5.0088160	-1.2422500	-0.5202870
13	H	3.9052200	-1.2928420	-1.9318480
14	H	3.5461730	-2.2816940	-0.4762370
15	H	-3.1904860	-3.3535910	-0.7993270
16	H	-1.4005420	-3.3355960	-0.7125580
17	H	-2.2428070	-2.5285530	-2.0805120
18	C	0.2456510	1.4160660	1.4799930
19	C	-0.5729000	2.0776180	0.8110520
20	C	-1.5250720	2.3288370	-0.1712820
21	H	0.9687500	1.4402030	2.2743660
22	H	-1.4509290	1.1588560	-0.5033960
23	C	-2.9574730	2.5703970	0.2955550
24	H	-3.0706830	3.6117750	0.6054270
25	H	-3.6415090	2.3724100	-0.5296970
26	H	-3.2223520	1.9186320	1.1279870
27	C	-1.0764410	3.1467830	-1.3785320
28	H	-0.0599690	2.8908470	-1.6780670
29	H	-1.7509830	2.9514590	-2.2135560
30	H	-1.1208460	4.2124940	-1.1428840

Energy = -3883.2370

Enthalpy = -3882.9994

Free Energy (1 M) = -3883.0703

# of imaginary frequencies: 1

Isopropylacetylene ene product

1	Se	0.5116160	-0.5003060	-0.7287480
2	N	-0.3413980	0.6377720	0.4900050
3	N	1.8286680	-1.1478930	0.2346090
4	S	-1.5081390	1.7173750	-0.0372170
5	C	-0.6885520	3.2870360	0.0886390
6	O	-2.5978320	1.6729000	0.9200730
7	O	-1.7528250	1.4286620	-1.4405950
8	S	3.1994940	-0.2473310	0.1840980
9	C	3.1629380	0.6983700	1.6965430

10	O	3.1864170	0.7115050	-0.9301010
11	O	4.3288680	-1.1660450	0.2672940
12	H	4.0770220	1.2902190	1.7329350
13	H	3.1178670	0.0030710	2.5326740
14	H	2.2838860	1.3414720	1.6753340
15	H	-1.4002280	4.0425090	-0.2429310
16	H	0.1864370	3.2670770	-0.5587270
17	H	-0.4104460	3.4429090	1.1292300
18	C	-0.6392960	-2.0425070	-0.5381700
19	C	-1.8556070	-1.8770090	-0.1195630
20	C	-3.0507220	-1.6067380	0.3310080
21	H	-0.1604930	-2.9615440	-0.8538490
22	H	-0.5778380	0.1947020	1.3745460
23	C	-4.1693830	-1.2277560	-0.5999560
24	H	-5.0116540	-1.9124200	-0.4664330
25	H	-4.5128650	-0.2206670	-0.3464330
26	H	-3.8570920	-1.2416250	-1.6434290
27	C	-3.3552110	-1.6390730	1.8040990
28	H	-2.4915320	-1.9426300	2.3957820
29	H	-3.6731550	-0.6414850	2.1199660
30	H	-4.1794500	-2.3311710	1.9974150

Energy = -3883.3000

Enthalpy = -3883.0573

Free Energy (1 M) = -3883.1297

# of imaginary frequencies: 0

HCCCH2CH2OAc

1	C	-3.9524690	0.3923150	-0.0001010
2	C	-2.8831190	-0.1538170	0.0000100
3	C	-1.5712370	-0.7954440	0.0001080
4	H	-4.9039750	0.8709900	-0.0001390
5	H	-1.4768800	-1.4363500	-0.8808350
6	C	-0.4521830	0.2379630	0.0000500
7	H	-0.4989210	0.8728960	0.8869630
8	H	-0.4990490	0.8729430	-0.8868270
9	H	-1.4769220	-1.4362310	0.8811460
10	O	0.7791570	-0.4955340	-0.0000550
11	C	1.9099340	0.2228370	-0.0000720
12	O	1.9200520	1.4300600	0.0000610

13	C	3.1205300	-0.6627880	-0.0000400
14	H	3.1058800	-1.3064750	0.8815430
15	H	3.1058690	-1.3065670	-0.8815540
16	H	4.0215910	-0.0538230	-0.0000720

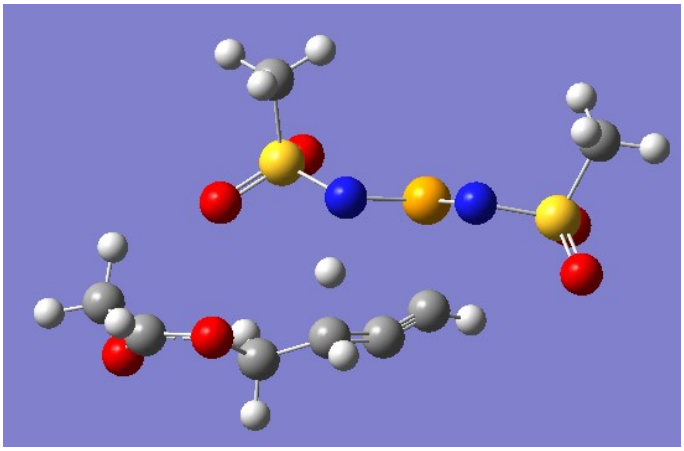
Energy = -383.8339

Enthalpy = -383.6953

Free Energy (1 M) = -383.7410

# of imaginary frequencies: 0

HCCCH2CH2OAc ene TS



1	Se	-1.3022760	0.5187780	0.4547770
2	N	0.2158990	0.6818520	-0.4197270
3	N	-2.2139270	-0.1520770	-0.8732500
4	S	1.2686150	1.8381020	0.1914890
5	C	1.0784310	3.1814790	-0.9573680
6	O	2.6058410	1.2900050	0.0452360
7	O	0.8358270	2.2777890	1.5149640
8	S	-3.7033540	-0.6795600	-0.4231290
9	C	-4.8164140	0.3865010	-1.3129340
10	O	-3.8976560	-0.4580380	1.0211810
11	O	-3.8977340	-2.0367410	-0.9154540
12	H	-5.8277830	0.0456330	-1.0930330
13	H	-4.5999410	0.2932340	-2.3756100
14	H	-4.6646190	1.4075930	-0.9682670
15	H	1.7858880	3.9522070	-0.6523770
16	H	0.0554550	3.5486270	-0.8994440
17	H	1.3104640	2.8095820	-1.9532280
18	C	-0.8647940	-1.3195010	1.6099300

19	C	0.1114410	-1.8035530	1.0051510
20	C	1.1299860	-1.8516080	0.0756760
21	H	-1.6205710	-1.4690340	2.3584990
22	H	0.8392790	-0.6929130	-0.3320300
23	C	2.5689860	-1.8075570	0.5525640
24	H	2.8712760	-2.7732930	0.9631070
25	H	2.7119870	-1.0342330	1.3076390
26	H	0.9473910	-2.5124410	-0.7724360
27	O	3.3473860	-1.5126960	-0.6041790
28	C	4.6037120	-1.0932540	-0.3896560
29	O	5.1064360	-1.0666710	0.7063420
30	C	5.2555220	-0.6583320	-1.6661630
31	H	6.3291820	-0.5636740	-1.5196030
32	H	5.0389000	-1.3621060	-2.4701330
33	H	4.8404830	0.3130130	-1.9463670

Energy = -4071.7940

Enthalpy = -4071.5393

Free Energy (1 M) = -4071.6182

# of imaginary frequencies: 1

HCCCH2CH2OAc ene product

1	Se	1.2375260	-0.6338990	-0.5797070
2	N	0.3439840	0.5488930	0.5572410
3	N	2.6771170	-1.0217640	0.3425630
4	S	-0.9407970	1.4775770	0.0024390
5	C	-0.1333110	2.9395660	-0.5976350
6	O	-1.7239100	1.8062190	1.1777990
7	O	-1.5565190	0.7919860	-1.1212530
8	S	3.9258710	0.0146800	0.0808790
9	C	3.9016560	1.0986180	1.4969440
10	O	3.6988050	0.8445350	-1.1110710
11	O	5.1575710	-0.7616600	0.1402260
12	H	4.7448280	1.7815080	1.3972330
13	H	3.9996330	0.4903650	2.3941630
14	H	2.9582340	1.6431770	1.4941660
15	H	-0.9167950	3.5942170	-0.9780800
16	H	0.5505200	2.6576990	-1.3969620
17	H	0.3955100	3.4006170	0.2338660
18	C	0.2964010	-2.2622610	-0.1649340

19	C	-0.8613640	-2.2127480	0.4143940
20	C	-2.0279950	-2.1068160	0.9781340
21	H	0.8040100	-3.1500090	-0.5219930
22	H	0.2031210	0.2070990	1.5052660
23	C	-3.2829790	-1.9084430	0.1783320
24	H	-3.9634580	-2.7539000	0.3092230
25	H	-3.0620930	-1.7853870	-0.8810110
26	H	-2.1101220	-2.1572420	2.0603570
27	O	-3.9017520	-0.7255400	0.6931680
28	C	-4.7175960	-0.0495040	-0.1307390
29	O	-5.0163540	-0.4434420	-1.2312620
30	C	-5.1767600	1.2274610	0.5042580
31	H	-5.6989040	1.0089670	1.4378330
32	H	-4.3029110	1.8361190	0.7459140
33	H	-5.8373680	1.7613080	-0.1750520

Energy = -4071.8524

Enthalpy = -4071.5918

Free Energy (1 M) = -4071.6720

# of imaginary frequencies: 0

HCCCH2CH2CH2OAc

1	C	-4.6135220	-0.6244200	0.0003690
2	C	-3.5748160	-0.0208040	-0.0002010
3	C	-2.2999100	0.6922650	-0.0001830
4	H	-5.5367730	-1.1553400	0.0000720
5	H	-2.2601270	1.3452800	0.8777630
6	C	-1.0968300	-0.2607640	-0.0000630
7	H	-1.1377460	-0.9052150	-0.8820460
8	H	-1.1379250	-0.9052180	0.8819020
9	H	-2.2600510	1.3451530	-0.8782150
10	C	0.2036900	0.5160340	0.0000650
11	H	0.2923930	1.1506120	0.8858690
12	H	0.2923910	1.1509150	-0.8855220
13	O	1.2744020	-0.4409530	-0.0000870
14	C	2.5211440	0.0433940	-0.0001800
15	O	2.7689060	1.2258480	0.0002170
16	C	3.5376600	-1.0604760	0.0000270
17	H	3.3980340	-1.6895960	0.8812030
18	H	3.3989180	-1.6889940	-0.8817200

19	H	4.5399260	-0.6381340	0.0006560

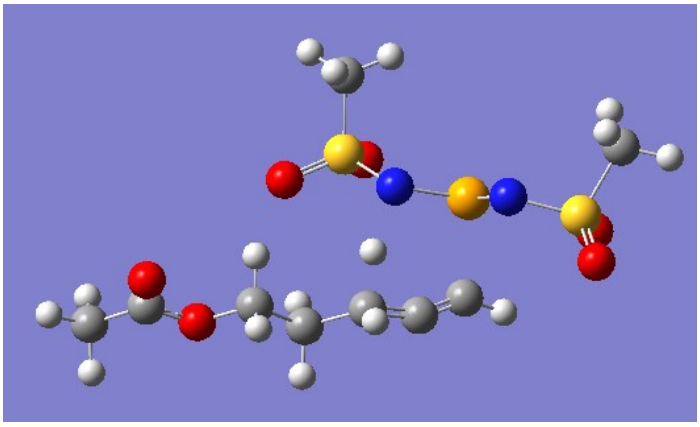
Energy = -423.1476

Enthalpy = -422.9791

Free Energy (1 M) = -423.0293

# of imaginary frequencies: 0

HCCCH2CH2CH2OAc ene TS



1	Se	-1.7174550	0.4816850	0.4309240
2	N	-0.1992810	0.7474930	-0.4215380
3	N	-2.5480960	-0.3076970	-0.8881300
4	S	0.7115830	2.0354480	0.1401710
5	C	0.3131820	3.3441940	-0.9961620
6	O	2.1013860	1.6597160	-0.0610520
7	O	0.2846720	2.4294090	1.4804140
8	S	-4.0038180	-0.9250180	-0.4467450
9	C	-5.1800400	0.0397840	-1.3713520
10	O	-4.2350290	-0.6883320	0.9902250
11	O	-4.0989350	-2.3021160	-0.9128690
12	H	-6.1657280	-0.3756380	-1.1636170
13	H	-4.9380330	-0.0511220	-2.4286990
14	H	-5.1157370	1.0745880	-1.0401670
15	H	0.9442900	4.1905240	-0.7259100
16	H	-0.7394860	3.5967030	-0.8833430
17	H	0.5338460	2.9984500	-2.0039070
18	C	-1.1586000	-1.2520420	1.6456540
19	C	-0.1060100	-1.6663670	1.1173650
20	C	0.9700020	-1.6593420	0.2540190
21	H	-1.9299180	-1.4625240	2.3636470
22	H	0.5743300	-0.5655370	-0.2230810

23	C	2.3812930	-1.4661770	0.7994890
24	H	2.6685680	-2.3532330	1.3691290
25	H	2.4047540	-0.6068080	1.4723120
26	H	0.8768810	-2.3682720	-0.5713610
27	C	3.3575900	-1.2508630	-0.3402420
28	H	3.0900110	-0.3684170	-0.9227230
29	H	3.3971800	-2.1192220	-1.0032860
30	O	4.6459420	-1.0521870	0.2560780
31	C	5.6627170	-0.7959060	-0.5756610
32	O	5.5363690	-0.7535560	-1.7759520
33	C	6.9403300	-0.5666620	0.1764840
34	H	6.8477950	0.3428000	0.7742060
35	H	7.1282410	-1.3962120	0.8598190
36	H	7.7658390	-0.4620180	-0.5238890

Energy = -4111.1106

Enthalpy = -4110.8256

Free Energy (1 M) = -4110.9086

# of imaginary frequencies: 1

HCCCH2CH2CH2OAc ene product

1	Se	1.5812100	-0.6587030	-0.4754650
2	N	0.8901730	0.6408980	0.6798840
3	N	3.1137210	-1.0545390	0.2804050
4	S	-0.4107090	1.5886070	0.2216470
5	C	0.3346740	3.1622740	-0.1208790
6	O	-1.2753170	1.7103890	1.3795450
7	O	-0.9239400	1.0321050	-1.0200880
8	S	4.3606330	-0.1068280	-0.2123700
9	C	4.5480590	1.0909020	1.0961310
10	O	4.0295160	0.6328820	-1.4387490
11	O	5.5592830	-0.9360220	-0.2267630
12	H	5.3944020	1.7263150	0.8373030
13	H	4.7353950	0.5549940	2.0247190
14	H	3.6296690	1.6734300	1.1593190
15	H	-0.4663990	3.8275400	-0.4415570
16	H	1.0686410	3.0263910	-0.9134530
17	H	0.7996710	3.5236370	0.7943250
18	C	0.6498780	-2.1951740	0.2242720
19	C	-0.5470150	-2.0527180	0.7035940

20	C	-1.7395390	-1.8563740	1.1847440
21	H	1.2096800	-3.1165360	0.1211990
22	H	0.8707080	0.3691590	1.6595600
23	C	-2.9987500	-1.9203470	0.3641790
24	H	-3.6238540	-2.7313020	0.7515560
25	H	-2.7627900	-2.1445930	-0.6773980
26	H	-1.8322710	-1.6460090	2.2484950
27	C	-3.7740540	-0.6155870	0.4537310
28	H	-3.2218740	0.2074500	-0.0012790
29	H	-3.9976260	-0.3529310	1.4907110
30	O	-5.0021990	-0.8214350	-0.2597980
31	C	-5.8508460	0.2125510	-0.3123380
32	O	-5.6278140	1.2745330	0.2172250
33	C	-7.0792890	-0.1279110	-1.1036310
34	H	-6.7979990	-0.3499390	-2.1351270
35	H	-7.5540120	-1.0190740	-0.6895250
36	H	-7.7734540	0.7090920	-1.0832850

Energy = -4111.1699

Enthalpy = -4110.8792

Free Energy (1 M) = -4110.9653

# of imaginary frequencies: 0

HCCCH2CH2Si(CH3)3

1	C	-3.0702490	0.9139600	-0.0136160
2	C	-2.4133650	-0.0925610	-0.0297140
3	C	-1.6077590	-1.3134690	-0.0558490
4	H	-3.6499300	1.8070730	0.0010180
5	H	-2.1952990	-2.0996790	-0.5407930
6	C	-0.2495090	-1.1514980	-0.7664330
7	H	0.2398240	-2.1323790	-0.7739510
8	H	-0.4144930	-0.8857800	-1.8167620
9	H	-1.4500730	-1.6426410	0.9765840
10	Si	0.9656780	0.0856020	0.0026780
11	C	2.6985890	-0.3987060	-0.5418440
12	H	2.7827490	-0.3923080	-1.6331890
13	H	3.4425200	0.2989710	-0.1449260
14	H	2.9562460	-1.4025900	-0.1904830
15	C	0.6049060	1.8369600	-0.5734980
16	H	0.6587370	1.9078870	-1.6644040

17	H	-0.3941610	2.1538080	-0.2635000
18	H	1.3337350	2.5381390	-0.1545230
19	C	0.8308450	-0.0073150	1.8755070
20	H	1.0101370	-1.0252040	2.2360270
21	H	1.5637120	0.6515590	2.3511460
22	H	-0.1639500	0.3004920	2.2129420

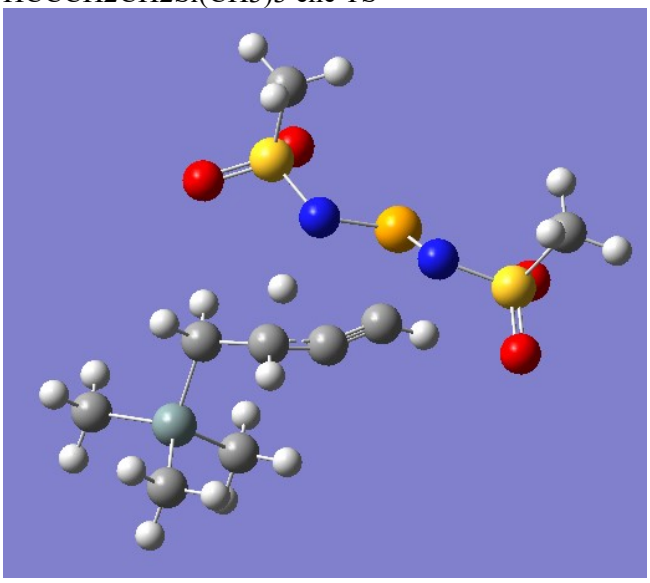
Energy = -564.6373

Enthalpy = -564.4376

Free Energy (1 M) = -564.4886

# of imaginary frequencies: 0

HCCCH2CH2Si(CH3)3 ene TS



1	Se	-1.5820900	0.3738540	0.4458000
2	N	-0.5697210	1.3125380	-0.6399290
3	N	-2.4300030	-0.5207360	-0.7938720
4	S	-0.0391500	2.7762580	-0.0359610
5	C	-1.2219100	3.9427630	-0.6751630
6	O	1.2418070	3.0295710	-0.6742280
7	O	-0.1050900	2.7962350	1.4245540
8	S	-3.3760550	-1.7164360	-0.1896570
9	C	-5.0274740	-1.2187110	-0.6296570
10	O	-3.2756860	-1.7480530	1.2811820
11	O	-3.0876520	-2.9589820	-0.8949810
12	H	-5.6974070	-2.0138560	-0.3036100
13	H	-5.0697040	-1.0974410	-1.7105310
14	H	-5.2540100	-0.2844670	-0.1196580
15	H	-0.8764760	4.9313990	-0.3737830
16	H	-2.1977430	3.7272320	-0.2438930
17	H	-1.2387560	3.8495090	-1.7590850
18	C	-0.1418910	-1.1498280	1.1074530
19	C	0.8196240	-1.0357170	0.3211200

20	C	1.5884520	-0.4781880	-0.6894700
21	H	-0.5831230	-1.7430300	1.8872310
22	H	0.7336530	0.3807430	-0.8616840
23	C	2.9172090	0.1867160	-0.3591370
24	H	3.1840850	0.8444840	-1.1901620
25	H	2.8023630	0.8253240	0.5216250
26	H	1.5665480	-1.0535610	-1.6173740
27	Si	4.3300140	-1.0469630	-0.0530800
28	C	3.8605660	-2.1382630	1.4008130
29	H	2.9774700	-2.7474980	1.1833540
30	H	4.6786240	-2.8239760	1.6421740
31	H	3.6490420	-1.5399710	2.2921960
32	C	4.5743270	-2.0924930	-1.5921050
33	H	4.8044700	-1.4675640	-2.4602640
34	H	5.4028180	-2.7937540	-1.4536170
35	H	3.6801020	-2.6790700	-1.8241800
36	C	5.8755840	-0.0588090	0.3319540
37	H	5.7320120	0.5651020	1.2190520
38	H	6.7235160	-0.7240030	0.5208260
39	H	6.1407580	0.5960980	-0.5032970

Energy = -4252.6042

Enthalpy = -4252.2876

Free Energy (1 M) = -4252.3731

# of imaginary frequencies: 1

HCCCH2CH2Si(CH3)3 ene product

1	Se	1.3714130	-0.4634070	-0.5995540
2	N	1.0710420	0.9788850	0.5564660
3	N	2.4834740	-1.4522530	0.3316560
4	S	0.2427350	2.3317660	0.0073640
5	C	1.5489350	3.4931480	-0.3007710
6	O	-0.5664670	2.8007820	1.1160350
7	O	-0.3783510	1.9860440	-1.2610660
8	S	4.0648430	-1.0794660	0.0992410
9	C	4.5008370	-0.1016120	1.5261350
10	O	4.2607930	-0.2334710	-1.0870420
11	O	4.8230620	-2.3230590	0.1709190
12	H	5.5600630	0.1402440	1.4438070
13	H	4.3068270	-0.6944110	2.4180710
14	H	3.8934410	0.8024840	1.5179300
15	H	1.0788760	4.4047790	-0.6682570
16	H	2.2116340	3.0693970	-1.0537050
17	H	2.0738560	3.6721400	0.6353720
18	C	-0.2078970	-1.5032450	-0.2018880
19	C	-1.2155580	-0.9450840	0.3925320
20	C	-2.1895350	-0.3123060	0.9876120
21	H	-0.1413680	-2.5180070	-0.5756970
22	H	0.7741940	0.6983460	1.4886300
23	C	-3.2822500	0.4285950	0.2886220
24	H	-3.5697390	1.2967410	0.8885220

25	H	-2.9352990	0.7923520	-0.6824470
26	H	-2.2232390	-0.3690960	2.0740320
27	Si	-4.8236940	-0.6543870	0.0015000
28	C	-6.1555410	0.4345940	-0.7444140
29	H	-7.0589110	-0.1465950	-0.9530800
30	H	-6.4271330	1.2462370	-0.0629360
31	H	-5.8172850	0.8802770	-1.6845720
32	C	-4.3502220	-2.0321920	-1.1794480
33	H	-3.5379180	-2.6392180	-0.7684290
34	H	-5.2014930	-2.6929270	-1.3690030
35	H	-4.0166840	-1.6267750	-2.1394790
36	C	-5.3902170	-1.3650170	1.6430050
37	H	-4.6186510	-2.0026060	2.0852470
38	H	-5.6237760	-0.5698090	2.3574230
39	H	-6.2901970	-1.9731820	1.5108110

Energy = -4252.6646

Enthalpy = -4252.3426

Free Energy (1 M) = -4252.4304

# of imaginary frequencies: 0

CH3CH2CCCH2OAc

1	C	0.9388610	-0.5173270	-0.2084720
2	C	-0.4444000	-0.9157510	0.0031990
3	H	-0.5754650	-1.3639750	0.9908890
4	H	-0.7592650	-1.6481930	-0.7438150
5	C	2.0892880	-0.2167320	-0.3853270
6	C	3.4899560	0.1574380	-0.5742060
7	H	3.5311500	1.0257930	-1.2387620
8	H	4.0012400	-0.6560130	-1.0979600
9	C	4.2102900	0.4692630	0.7421870
10	H	5.2492170	0.7422330	0.5455730
11	H	3.7282480	1.3004510	1.2612120
12	H	4.2021440	-0.3988170	1.4047810
13	O	-1.2779350	0.2541430	-0.1000870
14	C	-2.5925780	0.0559890	0.0722430
15	O	-3.0676840	-1.0299090	0.3015910
16	C	-3.3583800	1.3387480	-0.0586330
17	H	-2.9955850	2.0611050	0.6748170
18	H	-3.1967280	1.7631280	-1.0513260
19	H	-4.4182150	1.1506580	0.0966180

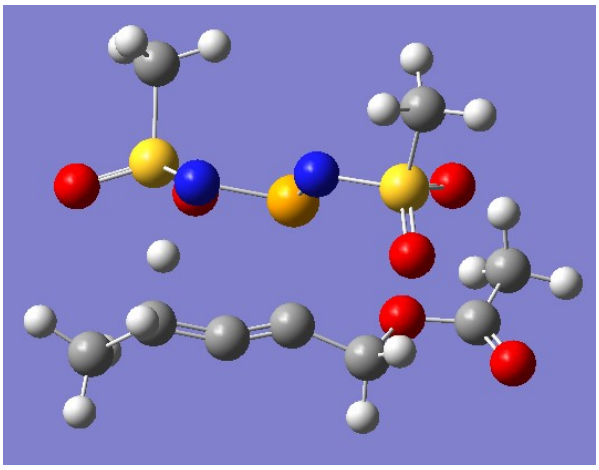
Energy = -423.1484

Enthalpy = -422.9796

Free Energy (1 M) = -423.0309

# of imaginary frequencies: 0

CH3CH2CCCH2OAc distal ene TS



1	Se	0.2489250	-0.3686290	-0.2954320
2	N	1.9144680	-0.7080080	0.1544240
3	N	-0.4756310	-1.6714400	0.6067320
4	S	3.0707690	-0.1888670	-0.9405230
5	C	3.3455540	-1.6196630	-1.9619950
6	O	4.2690510	0.0531660	-0.1555520
7	O	2.5508370	0.8913190	-1.7752490
8	S	-2.1160850	-1.6855580	0.5757500
9	C	-2.4406770	-3.4316460	0.5258040
10	O	-2.6316390	-1.0619020	-0.6525380
11	O	-2.6555170	-1.1553890	1.8278400
12	H	-3.5241160	-3.5454370	0.5540910
13	H	-1.9816750	-3.8909730	1.3990540
14	H	-2.0285250	-3.8339920	-0.3970760
15	H	4.1628820	-1.3650780	-2.6362710
16	H	2.4369250	-1.8314300	-2.5227420
17	H	3.6176130	-2.4516940	-1.3159190
18	C	-0.1697780	1.3436360	1.0889180
19	C	0.8056220	1.3144710	1.8682510
20	C	2.0234030	0.9150710	2.3833710
21	H	2.1327260	0.0804860	1.4630940
22	C	3.2169340	1.8570440	2.3361430
23	H	3.1600070	2.5682480	3.1623040
24	H	3.2443930	2.4072970	1.3954270
25	H	1.9468650	0.2962560	3.2786540
26	H	4.1381850	1.2835110	2.4286520
27	C	-1.5120120	1.9235470	0.8429250
28	H	-2.2724860	1.3118020	1.3348730
29	H	-1.5542240	2.9381100	1.2422330
30	O	-1.7225750	1.9287400	-0.5659960
31	C	-3.0059690	2.0231000	-0.9779010
32	O	-3.9141650	2.2283490	-0.2157250
33	C	-3.1085700	1.8210510	-2.4556890
34	H	-2.3266590	2.3745320	-2.9761940
35	H	-2.9648000	0.7563670	-2.6554020
36	H	-4.0923250	2.1283760	-2.8030150

Energy = -4111.1137

Enthalpy = -4110.8282

Free Energy (1 M) = -4110.9091

# of imaginary frequencies: 1

CH3CH2CCCH2OAc distal ene product

1	Se	-0.0120040	0.1096320	0.2291820
2	N	1.5939770	0.8004760	-0.4280640
3	N	-1.1740080	0.7768030	-0.9024500
4	S	3.0001060	0.6690250	0.4735360
5	C	3.2517030	2.3223010	1.0696070
6	O	4.0687610	0.3282430	-0.4461880
7	O	2.7005210	-0.1946940	1.6038960
8	S	-1.8905190	2.1600710	-0.3935930
9	C	-1.0505570	3.4524120	-1.2915010
10	O	-1.6614840	2.3990530	1.0389070
11	O	-3.2731010	2.1316620	-0.8562020
12	H	-1.5192160	4.3974400	-1.0186080
13	H	-1.1649200	3.2569290	-2.3561140
14	H	-0.0001540	3.4420400	-1.0034440
15	H	4.1555720	2.3041850	1.6777630
16	H	2.3869300	2.6044670	1.6678180
17	H	3.3726380	2.9793170	0.2104510
18	C	0.0569050	-1.6526820	-0.6047370
19	C	1.2124550	-2.1247890	-0.9554580
20	C	2.3999990	-2.5325640	-1.3011930
21	H	1.7394090	0.6577150	-1.4243110
22	C	3.3582430	-3.2382480	-0.3901200
23	H	3.6567190	-4.1939780	-0.8277560
24	H	2.9235800	-3.4120210	0.5936610
25	H	2.7211760	-2.3359170	-2.3221210
26	H	4.2580510	-2.6278420	-0.2769650
27	C	-1.2969220	-2.2860370	-0.7071890
28	H	-1.8701580	-1.8445430	-1.5234890
29	H	-1.2074280	-3.3620170	-0.8605610
30	O	-1.9548870	-2.0061640	0.5352690
31	C	-3.3016530	-2.0989410	0.5494460
32	O	-3.9302980	-2.5123350	-0.3897040
33	C	-3.8590160	-1.6121610	1.8504530
34	H	-3.3353950	-2.0791650	2.6855750
35	H	-3.7015660	-0.5328350	1.9174530
36	H	-4.9233130	-1.8296240	1.8993060

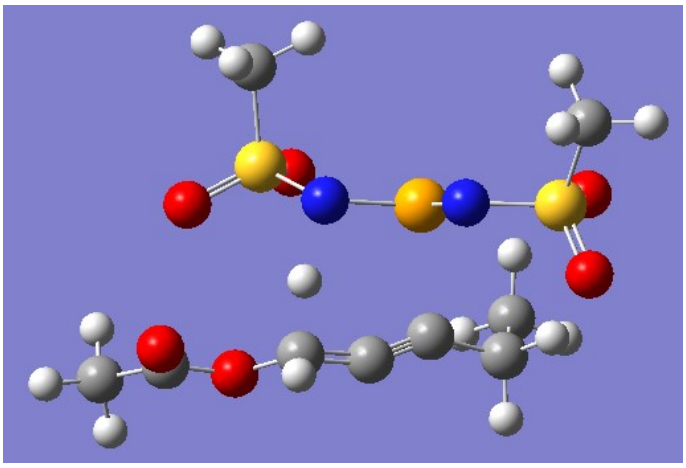
Energy = -4111.1734

Enthalpy = -4110.8830

Free Energy (1 M) = -4110.9678

# of imaginary frequencies: 0

CH3CH2CCCH2OAc proximal ene TS



1	Se	-0.8418010	0.4641850	0.3575610
2	N	0.6657080	0.9369260	-0.4129520
3	N	-1.7999970	0.4024230	-1.0950540
4	S	1.7693740	1.7042500	0.5990290
5	C	1.4769320	3.4264420	0.2672140
6	O	3.0837990	1.3526510	0.0917550
7	O	1.4594200	1.4294890	1.9986540
8	S	-3.3689320	-0.0054550	-0.8260990
9	C	-4.2472250	1.3206300	-1.6207360
10	O	-3.6694750	0.0211870	0.6153350
11	O	-3.6837200	-1.2435000	-1.5300520
12	H	-5.3087990	1.0899980	-1.5352870
13	H	-3.9423360	1.3544420	-2.6649580
14	H	-4.0063610	2.2497650	-1.1083510
15	H	2.2227360	3.9793740	0.8379580
16	H	0.4711430	3.6817940	0.5964670
17	H	1.6012920	3.5914530	-0.8009950
18	C	-0.4545700	-1.7861820	0.6393430
19	C	0.5617020	-1.9229540	-0.0676440
20	C	1.6112280	-1.5502170	-0.8881450
21	H	1.2598040	-0.3285360	-0.8700510
22	H	1.5771360	-1.8418060	-1.9363480
23	O	2.8767450	-1.6492320	-0.2937970
24	C	3.9214660	-1.2223310	-1.0513910
25	O	3.7876580	-0.8792250	-2.1949030
26	C	5.1895100	-1.2440670	-0.2623230
27	H	6.0377790	-1.0990190	-0.9272140
28	H	5.1456190	-0.4279490	0.4624230
29	H	5.2861010	-2.1817670	0.2855760
30	C	-1.5209630	-2.4191240	1.4514880
31	H	-2.4765260	-2.2770640	0.9401360
32	H	-1.3150030	-3.4915480	1.4555040
33	C	-1.5972180	-1.8767210	2.8792190
34	H	-2.3503590	-2.4364790	3.4354510
35	H	-0.6389930	-1.9801450	3.3916340
36	H	-1.8896480	-0.8247490	2.8920660

Energy = -4111.1079

Enthalpy = -4110.8232

Free Energy (1 M) = -4110.9049

# of imaginary frequencies: 1

CH3CH2CCCH2OAc proximal ene product

1	Se	-1.0047700	0.3156600	-0.4621870
2	N	-0.0479080	-1.0659020	0.3464620
3	N	-2.2711000	0.6173250	0.7120060
4	S	1.1430060	-1.8747000	-0.5160520
5	C	0.4275550	-3.4781850	-0.7732430
6	O	2.2992220	-2.0020860	0.3500620
7	O	1.2568370	-1.1985650	-1.7976110
8	S	-3.6534120	-0.2264400	0.4447030
9	C	-3.5770140	-1.5793540	1.6048430
10	O	-3.6877670	-0.8057330	-0.9054190
11	O	-4.7668200	0.6281670	0.8393230
12	H	-4.4961680	-2.1540610	1.4954470
13	H	-3.4968270	-1.1640250	2.6076970
14	H	-2.7069760	-2.1885700	1.3634980
15	H	1.1532840	-4.0595040	-1.3411790
16	H	-0.4957980	-3.3507040	-1.3355680
17	H	0.2426260	-3.9290080	0.1999760
18	C	0.1031960	1.8447480	0.0962330
19	C	1.2936110	1.5574960	0.5134320
20	C	2.4527830	1.1819770	0.9807100
21	H	0.2032730	-0.8894000	1.3163030
22	H	2.6323050	0.9865690	2.0313460
23	O	3.5164300	1.0135580	0.1380810
24	C	4.6578970	0.4707750	0.6637730
25	O	4.7756900	0.2172820	1.8293350
26	C	5.6694610	0.2558990	-0.4135830
27	H	5.2899630	-0.4961350	-1.1089640
28	H	5.8225250	1.1800580	-0.9727780
29	H	6.6048850	-0.0829520	0.0247540
30	C	-0.5579570	3.1840010	-0.0801090
31	H	-1.4430330	3.2125100	0.5615020
32	H	0.1409450	3.9375000	0.2878370
33	C	-0.9489270	3.4807120	-1.5294800
34	H	-1.3707410	4.4846600	-1.5985960
35	H	-0.0815270	3.4234860	-2.1906850
36	H	-1.7093750	2.7860250	-1.8995330

Energy = -4111.1656

Enthalpy = -4110.8754

Free Energy (1 M) = -4110.9596

# of imaginary frequencies: 0

CH3CH2CCCH2CH2OAc

1	C	2.7665830	-0.5264750	-0.1974540
2	C	1.6187250	-0.8535530	-0.0459370

3	C	0.2155350	-1.2257300	0.1276290
4	H	0.0577130	-1.6275190	1.1327110
5	H	-0.0507090	-2.0147910	-0.5816450
6	C	4.1613180	-0.1136710	-0.3608990
7	H	4.8114710	-0.9412790	-0.0607970
8	H	4.3569430	0.0637630	-1.4228740
9	C	-0.6995580	-0.0275070	-0.0851680
10	H	-0.5953190	0.3761280	-1.0943520
11	H	-0.4842650	0.7670930	0.6320960
12	O	-2.0426520	-0.4937530	0.1068770
13	C	-3.0223760	0.4076320	-0.0328100
14	O	-2.8164820	1.5654920	-0.3073570
15	C	-4.3706800	-0.2097940	0.1943570
16	H	-4.5280680	-1.0229060	-0.5168660
17	H	-4.4168460	-0.6338790	1.1992310
18	H	-5.1453120	0.5439610	0.0736890
19	C	4.5091200	1.1407170	0.4486600
20	H	5.5565030	1.4096200	0.2950090
21	H	3.8885790	1.9854670	0.1415210
22	H	4.3503850	0.9707190	1.5158470

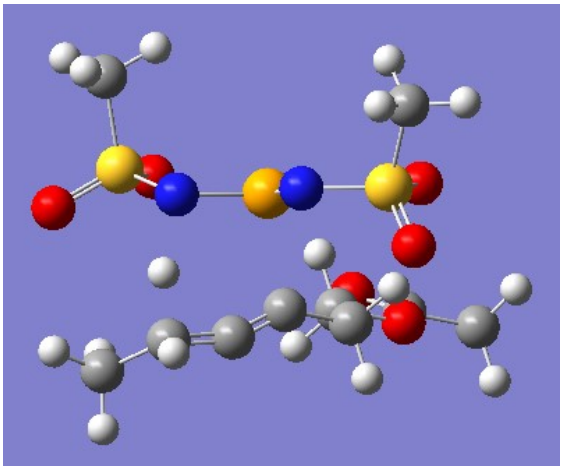
Energy = -462.2809

Enthalpy = -462.2676

Free Energy (1 M) = -462.3228

# of imaginary frequencies: 0

CH3CH2CCCH2CH2OAc distal ene TS



1	Se	-0.7400550	0.4025210	-0.4014090
2	N	-2.1912260	-0.5372590	-0.0676730
3	N	-1.3933760	1.9323430	0.1292320
4	S	-2.3019680	-1.9839040	-0.9056080
5	C	-3.2960600	-1.5658460	-2.3206720
6	O	-3.0675070	-2.8769090	-0.0532470
7	O	-0.9838550	-2.4141380	-1.3670730
8	S	-0.3363360	3.1800250	0.0235490
9	C	-1.1763760	4.3274540	-1.0463710
10	O	0.9095490	2.7524460	-0.6383880

11	O	-0.1958500	3.8115830	1.3304110
12	H	-0.5494190	5.2163940	-1.1110150
13	H	-2.1399270	4.5666250	-0.6002040
14	H	-1.2989370	3.8638170	-2.0230740
15	H	-3.4619930	-2.4946380	-2.8661140
16	H	-2.7520760	-0.8504330	-2.9347230
17	H	-4.2360510	-1.1498690	-1.9640150
18	C	0.5141790	-0.1559220	1.3619160
19	C	-0.3612930	-0.5927500	2.1415410
20	C	-1.5985330	-1.0349540	2.5634300
21	H	-2.0709080	-0.8320310	1.4136570
22	H	-2.1322120	-0.3339750	3.2063040
23	C	-1.8040380	-2.5080100	2.8902960
24	H	-1.4471970	-2.7143850	3.9011070
25	H	-2.8647480	-2.7497180	2.8361140
26	H	-1.2683050	-3.1447680	2.1864670
27	C	1.9496650	0.1656310	1.1707180
28	H	2.0494300	1.1267630	0.6607690
29	H	2.4143140	0.2535530	2.1544710
30	C	2.6405800	-0.9240670	0.3601030
31	H	2.6043880	-1.8856170	0.8763690
32	H	2.1855010	-1.0445460	-0.6259960
33	O	3.9990720	-0.5040700	0.2116680
34	C	4.8032030	-1.3067350	-0.5018670
35	O	4.4226430	-2.3380350	-0.9991500
36	C	6.1916810	-0.7481850	-0.5903350
37	H	6.1649470	0.2134620	-1.1068240
38	H	6.5875250	-0.5759890	0.4120100
39	H	6.8321350	-1.4406160	-1.1316670

Energy = -4150.4314

Enthalpy = -4150.1159

Free Energy (1 M) = -4150.2022

# of imaginary frequencies: 1

CH3CH2CCCH2CH2OAc distal ene product

1	Se	0.4013000	0.3106120	0.1844600
2	N	2.1457360	-0.1118100	-0.3296950
3	N	0.0272860	1.6669810	-0.8607160
4	S	3.0655640	-1.1658800	0.5958430
5	C	4.1943390	-0.0805750	1.4319460
6	O	3.8055400	-2.0050750	-0.3270680
7	O	2.1765920	-1.7612200	1.5795670
8	S	0.3679110	3.1354240	-0.2145060
9	C	1.9178730	3.5996750	-0.9660450
10	O	0.5888300	3.0590700	1.2362600
11	O	-0.6485750	4.0654720	-0.6920200
12	H	2.1742340	4.5925710	-0.5976110
13	H	1.7832960	3.6099740	-2.0460480
14	H	2.6715590	2.8697140	-0.6733380
15	H	4.8240820	-0.7072770	2.0627650

16	H	3.6139580	0.6164840	2.0342360
17	H	4.7869850	0.4389840	0.6816240
18	C	-0.5679210	-1.0140880	-0.8822440
19	C	0.1030500	-2.0722800	-1.2241880
20	C	0.8223440	-3.1057530	-1.5573610
21	H	2.2662510	-0.2473660	-1.3305180
22	H	1.3409820	-3.0717750	-2.5133730
23	C	1.0002740	-4.3295230	-0.7093630
24	H	2.0577260	-4.4386490	-0.4543750
25	H	0.4209070	-4.2671970	0.2113120
26	H	0.6983540	-5.2200010	-1.2662730
27	C	-2.0169310	-0.7009650	-1.1433930
28	H	-2.1096710	0.3319130	-1.4875280
29	H	-2.3617220	-1.3567100	-1.9449040
30	C	-2.8769720	-0.9123520	0.0938440
31	H	-2.8429590	-1.9526020	0.4252310
32	H	-2.5642540	-0.2767850	0.9278860
33	O	-4.2158750	-0.5676490	-0.2766180
34	C	-5.1524090	-0.6731330	0.6768390
35	O	-4.9062230	-1.0459220	1.7981430
36	C	-6.5019130	-0.2686450	0.1632410
37	H	-6.4758720	0.7795190	-0.1416340
38	H	-6.7588910	-0.8637330	-0.7148020
39	H	-7.2486550	-0.4083300	0.9414180

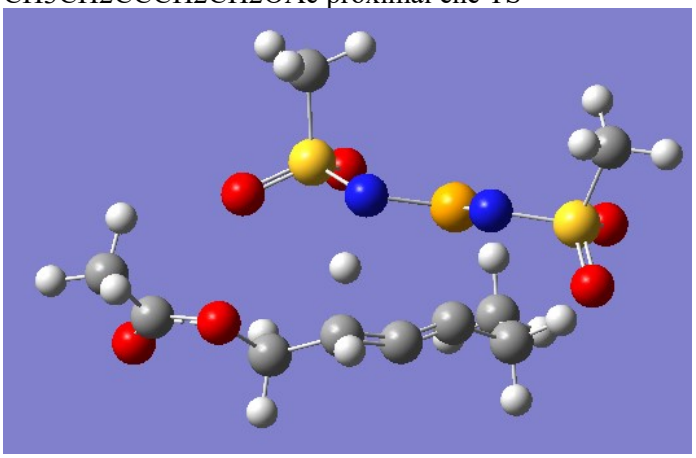
Energy = -4150.4876

Enthalpy = -4150.1670

Free Energy (1 M) = -4150.2549

# of imaginary frequencies: 0

CH3CH2CCCH2CH2OAc proximal ene TS



1	Se	-1.1607620	0.4804370	0.3665370
2	N	0.4195400	0.9341430	-0.2731630
3	N	-1.9476360	0.3918580	-1.1890150
4	S	1.4464320	1.6386410	0.8537410
5	C	1.2835890	3.3751540	0.5087220
6	O	2.7900630	1.2181810	0.4972450
7	O	0.9683240	1.3788570	2.2096150

8	S	-3.5209740	-0.0629590	-1.1083870
9	C	-4.3773610	1.3169910	-1.8359690
10	O	-3.9513260	-0.1900650	0.2954130
11	O	-3.7347340	-1.2222780	-1.9661500
12	H	-5.4338690	1.0522690	-1.8689320
13	H	-3.9863890	1.4697280	-2.8401700
14	H	-4.2134970	2.1932290	-1.2117140
15	H	1.9825840	3.8884250	1.1685640
16	H	0.2592450	3.6767550	0.7197370
17	H	1.5393410	3.5389630	-0.5360780
18	C	-0.8075870	-1.6910000	0.8075680
19	C	0.1491430	-1.8970510	0.0306660
20	C	1.1682470	-1.6094230	-0.8520350
21	H	0.9513250	-0.3517700	-0.7453670
22	C	2.6024070	-1.8113150	-0.4021670
23	H	2.8814480	-2.8659240	-0.4550860
24	H	2.7527860	-1.4523040	0.6164100
25	H	0.9752030	-1.8659970	-1.8938480
26	O	3.4051520	-1.0582740	-1.3090960
27	C	4.6661960	-0.8088880	-0.9275010
28	O	5.1563880	-1.2854470	0.0665400
29	C	5.3426590	0.1348560	-1.8737220
30	H	5.1256720	-0.1329990	-2.9080540
31	H	4.9461320	1.1372030	-1.6937440
32	H	6.4156110	0.1325830	-1.6949060
33	C	-1.7731970	-2.2262170	1.7989860
34	H	-2.7807630	-1.9211370	1.5063510
35	H	-1.7283050	-3.3154440	1.7355540
36	C	-1.4603580	-1.7537470	3.2213330
37	H	-2.1855350	-2.1833750	3.9142690
38	H	-0.4597860	-2.0659620	3.5260730
39	H	-1.5193400	-0.6659700	3.3044470

Energy = -4150.4312

Enthalpy = -4150.1169

Free Energy (1 M) = -4150.1989

# of imaginary frequencies: 1

CH3CH2CCCH2CH2OAc proximal ene product

1	Se	-1.1338080	0.3879420	-0.3561760
2	N	-0.1699000	-0.9119480	0.5740610
3	N	-2.6126500	0.5068410	0.5779230
4	S	1.1019450	-1.7219310	-0.1664050
5	C	0.2691070	-3.0486280	-1.0014100
6	O	1.9052080	-2.2548130	0.9178040
7	O	1.7055490	-0.8523650	-1.1619730
8	S	-3.7720400	-0.5597160	0.1191510
9	C	-3.6576870	-1.8741910	1.3193900
10	O	-3.4827600	-1.1441680	-1.1987410
11	O	-5.0633290	0.0924160	0.2986170
12	H	-4.4310860	-2.6031280	1.0794590

13	H	-3.8193490	-1.4482300	2.3078170
14	H	-2.6657820	-2.3183770	1.2432660
15	H	1.0363570	-3.6200400	-1.5228930
16	H	-0.4386310	-2.6224040	-1.7113430
17	H	-0.2367350	-3.6563710	-0.2542360
18	C	-0.3193390	2.0038140	0.3719330
19	C	0.8561990	1.8612200	0.9016480
20	C	2.0432410	1.6964520	1.4100230
21	H	0.0245700	-0.6907060	1.5479860
22	C	3.2846420	1.7350400	0.5673960
23	H	3.9345890	2.5609930	0.8685250
24	H	3.0428980	1.8362470	-0.4897380
25	H	2.1559300	1.5165570	2.4759500
26	O	3.9680390	0.4983590	0.7992570
27	C	4.7683150	0.0432850	-0.1766560
28	O	5.0078350	0.6700920	-1.1795860
29	C	5.2968690	-1.3180730	0.1590090
30	H	5.8616040	-1.2747110	1.0924520
31	H	4.4561990	-1.9984290	0.3100030
32	H	5.9361800	-1.6745840	-0.6453810
33	C	-1.1135830	3.2665990	0.1631800
34	H	-2.0681750	3.1609240	0.6852780
35	H	-0.5611250	4.0738550	0.6482510
36	C	-1.3519790	3.5964780	-1.3113260
37	H	-1.9667720	2.8377070	-1.8054520
38	H	-1.8835330	4.5457760	-1.3963710
39	H	-0.4073500	3.6788360	-1.8535650

Energy = -4150.4850

Enthalpy = -4150.1655

Free Energy (1 M) = -4150.2495

# of imaginary frequencies: 0

References:

1. Grünberg, M. F; Gooßen, L. J. Decarboxylative allylation of arylglyoxylic acid with allyl alcohol. *J. Organomet. Chem.* **2013**, *744*, 140-143.
2. Nishimura, T.; Guo, X.-X.; Uchiyama, N.; Katoh, T.; Hayashi, T. Steric Tuning of Silylacetylenes and Chiral Phosphine Ligands for Rhodium-Catalyzed Asymmetric Conjugate Alkynylation of Enones. *J. Am. Chem. Soc.* **2008**, *130*, 1576-1577.