A Concomitant Allylic Azide Rearrangement/Intramolecular Azide–Alkyne Cycloaddition Sequence

Rakesh H. Vekariya, Ruzhang Liu, and Jeffrey Aubé*

Department of Medicinal Chemistry, University of Kansas, Lawrence, Kansas 66045

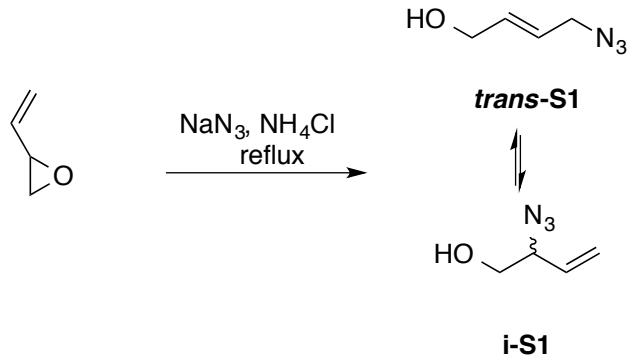
jaube@ku.edu

Supporting Information

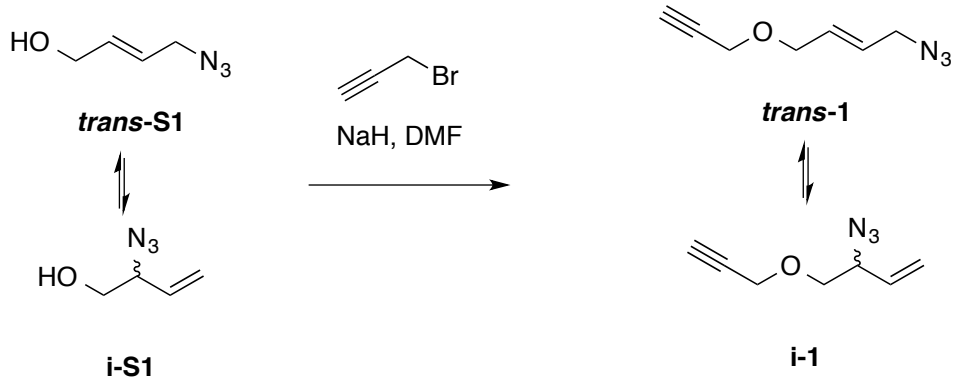
Corresponding Author:
Professor Jeffrey Aubé
Department of Medicinal Chemistry
Delbert M. Shankel Structural Biology Center
2034 Becker Drive, University of Kansas, Lawrence, Kansas 66045

Tel: 1.785.864.4496
Fax: 1.785.864.8179

Experimental Details:

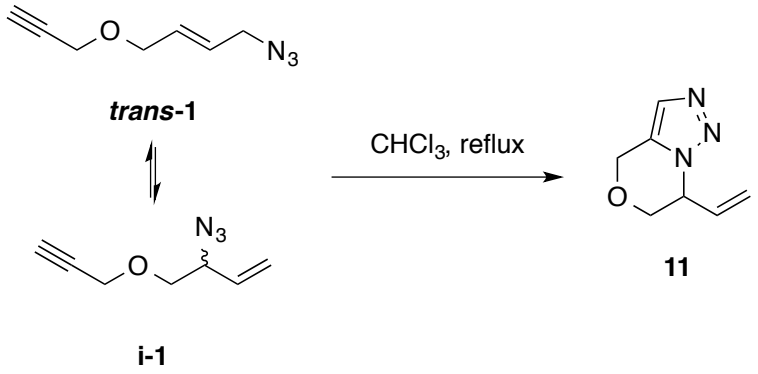


(*E*)-4-Azidobut-2-en-1-ol (***trans*-S1**), **2-azidobut-3-en-1-ol** (**i-S1**). To a solution of 2-vinyloxirane (370 mg, 5.28 mmol) and ammonium chloride (1.41 g, 26.4 mmol) in a mixed solvent of ethanol (16 mL) and water (2 mL), was added sodium azide (3.43 g, 52.8 mmol). The resulting mixture was refluxed for 24 h. After it was cooling to room temperature, water and dichloromethane were added. After separation, the aqueous layer was extracted with dichloromethane three times. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate and concentrated. The residue was purified by silica gel column chromatography (10-20% EtOAc/hexanes) to afford ***trans*-S1** and **i-S1** (280 mg, 47%, 96:4) as a colorless oil. Azides ***trans*-S1** and **i-S1**: R_f = 0.30 (50% EtOAc/hexanes). Azide ***trans*-S1**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.88-5.96 (m, 1H), 5.73-5.80 (m, 1H), 4.19 (d, *J* = 6.4 Hz, 2H), 3.79 (d, *J* = 6.4 Hz, 2H), 2.28 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.4, 124.1, 62.5, 52.2. Azides **i-S1** (diagnostic peaks only): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.85-5.93 (m, 1H), 5.73-5.80 (m, 1H), 5.36-5.43(m, 2H), 2.54 (br, 1H), 3.53-3.57 (m, 1H), 3.63-3.67 (m, 1H), 4.03-4.07 (m, 1H), 5.36-5.43(m, 2H), 5.41 (dt, *J* = 17.2 Hz, 1.2 Hz, 1H), 5.28 (dt, *J* = 10.4 Hz, 1.2 Hz, 1H), 4.34 (br, 1H), 3.40 (dd, *J* = 3.6 Hz, 12.3 Hz, 1H), 3.33 (dd, *J* = 7.2 Hz, 12.3 Hz, 1H), 2.08 (br, 1H).

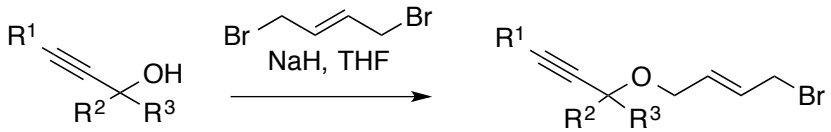


(*E*)-1-Azido-4-(prop-2-yn-1-yloxy)but-2-ene (*trans*-1) and **3-Azido-4-(prop-2-yn-1-yloxy)but-1-ene (i-1).** To a solution of a mixture of azides ***trans*-S1**, and **i-S1** (500 mg, 4.42 mmol) in anhydrous DMF (20 mL) at 0 °C under N_2 atmosphere was added sodium hydride (60% in mineral oil, 221 mg, 5.52 mmol). After the resulting mixture was stirred at 0 °C for 30 min, propargyl bromide (80% w/w in toluene, 821 mg, 5.52 mmol) was added slowly. The resulting mixture was stirred overnight, and quenched with saturated aqueous ammonium chloride. Products were extracted with diethyl ether three times. The combined

organic layers were washed with brine, dried over anhydrous sodium sulfate and concentrated. The residue was purified by silica gel column chromatography (0.5-2% EtOAc/hexanes) to afford a mixture of azides ***trans*-1**, and **i-1** (60 mg, 34%, 83:17) as a colorless oil. Azide ***trans*-1** and **i-1**: R_f = 0.30 (5% EtOAc/hexanes); IR (neat) 2859, 2100 cm^{-1}; HRMS (ESI) *m/z* calculated for $C_7H_{10}N_3O$ $(M+H)^+$ 152.0824, found: 152.0830. Azide ***trans*-1**: ^1H NMR (400 MHz, $CDCl_3$) δ 5.84 (q, *J* = 4.8 Hz, 2H), 4.17 (d, *J* = 2.4 Hz, 2H), 4.11 (d, *J* = 4.1 Hz, 2H), 3.80 (d, *J* = 4.6 Hz, 2H), 2.46 (t, *J* = 2.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 130.7, 126.6, 79.4, 74.7, 69.0, 57.3, 52.2. Azides **i-1** (diagnostic peaks only): ^1H NMR (400 MHz, $CDCl_3$) δ 5.79 (ddd, *J* = 17.3, 10.3, 7.1 Hz, 1H), 5.41 (dt, *J* = 17.1, 1.1 Hz, 2H), 5.36 (dt, *J* = 10.3, 1.0 Hz, 2H), 4.23 (t, *J* = 2.4 Hz, 1H), 4.10-4.16 (m, 1H), 3.65 (dd, *J* = 9.9, 4.4 Hz, 1H), 3.55 (dd, *J* = 9.9, 7.4 Hz, 1H), 2.48 (t, *J* = 2.4 Hz, 1H).



7-Vinyl-6,7-dihydro-4*H*-[1,2,3]triazolo[5,1-*c*][1,4]oxazine (11). A mixture of azides ***trans*-1**, and **i-1** (32 mg, 0.20 mmol) in chloroform (11 mL) under N_2 atmosphere was refluxed for 4 h. After the reaction was cooled to room temperature, solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography (20-50% EtOAc/hexanes) to afford triazole **11** (23 mg, 72%) as a colorless oil. Triazole **11**: R_f = 0.45 (100% EtOAc); IR (neat) 2923 cm^{-1}; HRMS (ESI) *m/z* calculated for $C_7H_{10}N_3O$ $(M+H)^+$ 152.0824, found: 152.0824; ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 (s, 1H), 5.99 (ddd, *J* = 17.4, 10.4, 7.2 Hz, 1H), 5.37-5.47 (m, 2H), 5.06 (q, *J* = 6.1 Hz, 1H), 4.94 (s, 2H), 4.12 (dd, *J* = 12.1, 4.3 Hz, 1H), 3.90 (dd, *J* = 12.1, 6.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.3, 130.4, 128.1, 120.7, 68.3, 62.5, 58.6.



S2a-g

	R^1	R^2	R^3	Yield (%)
S2a	H	Me	H	31
S2b	H	Ph	H	30
S2c	H	Ph	Me	5
S2d	Et	Me	H	5
S2e	Me	Et	H	15
S2f	Ph	Me	H	20
S2g	Ph	^{i}Pr	H	11

Compounds **S2a-g** were prepared using the following general procedure.

3-Butyn-2-ol (2.0 g, 2.23 mL, 2.85 mmol) was added dropwise via syringe to a suspension of NaH (60% in oil, 1.14 g, 2.85 mmol) in dry THF (25 mL) at 0 °C. The mixture was stirred at 0 °C for 30 min and then (*E*)-1,4-dibromo-2-butene (13.41 g, 6.27 mmol) was added and the reaction was heated at 50 °C for 24 h. The mixture was allowed to cool and then quenched with a mixture of Et_2O and H_2O and then poured onto Et_2O and 2M aqHCl. The aqueous layer was extracted with Et_2O (3 × 10 mL) and the combined organic layer was washed with water (1 × 20 mL) and brine, and dried (Na_2SO_4). Filtration and concentration gave a residue, which was purified by automated chromatography (Silica column, hexane/EtOAc 9.5:0.5) to give (*E*)-1-bromo-4-(but-3-yn-2-yloxy)but-2-ene (**S2a**, 1.82 g, 31%) as colorless oil. Compound **S2f** matches the literature characteristic.[S1]

(*E*)-1-Bromo-4-(but-3-yn-2-yloxy)but-2-ene (S2a). Obtained as colorless oil. R_f = 0.6 (10% EtOAc/hexanes); IR (neat) 3295, 2985, 1648 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.98 (dtt, *J* = 14.0, 7.3, 1.4 Hz, 1H), 5.86 (dddt, *J* = 15.0, 6.0, 5.2, 0.9 Hz, 1H), 4.32 – 4.23 (m, 1H), 4.19 (qd, *J* = 6.6, 2.0 Hz, 1H), 4.01 – 3.94 (m, 3H), 2.43 (d, *J* = 2.0 Hz, 1H), 1.45 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 131.4, 129.1, 83.6, 73.4, 68.0, 64.8, 32.0, 22.1.

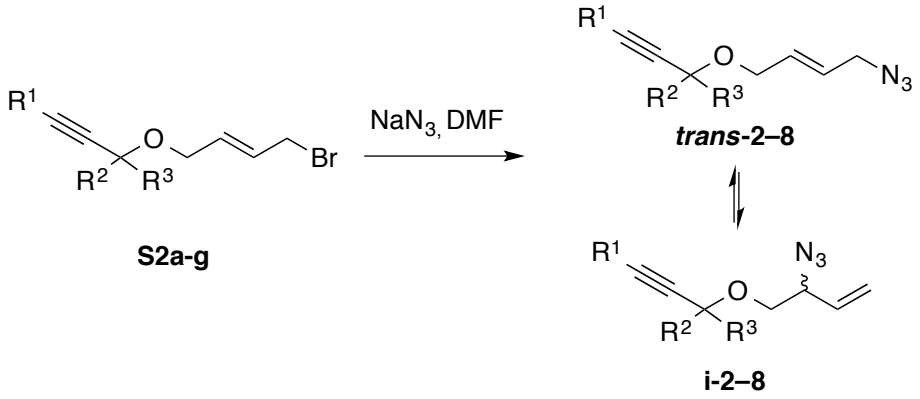
(*E*)-(1-(4-Bromobut-2-enyloxy)prop-2-ynyl)benzene (S2b). Obtained as colorless oil. R_f = 0.70 (10% EtOAc/hexanes); IR (neat) 3290, 2857, 1648 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (ddd, *J* = 7.6, 1.5, 0.7 Hz, 2H), 7.46 – 7.29 (m, 3H), 6.11 – 5.81 (m, 2H), 5.20 (d, *J* = 2.2 Hz, 1H), 4.26 – 4.17 (m, 1H), 4.17 – 4.05 (m, 1H), 3.96 (dd, *J* = 7.3, 0.8 Hz, 2H), 2.66 (d, *J* = 2.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.0, 131.2, 128.7, 128.6, 128.0, 127.5, 84.0, 76.6, 70.9, 67.6, 32.0.

(*E*)-(2-(4-Bromobut-2-enyloxy)but-3-yn-2-yl)benzene (S2c). Obtained as colorless oil. R_f = 0.7 (10% EtOAc/hexanes); IR (neat) 3291, 2988, 1446 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.48 (m, 2H), 7.40 – 7.34 (m, 2H), 7.33 – 7.28 (m, 1H), 6.00 – 5.90 (m, 1H), 5.90 – 5.81 (m, 1H), 4.24 – 4.05 (m, 1H), 4.05 – 3.85 (m, 2H), 3.79 – 3.58 (m, 1H), 2.73 (s, 1H), 1.76 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.4, 132.0, 128.5, 128.2, 128.1, 126.0, 83.9, 76.2, 75.8, 64.8, 32.9, 32.4.

(*E*)-2-(4-Bromobut-2-enyloxy)hex-3-yne (S2d). Obtained as colorless oil. R_f = 0.70 (10% EtOAc/hexanes); IR (neat) 2981, 1371 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.08 – 5.79 (m, 2H), 4.30 – 4.10 (m, 2H), 4.02 – 3.90 (m, 3H), 2.22 (qd, *J* = 7.5, 1.9 Hz, 2H), 1.41 (d, *J* = 6.5 Hz, 3H), 1.14 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 131.8, 128.8, 87.4, 79.1, 67.8, 65.2, 32.2, 22.6, 14.1, 12.5.

(*E*)-4-(4-Bromobut-2-enyloxy)hex-2-yne (S2e). Obtained as colorless oil. R_f = 0.70 (10% EtOAc/hexanes); IR (neat) 2969, 1724, 1458 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.07 – 5.78 (m, 2H), 4.34 – 4.19 (m, 1H), 4.03 – 3.88 (m, 4H), 1.86 (d, *J* = 2.1 Hz, 3H), 1.79 – 1.61 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 131.9, 128.7, 82.1, 78.1, 70.9, 67.9, 32.3, 29.2, 9.9, 3.7.

(*E*)-(3-(4-Bromobut-2-enyloxy)-4-methylpent-1-ynyl)benzene (S2g). Obtained as colorless oil. R_f = 0.75 (10% EtOAc/hexanes); IR (neat) 2962, 1489 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.41 (m, 2H), 7.31 (dd, *J* = 4.0, 2.6 Hz, 3H), 6.20 – 5.77 (m, 2H), 4.39 – 4.31 (m, 1H), 4.13 – 4.02 (m, 2H), 3.98 (d, *J* = 7.3 Hz, 2H), 2.08 – 1.99 (m, 1H), 1.11 – 1.03 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.0, 131.9, 128.7, 128.4, 128.3, 123.0, 87.1, 86.8, 75.4, 68.3, 33.5, 32.3, 18.8, 18.1.



S2a-g

	R^1	R^2	R^3	Yield (%)
2	H	Me	H	75
3	H	Ph	H	70
4	H	Ph	Me	89
5	Et	Me	H	64
6	Me	Et	H	56
7	Ph	Me	H	52
8	Ph	^{i}Pr	H	43

Compounds **2-8** were prepared using the following general procedure.

A suspension of (*E*)-1-bromo-4-(but-3-yn-2-yloxy)but-2-ene (**S2a**, 1.47 g, 7.23 mmol) and sodium azide (1.41 g, 2.17 mmol) in DMF (40 mL) was stirred for 3 h at room temperature. Saturated aq NH_4Cl was added. The aqueous layer was extracted with Et_2O (3 × 10 mL) and the combined organics washed with water (1 × 20 mL) and brine, and dried over Na_2SO_4. Filtration and concentration gave a residue, which

was purified by automated chromatography (Silica column, hexane/EtOAc 9.5:0.5) to give mixture of azides ***trans*-2**, and **i-2** (0.89 g, 75%, 67:33) as colorless oil.

(*E*)-1-Azido-4-(but-3-yn-2-yloxy)but-2-ene (*trans*-2), 3-azido-4-(but-3-yn-2-yloxy)but-1-ene (i-2). Obtained as colorless oil . Azides ***trans*-2** and **i-2** (67:33): R_f = 0.5 (10% EtOAc/hexanes); IR (neat) 2100 cm^{-1}; HRMS (ESI) m/z calculated for $(C_8H_{11}N_3O+H)^+$ 166.0980, found: 166.0976. Azide ***trans*-2**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.94 – 5.75 (m, 2H), 4.34 – 4.24 (m, 1H), 4.20 (qd, *J* = 6.6, 2.0 Hz, 1H), 4.06 – 3.92 (m, 1H), 3.83 – 3.76 (m, 2H), 2.43 (d, *J* = 2.0 Hz, 1H), 1.46 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 131.4, 126.3, 83.6, 73.3, 68.2, 64.7, 52.4, 22.1. Azide **i-2** (diagnostic peaks only): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.90 (d, *J* = 7.4 Hz, 1H), 3.51 (dd, *J* = 10.0, 4.3 Hz, 1H), 3.39 (dd, *J* = 9.9, 8.0 Hz, 1H).

(*E*)-(1-(4-Azidobut-2-enyloxy)prop-2-ynyl)benzene (*trans*-3), (1-((2-azidobut-3-en-1-yl)oxy)prop-2-yn-1-yl)benzene (i-3). Obtained as colorless oil . Azides ***trans*-3** and **i-3** (84:16): R_f = 0.6 (10% EtOAc/hexanes); IR (neat) 2097 cm^{-1}; HRMS (ESI) m/z calculated for $(C_{13}H_{13}N_3O+H)^+$ 228.1137, found: 228.1152. Azide ***trans*-3**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 8.1, 1.4 Hz, 2H), 7.47 – 7.30 (m, 3H), 6.03 – 5.74 (m, 2H), 5.22 (d, *J* = 2.2 Hz, 1H), 4.24 (ddt, *J* = 7.2, 5.1, 1.0 Hz, 1H), 4.14 (ddd, *J* = 6.4, 4.8, 0.7 Hz, 1H), 3.80 (d, *J* = 5.5 Hz, 2H), 2.66 (d, *J* = 2.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.1, 131.2, 128.8, 128.8, 127.6, 126.6, 81.5, 76.1, 70.8, 67.8, 52.4. Azide **i-3** (diagnostic peaks only): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.75 (ddd, *J* = 13.9, 6.9, 3.4 Hz, 2H), 5.40 (q, *J* = 1.1 Hz, 1H), 5.35 (q, *J* = 1.1 Hz, 1H), 5.33 (t, *J* = 1.1 Hz, 1H), 5.30 (t, *J* = 1.2 Hz, 1H), 3.74 (dd, *J* = 9.9, 4.2 Hz, 1H), 3.69 – 3.60 (m, 2H), 3.55 (dd, *J* = 9.9, 7.7 Hz, 1H), 2.68 (d, *J* = 2.2 Hz, 2H).

(*E*)-(2-((4-Azidobut-2-en-1-yl)oxy)but-3-yn-2-yl)benzene (*trans*-4), (2-((2-azidobut-3-en-1-yl)oxy)but-3-yn-2-yl)benzene (i-4). Obtained as colorless oil . Azides ***trans*-4** and **i-4** (64:36): R_f = 0.6 (10% EtOAc/hexanes); IR (neat) 2101 cm^{-1}; HRMS (ESI) m/z calculated for $(C_{14}H_{15}N_3O+H)^+$ 242.1293, found: 242.1322. Azide ***trans*-4**: ^{1}H NMR (400 MHz, $CDCl_3$) δ .68 – 7.57 (m, 2H), 7.38 (tt, *J* = 6.6, 1.0 Hz, 2H), 7.34 – 7.28 (m, 1H), 5.96 – 5.72 (m, 2H), 4.21 – 4.10 (m, 1H), 3.78 (dd, *J* = 5.9, 1.3 Hz, 2H), 3.75 – 3.66 (m, 1H), 2.74 (s, 1H), 1.77 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.4, 132.0, 128.5, 128.1, 126.0, 125.3, 83.9, 76.2, 75.8, 64.9, 52.5, 33.0. Azide **i-4** (diagnostic peaks only): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.46 (m, 1H), 3.27 (dd, *J* = 9.7, 4.3 Hz, 1H), 3.18 (dd, *J* = 9.8, 7.9 Hz, 1H).

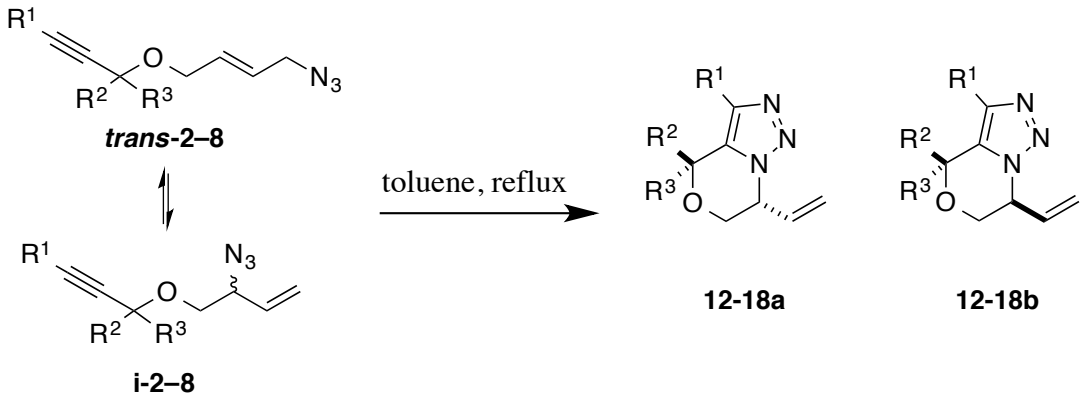
(*E*)-2-((4-Azidobut-2-en-1-yl)oxy)hex-3-yne (*trans*-5), 2-((2-azidobut-3-en-1-yl)oxy)hex-3-yne (i-5). Obtained as colorless oil . Azides ***trans*-5** and **i-5** (69:31): R_f = 0.6 (10% EtOAc/hexanes); IR (neat) 2098 cm^{-1}; HRMS (ESI) m/z calculated for $(C_{10}H_{15}N_3O+H)^+$ 194.1293, found: 194.1302. Azide ***trans*-5**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.96 – 5.72 (m, 2H), 4.32 – 4.22 (m, 1H), 4.18 (qt, *J* = 6.5, 1.9 Hz, 1H), 4.04 – 3.92 (m, 1H), 3.83 – 3.75 (m, 2H), 2.22 (qd, *J* = 7.5, 1.9 Hz, 2H), 1.41 (d, *J* = 6.6 Hz, 3H), 1.14 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 131.8, 125.9, 87.4, 79.2, 67.9, 65.1, 52.5, 22.6, 14.1, 12.5. Azide **i-5** (diagnostic peaks only): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.42 – 5.28 (m, 3H), 3.73 (dd, *J* = 10.1, 7.3 Hz, 1H), 3.49 (dd, *J* = 10.1, 4.4 Hz, 1H), 3.37 (dd, *J* = 10.0, 8.0 Hz, 1H), 2.77 – 2.64 (m, 1H).

(*E*)-4-((4-Azidobut-2-en-1-yl)oxy)hex-2-yne (*trans*-6), 4-((2-azidobut-3-en-1-yl)oxy)hex-2-yne (i-6). Obtained as colorless oil . Azides ***trans*-6** and **i-6** (86:14): R_f = 0.55 (10% EtOAc/hexanes); IR (neat) 2099 cm^{-1}; HRMS (ESI) m/z calculated for $(C_{10}H_{15}N_3O+H)^+$ 194.1293, found: 194.1288. Azide ***trans*-6**: ^{1}H NMR

(400 MHz, $CDCl_3$) δ 5.95 – 5.73 (m, 2H), 4.32 – 4.20 (m, 1H), 4.04 – 3.91 (m, 2H), 3.79 (d, *J* = 5.7 Hz, 2H), 1.86 (d, *J* = 2.0 Hz, 3H), 1.79 – 1.61 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 131.9, 125.8, 82.1, 78.1, 70.8, 68.0, 52.5, 29.2, 9.9, 3.7. Azide **i-6** (diagnostic peaks only): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.44 – 5.24 (m, 4H), 3.48 (dd, *J* = 10.0, 4.4 Hz, 1H), 3.36 (dd, *J* = 10.0, 8.0 Hz, 1H).

(*E*)-(3-(4-Azidobut-2-enyloxy)but-1-ynyl)benzene (*trans*-7), (3-((2-azidobut-3-en-1-yl)oxy)but-1-yn-1-yl)benzene (i-7). Obtained as colorless oil . Azides ***trans*-7** and **i-7** (81:19): R_f = 0.6 (10% EtOAc/hexanes); IR (neat) 2095 cm^{-1}; HRMS (ESI) m/z calculated for $(C_{14}H_{15}N_3O+H)^+$ 242.1293, found: 242.1303. Azide ***trans*-7**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.37 (m, 2H), 7.36 – 7.29 (m, 3H), 6.06 – 5.75 (m, 2H), 4.44 (q, *J* = 6.6 Hz, 1H), 4.35 (ddd, *J* = 13.0, 4.8, 1.1 Hz, 1H), 4.08 (ddd, *J* = 13.0, 5.7, 0.9 Hz, 1H), 3.80 (d, *J* = 5.7 Hz, 2H), 1.55 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 131.9, 131.6, 128.5, 128.4, 126.2, 122.8, 100.1, 88.9, 85.4, 68.3, 65.4, 52.5, 22.3. Azide **i-7** (diagnostic peaks only): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.48 – 5.38 (m, 1H), 5.33 (ddt, *J* = 17.0, 2.2, 1.1 Hz, 2H), 5.30 – 5.23 (m, 2H), 3.83 (dd, *J* = 10, 4.1 Hz, 1H), 3.53 (dd, *J* = 10.0, 4.3 Hz, 1H), 3.41 (dd, *J* = 10.0, 8.0 Hz, 1H).

(*E*)-(3-((4-Azidobut-2-en-1-yl)oxy)-4-methylpent-1-yn-1-yl)benzene (*trans*-8), (3-((2-azidobut-3-en-1-yl)oxy)-4-methylpent-1-yn-1-yl)benzene (i-8). Obtained as colorless oil . Azides ***trans*-8** and **i-8** (74:26): R_f = 0.65 (10% EtOAc/hexanes); IR (neat) 2099 cm^{-1}; HRMS (ESI) m/z calculated for $(C_{16}H_{19}N_3O+H)^+$ 270.1606, found: 270.1614. Azide ***trans*-8**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (ddd, *J* = 3.7, 2.7, 1.1 Hz, 2H), 7.39 – 7.28 (m, 3H), 6.01 – 5.76 (m, 2H), 4.43 – 4.30 (m, 1H), 4.15 – 4.01 (m, 2H), 3.86 – 3.74 (m, 2H), 2.04 (pd, *J* = 6.8, 5.8 Hz, 1H), 1.07 (dd, *J* = 11.0, 6.8 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 131.9, 131.9, 128.4, 125.8, 123.0, 87.1, 86.7, 75.3, 68.5, 52.5, 33.5, 18.8, 18.1. Azide **i-8** (diagnostic peaks only): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.45 – 5.26 (m, 4H), 3.94 (dd, *J* = 9.9, 4.0 Hz, 1H), 3.87 (dd, *J* = 10.0, 7.0 Hz, 1H), 3.58 (dd, *J* = 10.0, 4.4 Hz, 1H), 3.46 (dd, *J* = 10.0, 8.0 Hz, 1H).

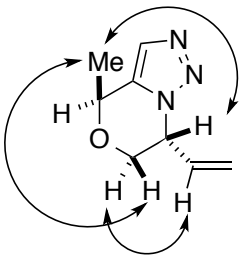


	R^1	R^2	R^3	Yield (%)	dr (a:b)
12	H	Me	H	85	1.7:1
13	H	Ph	H	83	1.4:1
14	H	Ph	Me	76	1.3:1
15	Et	Me	H	93	1.9:1
16	Me	Et	H	88	1.5:1
17	Ph	Me	H	84	2:1
18	Ph	^{i}Pr	H	84	1.5:1

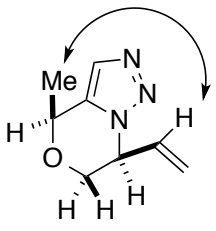
Compounds **12-18** were prepared using the following general procedure.

(*E*)-1-Azido-4-(but-3-yn-2-yloxy)but-2-ene (***trans*-2**, 0.22 g) was dissolved in toluene (15 mL). The reaction mixture was heated at reflux for 1 h. The solvent was evaporated after cooling the reaction mixture to room temperature. The residue was purified by automated chromatography (Silica column, hexane:EtOAc/9:1) to give **12a** (0.13 g, 58%) and **12b** (0.06 g, 27%) as colorless solid.

(4*S,7*R**)-4-Methyl-7-vinyl-6,7-dihydro-4*H*-[1,2,3]triazolo[5,1-*c*][1,4]oxazine (12a), (4*S**,7*S**)-4-methyl-7-vinyl-6,7-dihydro-4*H*-[1,2,3]triazolo[5,1-*c*][1,4]oxazine (12b). 12a**: Obtained as colorless solid (0.13, 57%). R_f = 0.3 (10% EtOAc/hexanes); mp 82-84 °C; IR (neat) 2985 cm^{-1}; HRMS (ESI) m/z calculated for $(C_8H_{11}N_3O+H)^+$ 166.0980, found: 166.0976. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 1.0 Hz, 1H), 5.93 (ddd, *J* = 17.1, 10.3, 7.8 Hz, 1H), 5.66 – 5.45 (m, 2H), 4.98 (dddq, *J* = 9.8, 7.8, 5.0, 1.0 Hz, 1H), 4.89 (qt, *J* = 6.5, 1.0 Hz, 1H), 4.23 (dd, *J* = 12.2, 5.0 Hz, 1H), 3.69 (dd, *J* = 12.2, 10.0 Hz, 1H), 1.57 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.7, 131.2, 128.8, 122.1, 69.4, 68.1, 59.3, 20.4. **12b**: Obtained as colorless oil (0.62, 28%). R_f = 0.25 (10% EtOAc/Hexane); IR (neat) 2973 cm^{-1}; HRMS (ESI) m/z calculated for $(C_8H_{11}N_3O+H)^+$ 166.0980, found: 166.0990; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, *J* = 0.9 Hz, 1H), 6.05 (ddd, *J* = 17.0, 10.4, 6.6 Hz, 1H), 5.35 (ddd, *J* = 10.3, 1.2, 0.7 Hz, 1H), 5.16 (ddd, *J* = 17.1, 1.3, 0.6 Hz, 1H), 5.06 (ddd, *J* = 6.7, 3.4, 1.6 Hz, 1H), 4.90 (qt, *J* = 6.6, 0.9 Hz, 1H), 4.19 (dd, *J* = 12.1, 1.6 Hz, 1H), 4.03 (dd, *J* = 12.1, 3.6 Hz, 1H), 1.58 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.3, 134.4, 128.5, 119.3, 69.3, 67.6, 57.8, 20.7. The following NOE correlations were used to assign **12a** and **12b**:

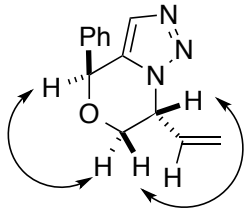


12a

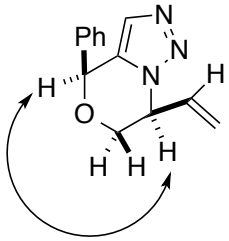


12b

(4*S*,7R)-4-Phenyl-7-vinyl-6,7-dihydro-4*H*-[1,2,3]triazolo[5,1-*c*][1,4]oxazine (13a), (4*S*,7S**)-4-phenyl-7-vinyl-6,7-dihydro-4*H*-[1,2,3]triazolo[5,1-*c*][1,4]oxazine (13b). 13a**: Obtained as colorless solid (0.06, 46%). R_f = 0.3 (10% EtOAc/hexanes); mp 65-67 °C; IR (neat) 2859, 1454 cm^{-1}; HRMS (ESI) m/z calculated for $(C_{13}H_{13}N_3O+H)^+$ 228.1137, found: 228.1138. ^{1}H NMR (400 MHz, $CDCl_3$) δ7.46 – 7.38 (m, 3H), 7.38 – 7.32 (m, 2H), 7.31 (d, *J* = 0.7 Hz, 1H), 6.02 (ddd, *J* = 17.3, 10.3, 7.7 Hz, 1H), 5.82 (s, 1H), 5.57 (t, *J* = 13.8 Hz, 2H), 5.20 – 5.08 (m, 1H), 4.32 (dd, *J* = 12.2, 4.9 Hz, 1H), 3.87 (dd, *J* = 12.2, 9.1 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.7, 134.0, 131.5, 130.6, 129.7, 129.1, 127.9, 122.1, 75.7, 67.8, 59.4, 29.9. **13b**: Obtained as colorless solid (0.05, 38%). R_f = 0.25 (10% EtOAc/Hexane); mp 136-138 °C; IR (neat) 1074 cm^{-1}; HRMS (ESI) m/z calculated for $(C_{13}H_{13}N_3O+H)^+$ 228.1137, found: 228.1137; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 – 7.37 (m, 3H), 7.37 – 7.31 (m, 2H), 6.13 (ddd, *J* = 17.0, 10.4, 6.5 Hz, 1H), 5.84 (s, 1H), 5.43 (dd, *J* = 10.4, 0.5 Hz, 1H), 5.35 – 5.25 (m, 1H), 5.22 – 5.12 (m, 1H), 4.20 (ddd, *J* = 15.9, 12.2, 3.2 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.8, 134.1, 129.7, 129.2, 127.9, 119.9, 75.5, 67.3, 58.2, 29.9. The following NOE correlations were used to assign **13a** and **13b**:

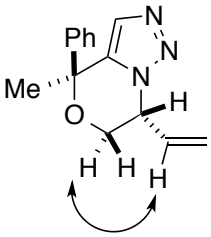


13a

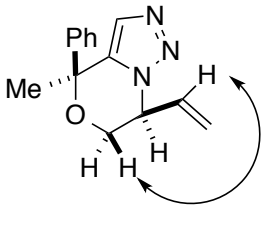


13b

(4*S*,7R)-4-Methyl-4-phenyl-7-vinyl-6,7-dihydro-4*H*-[1,2,3]triazolo[5,1-*c*][1,4]oxazine (14a), (4*S*,7S**)-4-methyl-4-phenyl-7-vinyl-6,7-dihydro-4*H*-[1,2,3]triazolo[5,1-*c*][1,4]oxazine (14b).** Obtained as colorless oil (0.07, 76%). R_f = 0.3 (10% EtOAc/hexanes); IR (neat) 2925 cm^{-1}; HRMS (ESI) m/z calculated for $(C_{14}H_{15}N_3O+H)^+$ 242.1293, found: 242.1318. **14a:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.40 – 7.28 (m, 5H), 5.88 – 5.70 (m, 1H), 5.58 – 5.43 (m, 2H), 5.01 – 4.97 (m, 1H), 4.00 (dd, *J* = 12.4, 5.3 Hz, 1H), 3.53 (dd, *J* = 12.5, 10.2 Hz, 1H), 1.83 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.2, 136.7, 131.3, 130.7, 128.9, 128.5, 125.9, 122.1, 63.8, 57.9, 31.6. **14b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.39 – 7.29 (m, 5H), 6.12 (ddd, *J* = 17.0, 10.4, 6.6 Hz, 1H), 5.38 (d, *J* = 10.4 Hz, 1H), 5.23 – 5.13 (m, 1H), 5.08 – 5.02 (m, 1H), 3.95 (dd, *J* = 12.4, 1.4 Hz, 1H), 3.88 (dd, *J* = 12.4, 3.6 Hz, 1H), 1.84 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.1, 136.3, 134.6, 131.0, 128.8, 128.5, 125.9, 119.1, 63.7, 59.3, 31.4. The following NOE correlations were used to assign **14a** and **14b**:

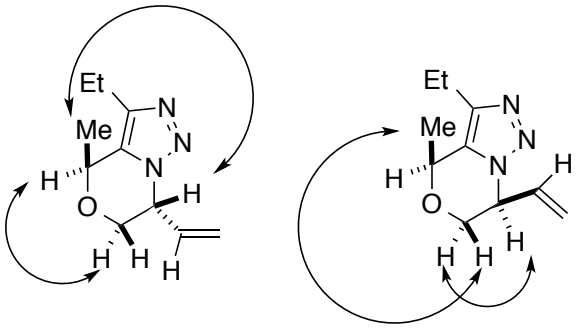


14a



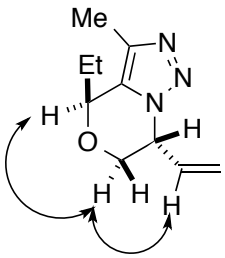
14b

(4*S,7*R**)-3-Ethyl-4-methyl-7-vinyl-6,7-dihydro-4*H*-[1,2,3]triazolo[5,1-*c*][1,4]oxazine (15a), (4*S**,7*S**)-3-ethyl-4-methyl-7-vinyl-6,7-dihydro-4*H*-[1,2,3]triazolo[5,1-*c*][1,4]oxazine (15b)**. **15a**: Obtained as colorless oil (0.03, 63%). R_f = 0.3 (10% EtOAc/hexanes); IR (neat) 2975 cm^{-1}; HRMS (ESI) m/z calculated for $(C_{10}H_{15}N_3O+H)^+$ 194.1293, found: 194.1299. ^1H NMR (400 MHz, $CDCl_3$) δ 5.93 (ddd, *J* = 17.1, 10.3, 7.7 Hz, 1H), 5.56 – 5.43 (m, 2H), 5.06 – 4.86 (m, 2H), 4.17 (dd, *J* = 12.1, 4.7 Hz, 1H), 3.68 (dd, *J* = 12.1, 8.8 Hz, 1H), 2.70 (hept, *J* = 7.3 Hz, 2H), 1.58 (d, *J* = 6.6 Hz, 3H), 1.27 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.4, 131.8, 130.5, 121.4, 69.4, 67.3, 59.4, 19.6, 19.3, 14.1. **15b**: Obtained as colorless oil (0.01, 30%). R_f = 0.25 (10% EtOAc/Hexane); IR (neat) 2975 cm^{-1}; HRMS (ESI) m/z calculated for $(C_{10}H_{15}N_3O+H)^+$ 194.1293, found: 194.1295; ^1H NMR (500 MHz, $CDCl_3$) δ 6.06 (ddd, *J* = 17.0, 10.3, 6.5 Hz, 1H), 5.42 – 5.31 (m, 1H), 5.27 – 5.17 (m, 1H), 5.01 (dt, *J* = 5.8, 2.8 Hz, 1H), 4.93 (q, *J* = 6.6 Hz, 1H), 4.11 (dd, *J* = 12.1, 2.5 Hz, 1H), 3.97 (dd, *J* = 12.1, 3.6 Hz, 1H), 2.70 (dq, *J* = 12.9, 7.4 Hz, 2H), 1.58 (d, *J* = 6.5 Hz, 3H), 1.28 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.1, 134.1, 130.3, 119.5, 69.2, 67.0, 58.2, 19.8, 19.2, 14. The following NOE correlations were used to assign **15a** and **15b**:

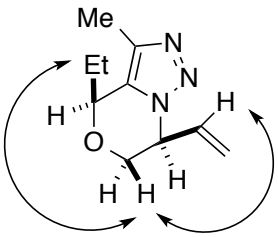


15a **15b**

(4*S,7*R**)-4-Ethyl-3-methyl-7-vinyl-6,7-dihydro-4*H*-[1,2,3]triazolo[5,1-*c*][1,4]oxazine (16a), (4*S**,7*S**)-4-ethyl-3-methyl-7-vinyl-6,7-dihydro-4*H*-[1,2,3]triazolo[5,1-*c*][1,4]oxazine (16b). 16a**: Obtained as colorless oil (0.09, 56%). R_f = 0.3 (10% EtOAc/hexanes); IR (neat) 2973 cm^{-1}; HRMS (ESI) m/z calculated for $(C_{10}H_{15}N_3O+H)^+$ 194.1293, found: 194.1291. ^1H NMR (400 MHz, $CDCl_3$) δ 5.92 (ddd, *J* = 17.1, 10.3, 7.7 Hz, 1H), 5.57 – 5.38 (m, 2H), 4.94 (dddd, *J* = 8.9, 7.8, 4.7, 0.9 Hz, 1H), 4.79 (dd, *J* = 7.8, 3.2 Hz, 1H), 4.17 (dd, *J* = 12.1, 4.6 Hz, 1H), 3.66 (dd, *J* = 12.0, 8.9 Hz, 1H), 2.32 (d, *J* = 0.8 Hz, 3H), 2.03 (dqd, *J* = 14.8, 7.4, 3.2 Hz, 1H), 1.86 (dp, *J* = 14.7, 7.4 Hz, 1H), 0.98 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.4, 131.7, 130.0, 121.5, 74.0, 67.3, 59.6, 26.0, 11.4, 8.9. **16b**: Obtained as colorless oil (0.05, 31%). R_f = 0.25 (10% EtOAc/Hexane); IR (neat) 2973 cm^{-1}; HRMS (ESI) m/z calculated for $(C_{10}H_{15}N_3O+H)^+$ 194.1293, found: 194.1292; ^1H NMR (500 MHz, $CDCl_3$) δ 6.04 (ddd, *J* = 17.0, 10.4, 6.5 Hz, 1H), 5.35 (dt, *J* = 10.4, 0.9 Hz, 1H), 5.20 (ddd, *J* = 17.1, 1.4, 0.7 Hz, 1H), 5.05 – 4.96 (m, 1H), 4.80 (dd, *J* = 7.2, 3.2 Hz, 1H), 4.13 (dd, *J* = 12.0, 2.3 Hz, 1H), 3.95 (dd, *J* = 12.0, 3.5 Hz, 1H), 2.31 (d, *J* = 0.8 Hz, 3H), 2.01 (dtd, *J* = 14.8, 7.4, 3.3 Hz, 1H), 1.89 (dp, *J* = 14.6, 7.3 Hz, 1H), 0.95 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.2, 134.2, 129.7, 119.4, 73.8, 66.9, 58.2, 26.1, 11.3, 8.8. The following NOE correlations were used to assign **16a** and **16b**:

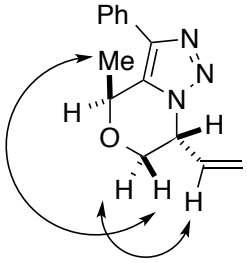


16a

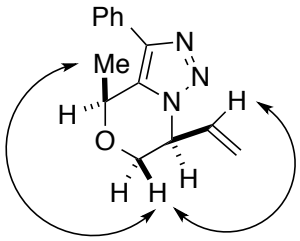


16b

(4*S,7*R**)-4-Methyl-3-phenyl-7-vinyl-6,7-dihydro-4H-[1,2,3]triazolo[5,1-c][1,4]oxazine (17a), (4*S**,7*S**)-4-methyl-3-phenyl-7-vinyl-6,7-dihydro-4H-[1,2,3]triazolo[5,1-c][1,4]oxazine (17b). 17a**: R_f = 0.3 (10% EtOAc/hexanes); mp 83-84 °C; IR (neat) 2984, 1607 cm^{-1}; HRMS (ESI) m/z calculated for $(C_{14}H_{15}N_3O+H)^+$ 242.1293, found: 242.1305. ^1H NMR (500 MHz, $CDCl_3$) δ 7.63 – 7.55 (m, 2H), 7.48 – 7.40 (m, 2H), 7.39 – 7.32 (m, 1H), 6.18 – 5.83 (m, 1H), 5.59 – 5.44 (m, 2H), 5.35 (q, *J* = 6.5 Hz, 1H), 5.21 – 4.95 (m, 1H), 4.22 (dd, *J* = 12, 4.5 Hz, 1H), 3.80 (dd, *J* = 12, 8.0 Hz, 1H), 1.43 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.4, 132.0, 131.36, 131.35, 128.85, 128.23, 127.9, 121.4, 69.8, 66.5, 59.7, 18.8. **17b**: R_f = 0.25 (10% EtOAc/Hexane); mp 103-105 °C; IR (neat) 2985, 1492 cm^{-1}; HRMS (ESI) m/z calculated for $(C_{14}H_{15}N_3O+H)^+$ 242.1293, found: 242.1308; ^1H NMR (500 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.50 – 7.39 (m, 2H), 7.39 – 7.30 (m, 1H), 6.12 (ddd, *J* = 17.0, 10.0, 6.7 Hz, 1H), 5.49 – 5.40 (m, 1H), 5.39 – 5.28 (m, 2H), 5.15 – 5.04 (m, 1H), 4.15 (dd, *J* = 12.0, 2.9 Hz, 1H), 4.06 (dd, *J* = 12.0, 3.6 Hz, 1H), 1.46 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.1, 133.7, 131.3, 131.2, 128.9, 128.2, 127.8, 120.1, 69.7, 66.5, 58.7, 19.0. The following NOE correlation were used to assign **17a** and **17b**:



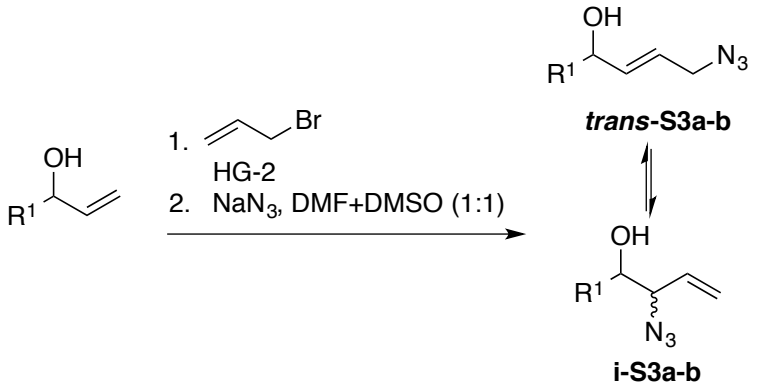
17a



17b

(4*S,7*R**)-4-*Iso*-propyl-3-phenyl-7-vinyl-6,7-dihydro-4*H*-[1,2,3]triazolo[5,1-*c*][1,4]oxazine (18a), (4*S**,7*S**)-4-*iso*-propyl-3-phenyl-7-vinyl-6,7-dihydro-4*H*-[1,2,3]triazolo[5,1-*c*][1,4]oxazine (18b). 18a**: Obtained as colorless solid (0.03, 56%). R_f = 0.3 (10% EtOAc/hexanes); mp 160-162 °C; IR (neat) 2969, 1339 cm^{-1}; HRMS (ESI) m/z calculated for $(C_{16}H_{19}N_3O+H)^+$ 270.1606, found: 270.1584. ^1H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.53 (m, 2H), 7.45 – 7.40 (m, 2H), 7.38 – 7.33 (m, 1H), 5.96 (ddd, *J* = 17.2, 10.3, 8.0 Hz, 1H), 5.69 – 5.46 (m, 2H), 5.11 (dd, *J* = 2.4, 0.9 Hz, 1H), 5.07 – 4.97 (m, 1H), 4.23 (dd, *J* = 11.9, 4.6 Hz, 1H), 3.68 (dd, *J* = 11.9, 10.0 Hz, 1H), 2.20 (pd, *J* = 7.3, 2.8 Hz, 1H), 1.05 (d, *J* = 7.0 Hz, 3H), 0.55 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.5, 131.6, 131.1, 130.2, 128.8, 128.2, 128.1, 122.0, 77.8, 67.8, 60.5, 29.9, 19.2, 15.1. **18b**: Obtained as colorless solid (0.01, 29%). R_f = 0.25 (10% EtOAc/Hexane); mp 154-156

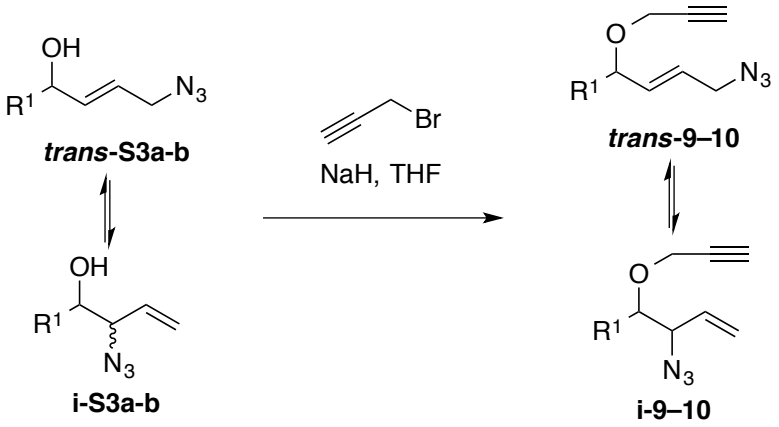
°C; IR (neat) 1091 cm^{-1}; HRMS (ESI) m/z calculated for $(C_{16}H_{19}N_3O+H)^+$ 270.1606, found: 270.1609; ^1H NMR (500 MHz, $CDCl_3$) δ 7.51 – 7.45 (m, 2H), 7.39 – 7.34 (m, 2H), 7.32 – 7.26 (m, 1H), 6.06 (ddd, *J* = 17.0, 10.4, 6.6 Hz, 1H), 5.42 – 5.20 (m, 2H), 5.03 (d, *J* = 2.4 Hz, 2H), 4.19 (dd, *J* = 11.9, 1.1 Hz, 1H), 3.96 (dd, *J* = 11.9, 3.2 Hz, 1H), 2.18 (pd, *J* = 6.9, 2.4 Hz, 1H), 1.01 (d, *J* = 7.0 Hz, 3H), 0.51 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.1, 134.3, 131.6, 130.0, 128.8, 128.2, 128.0, 119.6, 78.0, 67.3, 58.5, 29.8, 19.1, 15.5. Structures of **18a** and **18b** were defined by single X-ray crystallography.



	R^1	Yield (%)
S3a	Me	44
S3b	Ph	28

(*E*)-5-Azidopent-3-en-2-ol (*trans*-S3a), 3-azidopent-4-en-2-ol (i-S3a). To a solution of Hoveyda-Grubbs 2nd generation catalyst (HG-2) (0.21 g, 0.33 mmol) in CH_2Cl_2 (50 mL) under N_2 atmosphere at room temperature was slowly added a solution of but-3-en-2-ol (7.2 g, 100 mmol) and allyl bromide (300 mmol) in CH_2Cl_2 (10 mL). The resulting reaction mixture was stirred for 3 h. The solvent was concentrated in vacuum and the residue was dissolved in DMSO (10 mL) and DMF (10 mL), followed by addition of NaN_3 (26 g, 400 mmol) at room temperature. After being stirred for 3 h, Et_2O and H_2O were added and the aqueous layer was washed three times with Et_2O. The combined organic layers was washed with brine, dried (Na_2SO_4) and concentrated. The residue was purified by automated chromatography (Silica column, hexane/EtOAc 9.5:0.5) to give mixture of azides ***trans*-S3a**, and **i-S3a** (5.64 g, 44%, 57:43) as colorless oil. Azide ***trans*-S3a**: R_f = 0.45 (50% EtOAc/hexanes); IR (neat) 2096 cm^{-1}. HRMS (ESI) m/z calculated for $C_{10}H_{19}N_6O_2$ $(2M+H)^+$ 255.1569, found: 255.1590. ^1H NMR (400 MHz, $CDCl_3$) δ 5.77-5.86 (m, 1H), 5.64-5.75 (m, 1H), 4.27-4.37 (m, 1H), 3.74 (d, *J* = 5.7 Hz, 2H), 2.46 (br, 1H), 1.23-1.29 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.5, 122.4, 67.7, 52.1, 23.3. Azide **i-S3a**: ^1H NMR (400 MHz, $CDCl_3$) δ 5.84 (ddd, *J* = 17.2, 10.3, 8.2 Hz, 1H), 5.76 (ddd, *J* = 16.6, 10.6, 8.2 Hz, 1H), 5.44 (d, *J* = 10.1 Hz, 1H), 5.38 (d, *J* = 17.1 Hz, 1H), 5.33-5.40 (m, 2H), 3.86-3.91 (m, 1H), 3.80-3.85 (m, 1H), 3.74 (t, *J* = 7.6 Hz, 1H), 3.63-3.70 (m, 1H), 2.53 (br, 1H), 2.20 (br, 1H), 1.17 (d, *J* = 6.2 Hz, 3H), 1.17 (d, *J* = 6.3 Hz, 3H).

(*E*)-4-Azido-1-phenylbut-2-en-1-ol (*trans*-S3b), 2-azido-1-phenylbut-3-en-1-ol (i-S3b). Obtained as colorless oil . Azides ***trans*-S3b** and **i-S3b** (81:19): R_f = 0.3 (10% EtOAc/hexanes); IR (neat) 2097 cm^{-1}. Azide ***trans*-S3b**: ^1H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.28 (m, 5H), 5.99 (ddt, *J* = 15.3, 5.6, 1.2 Hz, 1H), 5.85 (dtd, *J* = 15.4, 6.2, 1.3 Hz, 1H), 5.30 – 5.23 (m, 1H), 3.81 (dt, *J* = 6.4, 1.0 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.4, 137.3, 128.8, 128.1, 126.4, 124.1, 74.3, 52.2. Azide **i-S3b** (diagnostic peaks only): ^1H NMR (400 MHz, $CDCl_3$) δ 5.74 – 5.61 (m, 2H), 4.73 (d, *J* = 5.2 Hz, 1H), 4.57 (d, *J* = 7.2 Hz, 1H).



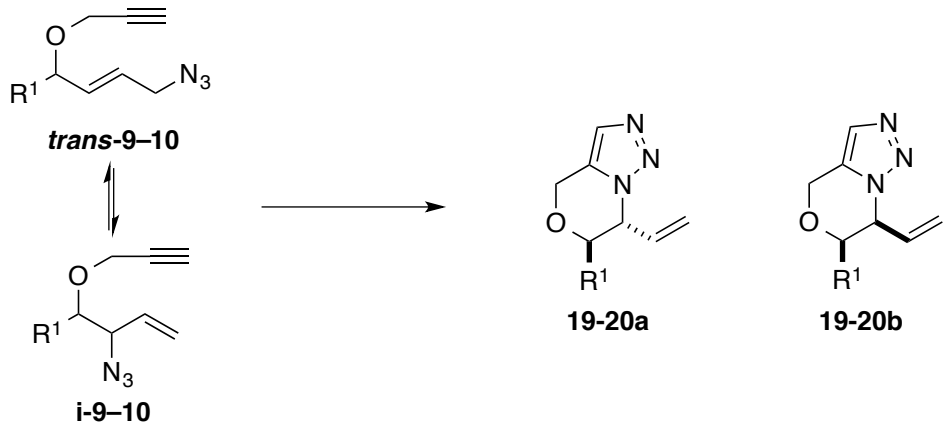
	R^1	Yield (%)
9	Me	34
10	Ph	41

Compounds **9-10** were prepared using the following general procedure:

Allylic azides ***trans*-S3a** and **i-S3a** (1.0 g, 7.86 mmol) were added dropwise via syringe to a suspension of NaH (60% in mineral oil, 0.47 g, 11.7 mmol) in dry THF (40 mL) at 0 °C. The mixture was stirred at 0 °C for 30 min and then propargyl bromide (80 wt% in toluene, 1.86 g, 15.7 mmol) was added and the reaction was stirred at room temperature for 12 h. The reaction mixture was quenched with a mixture of Et_2O and H_2O and then poured onto Et_2O and 2M aq HCl. The aqueous layer was extracted with Et_2O (3 X 10 mL) and the combined organic layer was washed with water (1 × 20 mL) and brine, and dried (Na_2SO_4). Filtration and concentration gave a residue, which was purified by automated chromatography (Silica column, hexane/EtOAc 9.5:0.5) to give azides ***trans*-9**, and **i-9** (0.44 g, 34%, 88:12) as colorless oil.

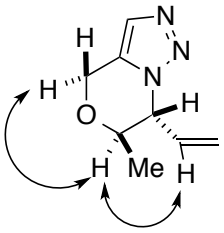
(*E*)-1-Azido-4-(prop-2-yn-1-yloxy)pent-2-ene (*trans*-9), 3-azido-4-(prop-2-yn-1-yloxy)pent-1-ene (i-9). Obtained as colorless oil . Azides ***trans*-9** and **i-9**: R_f = 0.6 (10% EtOAc/hexanes); IR (neat) 2100 cm^{-1}; HRMS (ESI) m/z calculated for $(C_8H_{11}N_3O+H)^+$ 266.0980, found: 266.1000. Azide ***trans*-9**: ^1H NMR (400 MHz, $CDCl_3$) δ 5.83 – 5.70 (m, 1H), 5.64 (ddt, *J* = 15.4, 7.4, 1.1 Hz, 1H), 4.28 – 3.95 (m, 3H), 3.88 – 3.72 (m, 2H), 2.41 (t, *J* = 2.4 Hz, 1H), 1.29 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.4, 125.8, 80.1, 74.6, 74.2, 6.4, 52.2, 21.5. Azide **i-9** (diagnostic peaks only): ^1H NMR (400 MHz, $CDCl_3$) δ 4.26 (dd, *J* = 3.5, 2.4 Hz, 1H), 4.23 (dd, *J* = 4.7, 2.4 Hz, 1H).

(*E*)-(4-Azido-1-(prop-2-yn-1-yloxy)but-2-en-1-yl)benzene (*trans*-10) (2-azido-1-(prop-2-yn-1-yloxy)but-3-en-1-yl)benzene (i-10). Obtained as colorless oil . Azides ***trans*-10** and **i-10** (74:26): R_f = 0.6 (10% EtOAc/hexanes); IR (neat) 2101 cm^{-1}; HRMS (ESI) m/z calculated for $(C_{13}H_{13}N_3O+H)^+$ 228.1137, found: 228.1164. Azide ***trans*-10**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.28 (m, 5H), 5.98 – 5.76 (m, 2H), 5.09 (dd, *J* = 6.3, 1.0 Hz, 1H), 4.18 (dd, *J* = 15.8, 2.4 Hz, 1H), 4.07 (dd, *J* = 15.8, 2.4 Hz, 1H), 3.86 – 3.74 (m, 2H), 2.44 (t, *J* = 2.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.63, 135.08, 128.80, 128.33, 127.31, 125.91, 79.97, 79.69, 74.75, 55.53, 52.31. Azide **i-10** (diagnostic peaks only): ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.61 (d, *J* = 5.6 Hz, 1H), 4.54 (d, *J* = 7.0 Hz, 1H), 4.24 (t, *J* = 2.6 Hz, 1H), 3.93 (d, *J* = 2.4 Hz, 1H), 3.89 (d, *J* = 2.3 Hz, 1H).

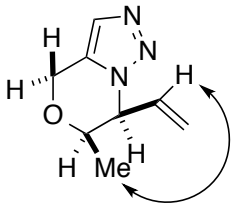


	R^1	Yield (%)	dr (a:b)
19	Me	79	1:1
20	Ph	82	1:1

(6*R,7*R**)-6-Methyl-7-vinyl-6,7-dihydro-4*H*-[1,2,3]triazolo[5,1-*c*][1,4]oxazine (19a), (6*R**,7*S**)-6-methyl-7-vinyl-6,7-dihydro-4*H*-[1,2,3]triazolo[5,1-*c*][1,4]oxazine (19b).** (*E*)-1-Azido-4-(prop-2-yn-1-yloxy)pent-2-ene (***trans*-9**, 0.43 g) was dissolved in toluene (25 mL). The reaction mixture was heated at reflux for 1 h. The solvent was evaporated after cooling the reaction mixture to room temperature. The residue was purified by automated chromatography (Silica column, hexane:EtOAc/9:1) to give **19a** (0.16 g, 38%) and **19b** (0.18, 41%) as colorless oil. **19a**: R_f = 0.3 (50% EtOAc/hexanes); IR (neat) 2984 cm^{-1}; HRMS (ESI) m/z calculated for $(C_8H_{11}N_3O+H)^+$ 166.0980, found: 166.1012. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (t, *J* = 0.9 Hz, 1H), 5.83 (ddd, *J* = 17.0, 10.1, 8.6 Hz, 1H), 5.66 – 5.54 (m, 2H), 5.06 (d, *J* = 15.0 Hz, 1H), 4.83 (dt, *J* = 15.1, 1.0 Hz, 1H), 4.55 (t, *J* = 8.9 Hz, 1H), 3.71 (dq, *J* = 9.1, 6.2 Hz, 1H), 1.41 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 131.7, 130.7, 128.3, 123.3, 74.4, 66.0, 61.8, 17.5. **19b**: R_f = 0.25 (50% EtOAc/Hexane); IR (neat) 2985 cm^{-1}; HRMS (ESI) m/z calculated for $(C_8H_{11}N_3O+H)^+$ 166.0980, found: 166.1016; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (t, *J* = 0.9 Hz, 1H), 5.89 (ddd, *J* = 17.1, 10.2, 8.1 Hz, 1H), 5.41 (dt, *J* = 10.2, 0.8 Hz, 1H), 5.29 (dt, *J* = 17.1, 1.0 Hz, 1H), 5.08 (dd, *J* = 15.1, 0.8 Hz, 1H), 4.98 – 4.91 (m, 1H), 4.85 (dt, *J* = 15.2, 0.9 Hz, 1H), 4.03 (qd, *J* = 6.5, 3.1 Hz, 1H), 1.34 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 131.2, 130.0, 127.9, 121.4, 72.8, 62.6, 62.2, 17.3. The following NOE correlations were used to assign **19a** and **19b**:

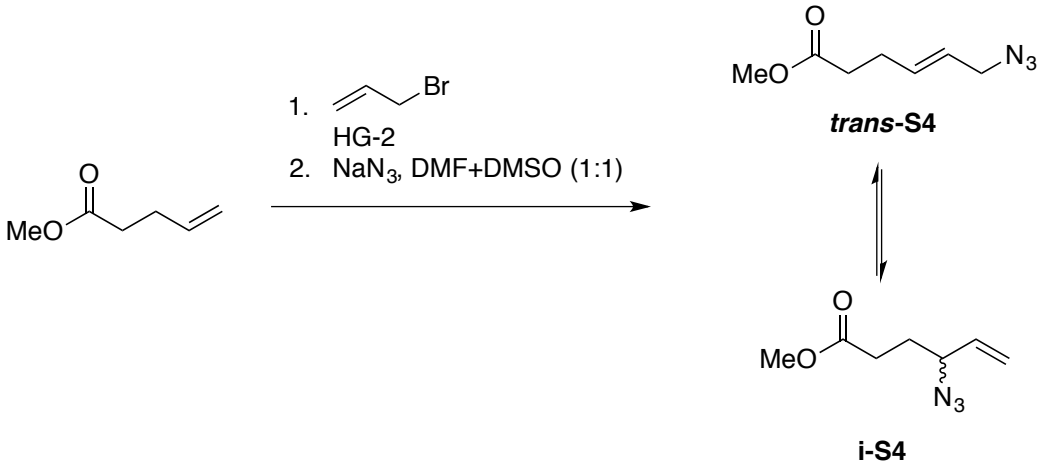


19a



19b

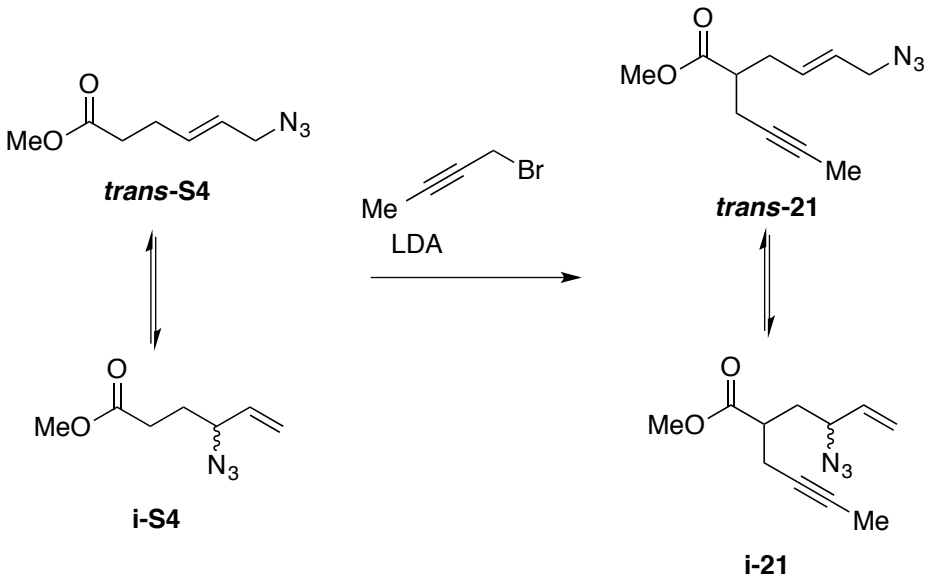
(6*R,7*R**)-6-Phenyl-7-vinyl-6,7-dihydro-4*H*-[1,2,3]triazolo[5,1-*c*][1,4]oxazine (20a), (6*R**,7*S**)-6-phenyl-7-vinyl-6,7-dihydro-4*H*-[1,2,3]triazolo[5,1-*c*][1,4]oxazine (20b).** Obtained as colorless solid. **20a** and **20b**: R_f = 0.3 (50% EtOAc/hexanes); IR (neat) 2857 cm^{-1}; HRMS (ESI) m/z calculated for $(C_{13}H_{13}N_3O+H)^+$ 228.1137, found: 228.1171. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 – 7.55 (m, 2H), 7.47 – 7.31 (m, 10H), 5.86 (ddd, *J* = 17.1, 10.3, 8.2 Hz, 1H), 5.66 (ddd, *J* = 17.0, 10.4, 6.5 Hz, 1H), 5.43 – 5.28 (m, 3H), 5.22 – 5.10 (m, 3H), 5.09 – 4.94 (m, 4H), 4.83 (dt, *J* = 17.1, 1.0 Hz, 1H), 4.58 (d, *J* = 9.0 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.1, 136.1, 130.9, 130.7, 130.6, 130.2, 129.3, 128.8, 128.7, 128.5, 128.4, 128.0, 127.8, 125.9, 123.3, 120.5, 81.1, 78.2, 65.2, 62.67, 62.65, 62.2.



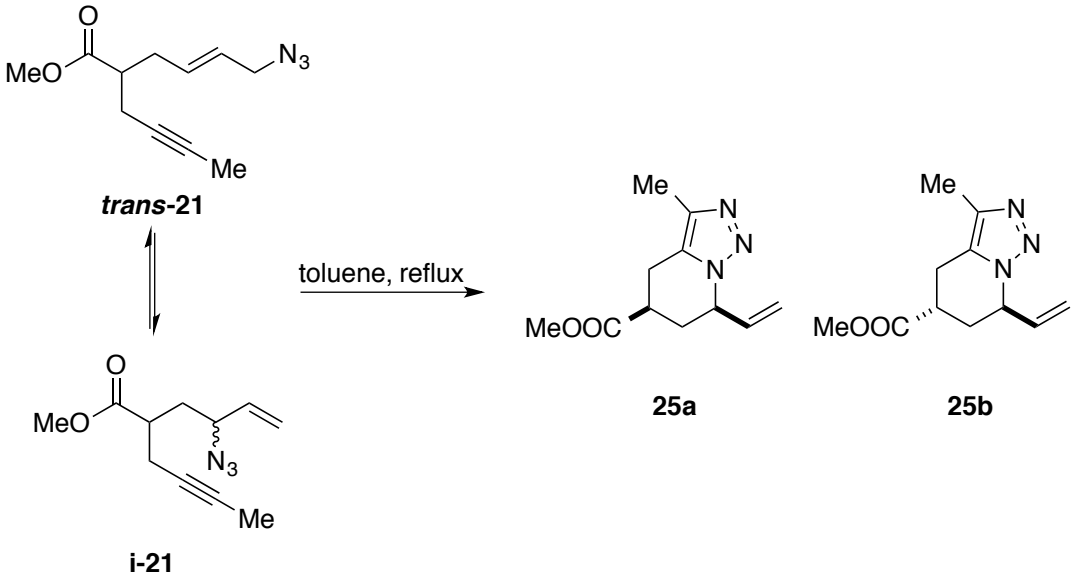
***trans*-S4**

i-S4

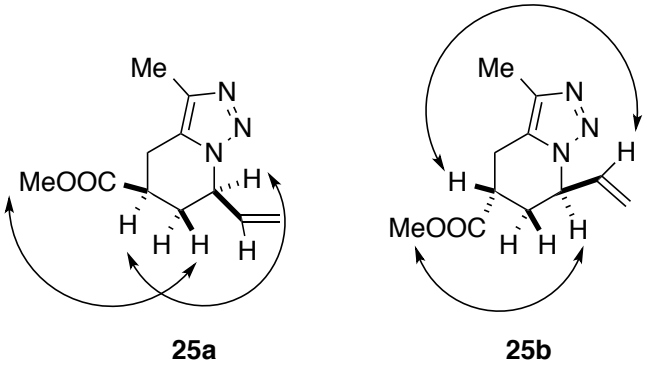
Methyl (*E*)-6-azidohex-4-enoate (*trans*-S4) methyl 4-azidohex-5-enoate (i-S4). Following the general procedure for 7a, methyl 4-pentenoate (2.0 g, 17.50 mmol), allyl bromide (6.35 g, 52.50 mmol), HG-2 (0.22 g, 0.35 mmol), and NaN_3 (4.55 g, 70 mmol) afforded azides ***trans*-S4** and **i-S4** (62:38 ratio, 1.05 g, 39%) as colorless oil. Azides ***trans*-S4** and **i-S4**: R_f = 0.3 (10% EtOAc/hexanes); IR (neat) 2098, 1738 cm^{-1}. Azide ***trans*-S4**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.86 – 5.64 (m, 1H), 5.64 – 5.48 (m, 1H), 3.87 – 3.69 (m, 2H), 3.68 (s, 3H), 2.56 – 2.32 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.31, 134.60, 124.37, 52.71, 51.79, 33.65, 27.57. Azide **i-S4** (diagnostic peaks only): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.38 – 5.25 (m, 2H), 3.92 (q, *J* = 7.3 Hz, 1H), 3.88 – 3.82 (m, 1H), 1.94 – 1.78 (m, 2H).

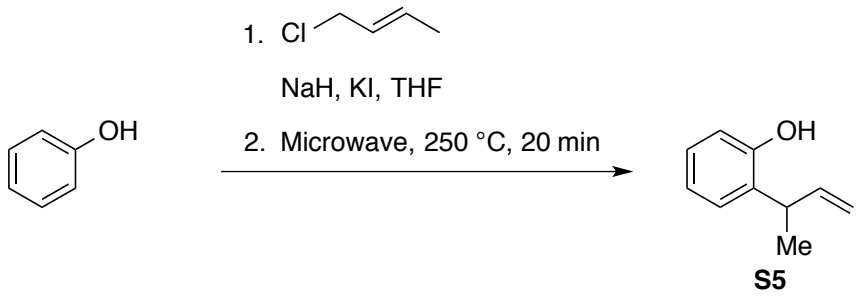


Methyl (*E*)-6-azido-2-(but-2-yn-1-yl)hex-4-enoate (*trans*-21) methyl 4-azido-2-(but-2-yn-1-yl)hex-5-enoate (i-21). To a solution of diisopropylamine (0.25 g, 2.51 mmol)in anhydrous THF (6 mL) under N_2 atmosphere at 0 °C was slowly added *n*-BuLi (0.9 mL, 2.5 M in hexane, 2.32 mmol). The ice bath was removed after 10 min and the reaction stirred for another 20 min. In another flask azides ***trans*-S4** and **i-S4** (0.3 g, 1.92 mmol) were dissolved in THF (10 mL) at -78 °C and to this prepared LDA was slowly added at -78 °C. The reaction mixture was stirred for 30 min and then propargyl bromide (80 wt% in toluene, 0.44 g, 3.28 mmol) was added. The resulting mixture was stirred for 1 h at -78 °C. NH_4Cl and H_2O were added. The aqueous layer was extracted with Et_2O (3 × 10 mL) and the combined organics washed with water (1 × 20 mL) and brine, and dried over Na_2SO_4. Filtration and concentration gave a residue, which was purified by automated chromatography (Silica column, hexane/EtOAc 9:1) to give mixture of azides ***trans*-21**, and **i-21** (0.11 g, 26%, 71:29) as colorless oil. Azides ***trans*-21** and **i-21**: R_f = 0.3 (10% EtOAc/hexanes); IR (neat) 2098, 1736 cm^{-1}; HRMS (ESI) m/z calculated for $(C_{11}H_{15}N_3O+H)^+$ 222.1243, found: 222.1233. Azide ***trans*-21**: ^1H NMR (400 MHz, $CDCl_3$) δ 5.79 – 5.50 (m, 2H), 3.77 – 3.62 (m, 5H), 2.69 – 2.55 (m, 1H), 2.54 – 2.31 (m, 4H), 1.77 (t, *J* = 2.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.4, 132.6, 126.0, 77.8, 75.7, 52.7, 52.0, 44.6, 33.7, 21.1, 3.6. Azide **i-21** (diagnostic peaks only): ^1H NMR (400 MHz, $CDCl_3$) δ 5.37 – 5.24 (m, 2H), 3.97 – 3.90 (m, 1H), 3.89 – 3.84 (m, 1H), 2.77 – 2.67 (m, 1H), 2.02 – 1.89 (m, 1H).



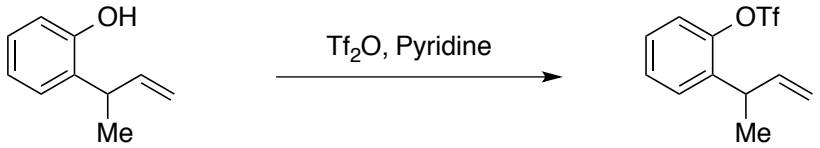
Methyl (5*R,7*R**)-3-methyl-7-vinyl-4,5,6,7-tetrahydro-[1,2,3]triazolo[1,5-*a*]pyridine-5-carboxylate (25a), methyl (5*S**,7*R**)-3-methyl-7-vinyl-4,5,6,7-tetrahydro-[1,2,3]triazolo[1,5-*a*]pyridine-5-carboxylate (25b).** Azides ***trans*-21** and **i-21** (0.10 g, 0.45 mmol) was dissolved in toluene (10 mL). The reaction mixture was heated at reflux for 24 h. The solvent was evaporated after cooling the reaction mixture to room temperature. The residue was purified by automated chromatography (Silica column, hexane:EtOAc/9:1) to give 0.08 g (80%) of the title products (anti:syn 1:1.5) as colorless yellow solid. R_f = 0.3 (50% EtOAc/hexanes); IR (neat) 1734 cm^{-1}; HRMS (ESI) m/z calculated for $(C_{11}H_{15}N_3O+H)^+$ 222.1243, found: 222.1286. **25a:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.05 (ddd, *J* = 17.4, 10.2, 7.5 Hz, 1H), 5.53 – 5.38 (m, 2H), 4.90 – 4.77 (m, 1H), 3.77 (s, 3H), 3.16 – 3.07 (m, 1H), 2.93 – 2.77 (m, 2H), 2.59 – 2.49 (m, 1H), 2.27 (d, *J* = 2.9 Hz, 3H), 2.00 (dt, *J* = 13.7, 11.7 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.4, 139.4, 135.3, 128.8, 119.5, 59.9, 52.6, 37.6, 33.1, 22.9, 10.1. **25b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.96 (ddd, *J* = 17.1, 10.6, 4.9 Hz, 1H), 5.30 (d, *J* = 9.8 Hz, 2H), 4.90 – 4.83 (m, 1H), 3.76 (s, 3H), 3.07 (dd, *J* = 16.2, 5.5 Hz, 1H), 3.03 – 2.95 (m, 1H), 2.87 (dd, *J* = 16.0, 9.9 Hz, 1H), 2.37 (d, *J* = 13.8 Hz, 1H), 2.27 (d, *J* = 2.7 Hz, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.7, 139.2, 136.0, 128.5, 118.1, 56.9, 52.6, 33.8, 30.8, 22.5, 10.1. The following NOE correlations were used to assign **25a** and **25b**:





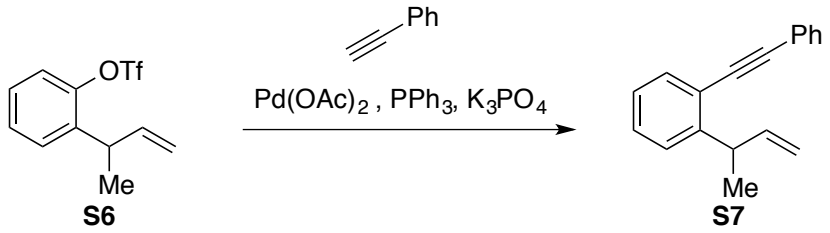
S5

2-(But-3-en-2-yl)phenol (S5). Following the general procedure for **S2a,** phenol (10 g, 106 mmol), crotyl chloride (14.43 g, 159.3 mmol), NaH (3.8 g, 159.3 mmol) afforded (*E*)-(but-2-en-1-yloxy)benzene (8.3 g), which was used as crude for the next reaction. The crude was dissolved in DMF (5 mL) and irradiated in microwave for 20 min at 250 °C. The reaction mixture was cooled and H_2O was added. The aqueous layer was extracted with Et_2O (3 × 10 mL) and the combined organics washed with water (1 × 20 mL) and brine, and dried over Na_2SO_4. Filtration and concentration gave a residue, which was purified by automated chromatography (Silica column, hexane/EtOAc 9.5:0.5) to give 2-(but-3-en-2-yl)phenol (**S5**, 5.2 g, 33%) as colorless oil. R_f = 0.30 (10% EtOAc/Hexanes); IR (neat) 3466 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ7.22 – 7.08 (m, 2H), 6.93 (td, *J* = 7.5, 1.3 Hz, 1H), 6.89 – 6.72 (m, 1H), 6.10 (ddd, *J* = 17.3, 10.3, 5.9 Hz, 1H), 5.24 – 5.19 (m, 1H), 5.19 – 5.16 (m, 1H), 5.12 (s, 1H), 3.72 (ddt, *J* = 7.4, 5.9, 1.6 Hz, 1H), 1.41 (d, *J* = 7.1 Hz, 3H).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.8, 142.5, 130.5, 128.1, 127.7, 121.1, 116.3, 114.5, 37.8, 18.9.



S5 **S6**

2-(But-3-en-2-yl)phenyl trifluoromethanesulfonate (S6). 2-(But-3-en-2-yl)phenol (**S5**, 0.74 g, 4.99 mmol) dissolved in CH_2Cl_2 (20 mL) and cooled to 0 °C. Pyridine (0.79 g, 9.98 mmol) was added to it at 0 °C and Tf_2O (1.69 g, 5.99 mmol) was added very slowly for 20 min. The reaction mixture was stirred for 10 min at 0 °C. Reaction was quenched by aq HCl. The aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL) and the combined organics washed with water (1 × 20 mL) and brine, and dried over Na_2SO_4. Filtration and concentration gave a residue, which was purified by automated chromatography (Silica column, hexane) to give **S6** (1.0 g, 71%) of as colorless oil. R_f = 0.8 (10% EtOAc/hexanes); IR (neat) 1213 cm^{-1}; HRMS (ESI) m/z calculated for $(C_{11}H_{11}F_3O_3S\text{-}H)^+$ 279.0303, found: 279.0301. ^1H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 2H), 7.32 – 7.26 (m, 2H), 5.96 (ddd, *J* = 17.2, 10.4, 5.9 Hz, 1H), 5.18 – 5.04 (m, 2H), 3.87 (qdt, *J* = 7.1, 5.8, 1.6 Hz, 1H), 1.37 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.4, 141.0, 138.3, 129.3, 128.7, 128.0, 121.4, 118.7 (*J* = 319.7), 114.7, 36.0, 20.1.

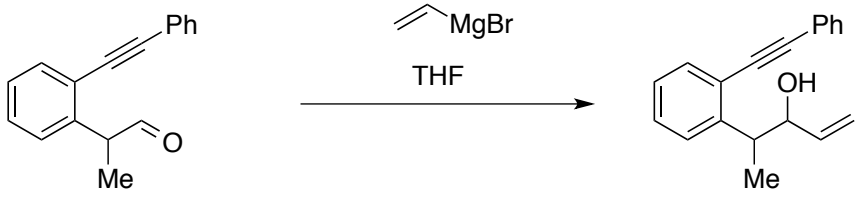


S6 **S7**

1-(But-3-en-2-yl)-2-(phenylethynyl)benzene (S7). 2-(But-3-en-2-yl)phenyl trifluoromethanesulfonate (**S6**, 1.51 g, 5.41 mmol) was dissolved in DMSO (10 mL) under N_2 atmosphere. Ethynylbenzene (0.83 g, 8.12 mmol), $Pd(OAc)_2$ (0.04 g, 0.16 mmol), PPh_3 (0.17 g, 0.65 mmol), and K_3PO_4 (2.29 g, 6.49 mmol) were added to it. The resulting reaction mixture was heated at 80 °C for 24 h. The reaction was quenched by H_2O. The aqueous layer was extracted with Et_2O (3 × 10 mL) and the combined organics washed with water (1 × 20 mL) and brine, and dried over Na_2SO_4. Filtration and concentration gave a residue, which was purified by automated chromatography (Silica column, hexane) to give **S7** (1.0 g, 80%) of as colorless oil. R_f = 0.8 (hexane); IR (neat) 1637 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.48 (m, 3H), 7.47 – 7.13 (m, 6H), 6.11 (ddd, *J* = 17.3, 10.3, 5.9 Hz, 1H), 5.26 – 5.05 (m, 2H), 4.18 (ttd, *J* = 7.1, 5.5, 1.7 Hz, 1H), 1.44 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.5, 142.4, 132.5, 131.6, 128.8, 128.5, 128.4, 126.5, 126.1, 123.6, 122.4, 113.6, 93.4, 88.2, 40.6, 19.9.

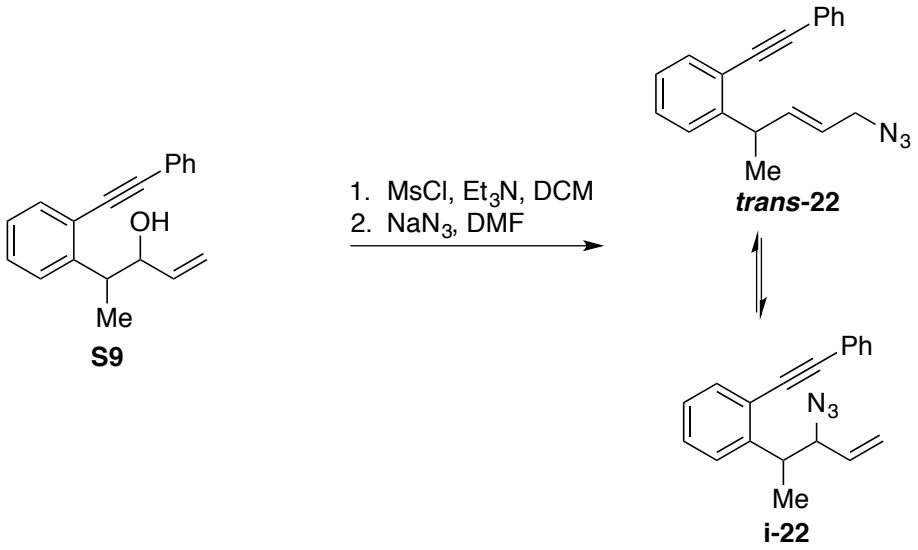
S7 **S8**

2-(2-(Phenylethynyl)phenyl)propanal (S8). 1-(But-3-en-2-yl)-2-(phenylethynyl)benzene (**S7**, 1.58 g, 6.77 mmol) was dissolved in anhydrous CH_2Cl_2 (100 mL) under N_2 atmosphere. The solution was cooled to -78 °C, and the stream of O_3/O_2 was introduced through a disposable pipet for a period of 20 min. The reaction was then purged with O_2 followed by N_2. The reaction was quenched with dimethylsulfide (2.1 g, 3.38 mmol). H_2O was added to the reaction mixture. . The aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL) and the combined organics washed with water (1 × 20 mL) and brine, and dried over Na_2SO_4. Filtration and concentration gave a residue, which was purified by automated chromatography (Silica column, hexane:EtOAc/9:1) to give **S8** (0.46 g, 29%) of as colorless oil. R_f = 0.6 (10% EtOAc/hexanes); IR (neat) 1637 cm^{-1}; HRMS (ESI) m/z calculated for $(C_{17}H_{14}O\text{-}H)^+$ 233.0967, found: 233.0951. ^1H NMR (400 MHz, $CDCl_3$) δ 9.83 (s, 1H), 7.64 – 7.60 (m, 1H), 7.56 – 7.50 (m, 2H), 7.40 – 7.34 (m, 4H), 7.31 (td, *J* = 7.5, 1.5 Hz, 1H), 7.18 (dd, *J* = 7.6, 1.4 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 1H), 1.51 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.3, 140.2, 133.0, 131.6, 129.2, 128.8, 128.6, 128.1, 127.6, 123.6, 122.9, 94.3, 87.4, 51.4, 14.3.



S8 **S9**

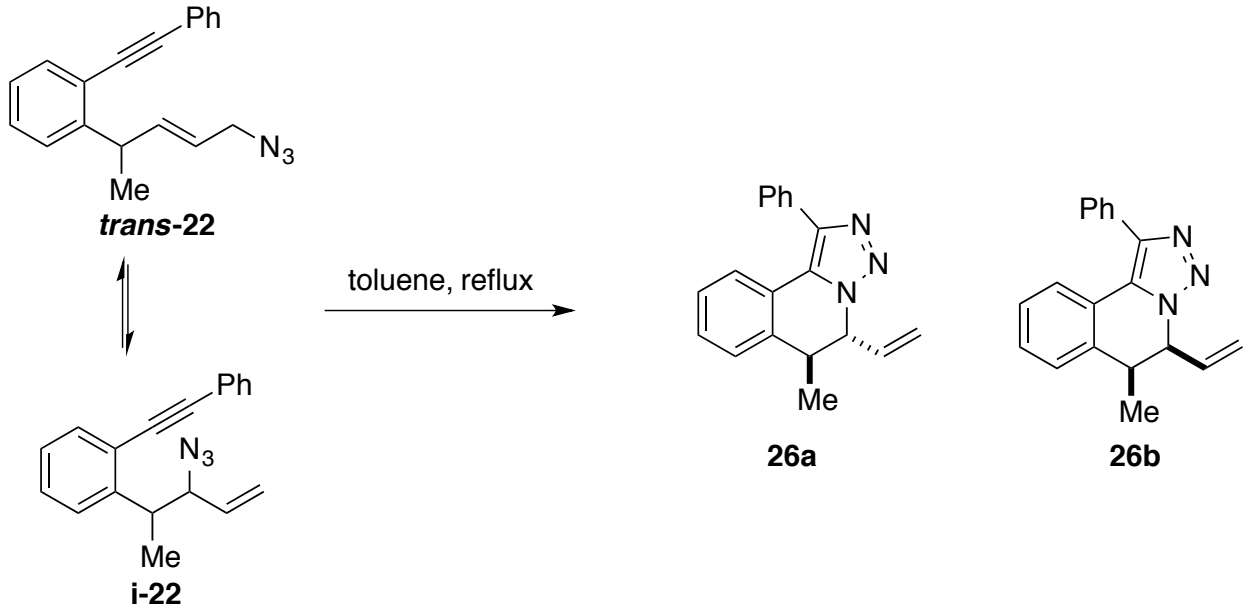
4-(2-(Phenylethynyl)phenyl)pent-1-en-3-ol (S9). To a stirred solution of vinylmagnesium bromide (0.74 g, 5.63 mmol) in anhydrous THF (30 mL) at -78 °C under N_2 atmosphere was slowly added a solution of 2-(2-(phenylethynyl)phenyl)propanal (**S8**, 0.05 g, 0.21 mmol) in anhydrous THF (5 mL). The reaction mixture was stirred for 2 h at -78 °C and then brought to room temperature. The reaction was quenched with aq NH_4Cl solution. The aqueous layer was extracted with EtOAc (3 × 10 mL) and the combined organics washed with water (1 × 20 mL) and brine, and dried over Na_2SO_4. Filtration and concentration gave a residue, which was purified by automated chromatography (Silica column, hexane:EtOAc/9:1) to give **S9** (0.02 g, 29%) of as colorless oil. R_f = 0.4 (10% EtOAc/hexanes); IR (neat) 3415 cm^{-1}; HRMS (ESI) m/z calculated for $(C_{19}H_{18}O+NH_4)^+$ 280.1702, found: 280.1725. ^1H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.46 (m, 3H), 7.44 – 7.29 (m, 5H), 7.22 (ddd, *J* = 7.6, 5.2, 3.4 Hz, 1H), 5.94 (ddd, *J* = 17.2, 10.5, 5.7 Hz, 1H), 5.30 – 5.05 (m, 2H), 4.45 (q, *J* = 4.9 Hz, 1H), 3.70 – 3.56 (m, 1H), 1.36 (d, *J* = 7.1 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.7, 139.6, 132.6, 131.6, 128.6, 128.5, 128.5, 127.2, 126.4, 123.4, 122.9, 115.4, 93.8, 88.2, 76.4, 42.8, 14.2.



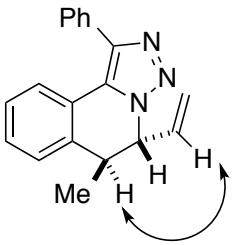
S9 ***trans*-22** **i-22**

(*E*)-1-(5-Azidopent-3-en-2-yl)-2-(phenylethynyl)benzene (*trans*-22), 1-(3-azidopent-4-en-2-yl)-2-(phenylethynyl)benzene (i-22). Triethylamine was added to a solution of 4-(2-(phenylethynyl)phenyl)pent-1-en-3-ol (**S9**, 0.05 g, 0.20 mmol) and methanesulfonyl chloride (0.04 g, 0.30 mmol) in CH_2Cl_2 (5 mL) under N_2 atmosphere at 0 °C. The reaction mixture was stirred at room temperature for 2 h. H_2O was added, and the aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL). The combined organics washed with water (1 × 20 mL) and brine, and dried over Na_2SO_4. Filtration and concentration gave a residue. A suspension of the residue and sodium azide (0.04 g, 0.61 mmol) in DMF (10 mL) was stirred for 3 h at room temperature. Saturated solution of aq NH_4Cl was added. The

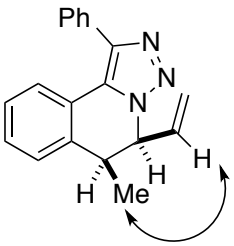
aqueous layer was extracted with Et_2O (3 × 10 mL) and the combined organics washed with water (1 × 20 mL) and brine, and dried over Na_2SO_4. Filtration and concentration gave a residue, which was purified by automated chromatography (Silica column, hexane/EtOAc 9.5:0.5) to give mixture of azides ***trans*-22**, and **i-22** (0.03 g, 52%, 85:15) as colorless oil. Azides ***trans*-22** and **i-22**: R_f = 0.7 (10% EtOAc/hexanes); IR (neat) 2097 cm^{-1}; HRMS (ESI) m/z calculated for $(C_{19}H_{17}N_3+H)^+$ 288.1501, found: 288.1513. Azide ***trans*-22**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.48 (m, 3H), 7.40 – 7.28 (m, 4H), 7.25 – 7.18 (m, 1H), 6.01 (ddt, *J* = 15.3, 6.1, 1.2 Hz, 1H), 5.63 (dtd, *J* = 15.2, 6.6, 1.6 Hz, 1H), 4.20 (p, *J* = 6.9 Hz, 1H), 3.76 (dt, *J* = 6.6, 1.2 Hz, 2H), 1.45 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.8, 140.4, 132.6, 131.6, 128.9, 128.6, 128.5, 126.5, 126.3, 123.5, 122.4, 122.3, 93.7, 88.0, 52.9, 39.6, 20.4. Azide **i-22** (diagnostic peaks only): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.91 – 5.69 (m, 1H), 5.37 – 5.15 (m, 2H), 4.29 (t, *J* = 7.6 Hz, 1H), 3.62 (dt, *J* = 13.3, 6.9 Hz, 1H).



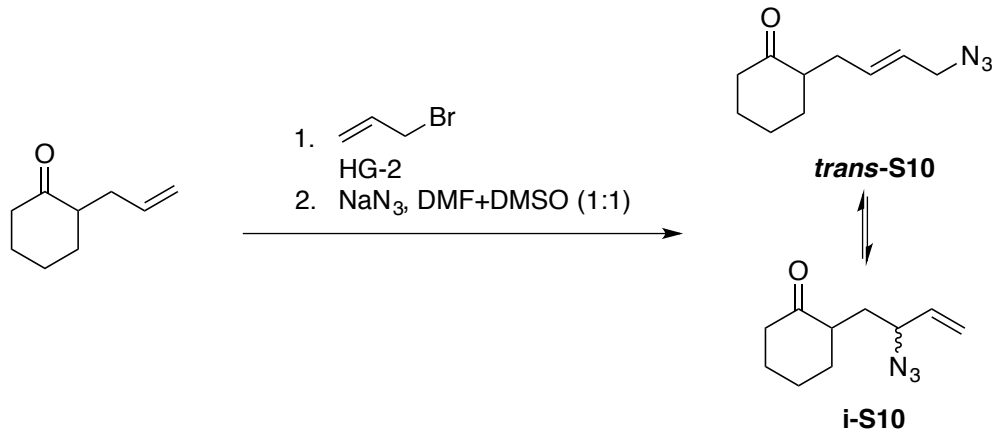
(5*S,6*R**)-6-Methyl-1-phenyl-5-vinyl-5,6-dihydro-[1,2,3]triazolo[5,1-*a*]isoquinoline (26a) and (5*S**,6*S**)-6-methyl-1-phenyl-5-vinyl-5,6-dihydro-[1,2,3]triazolo[5,1-*a*]isoquinoline (26b).** Azides ***trans*-22** and **i-22** (0.03 g) was dissolved in toluene (10 mL). The reaction mixture was heated at reflux for 12 h. The solvent was evaporated after cooling the reaction mixture to room temperature. The residue was purified by automated chromatography (Silica column, hexane:EtOAc/8:2) to give **26a** and **26b** (0.02 g, 80%) (**26a**:**26b**/1.4:1) as colorless solid. **26a** and **26b:** R_f = 0.3 (20% EtOAc/hexanes); IR (neat) 2926 cm^{-1}; HRMS (ESI) m/z calculated for $(C_{19}H_{17}N_3+H)^+$ 288.1501, found: 288.1473. **26a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 – 7.71 (m, 3H), 7.51 – 7.40 (m, 4H), 7.37 – 7.29 (m, 2H), 5.81 (ddd, *J* = 17.1, 10.4, 5.8 Hz, 1H), 5.25 – 5.20 (m, 1H), 5.13 (dt, *J* = 10.6, 0.8 Hz, 1H), 5.00 – 4.89 (m, 1H), 3.30 (qd, *J* = 7.2, 2.3 Hz, 1H), 1.32 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.2, 137.2, 134.8, 131.9, 129.6, 128.8, 128.7, 128.6, 127.9, 127.6, 126.6, 124.7, 123.6, 118.2, 63.8, 40.4, 20.8. **26b** (diagnostic peaks only): ^{1}H NMR (500 MHz, $CDCl_3$) δ5.89 – 5.83 (m, 1H), 5.34 – 5.26 (m, 2H), 5.23 (dq, *J* = 5.7, 2.0 Hz, 2H), 3.52 (qd, *J* = 7.0, 4.9 Hz, 1H), 1.43 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.3, 136.8, 131.8, 131.0, 127.5, 124.5, 120.8, 63.4, 38.1, 14.4. The following NOE correlations were used to assign **26a** and **26b**:



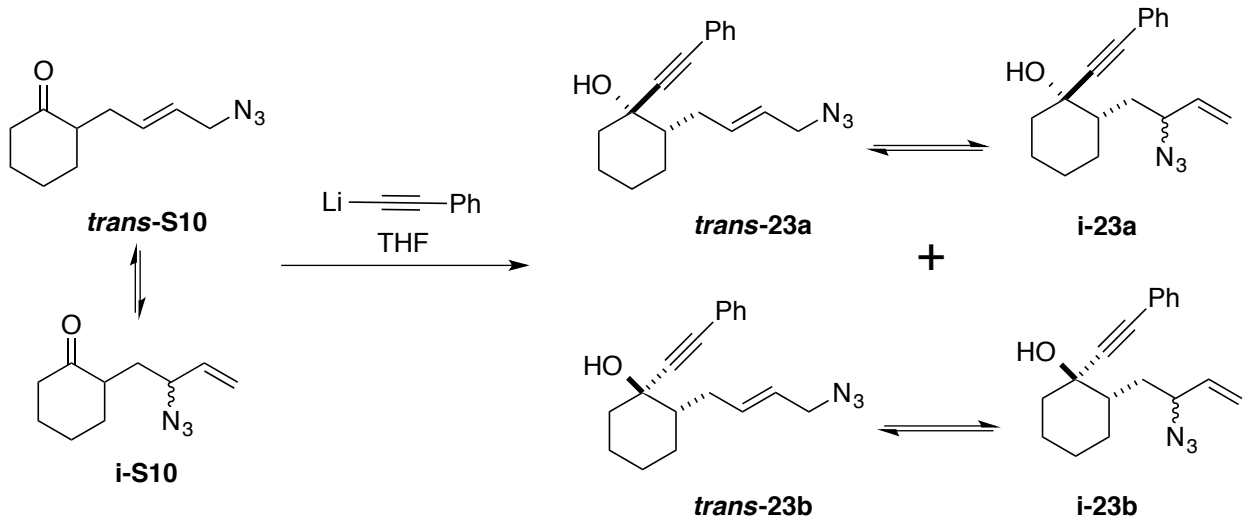
26a



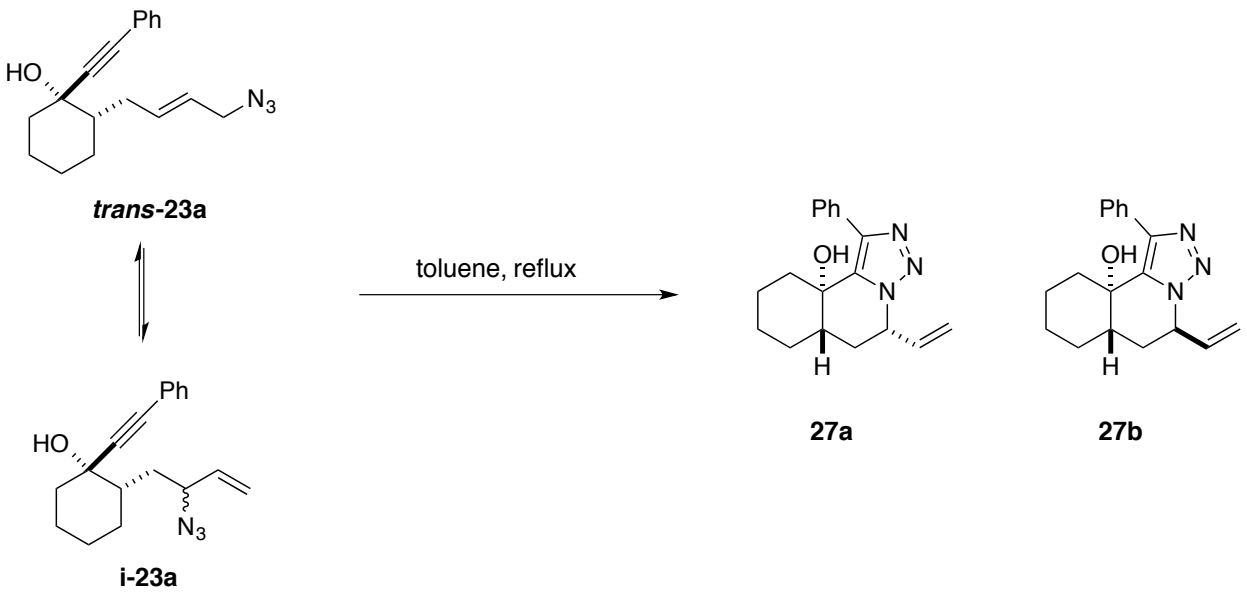
26b



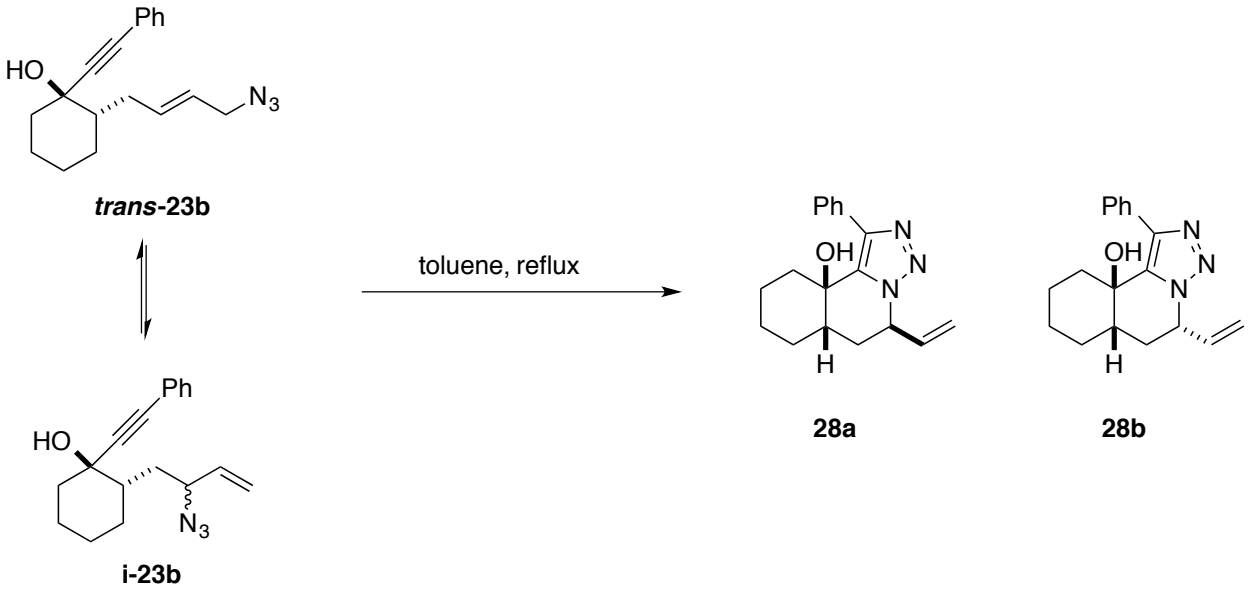
(*E*)-2-(4-Azidobut-2-en-1-yl)cyclohexan-1-one (*trans*-S10), 2-(2-azidobut-3-en-1-yl)cyclohexan-1-one (i-S10). Following the general procedure for **S3**, methyl 2-allylyclohexanone (2.0 g, 14.40 mmol), allyl bromide (5.25 g, 43.4 mmol), HG-2 (0.18 g, 0.28 mmol), and NaN_3 (3.74 g, 57.60 mmol) afforded azides ***trans*-S10** and **i-S10** (81:19 ratio, 1.53 g, 55%) as colorless oil. Azides ***trans*-S10** and **i-S10**: R_f = 0.3 (10% EtOAc/hexanes); IR (neat) 2096, 1709 cm^{-1}. Azide ***trans*-S10**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.84 – 5.65 (m, 1H), 5.61 – 5.46 (m, 1H), 3.68 (d, *J* = 6.6 Hz, 2H), 2.53 (dtd, *J* = 14.4, 5.8, 1.3 Hz, 1H), 2.46 – 2.22 (m, 3H), 2.19 – 1.93 (m, 3H), 1.86 (dtd, *J* = 9.3, 3.5, 1.9 Hz, 1H), 1.75 – 1.54 (m, 2H), 1.46 – 1.27 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 212.2, 134.6, 124.8, 52.8, 50.4, 42.2, 33.6, 32.3, 28.0, 25.1. Azide **i-S10** (diagnostic peaks only): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.34 – 5.15 (m, 2H), 4.05 – 3.91 (m, 1H), 3.91 – 3.78 (m, 1H).



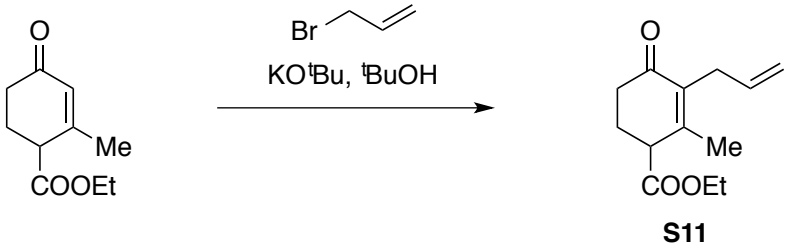
(1*R,2*R**)-2-((*E*)-4-Azidobut-2-en-1-yl)-1-(phenylethynyl)cyclohexan-1-ol (*trans*-23a), (1*R**,2*R**)-2-(2-azidobut-3-en-1-yl)-1-(phenylethynyl)cyclohexan-1-ol(i-23a), (1*R**,2*S**)-2-((*E*)-4-azidobut-2-en-1-yl)-1-(phenylethynyl)cyclohexan-1-ol (*trans*-23b), (1*R**,2*S**)-2-(2-azidobut-3-en-1-yl)-1-(phenylethynyl)cyclohexan-1-ol (i-23b).** Azides ***trans*-S10** and **i-S10** (0.3 g, 1.55 mmol) were dissolved in THF (10 mL) at -78 °C and stirred for 30 min. Then lithium phenylacetylide (1M in THF, 0.17 g, 1.55 mmol) was added to the reaction mixture and stirred for 2 h at -78 °C. The reaction was brought to room temperature and stirred for 2 h. NH_4Cl and H_2O were added. The aqueous layer was extracted with Et_2O (3 × 10 mL) and the combined organics washed with water (1 × 20 mL) and brine, and dried over Na_2SO_4. Filtration and concentration gave a residue, which was purified by automated chromatography (Silica column, hexane/EtOAc 9:1) to give mixture of azides ***trans*-23a**, **i-23a** (0.12 g, 25%), and ***trans*-23b,** and **i-23b** (0.12 g, 26%) (**23a:23b**/1:1) of as colorless oil. Azides ***trans*-23a** and **i-23a** (81:19) : R_f = 0.3 (20% EtOAc/hexanes); IR (neat) 2100 cm^{-1}; HRMS (ESI) m/z calculated for $(C_{18}H_{21}N_3O+H)^+$ 296.1763, found: 296.1768. Azide ***trans*-23a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.36 (m, 2H), 7.31 (ddd, *J* = 3.8, 2.6, 1.5 Hz, 3H), 5.93 – 5.70 (m, 1H), 5.66 – 5.50 (m, 1H), 3.93 – 3.83 (m, 1H), 3.78 – 3.66 (m, 1H), 2.84 – 2.63 (m, 1H), 2.30 – 1.95 (m, 2H), 1.89 – 1.58 (m, 6H), 1.44 – 1.19 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.9, 131.8, 128.4, 128.4, 124.6, 122.9, 93.6, 84.0, 70.3, 53.0, 46.0, 40.0, 34.0, 26.1, 25.0, 21.3. Azide **i-23a** (diagnostic peaks only): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.53 – 5.37 (m, 1H), 5.36 – 5.21 (m, 3H), 4.02 (q, *J* = 7.7 Hz, 1H), 3.94 (ddd, *J* = 11.1, 7.3, 4.2 Hz, 1H), 3.87 (d, *J* = 7.3 Hz, 3H). Azides ***trans*-23b** and **i-23b** (83:17): R_f = 0.25 (20% EtOAc/hexanes); IR (neat) 2099 cm^{-1}; HRMS (ESI) m/z calculated for $(C_{18}H_{21}N_3O+H)^+$ 296.1763, found: 296.1771. Azide ***trans*-23b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.38 (m, 2H), 7.37 – 7.29 (m, 3H), 5.92 – 5.72 (m, 1H), 5.69 – 5.51 (m, 1H), 3.73 (d, J = 6.6 Hz, 2H), 2.75 (dddd, J = 14.2, 6.8, 4.2, 1.4 Hz, 1H), 2.21 (s, 1H), 2.17 – 1.98 (m, 2H), 1.90 – 1.58 (m, 5H), 1.35 – 1.13 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.0, 131.8, 128.5, 128.5, 124.7, 122.9, 90.1, 86.9, 73.3, 53.0, 48.0, 41.5, 34.2, 29.5, 25.6, 24.3. Azide **i-23b** (diagnostic peaks only): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.36 – 5.24 (m, 3H), 4.09 (q, *J* = 7.5 Hz, 1H), 4.05 – 3.94 (m, 1H).



(5*R,6a*R**,10a*R**)-1-Phenyl-5-vinyl-6,6a,7,8,9,10-hexahydro-[1,2,3]triazolo[5,1-*a*]isoquinolin-10a(5*H*)-ol (27a), (5*S**,6a*R**,10a*R**)-1-phenyl-5-vinyl-6,6a,7,8,9,10-hexahydro-[1,2,3]triazolo[5,1-*a*]isoquinolin-10a(5*H*)-ol (27b).** Azides ***trans*-23a** and **i-23a** (0.09 g, 0.30 mmol) were dissolved in toluene (10 mL). The reaction mixture was heated at reflux for 15 h. The solvent was evaporated after cooling the reaction mixture to room temperature. The residue was purified by automated chromatography (Silica column, hexane:EtOAc/8:2) to give **27a** (0.06 g, 65%) and **27b** (0.03 g, 32%) (**27a**:**27b** 2.9:1) as colorless solid. **27a**: R_f = 0.3 (50% EtOAc/hexanes); mp 227-229 °C; IR (neat) 981 cm^{-1}; HRMS (ESI) m/z calculated for $(C_{18}H_{21}N_3O+H)^+$ 296.1763, found: 296.1743. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 – 7.61 (m, 2H), 7.49 – 7.32 (m, 3H), 6.13 (ddd, *J* = 17.4, 10.2, 7.6 Hz, 1H), 5.48 (dt, *J* = 17.2, 1.0 Hz, 1H), 5.40 (dt, *J* = 10.1, 0.9 Hz, 1H), 4.97 – 4.88 (m, 1H), 2.27 (dd, *J* = 13.9, 3.5 Hz, 1H), 1.99 (s, 1H), 1.85 (ddd, *J* = 13.9, 5.5, 2.3 Hz, 1H), 1.78 (dddd, *J* = 12.8, 10.8, 4.3, 2.3 Hz, 2H), 1.70 – 1.45 (m, 4H), 1.38 – 1.14 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.5, 136.4, 135.3, 132.5, 129.8, 128.4, 128.3, 118.7, 67.0, 61.9, 42.0, 34.3, 32.2, 26.7, 25.5, 20.8. **27b**: R_f = 0.25 (50% EtOAc/Hexane); mp 155-157 °C; HRMS (ESI) m/z calculated for $(C_{18}H_{21}N_3O+H)^+$ 296.1763, found: 296.1776; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 – 7.63 (m, 2H), 7.55 – 7.33 (m, 3H), 6.04 (ddd, *J* = 17.1, 10.3, 5.2 Hz, 1H), 5.39 – 5.25 (m, 2H), 4.95 (dd, *J* = 17.1, 1.5 Hz, 1H), 2.51 – 2.39 (m, 1H), 2.32 (dt, *J* = 13.8, 3.5 Hz, 1H), 1.94 – 1.85 (m, 1H), 1.83 – 1.73 (m, 1H), 1.74 – 1.42 (m, 4H), 1.39 – 1.17 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.2, 136.7, 135.3, 132.4, 129.7, 128.4, 128.3, 117.5, 67.1, 58.6, 37.7, 34.0, 29.9, 26.6, 25.5, 20.8.

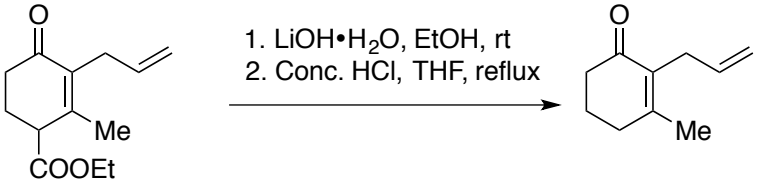


(5*R,6a*S**,10a*R**)-1-Phenyl-5-vinyl-6,6a,7,8,9,10-hexahydro-[1,2,3]triazolo[5,1-*a*]isoquinolin-10a(5*H*)-ol (28a), (5*S**,6a*S**,10a*R**)-1-phenyl-5-vinyl-6,6a,7,8,9,10-hexahydro-[1,2,3]triazolo[5,1-*a*]isoquinolin-10a(5*H*)-ol (28b).** Azides ***trans*-23b** and **i-23b** (0.12 g, 0.40 mmol) was dissolved in toluene (10 mL). The reaction mixture was heated at reflux for 8 h. The solvent was evaporated after cooling the reaction mixture to room temperature. The residue was purified by automated chromatography (Silica column, hexane:EtOAc/8:2) to give **28a** and **28b** (0.11 g, 96%) (**28a**:**28b** 6.2:1) as colorless solid. **28a** and **28b:** R_f = 0.3 (50% EtOAc/hexanes); mp 182-184 °C; IR (neat) 2900 cm^{-1}; HRMS (ESI) m/z calculated for $(C_{18}H_{21}N_3O+H)^+$ 296.1763, found: 296.1789. **28a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 – 7.69 (m, 2H), 7.41 (tdd, *J* = 8.7, 6.6, 5.1 Hz, 3H), 6.09 (ddd, *J* = 16.9, 10.3, 6.5 Hz, 1H), 5.37 (dt, *J* = 10.5, 0.9 Hz, 1H), 5.33 – 5.21 (m, 1H), 5.12 (d, *J* = 7.0 Hz, 1H), 2.37 (s, 1H), 2.23 – 2.06 (m, 2H), 1.96 – 1.80 (m, 1H), 1.79 – 1.44 (m, 4H), 1.41 – 1.19 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.8, 136.7, 136.2, 132.3, 129.6, 128.4, 128.4, 118.3, 69.6, 57.5, 35.4, 31.7, 31.0, 27.3, 22.8, 22.8, 14.3. **28b** (diagnostic peaks only): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 – 7.80 (m, 2H), 6.15 (dd, *J* = 10.1, 7.4 Hz, 1H), 5.52 – 5.45 (m, 1H), 5.42 (d, *J* = 10.3 Hz, 1H), 4.90 (dt, *J* = 10.6, 6.1 Hz, 1H), 4.12 (q, *J* = 7.2 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 129.4, 128.5, 128.3, 119.0, 69.9, 61.1, 34.8, 34.2, 33.9, 26.7, 21.4, 14.4.



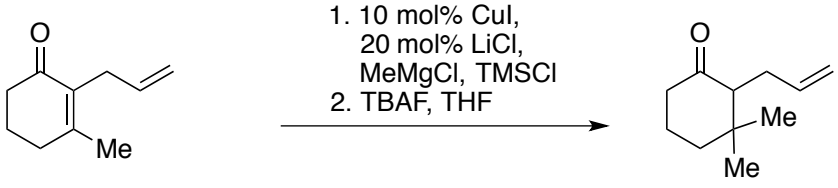
Ethyl 3-Allyl-2-methyl-4-oxocyclohex-2-ene-1-carboxylate (S11). Hagemann's ester (10 g, 54.80 mmol) was rapidly added to a stirred solution of potassium *tert*-butoxide (6.77 g, 60.30 mmol) in dry *tert*-butanol (30 mL). The red solution so formed turned into a straw-yellow suspension few minutes later after the addition. The reaction mixture was stirred for 15 min and then ally bromide (7.29 g, 5.22

mmol) was added in a single portion. The mixture was allowed to reflux for 12 h. The reaction mixture was allowed to cool to room temperature and then aq HCl and CH_2Cl_2 were added. the aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL). The combined organics washed with water (1 × 20 mL) and brine, and dried over Na_2SO_4. Filtration and concentration gave a residue, which was purified by automated chromatography (Silica column, hexane/EtOAc 9.5:0.5) to give **S11** (7.7 g, 63%) as colorless oil. R_f = 0.6 (10% EtOAc/hexanes); IR (neat) 1729, 1669 cm^{-1}; HRMS (ESI) m/z calculated for $(C_{13}H_{18}O_3+H)^+$ 223.1334, found: 223.1356. ^1H NMR (400 MHz, $CDCl_3$) δ 5.76 (ddt, *J* = 16.5, 10.5, 5.9 Hz, 1H), 5.05 – 4.89 (m, 2H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.31 (t, *J* = 5.0 Hz, 1H), 3.10 (ddt, *J* = 5.6, 3.5, 1.7 Hz, 2H), 2.59 (ddd, *J* = 16.9, 11.7, 5.2 Hz, 1H), 2.45 – 2.35 (m, 1H), 2.35 – 2.15 (m, 2H), 1.97 (d, *J* = 0.7 Hz, 3H), 1.28 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.1, 172.3, 151.7, 135.1, 135.0, 114.8, 61.4, 47.9, 34.7, 29.3, 25.8, 20.6, 14.3.



S11 **S12**

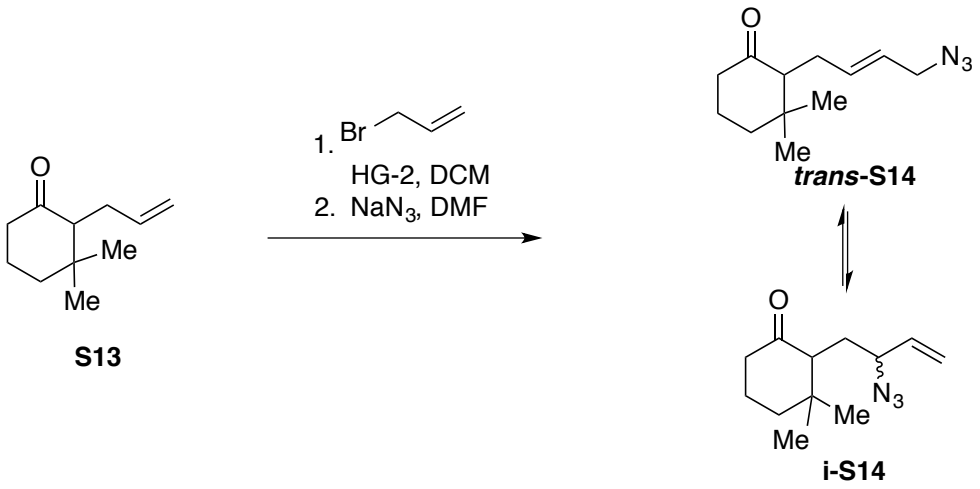
2-Allyl-3-methylcyclohex-2-en-1-one (S12). The compound **S12** was prepared following the procedure reported by aubé et al.[S2] The starting ester (**S11**, 7.68 g, 34.50 mmol) was dissolved in 1/1 mixture of ethanol and water (40 mL) and LiOH•H_2O (2.90 g, 6.91 mmol) was added as a powder. The mixture was stirred 3 h, concentrated, and the residue partitioned between water and Et_2O. The aqueous phase was acidified with 6 M aq HCl and extracted with CH_2Cl_2. The organic extracts combined, dried over Na_2SO_4, and concentrated. The residue was dissolved in a mixture of concentrated HCl (3 mL) in THF (50 mL) and heated for 24 h at 90 °C. The reaction mixture was allowed to cool to room temperature and then aq HCl and CH_2Cl_2 were added. The aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL). The combined organics washed with water (1 × 20 mL) and brine, and dried over Na_2SO_4. Filtration and concentration gave a residue, which was purified by automated chromatography (Silica column, hexane/EtOAc 9:1) to give **S12** (3.86 g, 74%) as dark yellow oil. R_f = 0.5 (20% EtOAc/hexanes); IR (neat) 1662 cm^{-1}; HRMS (ESI) m/z calculated for $(C_{10}H_{14}O+H)^+$ 151.1123, found: 151.1145. ^1H NMR (400 MHz, $CDCl_3$) δ 5.75 (ddt, *J* = 17.7, 9.4, 6.1 Hz, 1H), 5.01 – 4.87 (m, 2H), 3.06 (dt, *J* = 6.2, 1.5 Hz, 2H), 2.42 – 2.34 (m, 4H), 2.02 – 1.94 (m, 2H), 1.93 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.4, 157.0, 135.9, 133.2, 114.4, 37.8, 33.1, 29.4, 22.4, 21.3.



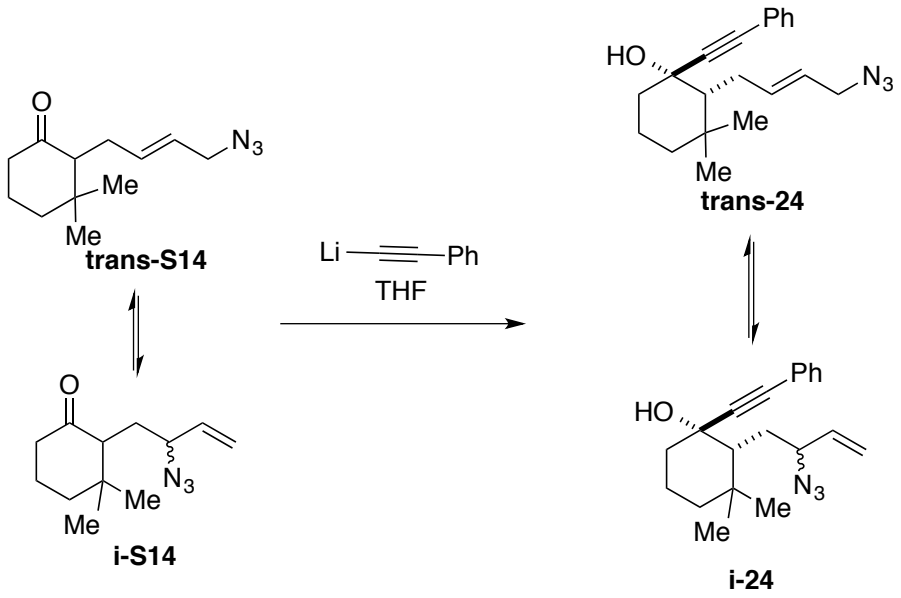
S12 **S13**

2-Allyl-3,3-dimethylcyclohexan-1-one (S13). Compound **S13** prepared following the procedure reported by Reetz and Kindler.[S3] Lithium chloride (0.11 g, 2.66 mmol) and CuI (0.25 g, 1.33 mmol) were

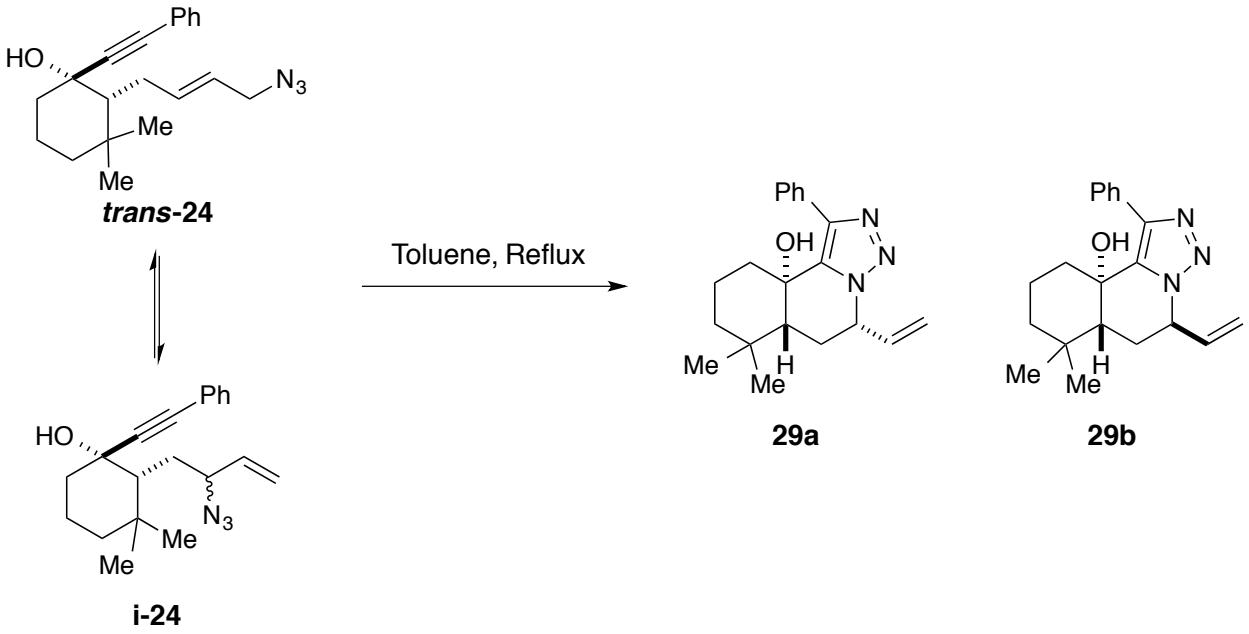
dissolved in anhydrous THF (90 mL) under argon at room temperature. The resulting solution was cooled to -40 °C (dry ice/acetonitrile), ketone **S12** (2.0 g, 13.30 mmol) and TMSCl (1.59 g, 14.60 mmol) were added, and the solution was stirred for 10 min. MeMgCl (3 M in THF, 1.49 g, 19.90 mmol) was added dropwise and left stirring at -40 °C for 1.5 h. The reaction mixture was then poured into saturated aq NH_4Cl (150 mL) and Et_2O (150 mL). The aqueous layer was extracted with Et_2O (3 × 10 mL). The combined organics washed with water (1 × 20 mL) and brine, and dried over Na_2SO_4. Filtration and concentration gave a residue, which was dissolved in THF (40 mL) and stirred with TBAF (1 M in THF, 20 mL, 19.90 mmol) at room temperature for 30 min under N_2 atmosphere. The mixture was poured into H_2O and Et_2O, and the aqueous layer was extracted with Et_2O (3 × 10 mL). The combined organics washed with water (1 × 20 mL) and brine, and dried over Na_2SO_4. Filtration and concentration gave a residue, which was purified by automated chromatography (Silica column, hexane/EtOAc 9:1) to give **S13** (1.67 g, 76%) as colorless oil. R_f = 0.5 (10% EtOAc/hexanes); IR (neat) 1709 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 5.76 (dddd, *J* = 17.2, 10.1, 7.2, 6.4 Hz, 1H), 5.11 – 4.77 (m, 2H), 2.45 (dddt, *J* = 14.1, 10.3, 6.4, 1.3 Hz, 1H), 2.39 – 2.18 (m, 3H), 2.06 (dddt, *J* = 14.2, 7.3, 2.9, 1.4 Hz, 1H), 1.97 – 1.72 (m, 2H), 1.70 – 1.54 (m, 2H), 1.07 (s, 3H), 0.79 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 212.8, 138.0, 115.3, 61.1, 41.4, 39.8, 39.3, 29.6, 28.8, 23.2, 22.2.



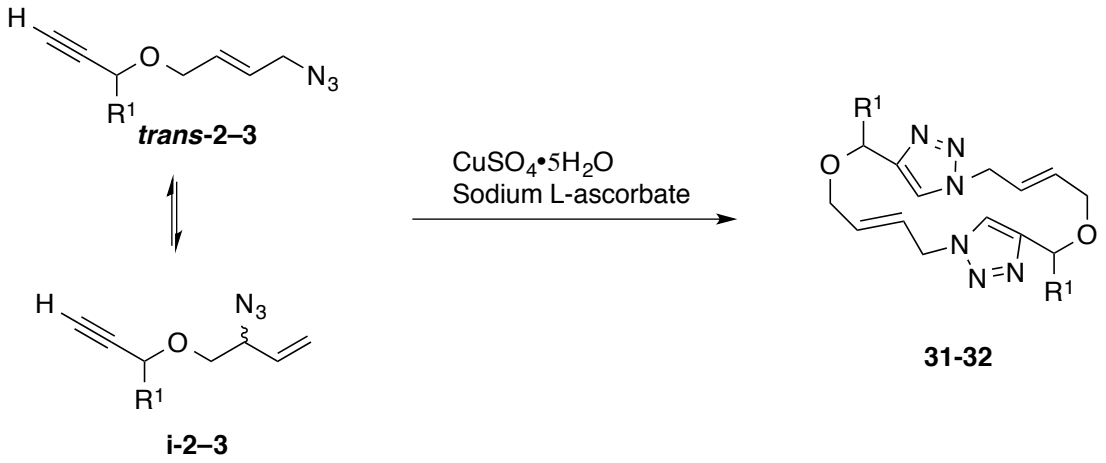
(*E*)-2-(4-Azidobut-2-en-1-yl)-3,3-dimethylcyclohexan-1-one (*trans*-S14), 2-(2-azidobut-3-en-1-yl)-3,3-dimethylcyclohexan-1-one (i-S14). Following the general procedure for **S3**, 2-allyl-3,3-dimethylcyclohexan-1-one (**S13,** 1.66 g, 9.95 mmol), allyl bromide (3.61 g, 29.80 mmol), HG-2 (0.12 g, 0.20 mmol), and NaN_3 (2.59 g, 39.80 mmol) afforded azides ***trans*-S14** and **i-S14** (72:28 ratio, 1.32 g, 60%) as colorless oil. Azides ***trans*-S14**and **i-S14**: R_f = 0.4 (10% EtOAc/hexanes); IR (neat) 2095, 1708 cm^{-1}; HRMS (ESI) m/z calculated for $(C_{12}H_{19}N_3O+NH_4)^+$ 239.1872, found: 239.1869. Azide ***trans*-S14**: ^1H NMR (400 MHz, $CDCl_3$) δ 5.72 (dddt, *J* = 15.1, 7.5, 6.3, 1.2 Hz, 1H), 5.51 (dtt, *J* = 15.0, 6.7, 1.3 Hz, 1H), 3.71 – 3.57 (m, 2H), 2.54 – 2.41 (m, 1H), 2.40 – 2.18 (m, 3H), 2.07 (dddd, *J* = 14.1, 7.7, 2.6, 1.2 Hz, 1H), 2.01 – 1.75 (m, 2H), 1.74 – 1.52 (m, 2H), 1.08 (s, 3H), 0.77 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 212.3, 136.3, 123.9, 61.4, 52.8, 41.6, 40.0, 39.8, 29.7, 27.0, 23.2, 21.7. Azide **i-S14** (diagnostic peaks only): ^1H NMR (400 MHz, $CDCl_3$) δ 5.37 – 5.12 (m, 2H), 3.88 – 3.77 (m, 1H), 1.42 – 1.27 (m, 1H).



(1*R,2*S**)-2-((*E*)-4-Azidobut-2-en-1-yl)-3,3-dimethyl-1-(phenylethynyl)cyclohexan-1-ol (*trans*-24), (1*R**,2*S**)-2-(2-azidobut-3-en-1-yl)-3,3-dimethyl-1-(phenylethynyl)cyclohexan-1-ol (i-24).** Azides ***trans*-S14** and **i-S14** (1.31 g, 5.93 mmol) were dissolved in THF (20 mL) at -78 °C and stirred for 30 min. Then lithium phenylacetylide (1M in THF, 5.93 mL, 5.93 mmol) was added to the reaction mixture and stirred for 2 h at -78 °C. The reaction was brought to room temperature and stirred for 2 h. NH_4Cl and H_2O were added. The aqueous layer was extracted with Et_2O (3 × 10 mL) and the combined organics washed with water (1 × 20 mL) and brine, and dried over Na_2SO_4. Filtration and concentration gave a residue, which was purified by automated chromatography (Silica column, hexane/EtOAc 9:1) to give mixture of azides ***trans*-24**, and **i-24** (1.12 g, 58%) of as colorless oil. Azides ***trans*-24** and **i-24** (68:32) : R_f = 0.4 (10% EtOAc/hexanes); IR (neat) 3256, 2100 cm^{-1}; HRMS (ESI) m/z calculated for $(C_{20}H_{25}N_3O+H)^+$ 324.2076, found: 324.2051. Azide ***trans*-24**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.34 (m, 2H), 7.30 (dp, *J* = 5.3, 1.7 Hz, 3H), 6.13 – 5.97 (m, 1H), 5.65 – 5.52 (m, 1H), 3.66 (d, *J* = 5.7 Hz, 2H), 2.75 – 2.59 (m, 1H), 2.42 – 2.32 (m, 1H), 2.16 – 2.03 (m, 1H), 1.81 (dddd, *J* = 10.0, 5.1, 2.8, 1.3 Hz, 2H), 1.71 (d, *J* = 3.1 Hz, 1H), 1.55 – 1.41 (m, 2H), 1.28 (ddt, *J* = 12.8, 9.2, 3.9 Hz, 1H), 1.03 (s, 3H), 0.95 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.6, 131.6, 128.4, 128.4, 128.4, 122.7, 94.8, 83.5, 71.3, 54.2, 53.0, 41.8, 41.6, 34.9, 32.5, 30.3, 22.1, 17.8. Azide **i-24** (diagnostic peaks only): ^{1}H NMR (400 MHz, $CDCl_3$) δ ^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.38 – 5.11 (m, 2H), 4.05 – 3.93 (m, 1H), 3.91 – 3.76 (m, 1H).



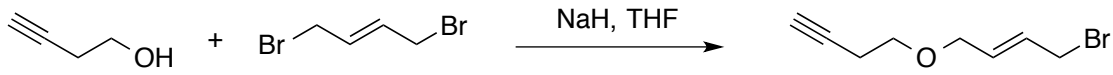
(5*R,6a*S**,10a*R**)-7,7-Dimethyl-1-phenyl-5-vinyl-6,6a,7,8,9,10-hexahydro-[1,2,3]triazolo[5,1-*a*]isoquinolin-10a(5*H*)-ol (29a), (5*S**,6a*S**,10a*R**)-7,7-dimethyl-1-phenyl-5-vinyl-6,6a,7,8,9,10-hexahydro-[1,2,3]triazolo[5,1-*a*]isoquinolin-10a(5*H*)-ol (29b).** Azides ***trans*-24** and **i-24** (1.12 g, 3.46 mmol) was dissolved in toluene (10 mL). The reaction mixture was heated at reflux for 24 h. The solvent was evaporated after cooling the reaction mixture to room temperature. The residue was purified by automated chromatography (Silica column, hexane:EtOAc/8:2) to give **29a** (0.63 g, 56%) and **29b** (0.19 g, 17%) (**29a**:**29b** 2.5:1). **29a**: Obtained as colorless solid. R_f = 0.3 (50% EtOAc/hexanes); mp 162-164 °C; IR (neat) 3259 cm^{-1}; HRMS (ESI) m/z calculated for $(C_{20}H_{25}N_3O+H)^+$ 324.2076, found: 324.2039. ^1H NMR (500 MHz, $CDCl_3$) δ 7.60 – 7.54 (m, 2H), 7.44 – 7.33 (m, 3H), 6.11 (ddd, *J* = 17.2, 10.2, 7.7 Hz, 1H), 5.50 (d, *J* = 17.2 Hz, 1H), 5.40 (d, *J* = 10.1 Hz, 1H), 4.84 (ddd, *J* = 11.7, 7.7, 5.5 Hz, 1H), 2.31 – 2.05 (m, 4H), 1.79 (qt, *J* = 14.0, 3.6 Hz, 1H), 1.55 – 1.46 (m, 1H), 1.44 – 1.34 (m, 1H), 1.31 – 1.15 (m, 3H), 1.06 (s, 3H), 0.99 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.7, 136.6, 136.5, 132.6, 129.9, 128.3, 128.3, 118.7, 68.6, 62.7, 49.2, 40.9, 35.4, 33.2, 32.4, 26.5, 21.6, 17.7. **29b**: Obtained as colorless oil. R_f = 0.25 (50% EtOAc/Hexane); HRMS (ESI) m/z calculated for $(C_{20}H_{25}N_3O+H)^+$ 324.2076, found: 324.2045; ^1H NMR (500 MHz, $CDCl_3$) δ 7.75 – 7.59 (m, 2H), 7.51 – 7.32 (m, 3H), 5.97 (ddd, *J* = 17.1, 10.5, 5.0 Hz, 1H), 5.29 (dd, *J* = 10.6, 1.6 Hz, 1H), 5.24 (ddt, *J* = 5.0, 3.3, 1.6 Hz, 1H), 4.93 (dd, *J* = 17.2, 1.7 Hz, 1H), 2.41 (ddd, *J* = 14.0, 12.8, 6.3 Hz, 1H), 2.37 – 2.28 (m, 1H), 1.93 (dt, *J* = 14.0, 1.6 Hz, 1H), 1.82 (qt, *J* = 13.8, 3.6 Hz, 2H), 1.59 (dd, *J* = 12.7, 1.7 Hz, 1H), 1.49 (dt, *J* = 13.5, 1.7 Hz, 1H), 1.39 (dt, *J* = 13.9, 3.5 Hz, 1H), 1.31 – 1.10 (m, 2H), 1.05 (s, 3H), 0.92 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.4, 136.5, 136.3, 132.4, 129.8, 128.3, 128.3, 117.7, 68.5, 58.8, 44.6, 40.9, 35.0, 32.9, 32.2, 23.8, 21.7, 17.7.



	R^1	Yield (%)
31	Me	78
32	Ph	70

(1^4*Z*,8^4*Z*,5*E*,12*E*)-2,9-Diphenyl-1^1*H*,8^1*H*-3,10-dioxa-1(4,1),8(1,4)-ditriazolacyclotetradecaphane-5,12-diene (32). Azides ***trans*-3** and **i-3** (0.50 g, 2.20 mmol) were dissolved in a mixture of *tert*-BuOH/H_2O (1:1, 40 mL). $CuSO_4$•$5H_2O$ (0.54 g, 2.20 mmol) and sodium L-ascorbate (0.87 g, 4.40 mmol) were added to it. The heterogenous mixture was stirred for 1 h. Then CH_2Cl_2 was added to dissolve the crude product. The aqueous layer was extracted with CH_2Cl_2 (3 X 10 mL) and the combined organic layer was washed with aq NH_4OH (1 × 20 mL) and brine, and dried (Na_2SO_4). Filtration and concentration gave a residue, which was purified by automated chromatography (Silica column, CH_2Cl_2:MeOH 9:1) to give **32** (0.35 g, 70%) as yellow oil. R_f = 0.5 (10% MeOH/CH_2Cl_2); IR (neat) 1453 cm^{-1}; HRMS (ESI) m/z calculated for $(C_{26}H_{26}N_6O_2+H)^+$ 455.2195, found: 455.2199. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.27 (m, 5H), 5.83 (tdd, *J* = 15.5, 12.9, 10.2, 7.2 Hz, 2H), 5.61 (s, 1H), 4.87 (d, *J* = 5.7 Hz, 2H), 4.04 (d, *J* = 4.9 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.8, 140.1, 132.5, 128.8, 128.3, 126.9, 125.4, 121.8, 76.4, 68.3, 51.9.

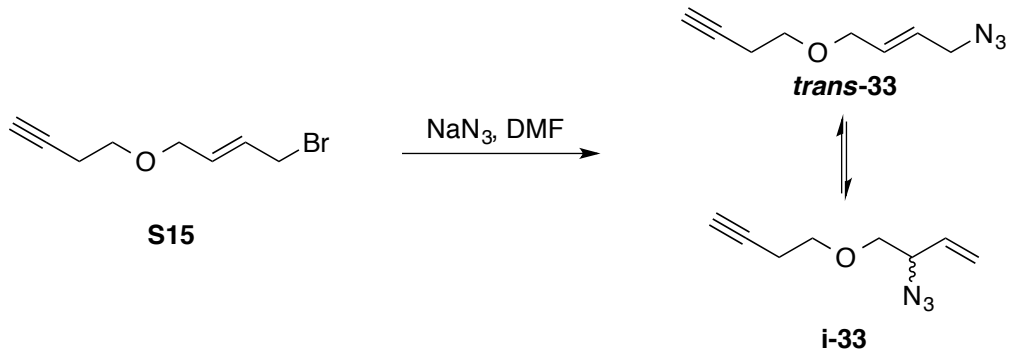
(1^4*Z*,8^4*Z*,5*E*,12*E*)-2,9-Dimethyl-1^1*H*,8^1*H*-3,10-dioxa-1(4,1),8(1,4)-ditriazolacyclotetradecaphane-5,12-diene (31). Obtained as yellow oil. R_f = 0.4 (10% MeOH/CH_2Cl_2); IR (neat) 1453 cm^{-1}; HRMS (ESI) m/z calculated for $(C_{16}H_{22}N_6O_2+H)^+$ 331.1882, found: 331.1898. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (s, 1H), 5.92 (dt, *J* = 15.4, 6.2 Hz, 1H), 5.83 (dt, *J* = 15.5, 5.1 Hz, 1H), 5.04 – 4.88 (m, 2H), 4.73 (q, *J* = 6.6 Hz, 1H), 4.02 (dt, *J* = 4.9, 1.5 Hz, 2H), 1.53 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.3, 132.9, 125.1, 120.8, 70.3, 68.0, 51.9, 21.5.



S15

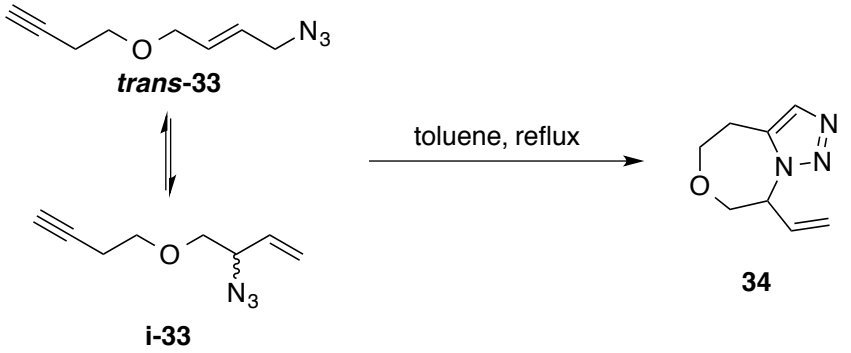
(*E*)-1-Bromo-4-(but-3-yn-1-yloxy)but-2-ene (S15). Following the general procedure for **S2a**, 3-butyn-1-ol (35, 2 g, 28.50 mmol), (*E*)-1,4-dibromobut-2-ene (12.19 g, 57 mmol), and NaH (1.14 g, 28.50 mmol) afforded **S15** (1.42 g, 24%) as colorless oil. R_f = 0.7 (10% EtOAc/hexanes); IR (neat) 2864 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.03 – 5.90 (m, 1H), 5.85 (dtt, *J* = 15.3, 5.5, 0.8 Hz, 1H), 4.08 – 4.00 (m, 2H), 4.00 –

3.91 (m, 2H), 3.57 (t, *J* = 6.9 Hz, 2H), 2.48 (td, *J* = 6.9, 2.7 Hz, 2H), 1.99 (t, *J* = 2.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 131.5, 128.9, 81.3, 70.4, 69.5, 68.5, 32.0, 20.0.



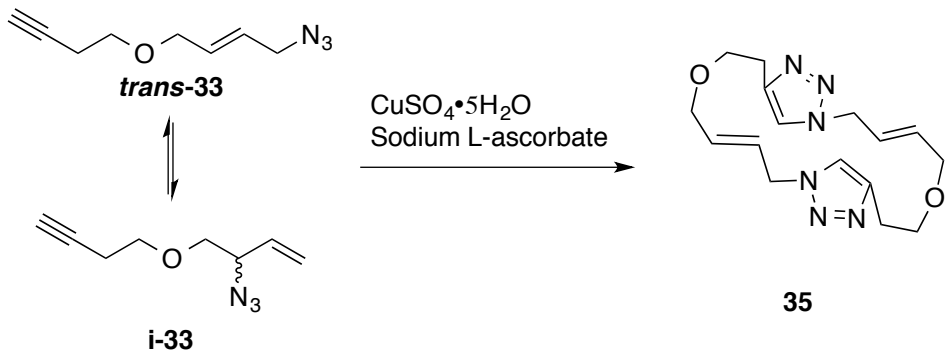
S15

(*E*)-1-Azido-4-(but-3-yn-1-yloxy)but-2-ene (*trans*-33), 3-azido-4-(but-3-yn-1-yloxy)but-1-ene (i-33). Following the general procedure for **2**, (*E*)-1-bromo-4-(but-3-yn-1-yloxy)but-2-ene (**S15**, 1.41 g, 6.90 mmol), and NaN_3 (1.35 g, 20 mmol) afforded a mixture of azides ***trans*-33** and **i-33** (0.87, 76%, 84:16) as a colorless oil. . Azides ***trans*-33** and **i-33** : R_f = 0.6 (10% EtOAc/hexanes); IR (neat) 2098 cm^{-1}; HRMS (ESI) m/z calculated for $(C_8H_{11}BrO+H)^+$ 166.0980, found: 166.1001. Azide ***trans*-33**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.92 – 5.73 (m, 2H), 4.10 – 4.04 (m, 2H), 3.79 (d, *J* = 5.6 Hz, 2H), 3.58 (t, *J* = 6.9 Hz, 2H), 2.48 (td, *J* = 6.8, 2.7 Hz, 2H), 1.99 (t, *J* = 2.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 131.6, 126.0, 81.3, 70.5, 69.5, 68.5, 52.4, 20.0. Azide **i-33** (diagnostic peaks only): ^{1}H NMR (400 MHz, $CDCl_3$) δ ^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.52 – 5.22 (m, 2H), 3.63 (t, *J* = 7.0 Hz, 2H), 3.49 (dd, *J* = 10.1, 7.5 Hz, 1H).



34

8-Vinyl-4,5,7,8-tetrahydro-[1,2,3]triazolo[1,5-*d*][1,4]oxazepine (34). Following the general procedure of **12**, azides ***trans*-33** and **i-33** (0.13 g, 0.79 mmol) afforded **34** (0.11 g, 81%) as colorless oil. R_f = 0.3 (50% EtOAc/hexanes); IR (neat) 2957 cm^{-1}; HRMS (ESI) m/z calculated for $(C_8H_{11}N_3O+H)^+$ 166.0980, found: 166.0977. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (s, 1H), 6.13 (ddd, *J* = 17.2, 10.6, 4.6 Hz, 1H), 5.48 (dp, *J* = 4.9, 1.8 Hz, 1H), 5.35 (dd, *J* = 10.6, 2.0 Hz, 1H), 4.84 (ddd, *J* = 17.2, 2.0, 0.6 Hz, 1H), 4.31 (dd, *J* = 13.3, 3.4 Hz, 1H), 4.25 – 4.07 (m, 1H), 3.82 (dd, *J* = 13.4, 1.6 Hz, 1H), 3.53 (ddd, *J* = 12.5, 10.7, 1.9 Hz, 1H), 3.17 – 2.91 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.6, 133.5, 132.8, 118.5, 72.8, 70.2, 65.3, 26.2.



(1^4*Z*,9^4*Z*,6*E*,14*E*)-1^1*H*,9^1*H*-4,12-Dioxa-1(4,1),9(1,4)-ditriazolacyclohexadecaphane-6,14-diene (35). Following the general procedure for compound **32,** compound **35** (78%) was obtained as yellow oil. R_f = 0.4 (10% MeOH/CH_2Cl_2); IR (neat) 1552 cm^{-1}; HRMS (ESI) m/z calculated for $(C_{16}H_{22}N_6O_2+H)^+$ 331.1882, found: 331.1884. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (s, 1H), 5.92 – 5.74 (m, 2H), 4.94 (dq, *J* = 2.7, 1.3 Hz, 2H), 4.00 (dd, *J* = 2.0, 1.0 Hz, 2H), 3.78 – 3.63 (m, 2H), 3.01 (t, *J* = 5.5 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.1, 132.6, 124.2, 121.5, 70.0, 69.6, 51.9, 26.8.

References:

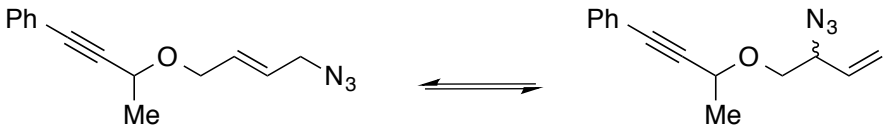
S1. Meng, T.; Hu, Y.; Zhao, Q.; Yu, T.; Wang, S. *Tetrahedron* **2011**, *67*, 8710.

S2. Liu, R.; Gutierrez, O.; Tantillo, D. J.; Aubé, J. *J. Am. Chem. Soc.* **2012**, *134*, 6528.

S3. Reetz, M. T.; Kindler, A. *J. Organomet. Chem.* **1995**, *502*, C5-C7.

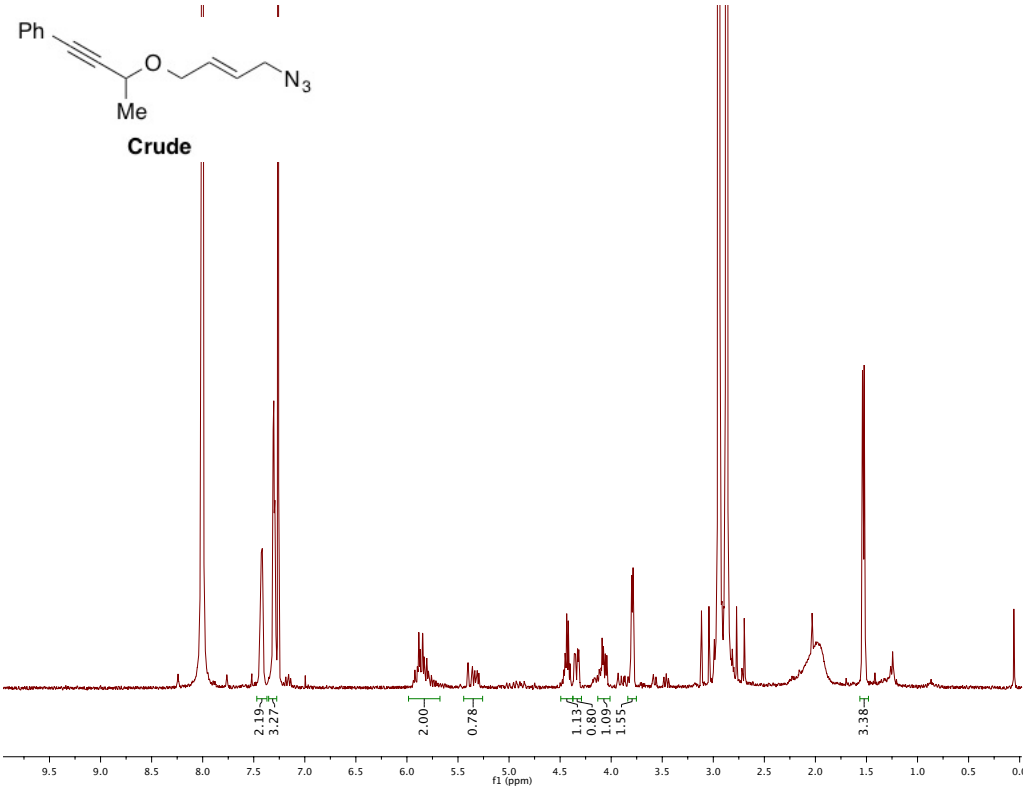
NMR Study of Rearrangement of Allylic Azide 7:

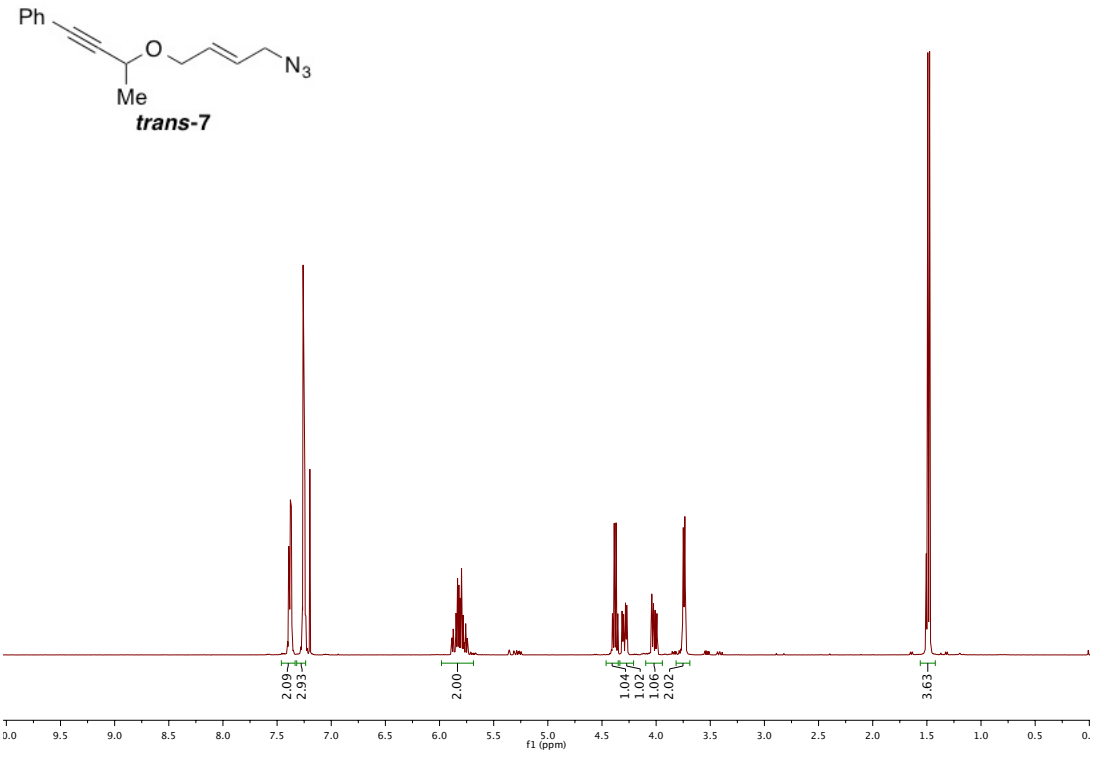
Compound **7** undergoes allylic azide rearrangement to afford a mixture of diastereomeric azides (plus, in principle a cis-configured alkene containing a terminal azide, although this was not detected in this case). Two diastereomers of the internal azide **i-7** are possible.

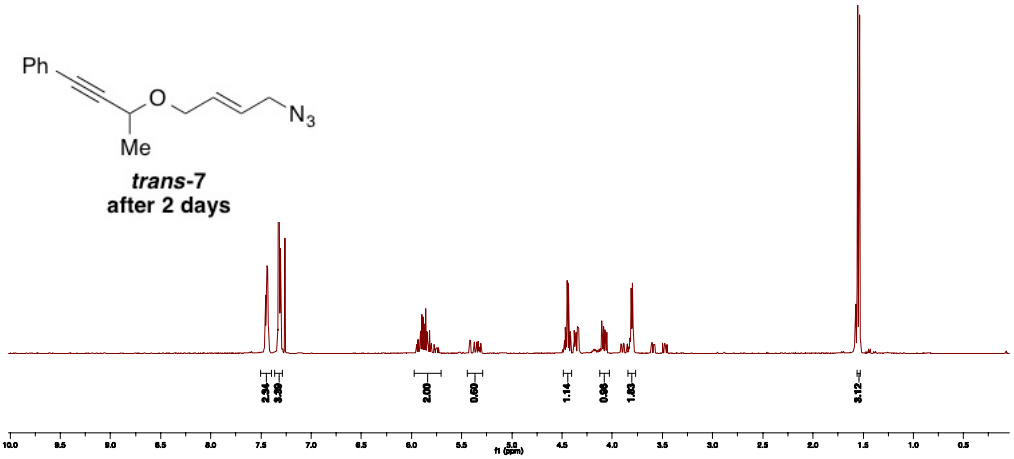


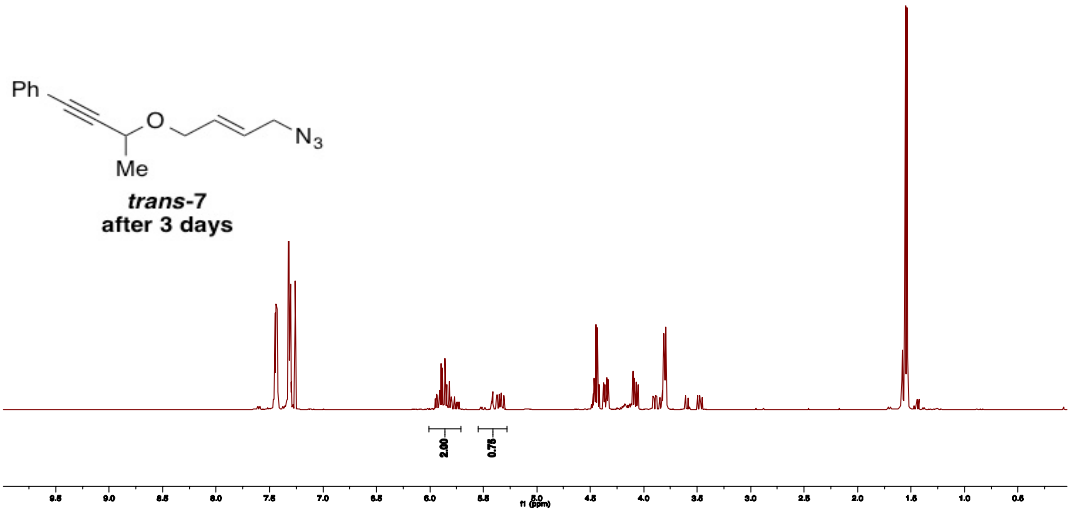
***trans*-7** **i-7**

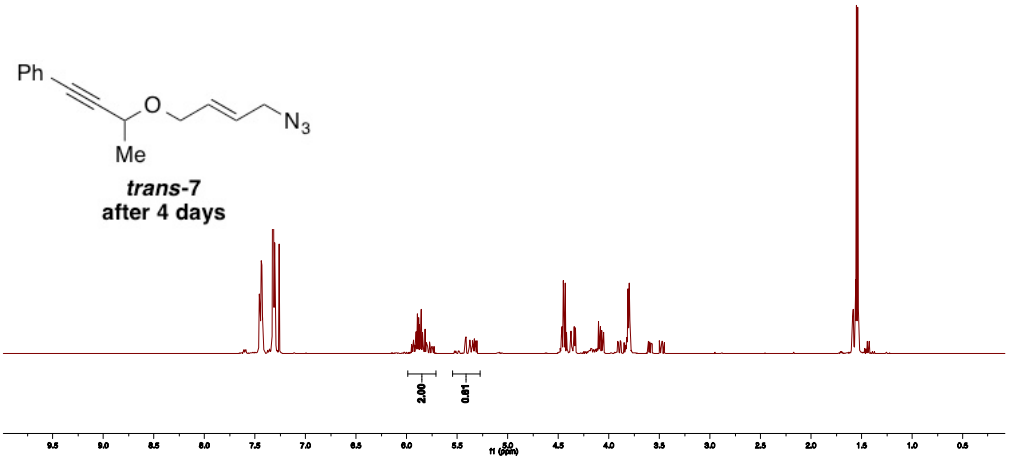
In the crude NMR of compound **7** as prepared by displacement of the corresponding bromide, all three of the isomers depicted above were present. A sample highly enriched in ***trans*-7** could isolated by column chromatography and was monitored by ^{1}H NMR at room temperature in $CDCl_3$ for a week, at which time no further spectral changes were observed, suggesting that equilibrium ratio was obtained at this point (see spectra on following pages).

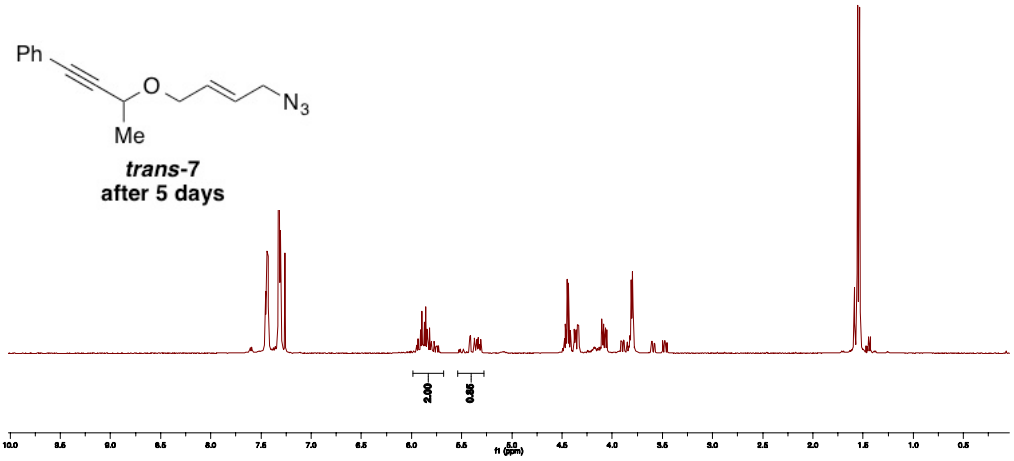

Ph
O
N3
Me
Crude
2.19
3.27
2.00
0.78
1.13
0.80
1.09
1.55
3.38
f1 (ppm)

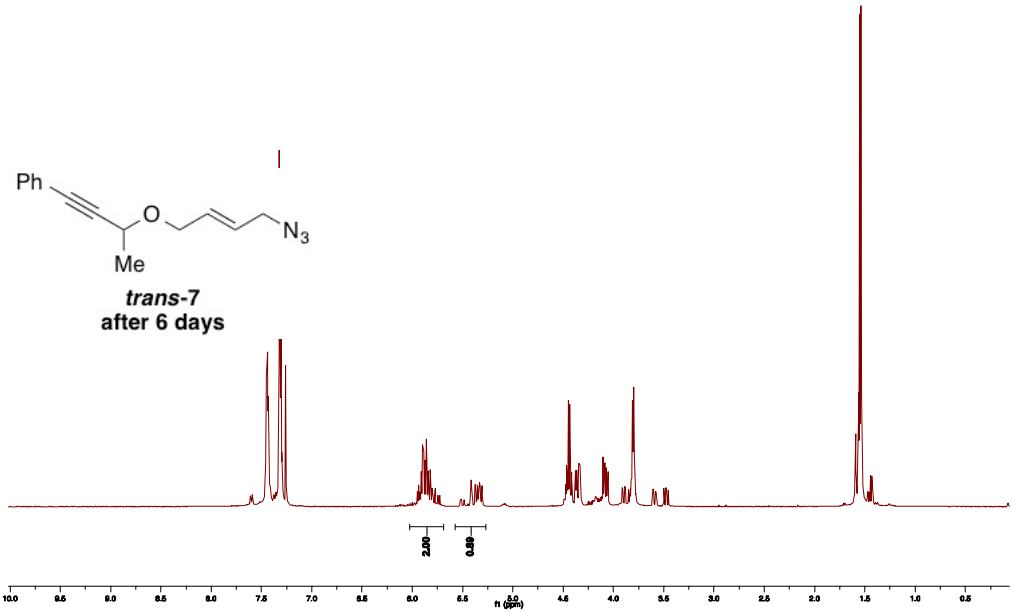

Ph
O
N3
Me
trans-7
2.09
2.93
2.00
1.04
1.02
1.06
2.02
3.63
f1 (ppm)

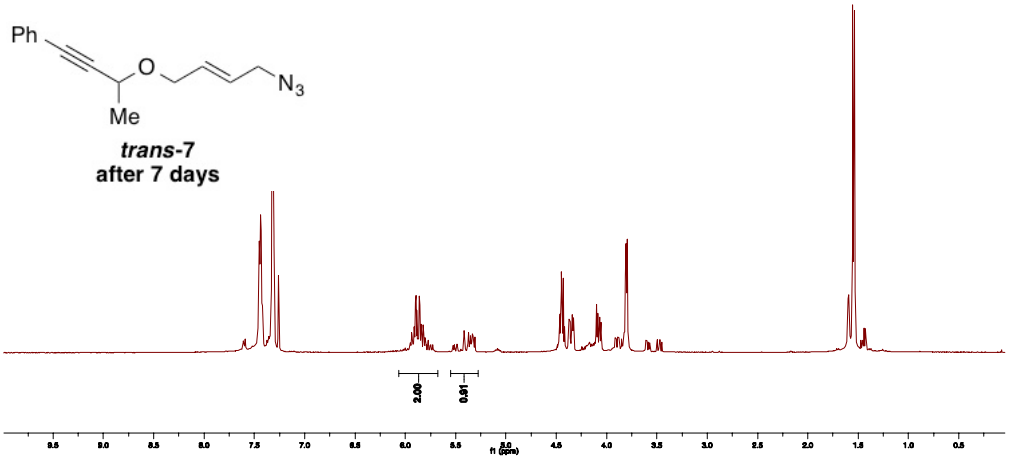

Ph
O
N3
Me
trans-7
after 2 days


Ph
O
N3
Me
trans-7
after 3 days

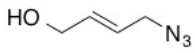

Ph
O
N3
Me
trans-7
after 4 days


Ph
O
N3
Me
trans-7
after 5 days
2.00
0.85
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

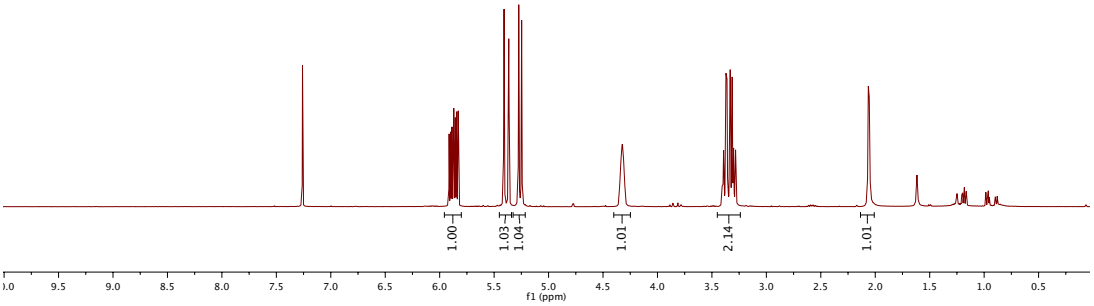

Ph
O
N3
Me
trans-7
after 6 days
2.00
0.89
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

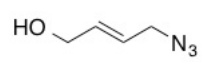

Ph
O
N3
Me
trans-7
after 7 days
2.00
0.91
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

Copies of ^{1}H and ^{13}C NMR spectra:

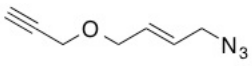


***trans*-S1**

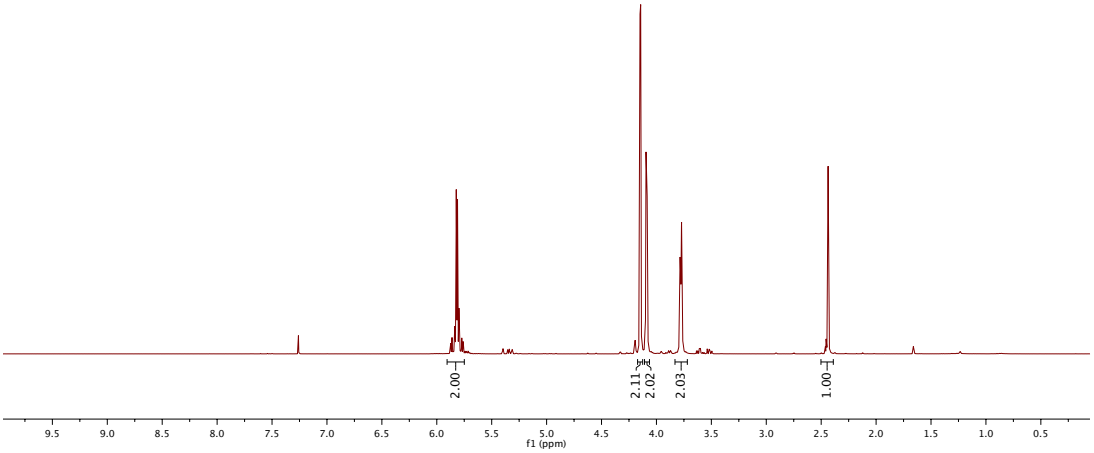


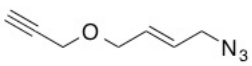


***trans*-S1**

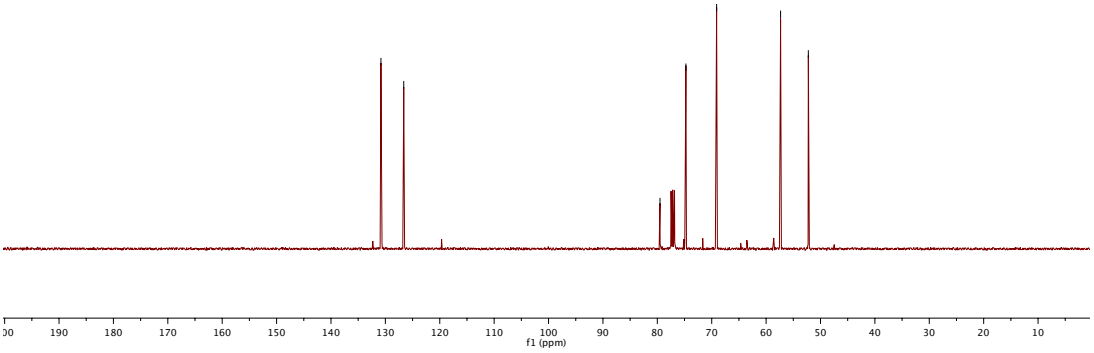


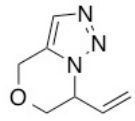
***trans*-1**



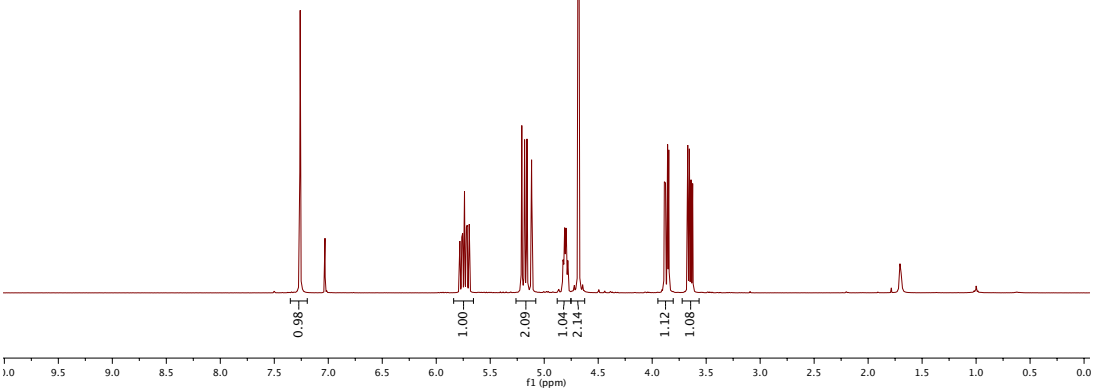


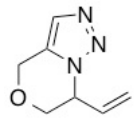
***trans*-1**





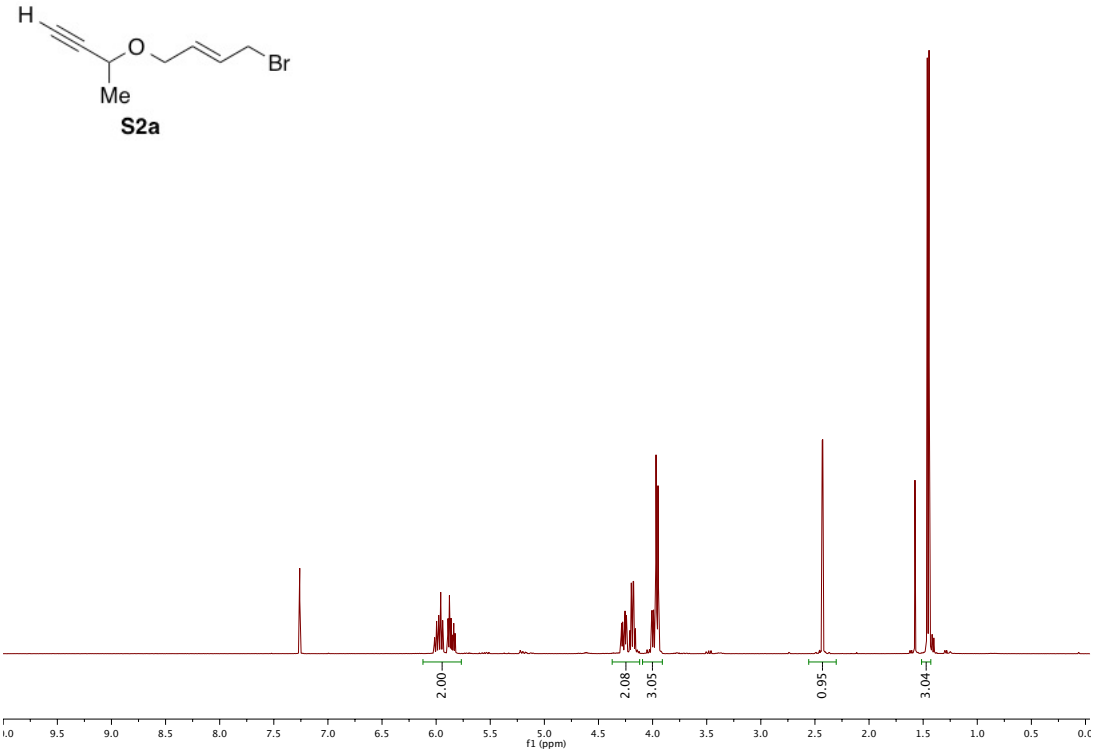
11

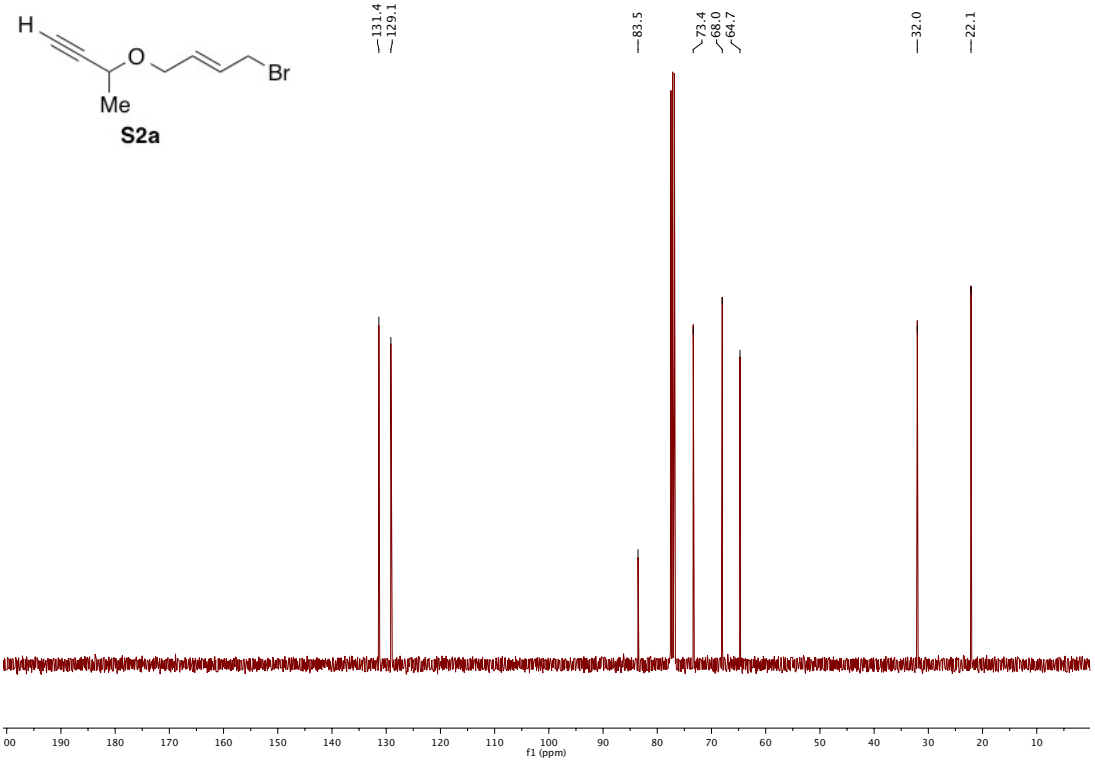

0.98
1.00
2.09
1.04
2.14
1.12
1.08
f1 (ppm)

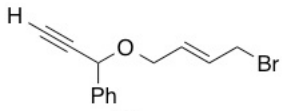


11

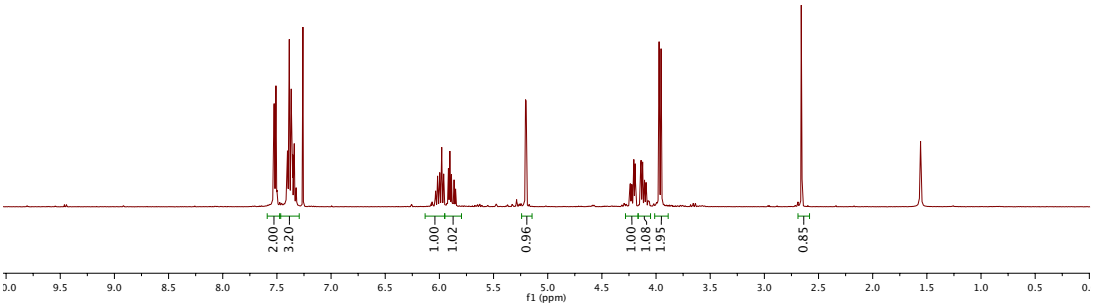
132.4
130.5
128.2
120.8
68.4
62.5
58.7
f1 (ppm)

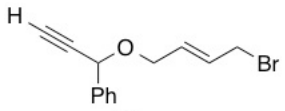

H
O
Br
Me
S2a
2.00
2.08
3.05
0.95
3.04
f1 (ppm)


H
O
Br
Me
S2a
131.4
129.1
83.5
73.4
68.0
64.7
32.0
22.1
f1 (ppm)


H
O
Br
Ph

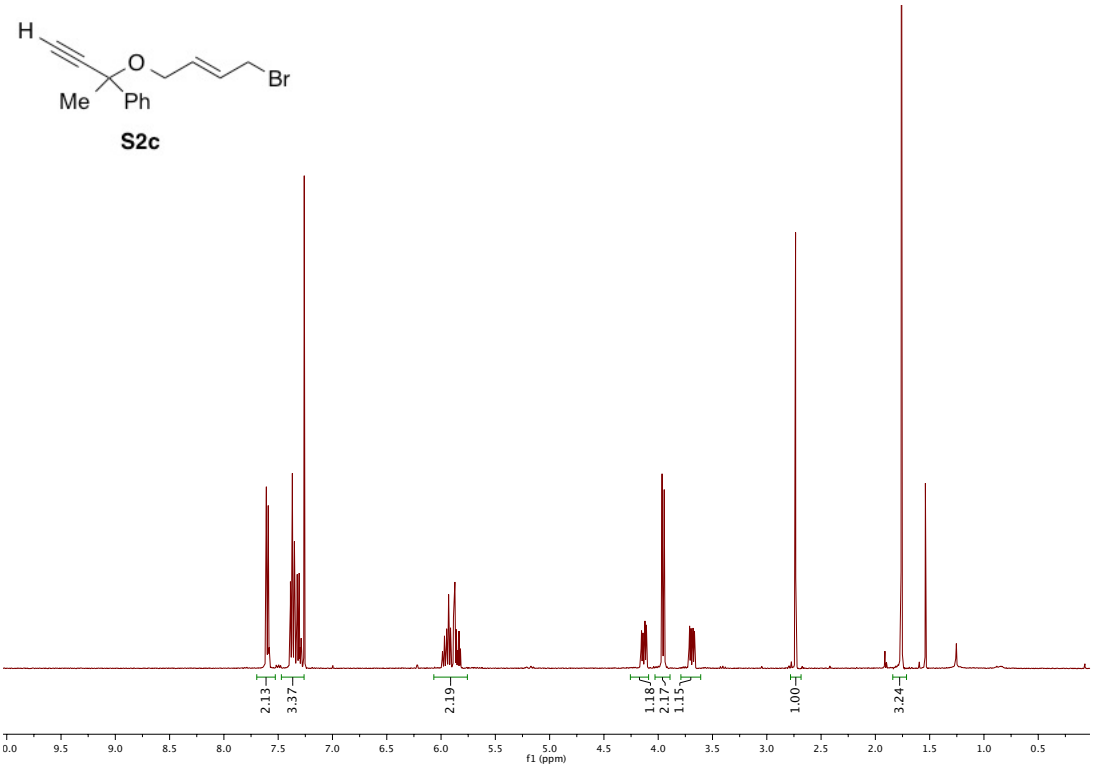
S2b

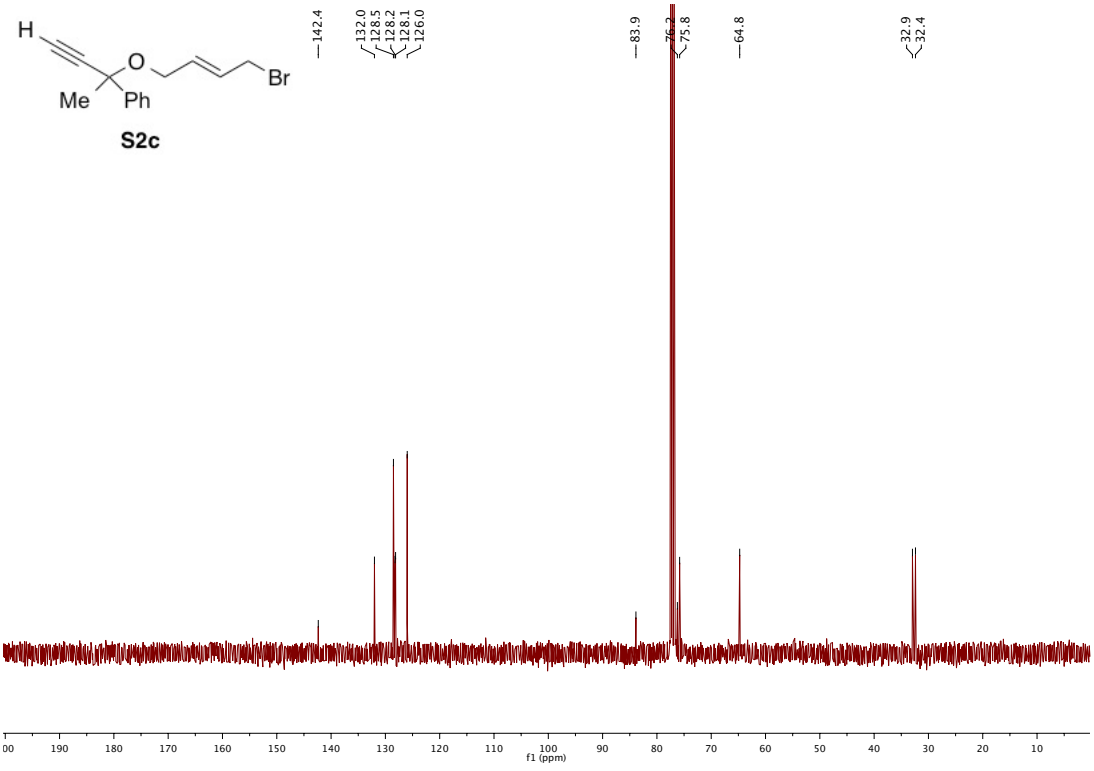

2.00
3.20
1.00
1.02
0.96
1.00
1.08
1.95
0.85
f1 (ppm)

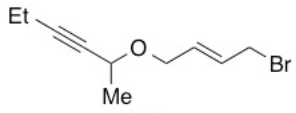

H
O
Br
Ph

S2b

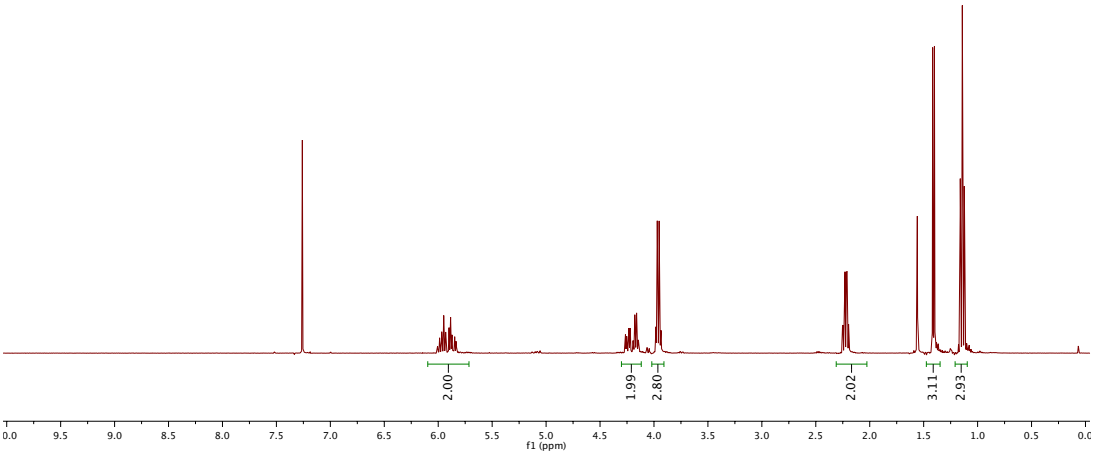
138.0
131.2
128.7
128.6
128.0
127.5
84.0
76.0
70.9
67.6
32.0
f1 (ppm)

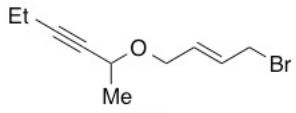

H
O
Br
Me
Ph
S2c
2.13
3.37
2.19
1.18
2.17
1.15
1.00
3.24
f1 (ppm)


H
O
Br
Me
Ph
S2c
142.4
132.0
128.5
128.2
128.1
126.0
83.9
76.2
75.8
64.8
32.9
32.4
f1 (ppm)


Et
O
Br
Me

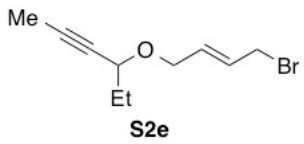
S2d


2.00
1.99
2.80
2.02
3.11
2.93
f1 (ppm)


Et
O
Br
Me

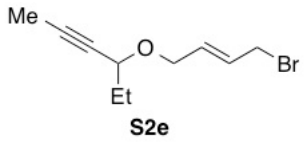
S2d

131.8
128.8
87.4
79.1
67.8
65.2
32.2
22.6
14.1
12.5
f1 (ppm)


Me
O
Br
Et

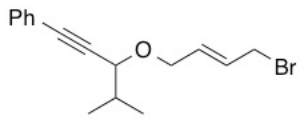
S2e

2.00
1.04
3.98
3.13
2.23
3.25
f1 (ppm)

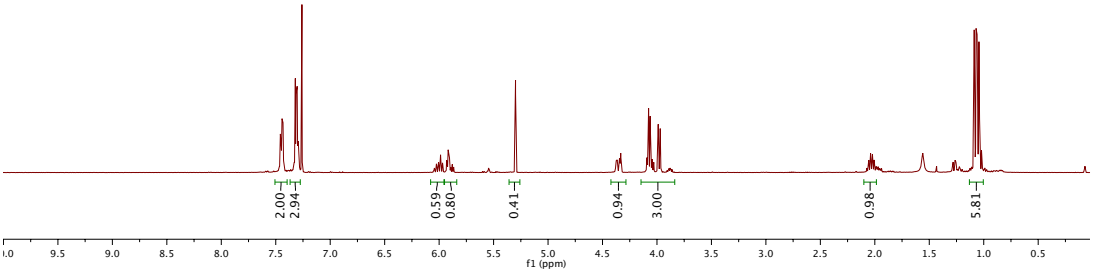

Me
O
Br
Et

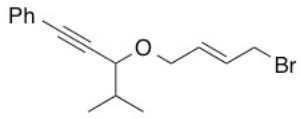
S2e

131.9
128.7
82.1
78.1
70.9
67.9
32.3
29.2
9.9
3.7
f1 (ppm)


Ph
O
Br

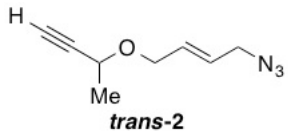
S2g


2.00
2.94
0.59
0.80
0.41
0.94
3.00
0.98
5.81
f1 (ppm)

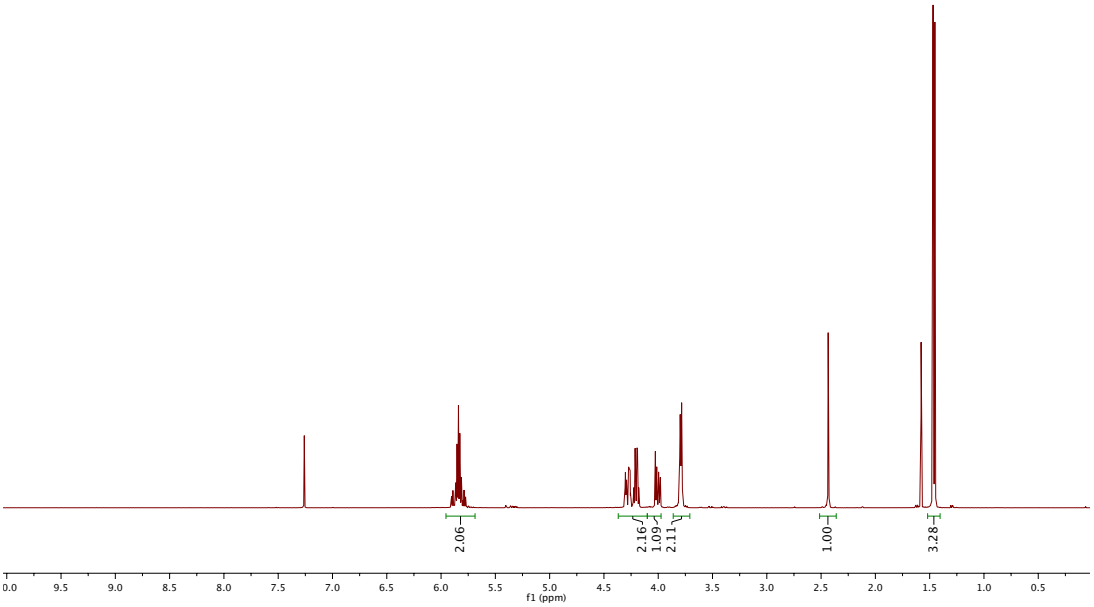

Ph
O
Br

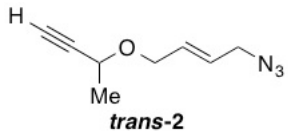
S2g

132.0
131.9
128.7
128.4
128.3
123.0
87.1
86.8
75.4
68.3
33.5
32.3
18.8
18.1
f1 (ppm)

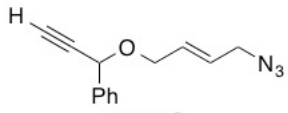


***trans*-2**

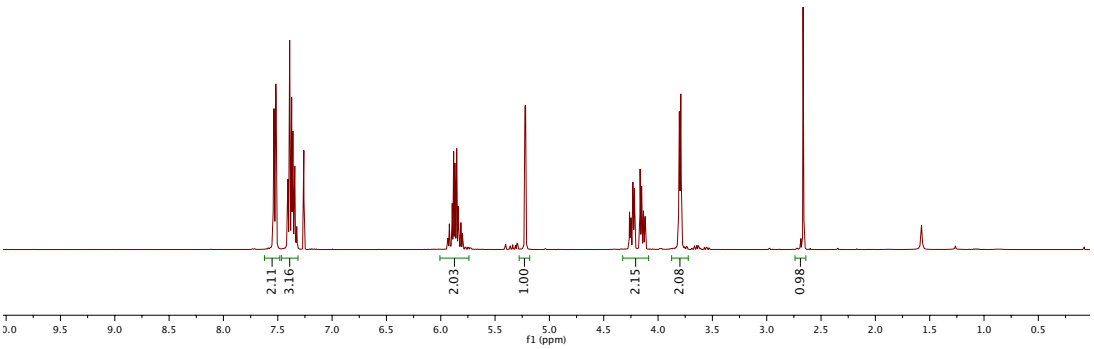


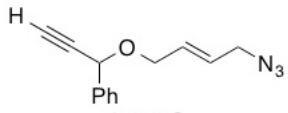


***trans*-2**

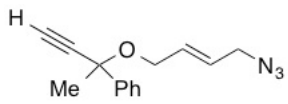


***trans*-3**

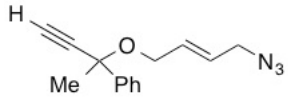




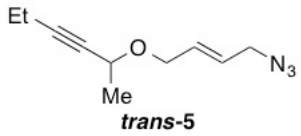
***trans*-3**



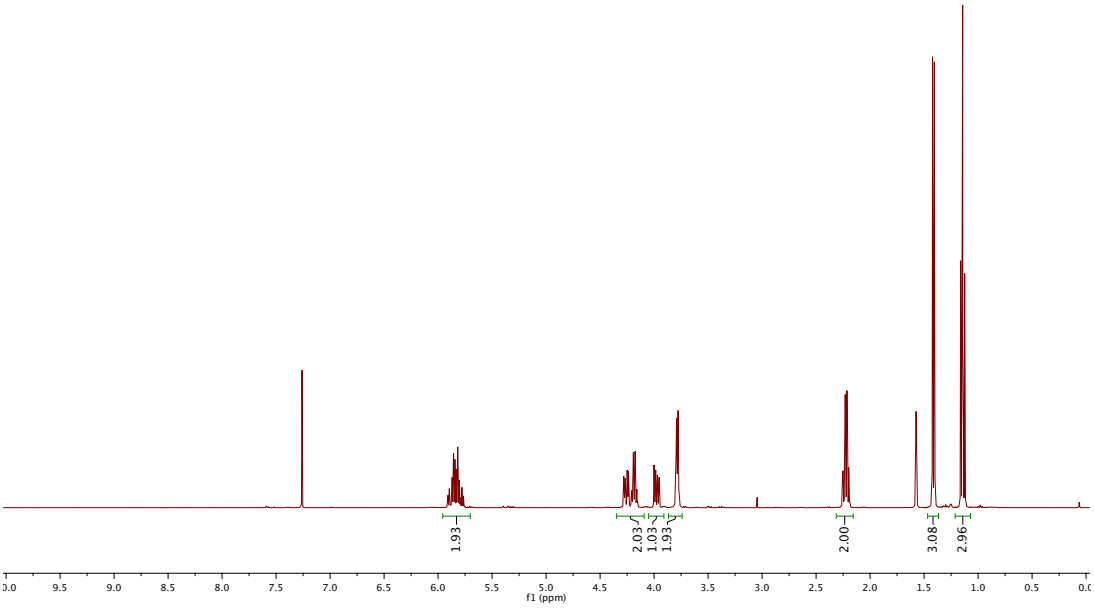
***trans*-4**

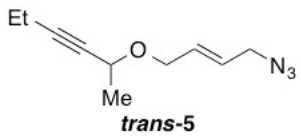


***trans*-4**

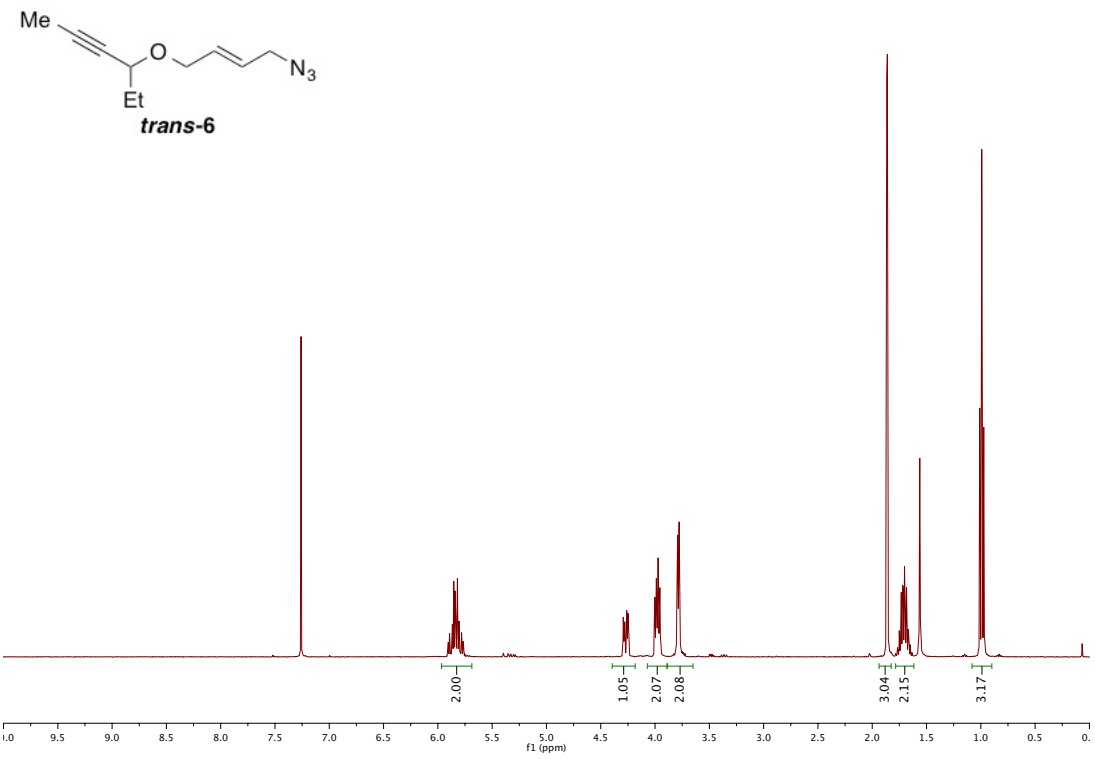


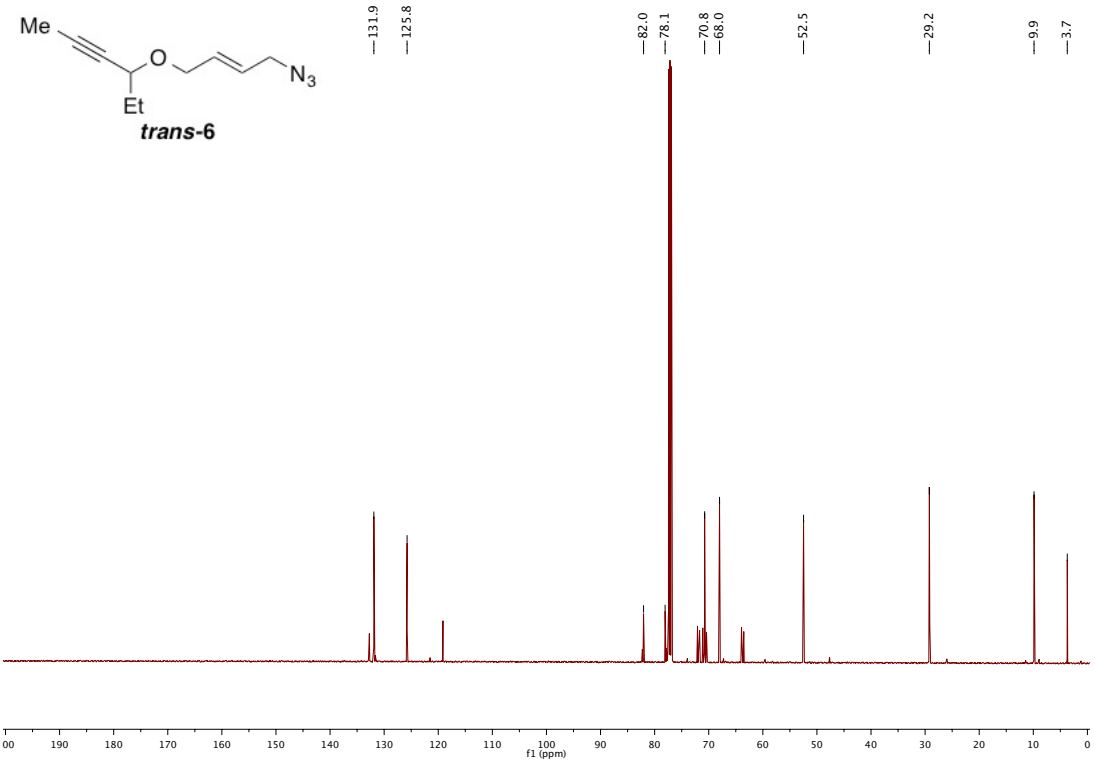
***trans*-5**

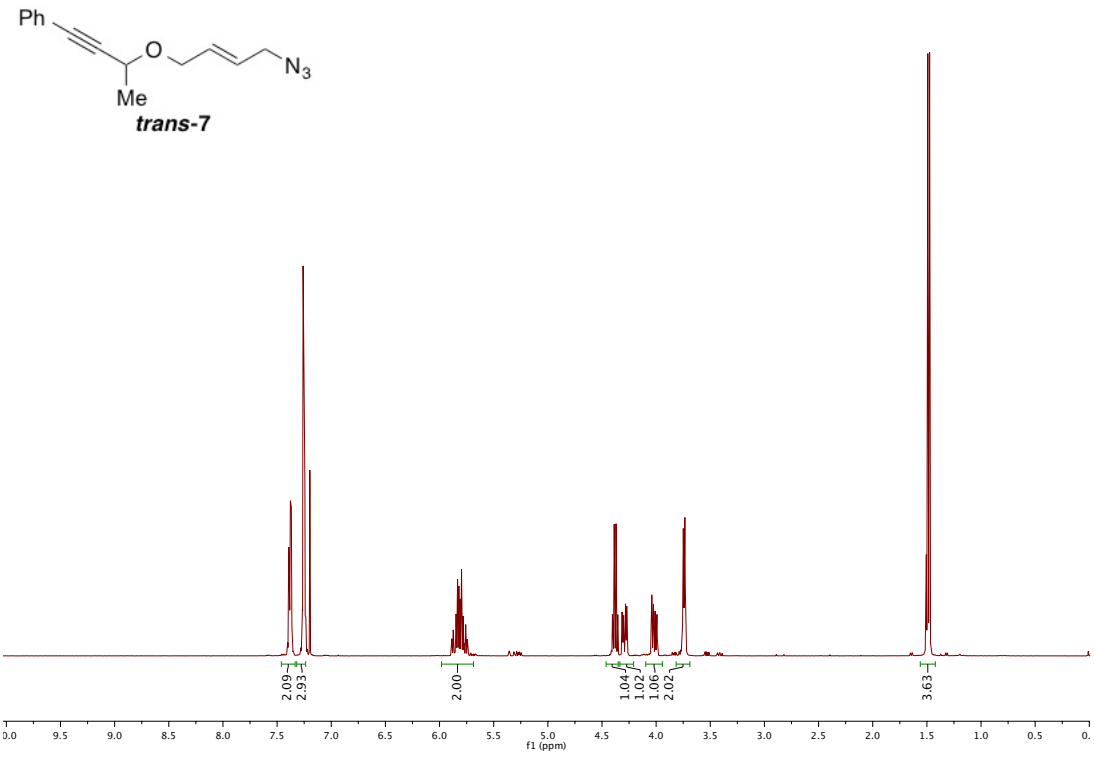


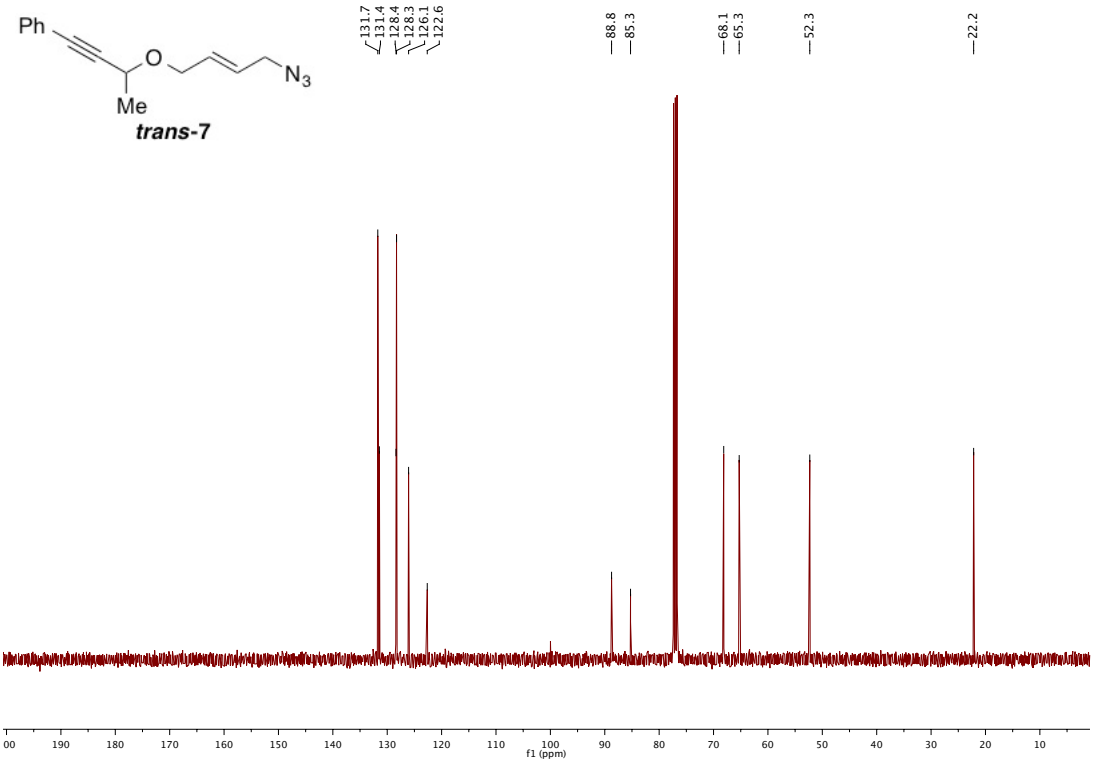


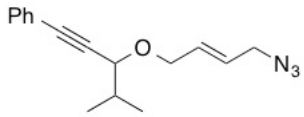
***trans*-5**


Me
O
N3
Et
trans-6
2.00
1.05
2.07
2.08
3.04
2.15
3.17
f1 (ppm)

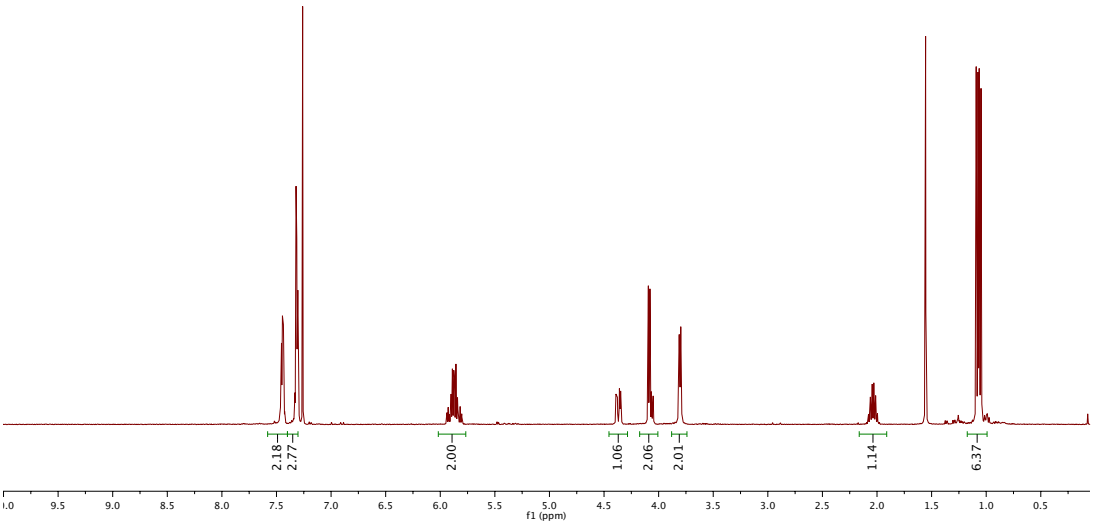

Me
O
N3
Et
trans-6
131.9
125.8
82.0
78.1
70.8
68.0
52.5
29.2
9.9
3.7
f1 (ppm)

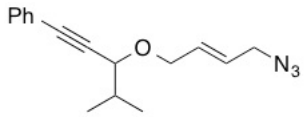

Ph
O
N3
Me
trans-7
2.09
2.93
2.00
1.04
1.02
1.06
2.02
3.63
f1 (ppm)


Ph
O
N3
Me
trans-7
131.7
131.4
128.4
128.3
126.1
122.6
88.8
85.3
68.1
65.3
52.3
22.2
f1 (ppm)

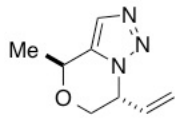


***trans*-8**

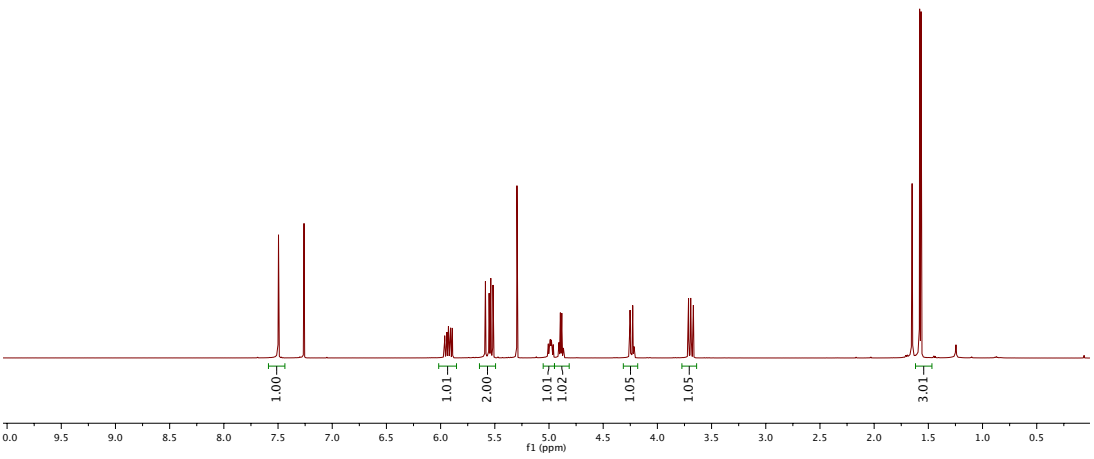


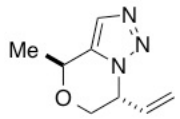


***trans*-8**


Me
N
N
N
O

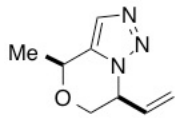
12a


1.00
1.01
2.00
1.01
1.02
1.05
1.05
3.01
f1 (ppm)

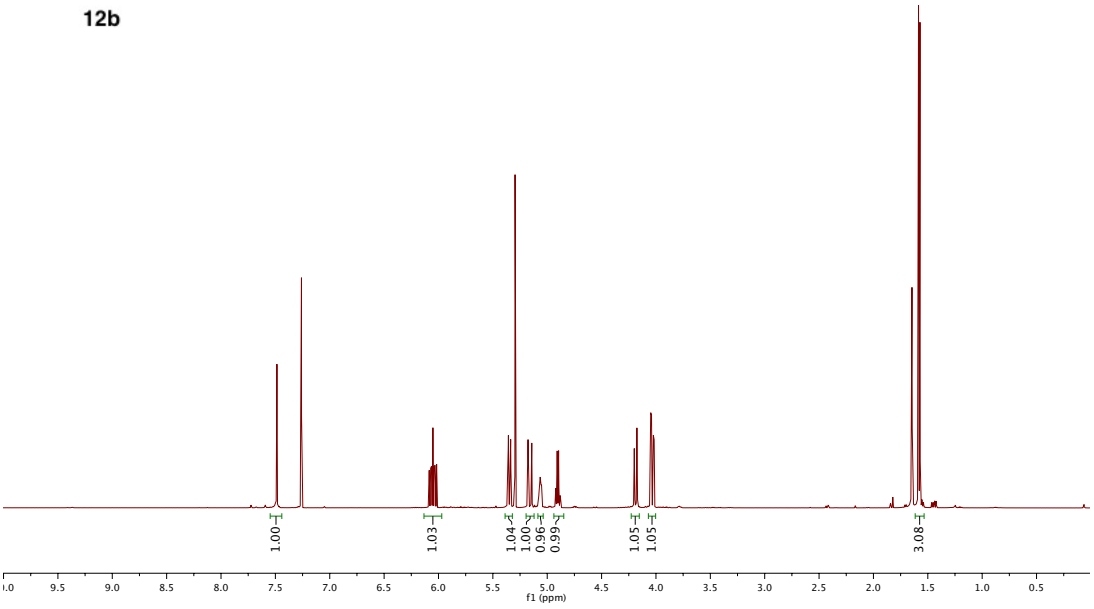

Me
N
N
N
O

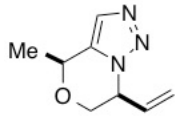
12a

135.7
131.2
128.8
122.1
69.4
68.1
59.3
20.4
f1 (ppm)


Me
N
N
N
O

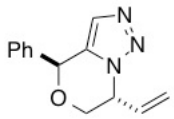
12b


1.00
1.03
1.04
1.00
0.96
0.99
1.05
1.05
3.08
f1 (ppm)

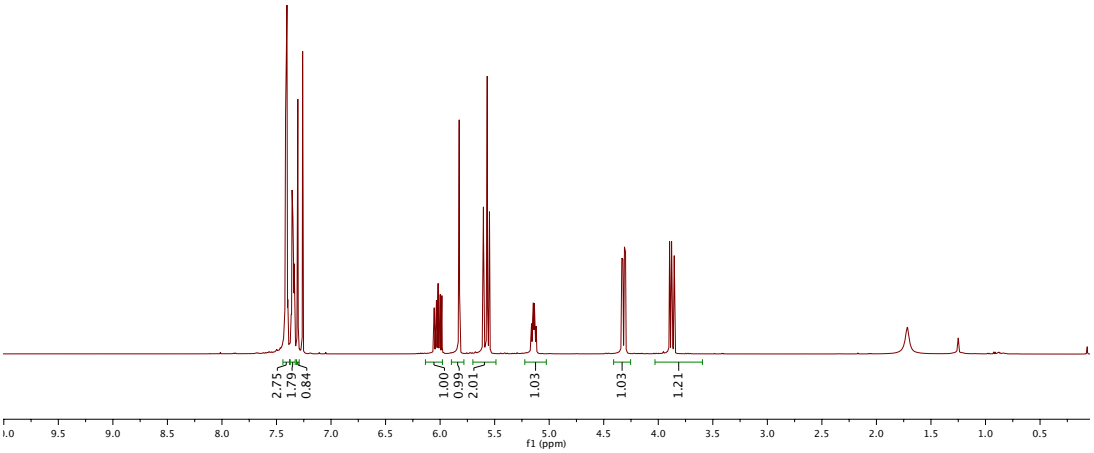

Me
N
N
N
O

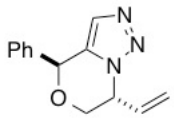
12b

135.3
134.4
128.5
119.3
69.3
67.6
57.8
20.7
f1 (ppm)


Ph
N
N
N
O

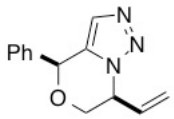
13a


2.75
1.79
0.84
1.00
0.99
2.01
1.03
1.03
1.21
f1 (ppm)


Ph
N
N
N
O

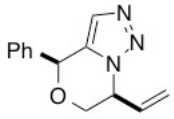
13a

137.6
134.0
131.5
130.5
129.6
129.1
127.8
122.0
75.6
67.7
59.3
f1 (ppm)


Ph
N
N
N
O

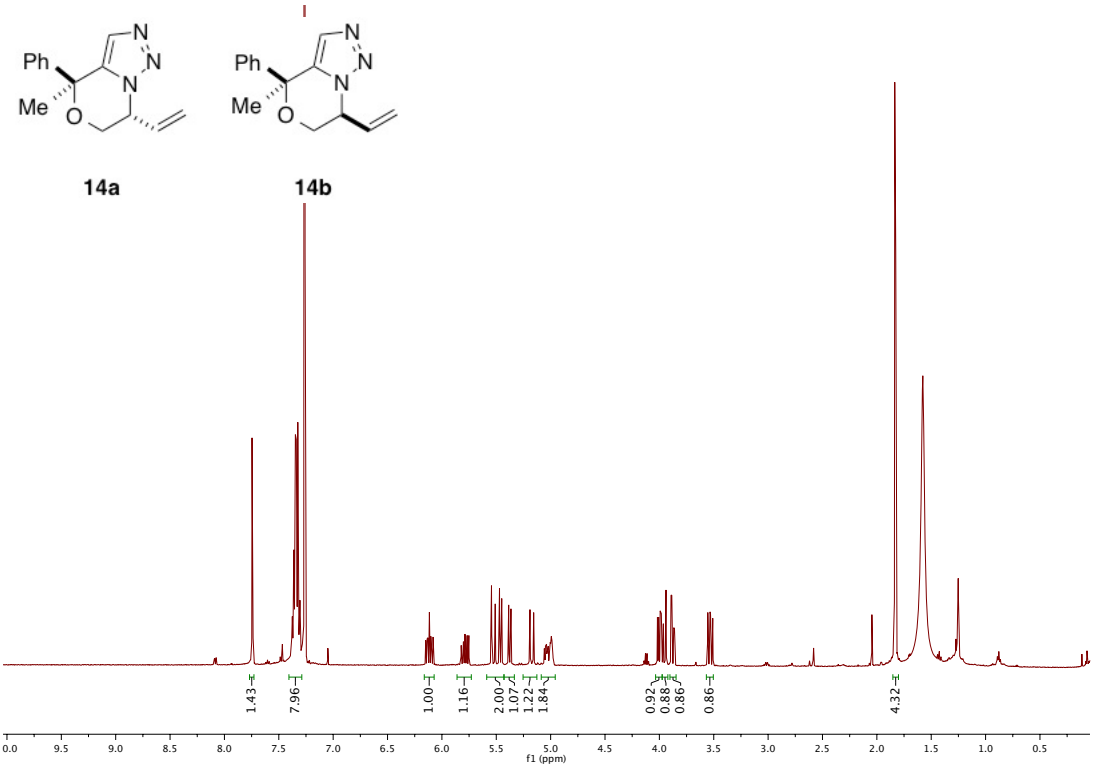
13b

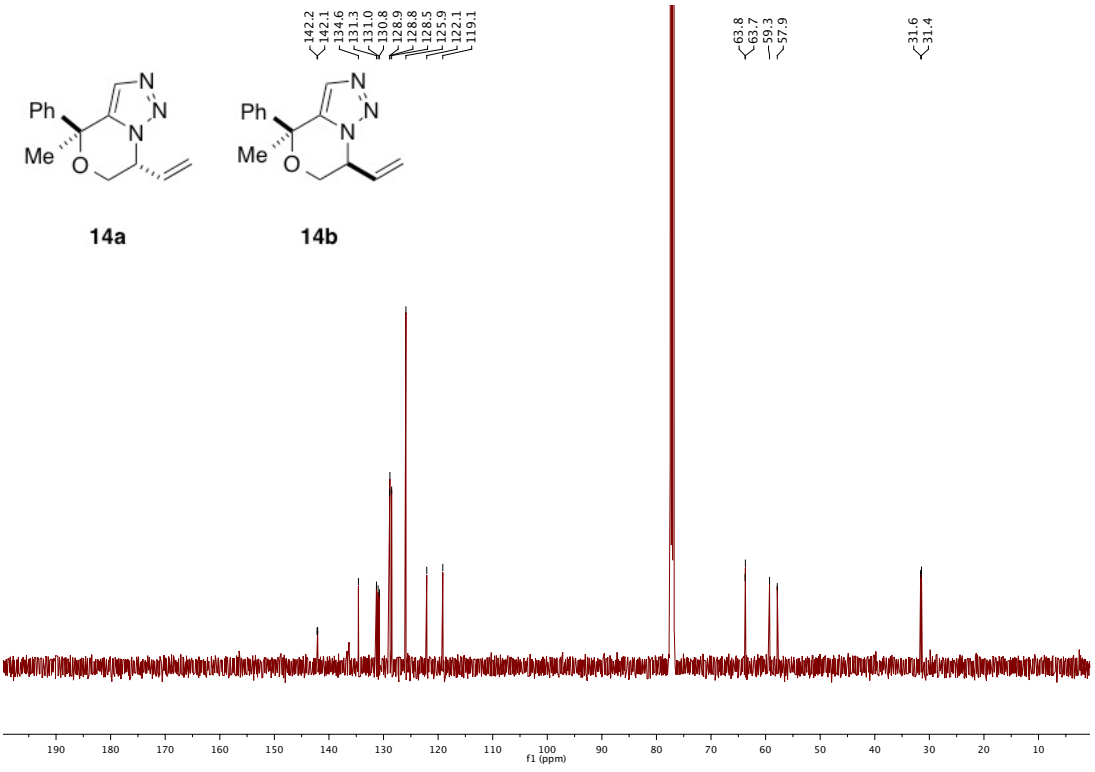
2.96
2.70
1.00
0.98
0.99
1.03
1.00
2.00
f1 (ppm)

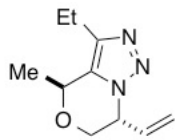

Ph
N
N
N
O

13b

137.7
134.0
129.6
129.6
129.1
127.8
120.2
119.8
75.4
67.2
58.1
f1 (ppm)

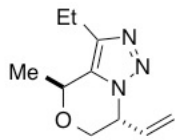

Ph
Me
O
N
N
N
14a
14b
1.43
7.96
1.00
1.16
2.00
1.07
1.22
1.84
0.92
0.88
0.86
4.32
f1 (ppm)


142.2
142.1
134.6
131.3
131.0
130.8
128.9
128.8
128.5
125.9
122.1
119.1
63.8
63.7
59.3
57.9
31.6
31.4
Ph
Me
O
N
N
N
14a
14b
f1 (ppm)


Et
N
N
Me
N
O

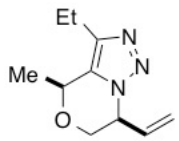
15a

1.00
1.91
1.90
1.03
0.99
2.02
2.89
3.10
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

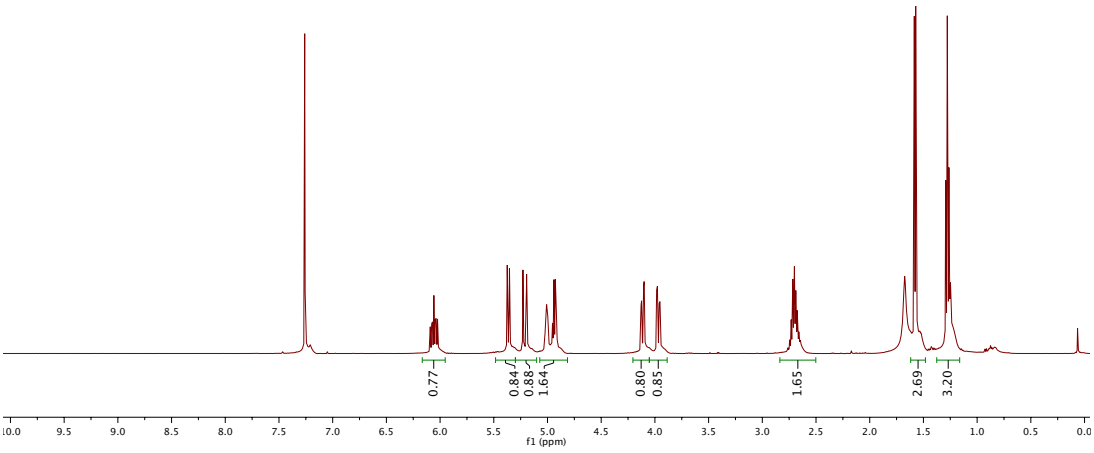

Et
N
N
Me
N
O

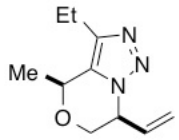
15a

143.3
131.8
130.5
121.4
69.4
67.3
59.4
19.6
19.2
14.1
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


Et
N
N
Me
N
O

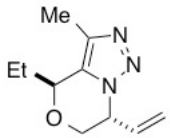
15b


0.77
0.84
0.88
1.64
0.80
0.85
1.65
2.69
3.20
f1 (ppm)


Et
N
N
Me
N
O

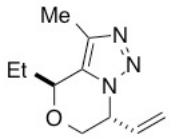
15b

143.1
134.1
130.3
119.5
69.2
67.0
58.2
19.8
19.2
14.0
f1 (ppm)


Me
Et
N
N
N
O

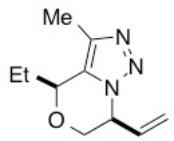
16a

1.00
1.86
0.95
0.96
0.99
0.99
2.78
1.00
1.07
2.91
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


Me
Et
N
N
N
O

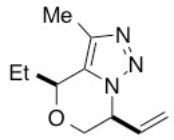
16a

137.4
131.7
130.0
121.5
73.9
67.3
59.6
26.0
11.4
8.9
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Me
N
N
Et
N
O

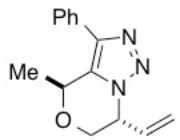
16b

1.00
1.14
1.06
1.10
1.06
0.86
1.12
3.17
3.14
f1 (ppm)


Me
N
N
Et
N
O

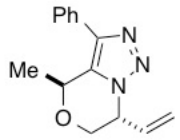
16b

137.2
134.2
129.7
119.4
73.8
66.9
58.2
26.1
11.3
8.8
f1 (ppm)


Ph
N
N
Me
N
O

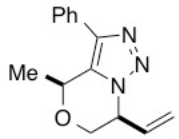
17a

1.90
1.83
0.93
0.95
1.90
1.01
0.98
1.00
1.01
2.75
f1 (ppm)


Ph
N
N
Me
N
O

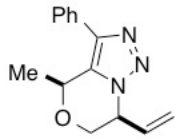
17a

142.3
131.9
131.3
131.3
128.8
128.2
127.8
121.3
69.7
66.4
59.6
18.8
f1 (ppm)


Ph
N
N
Me
N
O

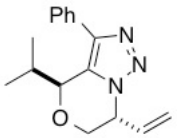
17b

1.94
1.96
0.94
1.00
0.95
1.89
0.96
1.98
2.88
f1 (ppm)

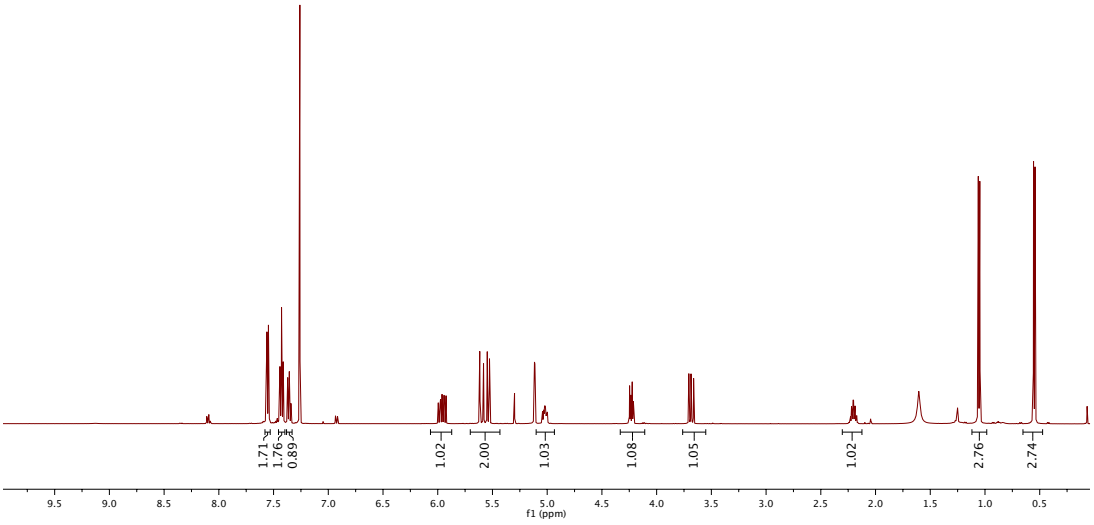

Ph
N
N
Me
N
O

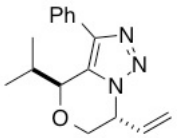
17b

142.0
133.6
131.3
131.1
128.8
128.1
127.7
120.0
69.7
66.4
58.6
18.9
f1 (ppm)


Ph
N
N
N
O

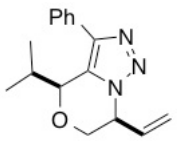
18a


1.71
1.76
0.89
1.02
2.00
1.03
1.08
1.05
1.02
2.76
2.74
f1 (ppm)


Ph
N
N
N
O

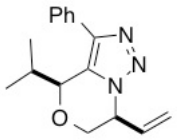
18a

142.5
131.6
131.1
130.2
128.8
128.2
128.1
122.0
77.8
67.7
60.5
29.9
19.2
15.1
f1 (ppm)


Ph
N
N
N
O

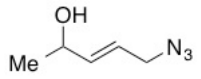
18b

1.92
1.98
0.93
1.00
1.93
1.84
1.01
0.97
1.04
2.87
2.75
f1 (ppm)

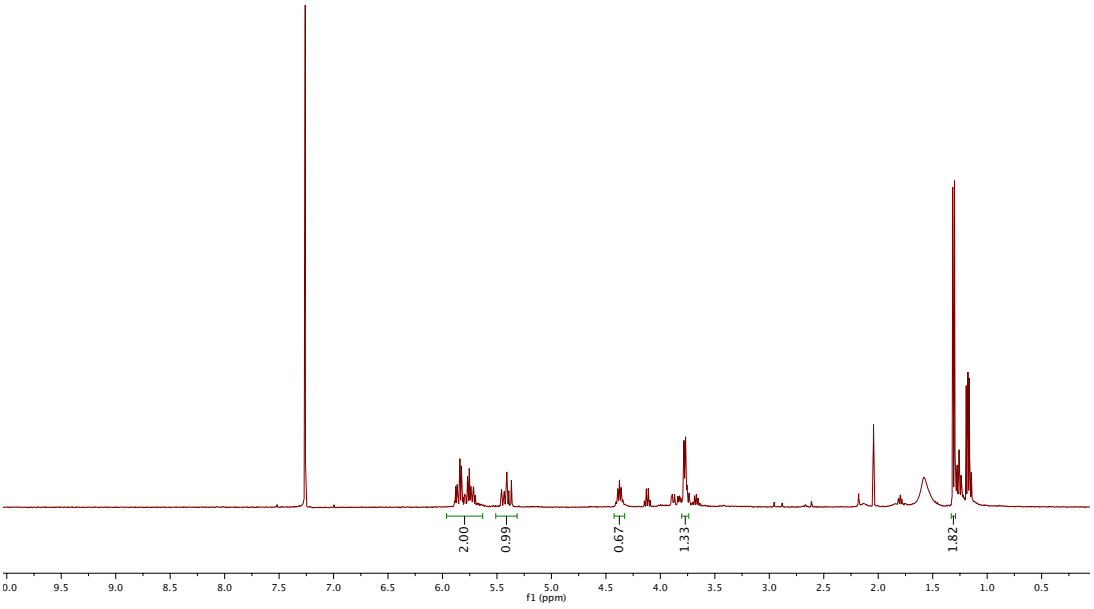

Ph
N
N
N
O

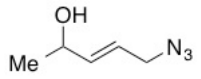
18b

142.1
134.3
131.6
130.0
128.8
128.2
128.0
119.6
77.9
67.3
58.5
29.8
19.1
15.5
f1 (ppm)

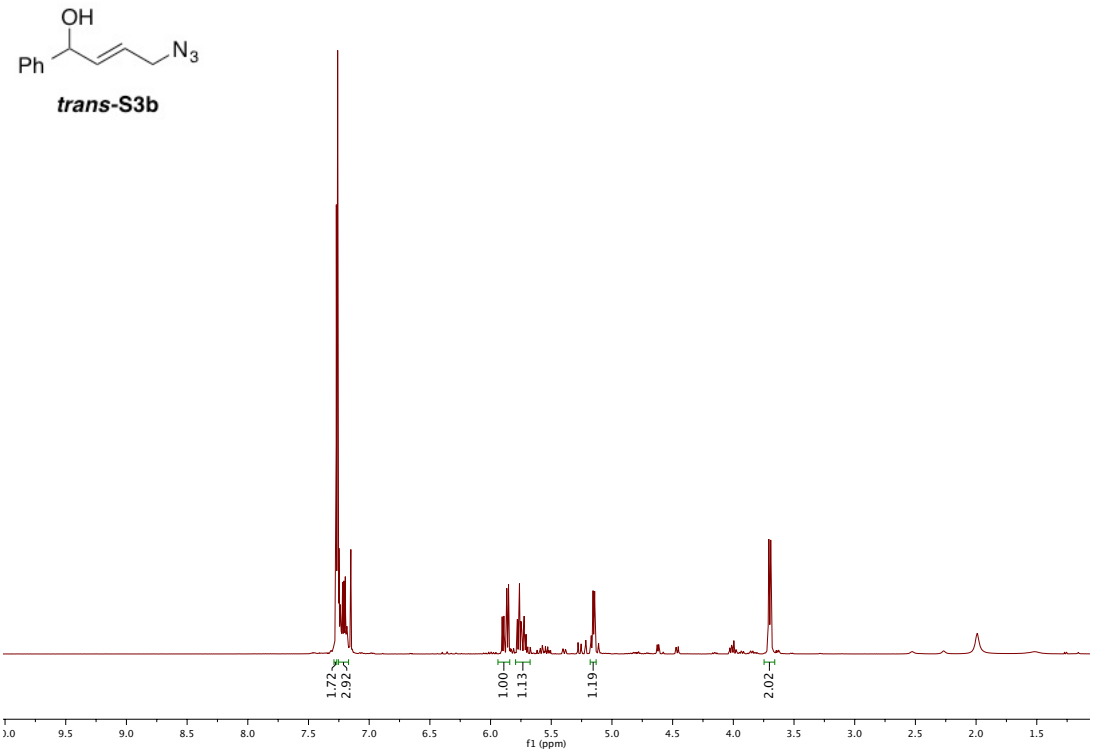


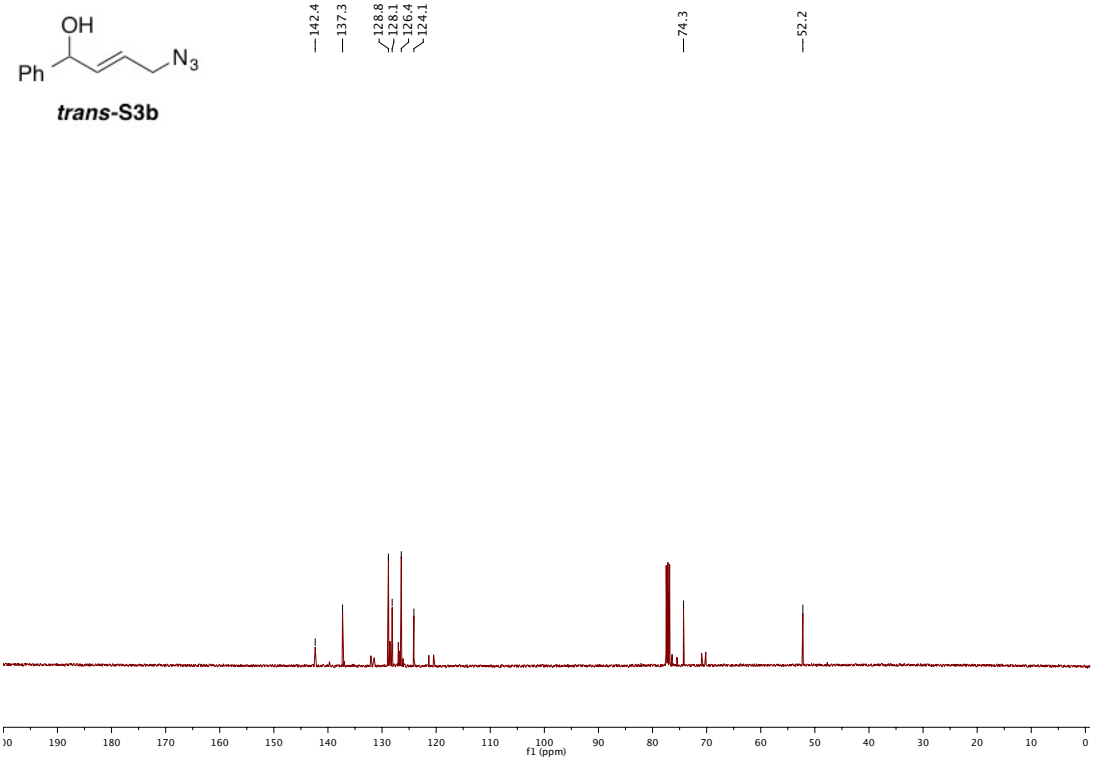
***trans*-S3a**

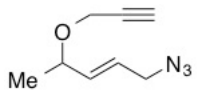




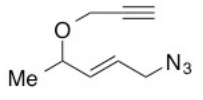
***trans*-S3a**


OH
Ph
N3
trans-S3b
1.72
2.92
1.00
1.13
1.19
2.02
f1 (ppm)

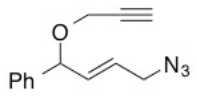

OH
Ph
N3
trans-S3b
142.4
137.3
128.8
128.1
126.4
124.1
74.3
52.2
f1 (ppm)



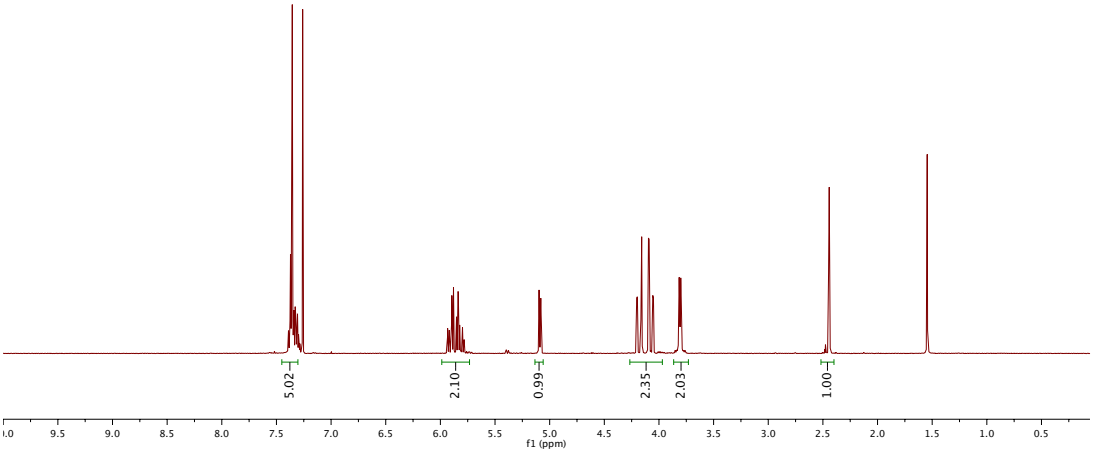
***trans*-9**

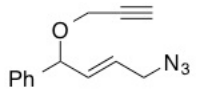


***trans*-9**

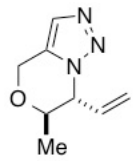


***trans*-10**

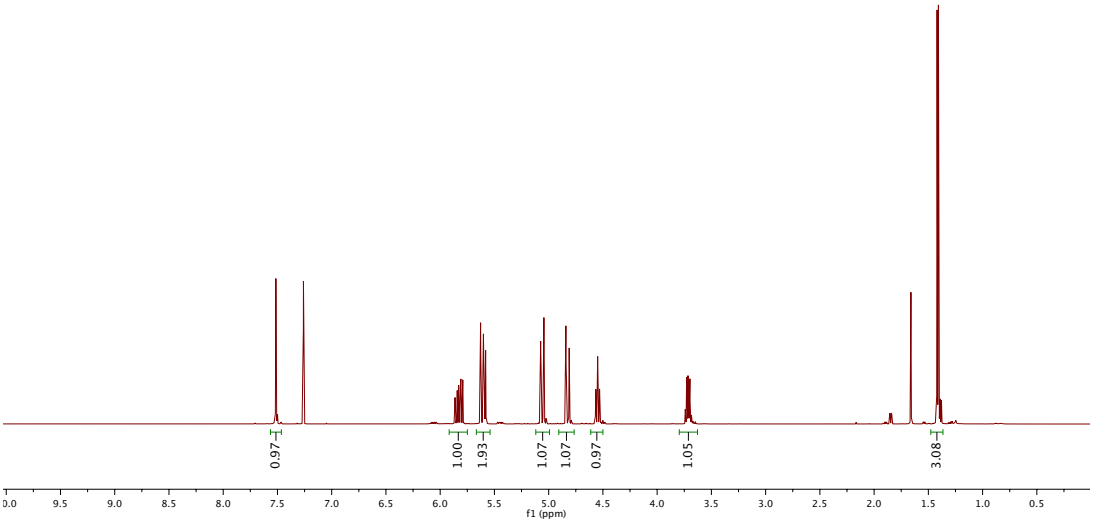


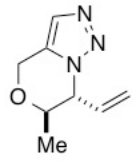


***trans*-10**


N
N
N
O
Me

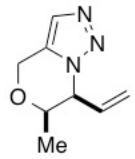
19a


0.97
1.00
1.93
1.07
1.07
0.97
1.05
3.08
f1 (ppm)


N
N
N
O
Me

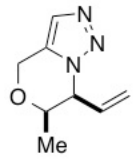
19a

131.7
130.7
128.3
123.3
74.4
66.0
61.8
17.5
f1 (ppm)


N
N
N
O
Me

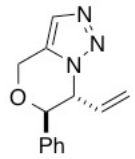
19b

1.00
1.00
1.01
1.00
1.11
0.95
1.14
1.08
2.94
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

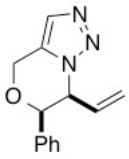

N
N
N
O
Me

19b

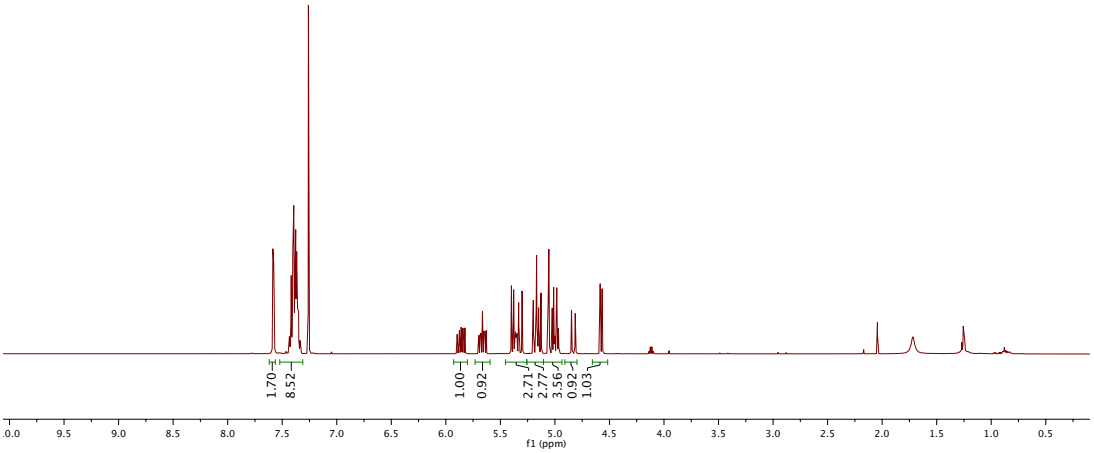
131.2
130.0
127.9
121.4
72.7
62.6
62.2
17.3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

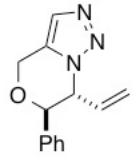


20a

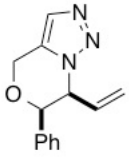


20b

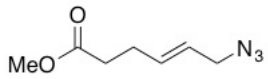




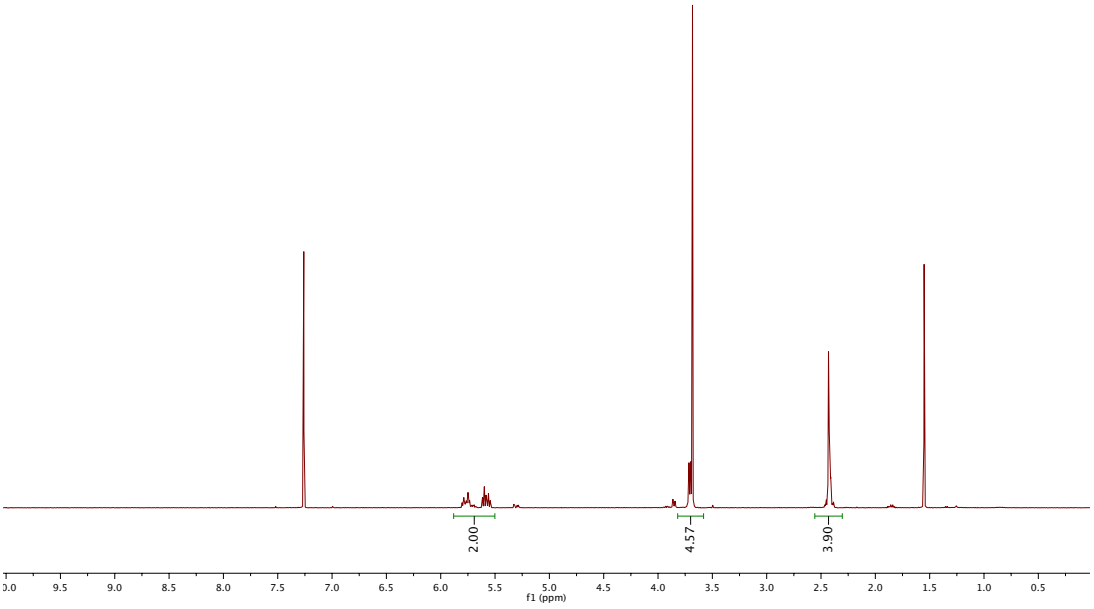
20a

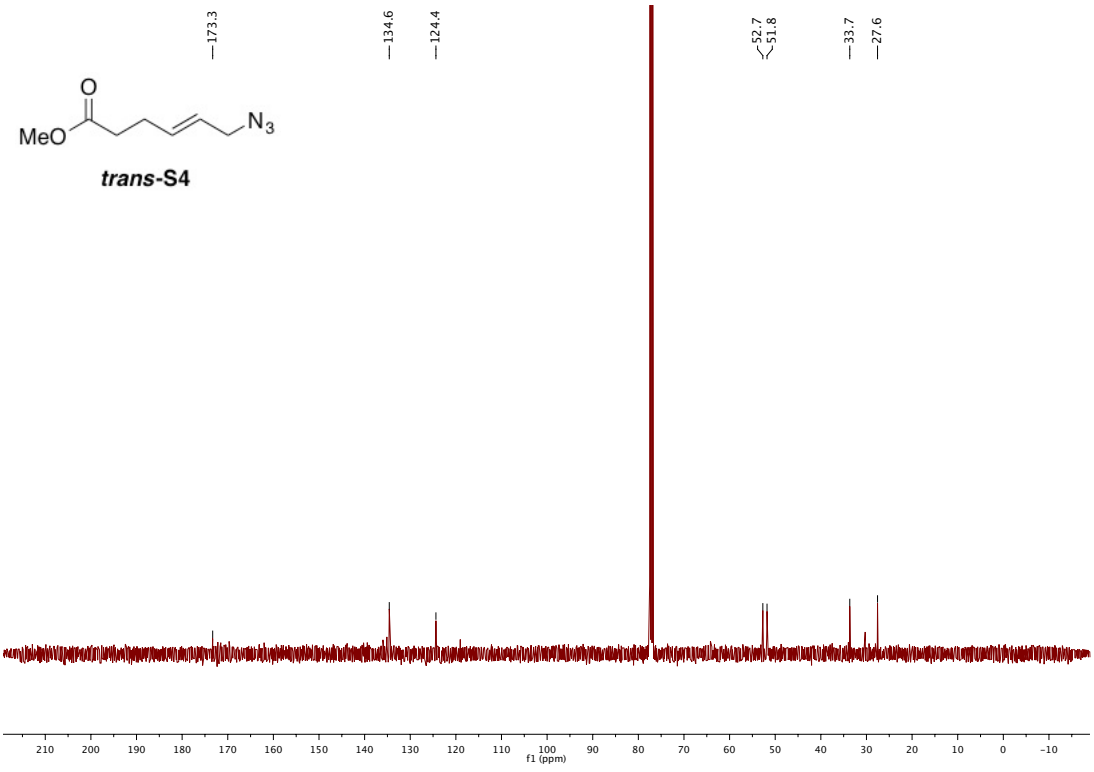


20b

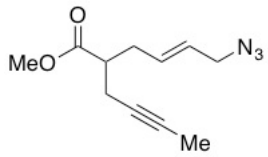


***trans*-S4**

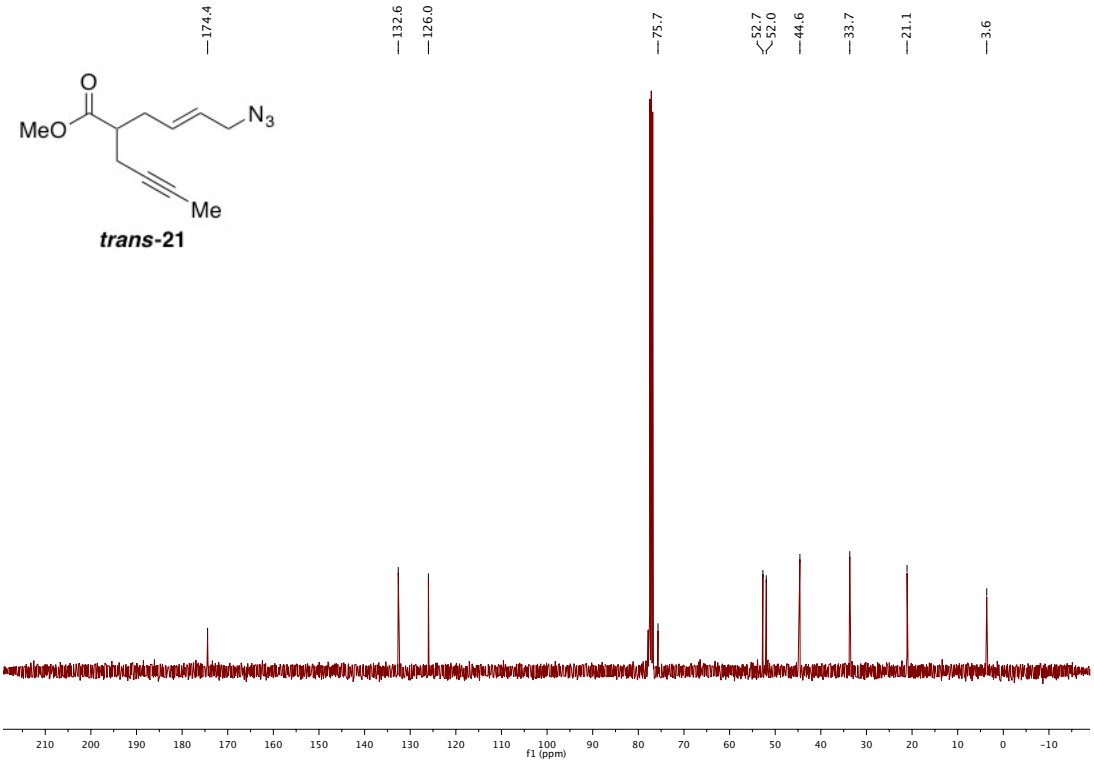




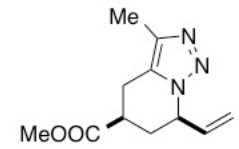
***trans*-S4**



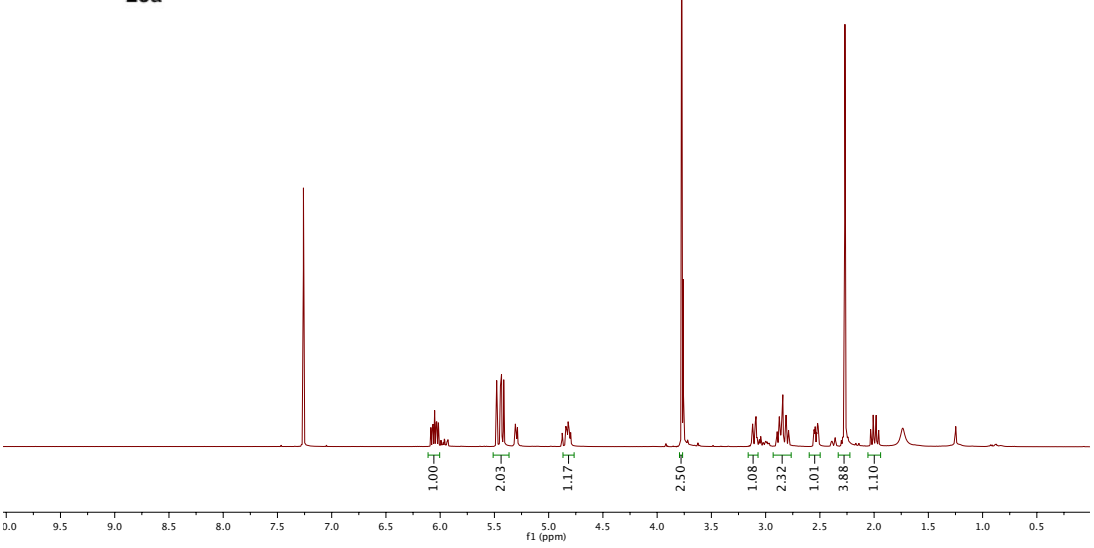
***trans*-21**

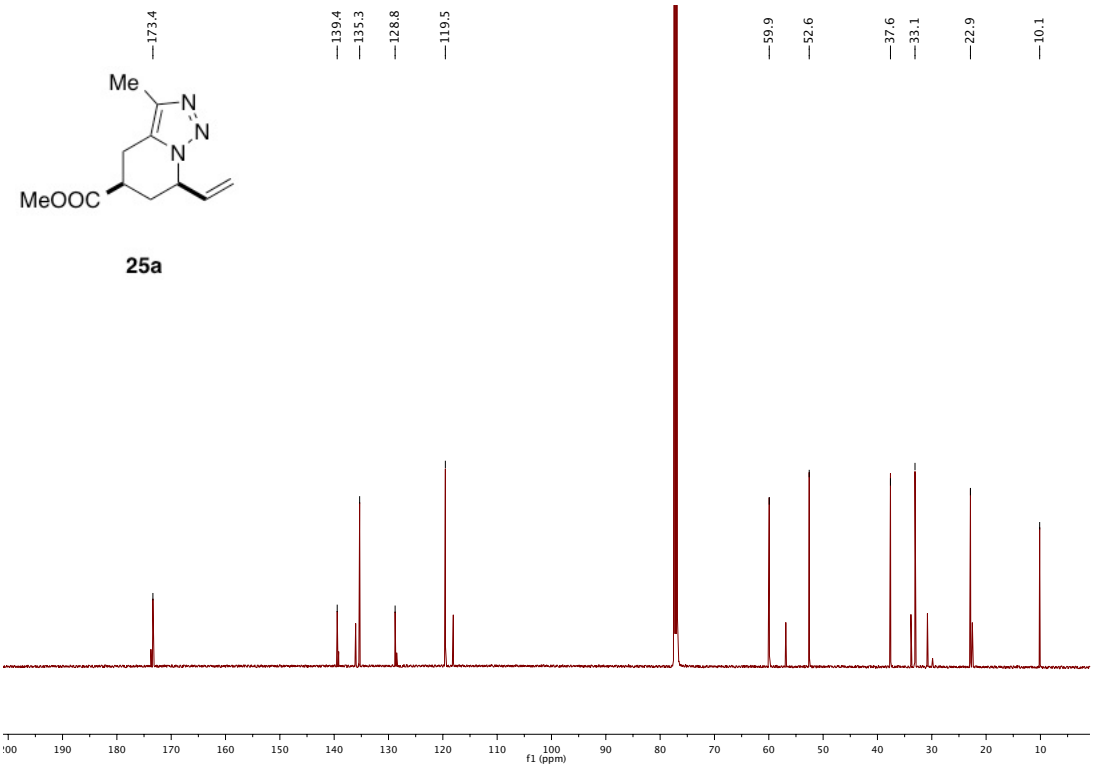


***trans*-21**


Me
N
N
N
MeOOC

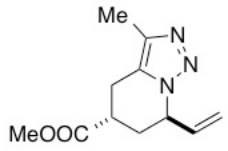
25a


1.00
2.03
1.17
2.50
1.08
2.32
1.01
3.88
1.10
f1 (ppm)

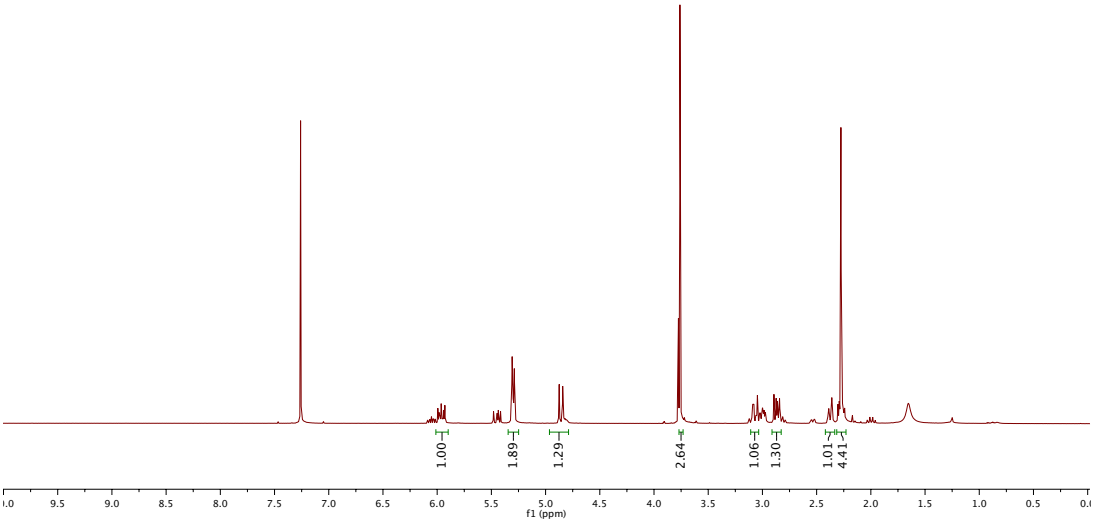

173.4
139.4
135.3
128.8
119.5
59.9
52.6
37.6
33.1
22.9
10.1
f1 (ppm)

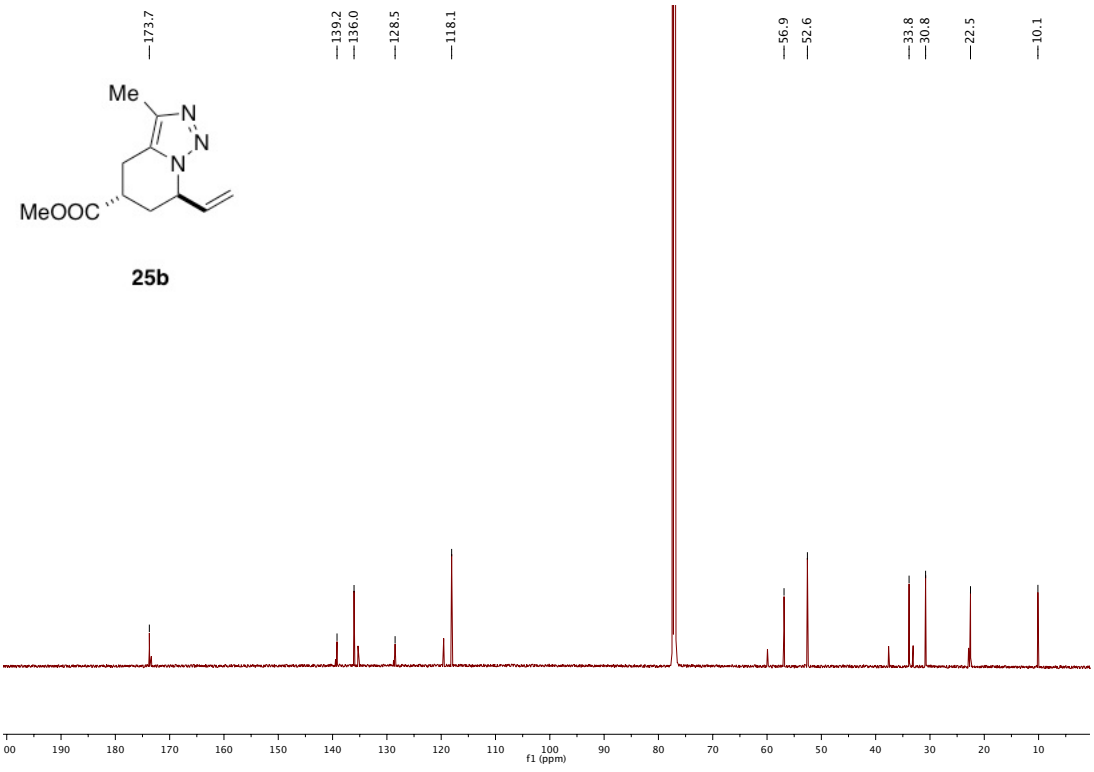
Me
N
N
N
MeOOC

25a


Me
N
N
N
MeOOC

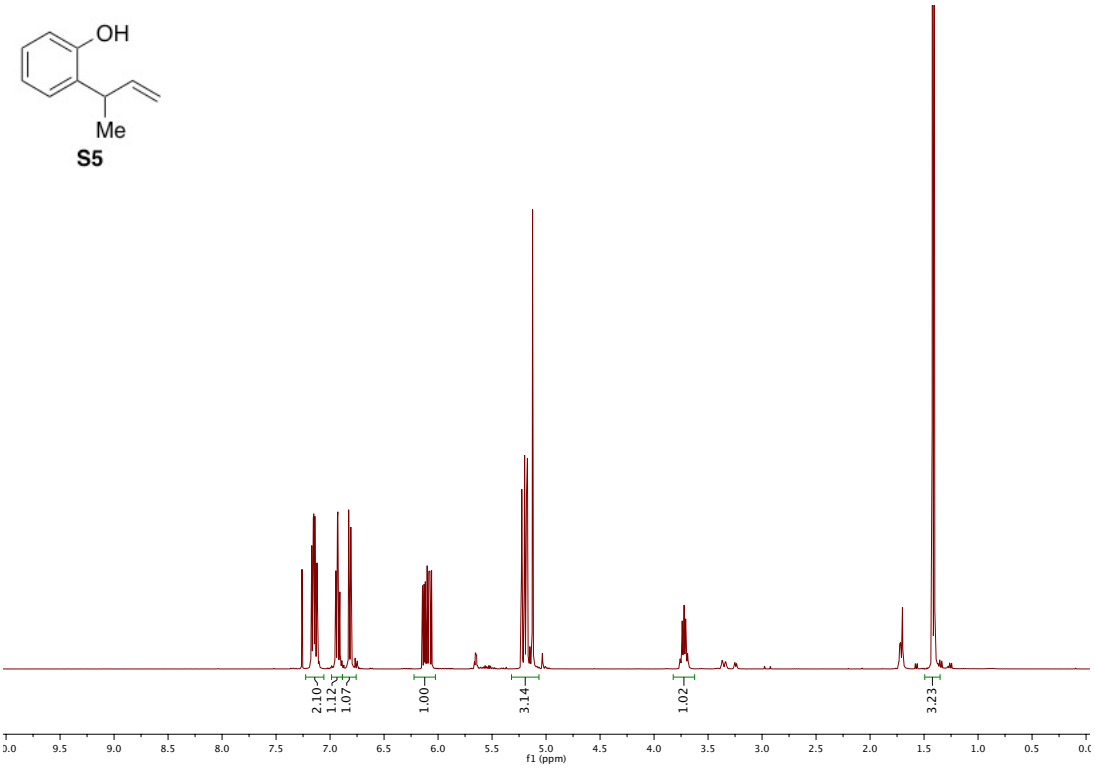
25b

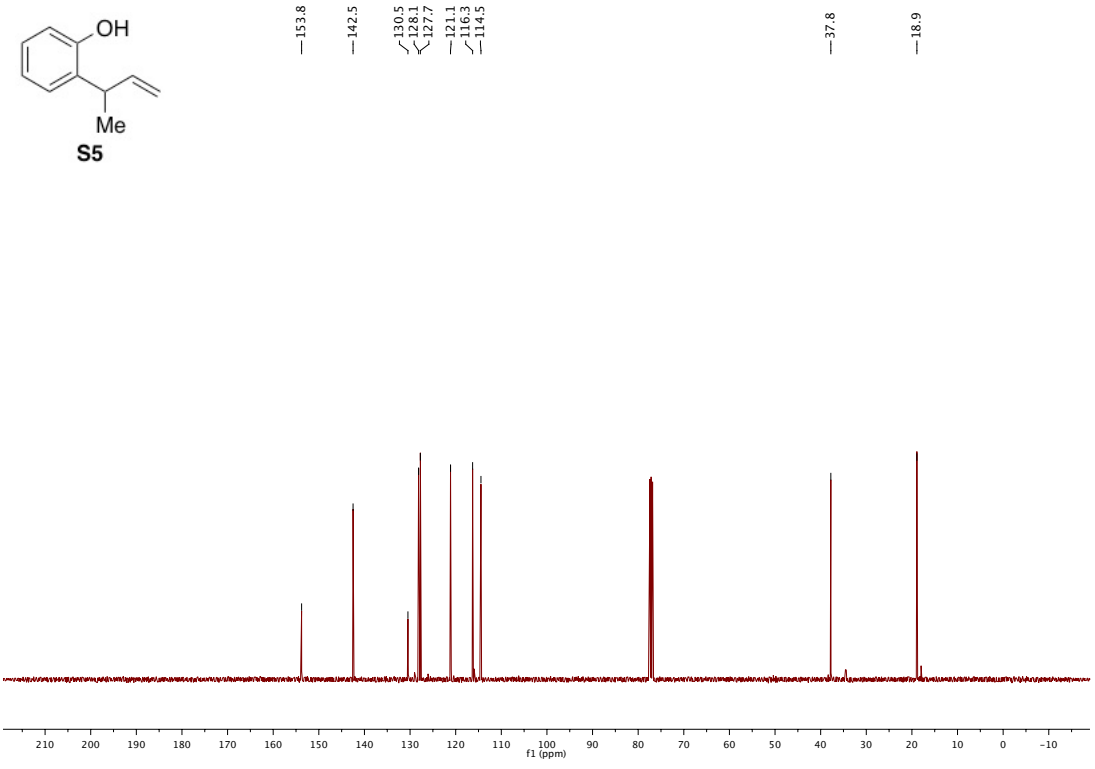

1.00
1.89
1.29
2.64
1.06
1.30
1.01
4.41
f1 (ppm)

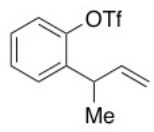

173.7
139.2
136.0
128.5
118.1
56.9
52.6
33.8
30.8
22.5
10.1
f1 (ppm)

Me
N
N
N
MeOOC

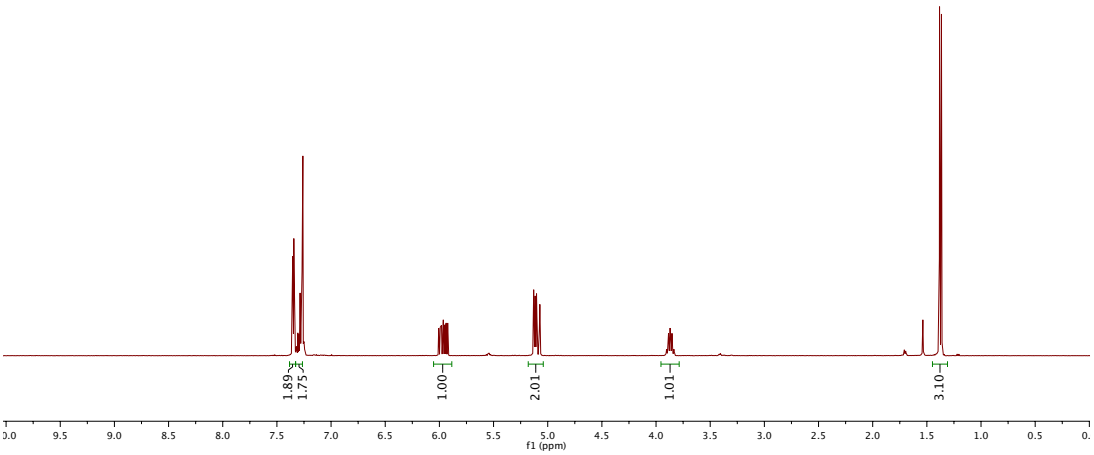
25b

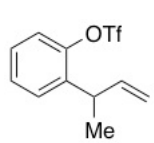

OH
Me
S5
2.10
1.12
1.07
1.00
3.14
1.02
3.23
f1 (ppm)


OH
Me
S5
153.8
142.5
130.5
128.1
127.7
121.1
116.3
114.5
37.8
18.9
f1 (ppm)


OTf
Me

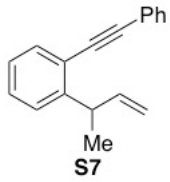
S6


1.89
1.75
1.00
2.01
1.01
3.10
f1 (ppm)

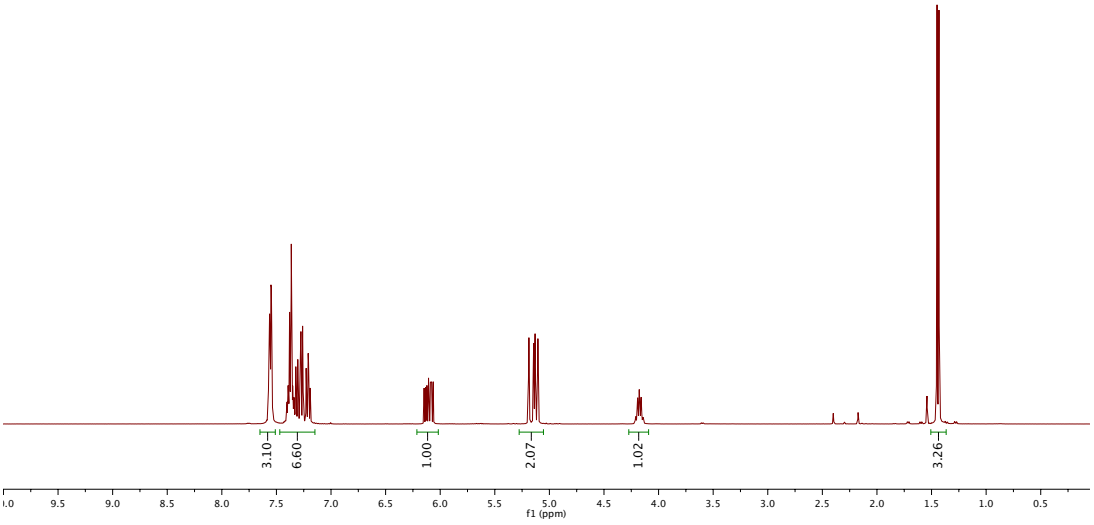

OTf
Me

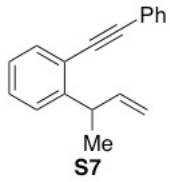
S6

147.4
141.0
138.3
129.3
128.7
128.0
121.4
120.3
117.1
114.7
36.0
20.1
f1 (ppm)


Ph
Me

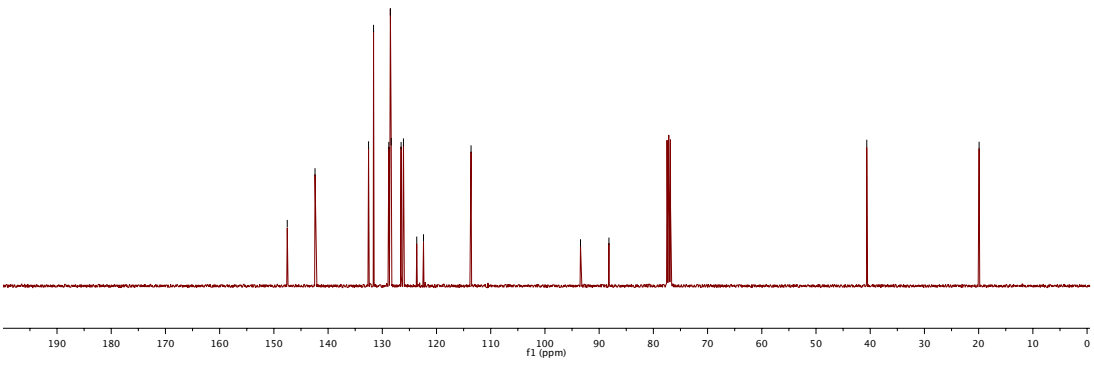
S7

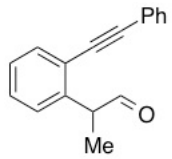

3.10
6.60
1.00
2.07
1.02
3.26
f1 (ppm)


Ph
Me

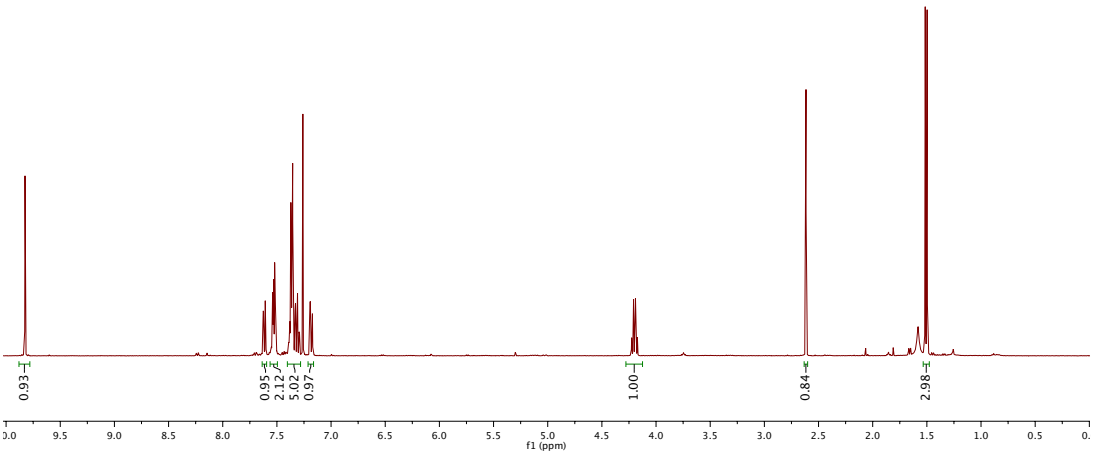
S7

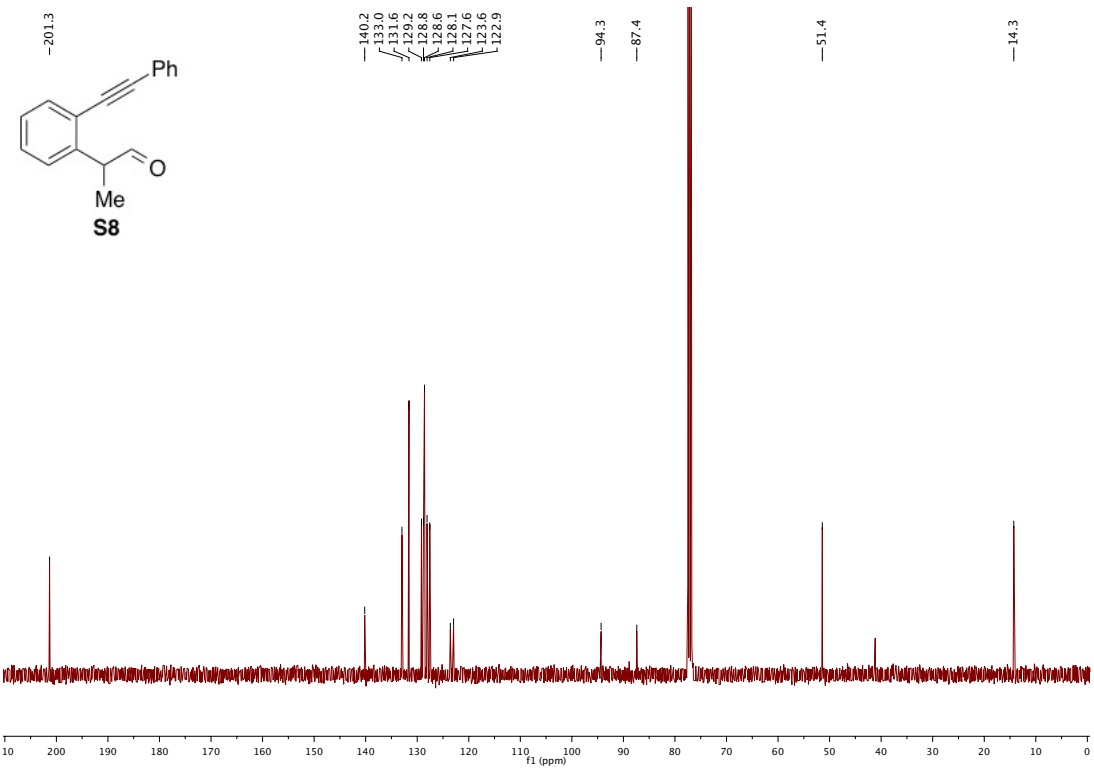

147.5
142.4
132.5
131.6
128.8
128.5
128.4
126.5
126.1
123.6
122.4
113.6
93.4
88.2
40.6
19.9


f1 (ppm)

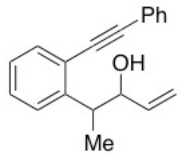

Ph
O
Me

S8

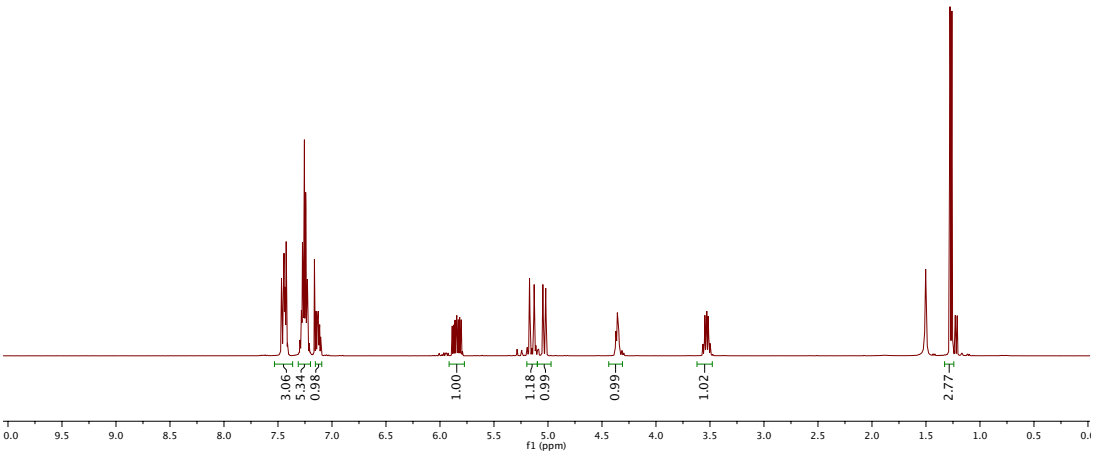

0.93
0.95
2.12
5.02
0.97
1.00
0.84
2.98
f1 (ppm)

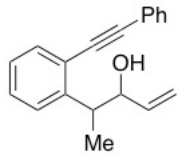

201.3
140.2
133.0
131.6
129.2
128.8
128.6
128.1
127.6
123.6
122.9
94.3
87.4
51.4
14.3
Ph
O
Me
f1 (ppm)

S8


Ph
OH
Me

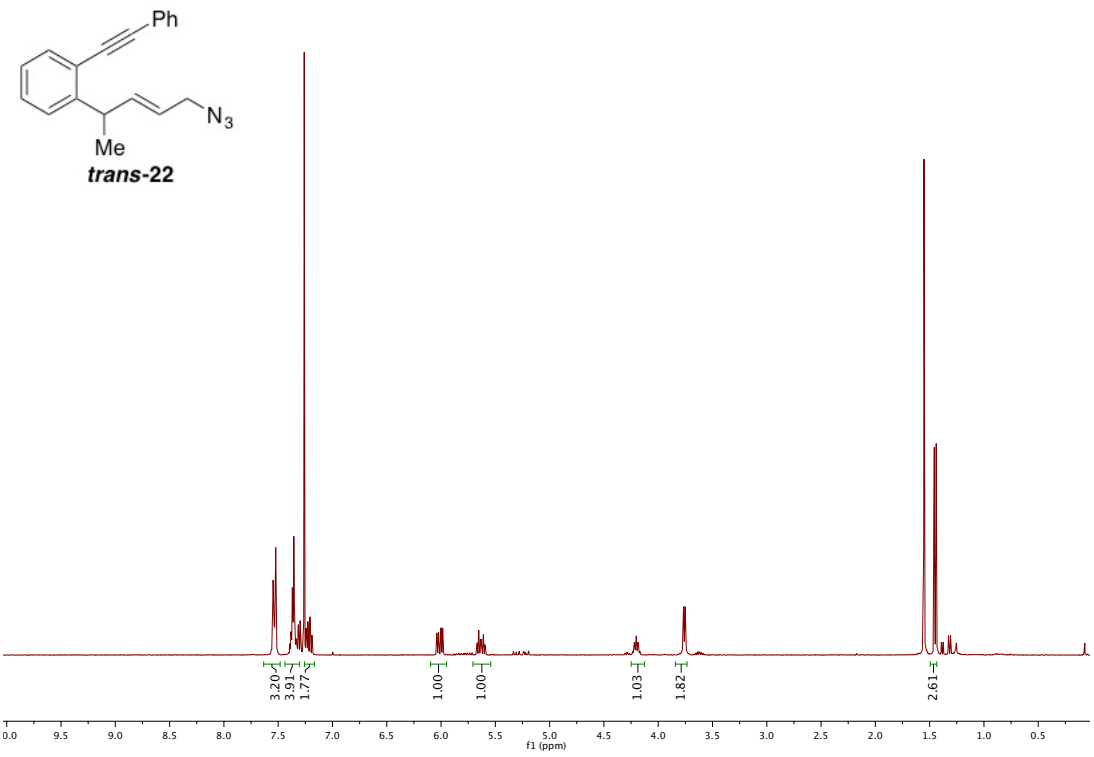
S9

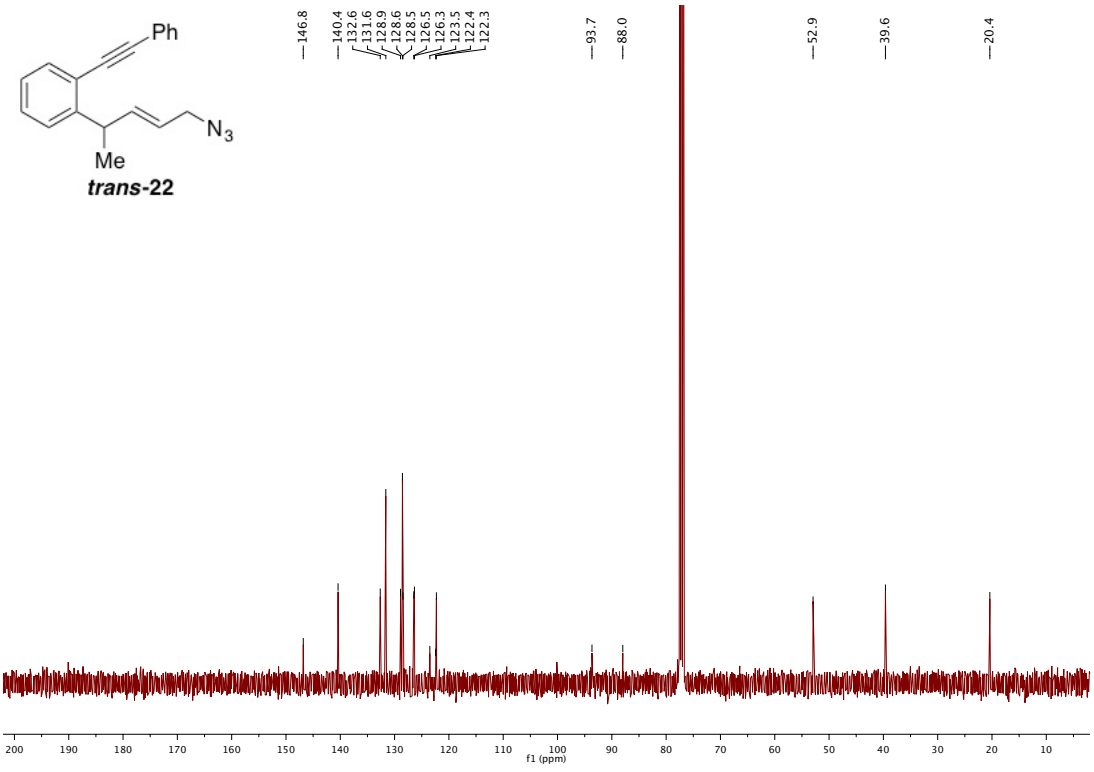

3.06
5.34
0.98
1.00
1.18
0.99
0.99
1.02
2.77
f1 (ppm)

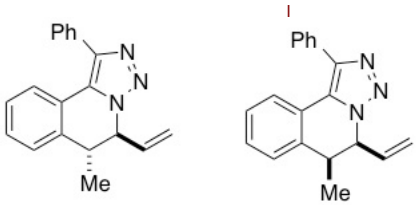

Ph
OH
Me

S9

145.7
139.6
132.6
131.6
128.6
128.5
128.5
127.2
126.4
123.4
122.9
115.4
93.8
88.2
76.4
42.8
14.2
f1 (ppm)

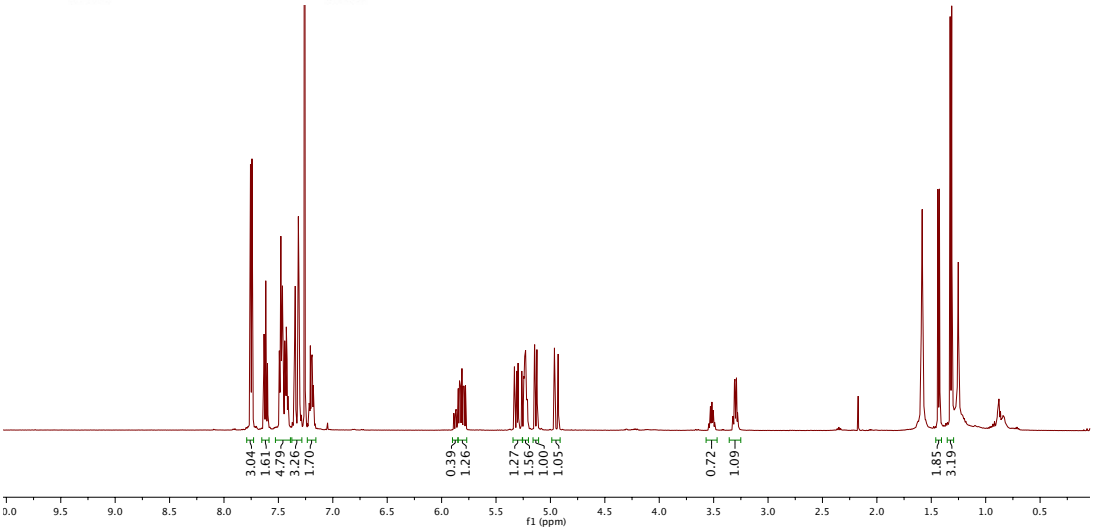

Ph
N3
Me
trans-22
3.20
3.91
1.77
1.00
1.00
1.03
1.82
2.61
f1 (ppm)

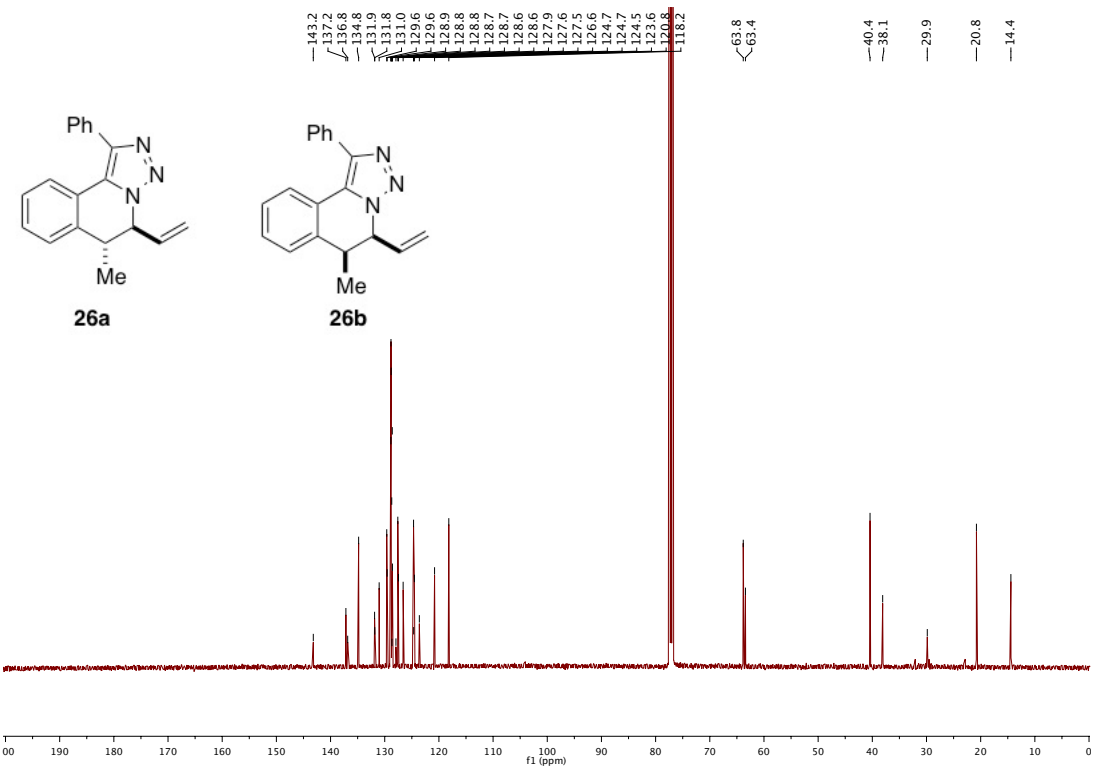

Ph
N3
Me
trans-22
146.8
140.4
132.6
131.6
128.9
128.6
128.5
126.5
126.3
123.5
122.4
122.3
93.7
88.0
52.9
39.6
20.4
f1 (ppm)



26a

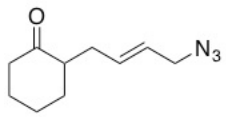
26b



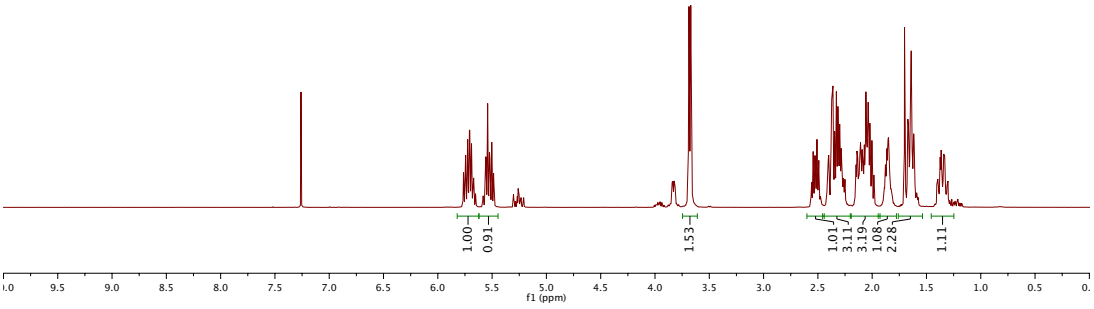


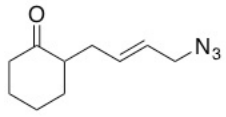
26a

26b

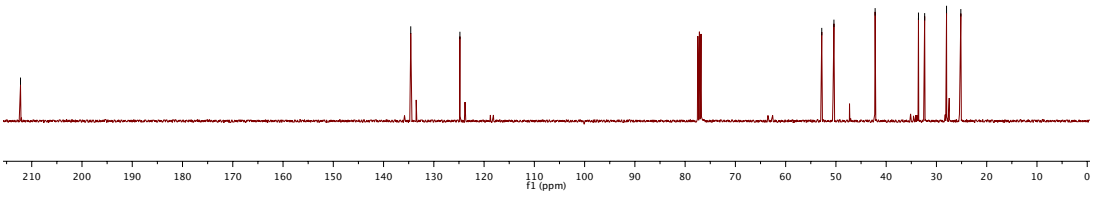


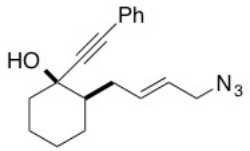
***trans*-S10**



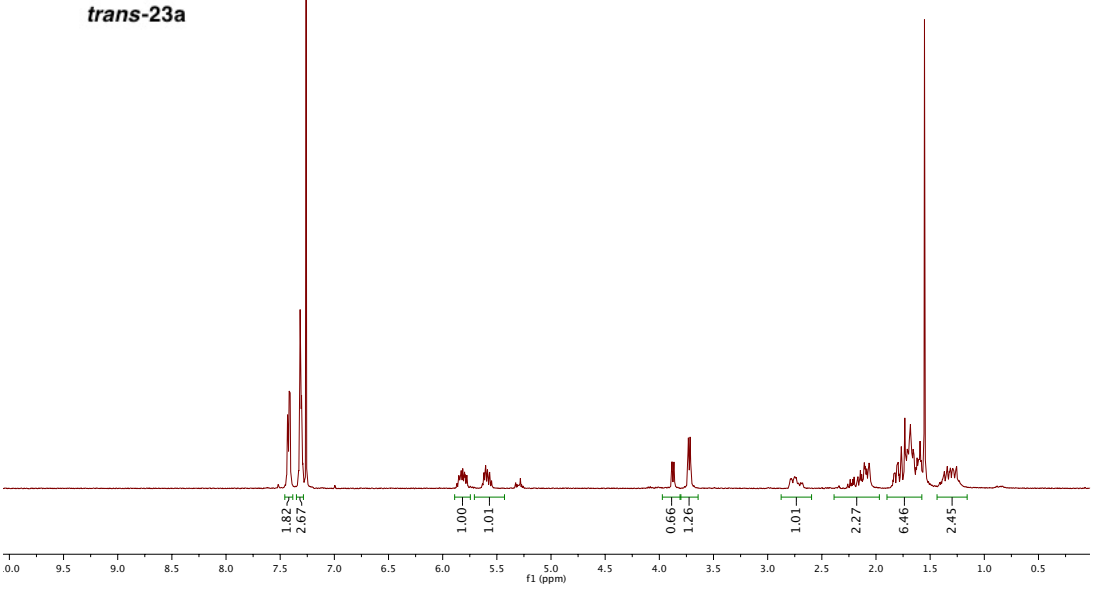


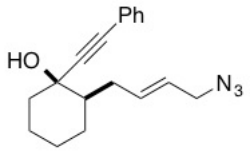
***trans*-S10**



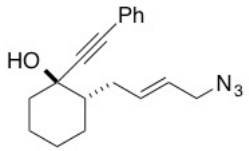


***trans*-23a**

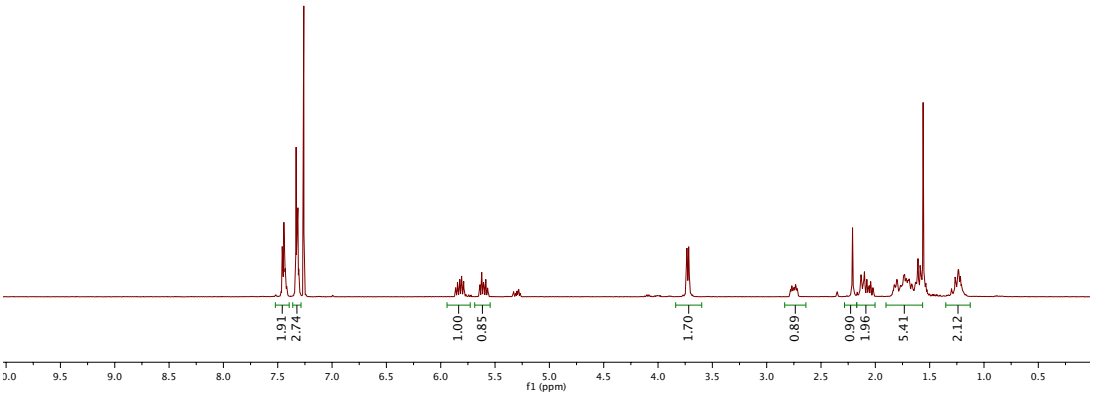


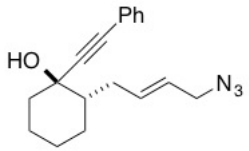


***trans*-23a**

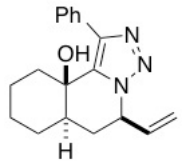


***trans*-23b**

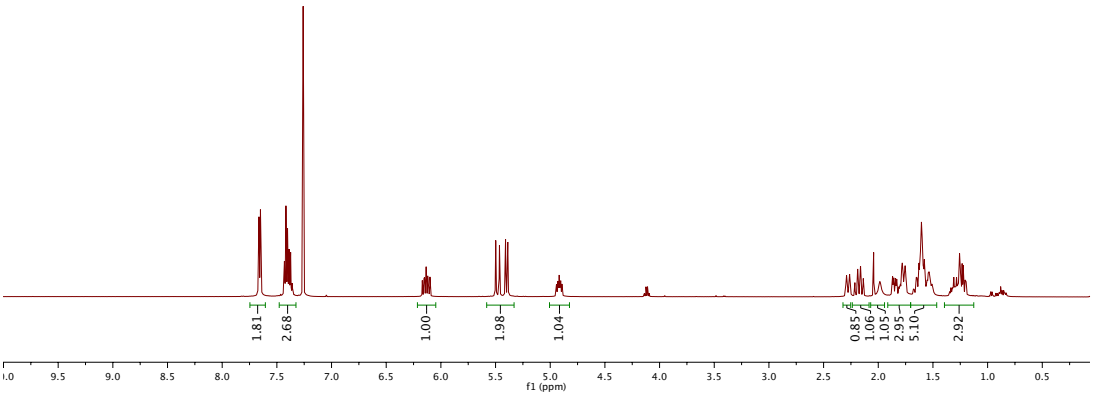


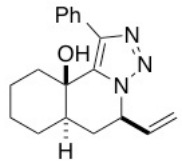


***trans*-23b**


Ph
OH
N
N
N
H

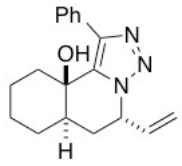
27a


1.81
2.68
1.00
1.98
1.04
0.85
1.06
1.05
2.95
5.10
2.92
f1 (ppm)


Ph
OH
N
N
N
H

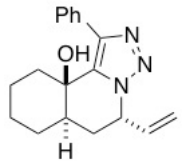
27a

144.5
136.4
135.3
132.5
129.8
128.4
128.3
118.7
67.0
61.9
42.0
34.3
32.2
26.7
25.5
20.8
f1 (ppm)


Ph
OH
N
N
N
H

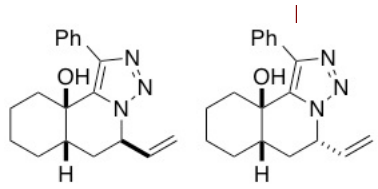
27b

1.74
2.91
1.00
1.84
0.99
0.92
1.04
1.00
1.09
9.05
3.85
f1 (ppm)


Ph
OH
N
N
N
H

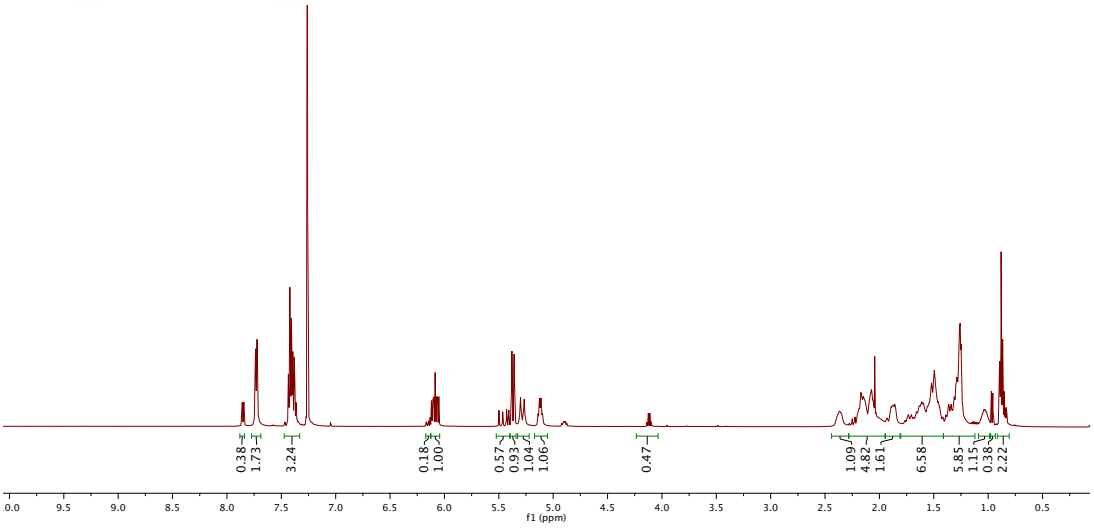
27b

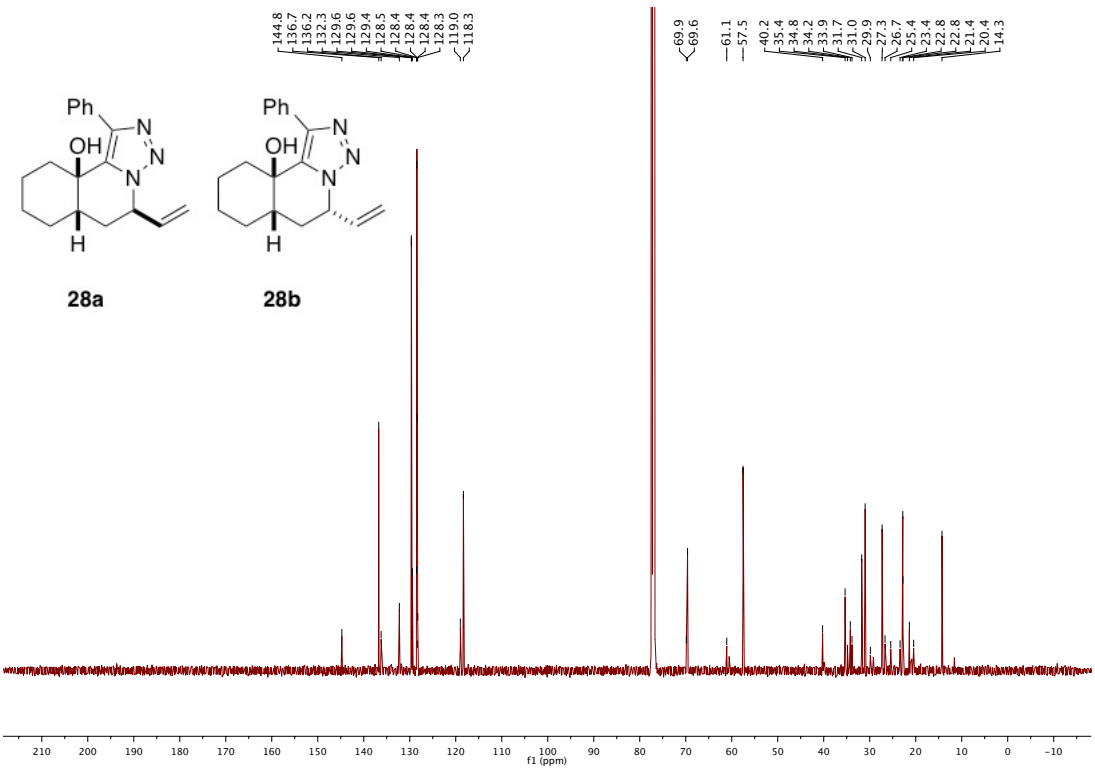
144.2
136.7
135.3
132.4
129.7
128.4
128.3
117.5
67.1
58.6
37.7
34.0
29.9
26.6
25.5
20.8
f1 (ppm)



28a

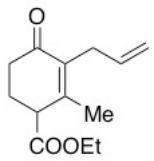
28b



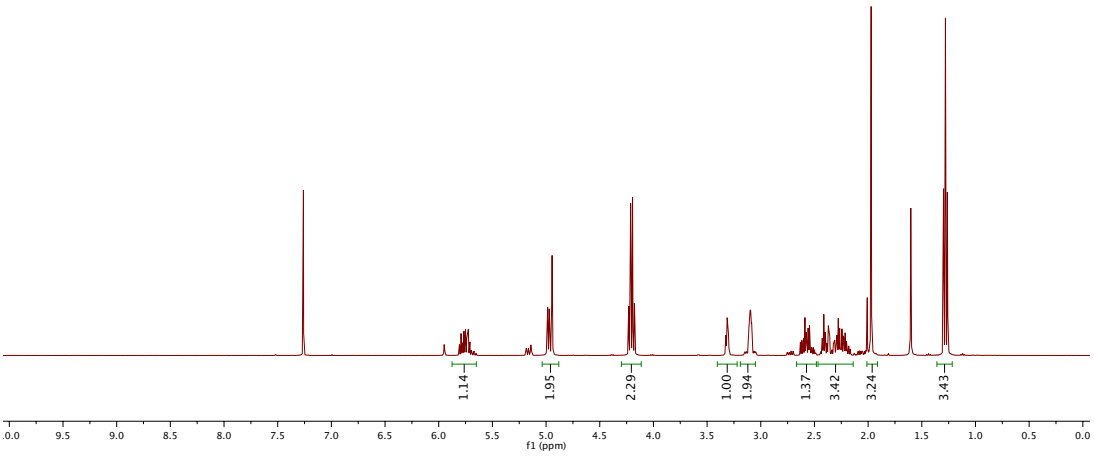


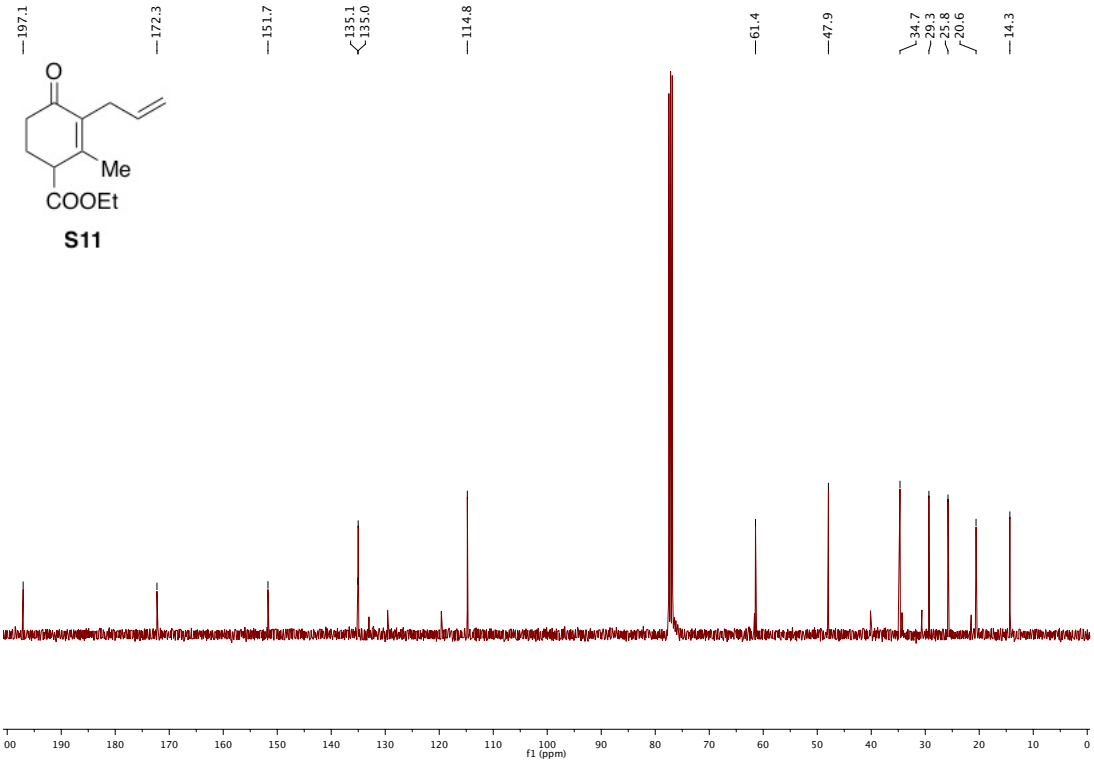
28a

28b

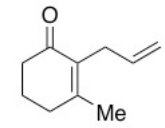

O
Me
COOEt

S11


1.14
1.95
2.29
1.00
1.94
1.37
3.42
3.24
3.43
f1 (ppm)

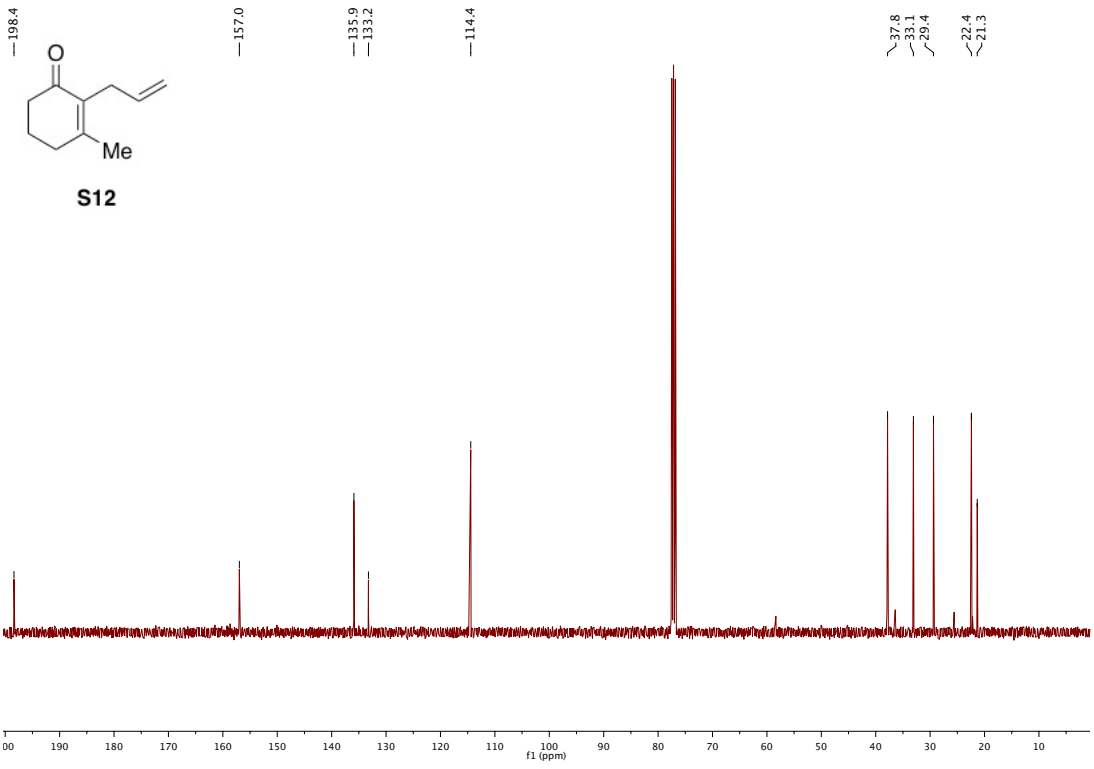

197.1
172.3
151.7
135.1
135.0
114.8
61.4
47.9
34.7
29.3
25.8
20.6
14.3
O
Me
COOEt
f1 (ppm)

S11


O
Me

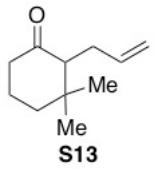
S12

1.00
2.01
2.08
4.56
5.65
0.85
f1 (ppm)


198.4
157.0
135.9
133.2
114.4
37.8
33.1
29.4
22.4
21.3
f1 (ppm)

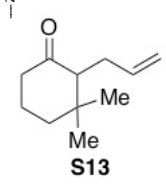
O
Me

S12


O
Me
Me

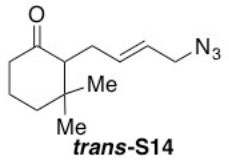
S13

1.00
2.06
1.15
3.19
1.15
2.39
3.12
3.24
3.19
f1 (ppm)

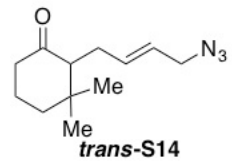

O
Me
Me

S13

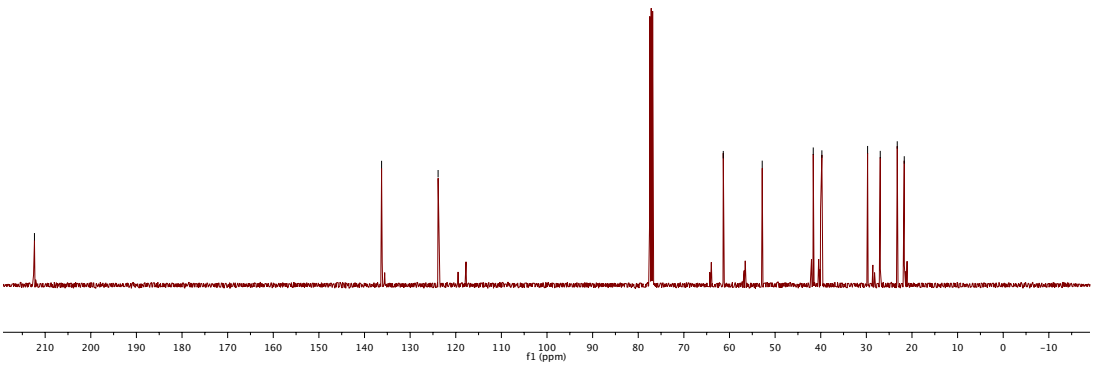
212.8
138.0
115.3
61.1
41.4
39.8
39.3
29.6
28.8
23.2
22.2
f1 (ppm)

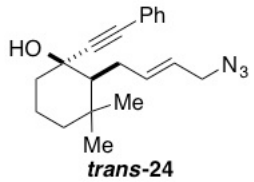


***trans*-S14**

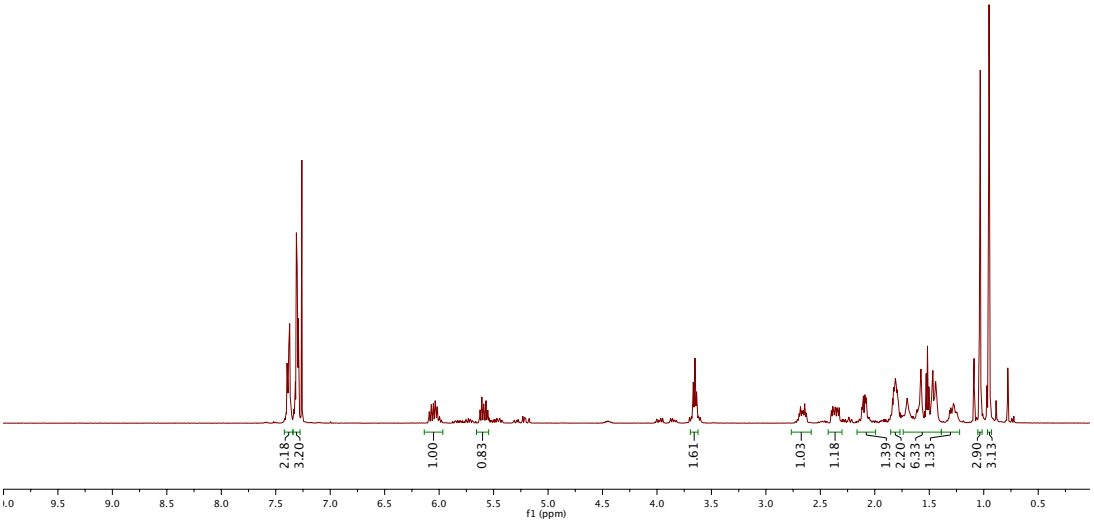


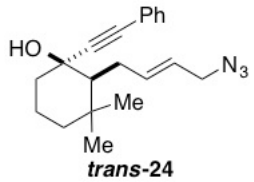
***trans*-S14**



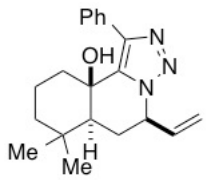


***trans*-24**

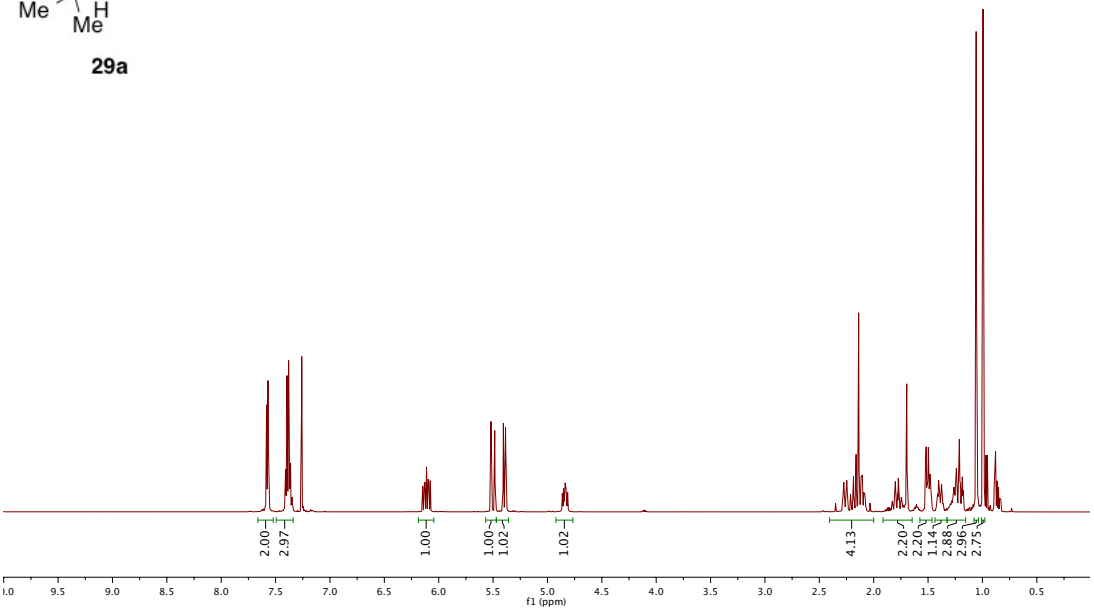


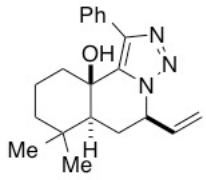


***trans*-24**


Ph
OH
N
N
N
Me
H
Me

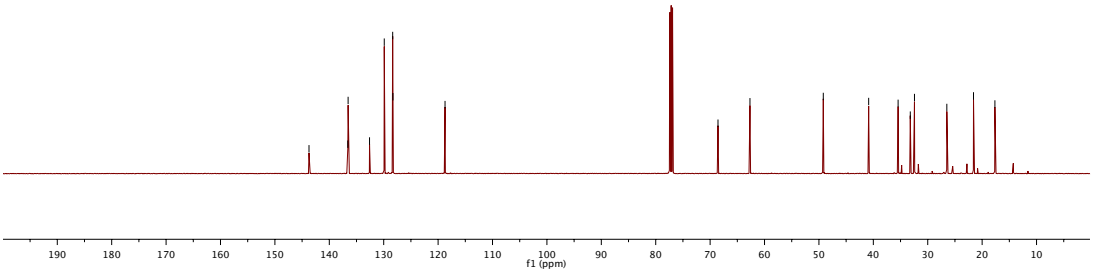
29a

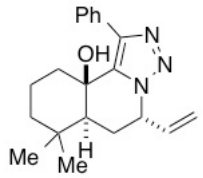

2.00
2.97
1.00
1.00
1.02
1.02
4.13
2.20
2.20
1.14
2.88
2.96
2.75
f1 (ppm)


Ph
OH
N
N
N
Me
H
Me

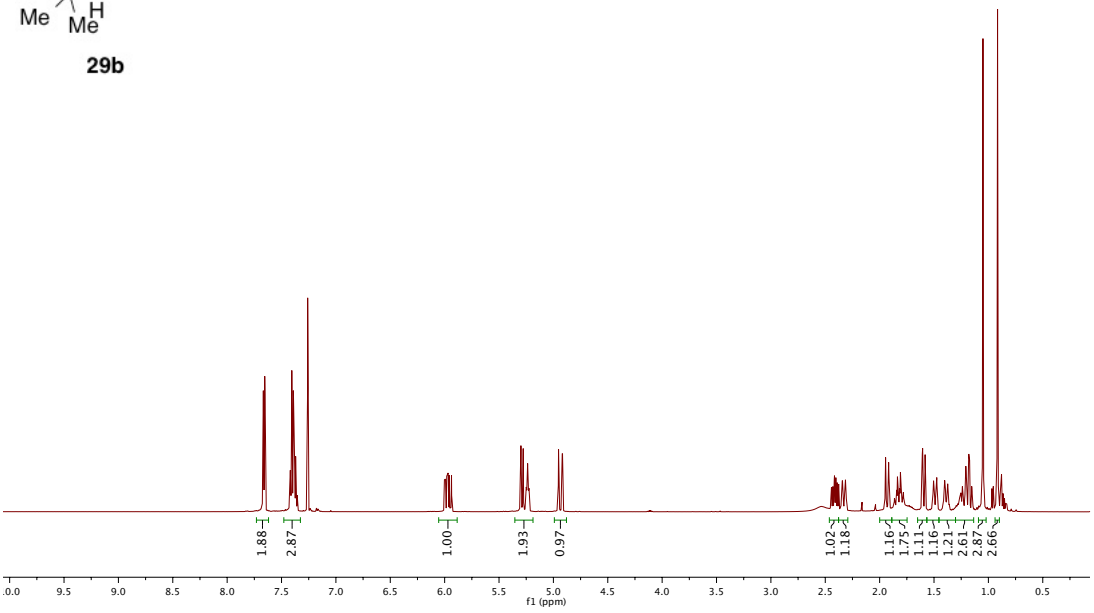
29a

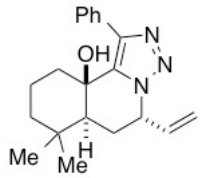

143.7
136.6
136.5
132.6
129.9
128.3
128.3
118.7
68.6
62.7
49.2
40.9
35.4
33.2
32.4
26.5
21.6
17.7


f1 (ppm)


Ph
OH
N
N
N
Me
Me
H

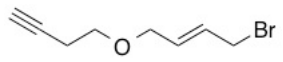
29b


1.88
2.87
1.00
1.93
0.97
1.02
1.18
1.16
1.75
1.11
1.16
1.21
2.61
2.87
2.66
f1 (ppm)

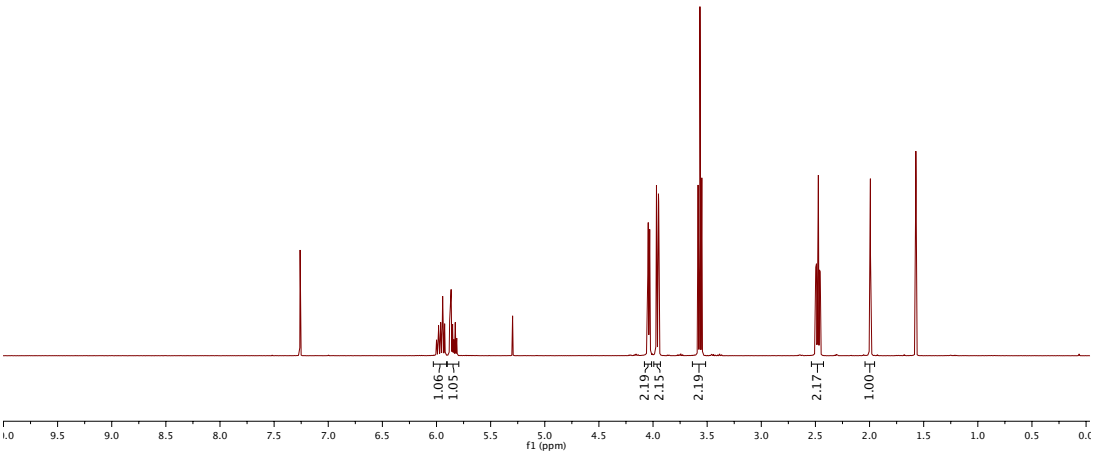

Ph
OH
N
N
N
Me
Me
H

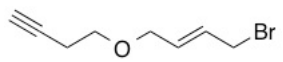
29b

143.4
136.5
136.3
132.4
129.8
128.3
128.3
117.7
68.5
58.8
44.6
40.9
35.0
32.9
32.2
23.8
21.7
17.7
f1 (ppm)


O
Br

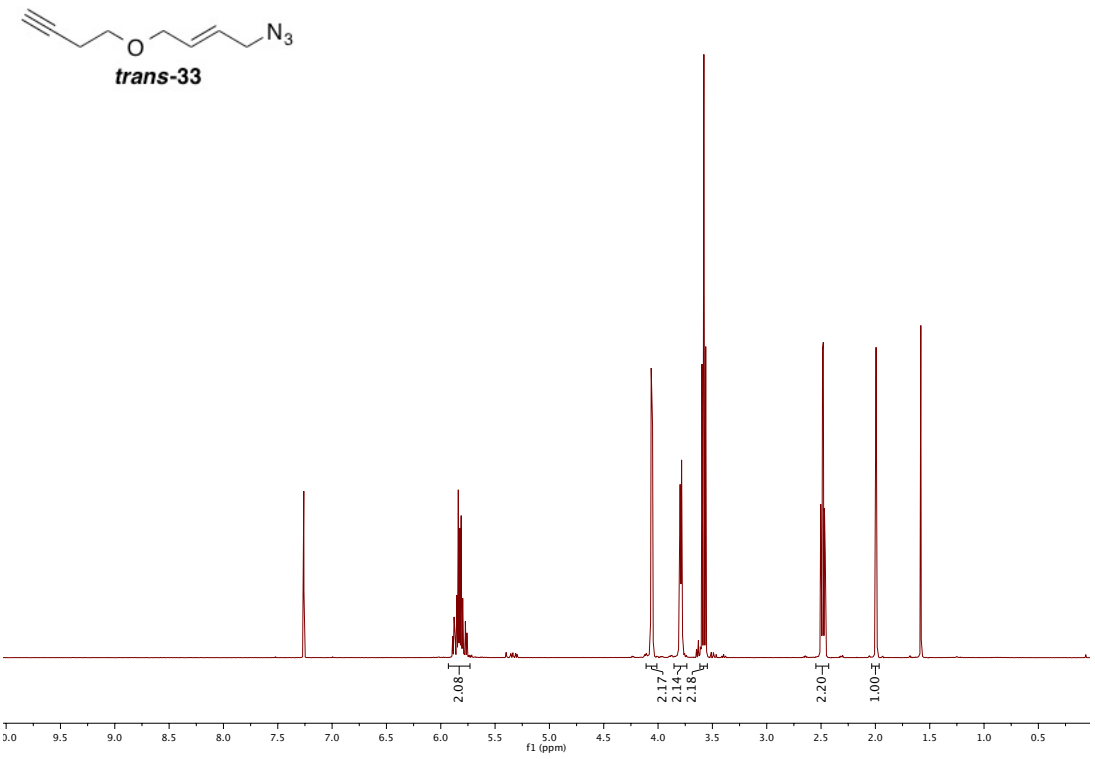
S15

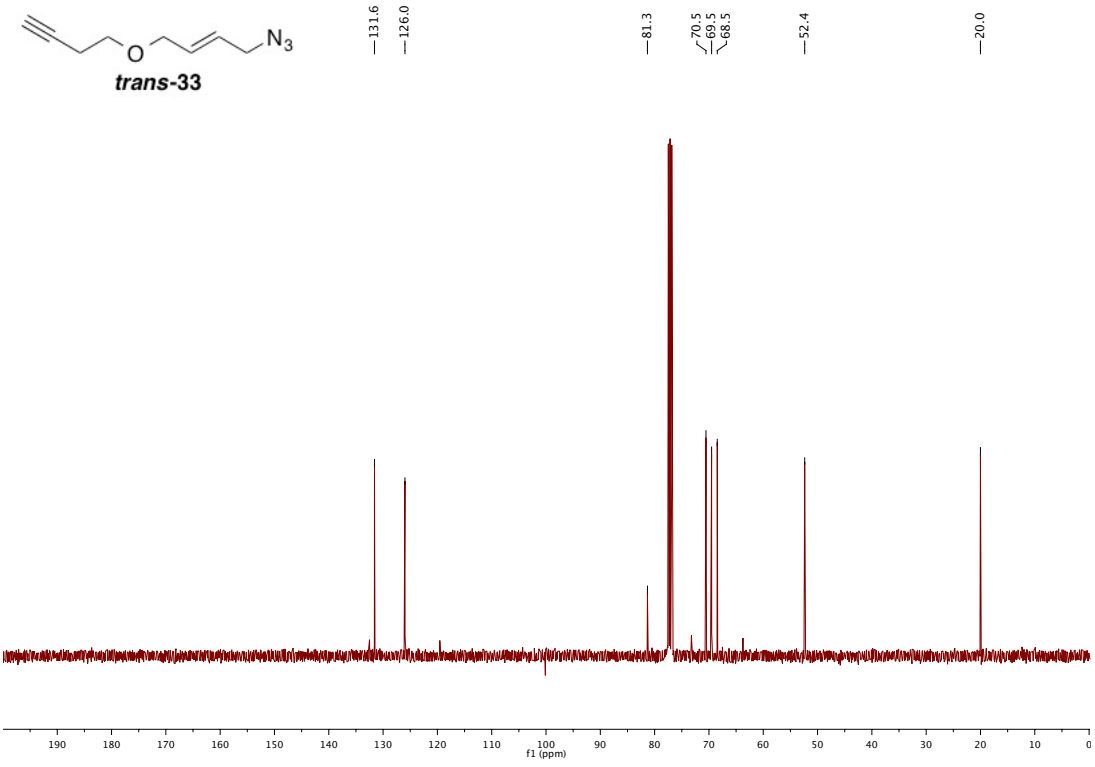

1.06
1.05
2.19
2.15
2.19
2.17
1.00
f1 (ppm)

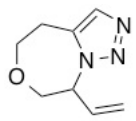

O
Br

S15

131.5
128.9
81.3
70.4
69.5
68.5
32.0
20.0
f1 (ppm)

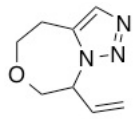

O
N3
trans-33
2.08
2.17
2.14
2.18
2.20
1.00
f1 (ppm)


O
N3
trans-33
131.6
126.0
81.3
70.5
69.5
68.5
52.4
20.0
f1 (ppm)



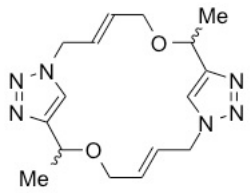
34

1.00
1.00
0.99
0.94
1.00
1.01
1.00
0.98
0.97
1.95
f1 (ppm)

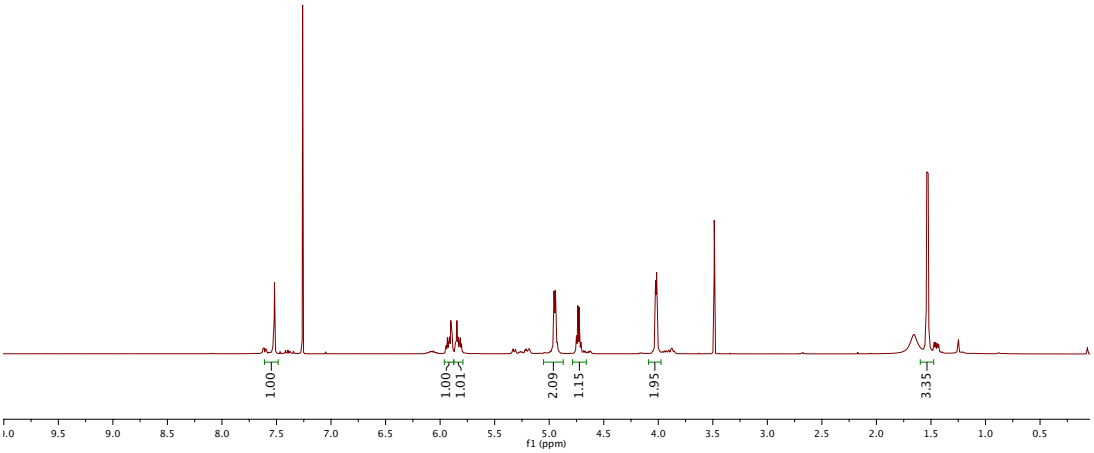


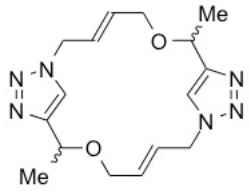
34

136.6
133.5
132.8
118.5
72.8
70.2
65.3
26.2
f1 (ppm)


Me
O
N
N
N
N
N
O
Me

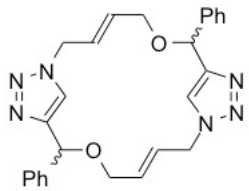
31


1.00
1.00
1.01
2.09
1.15
1.95
3.35
f1 (ppm)


Me
O
N
N
N
N
N
O
Me

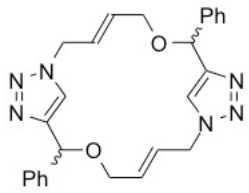
31

150.3
132.9
125.1
120.8
70.3
68.0
51.9
21.5
f1 (ppm)


Ph
O
N
N
N
N
N
N
O
Ph

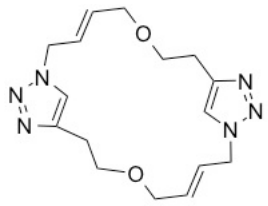
32

5.30
2.00
1.01
2.10
1.86
f1 (ppm)

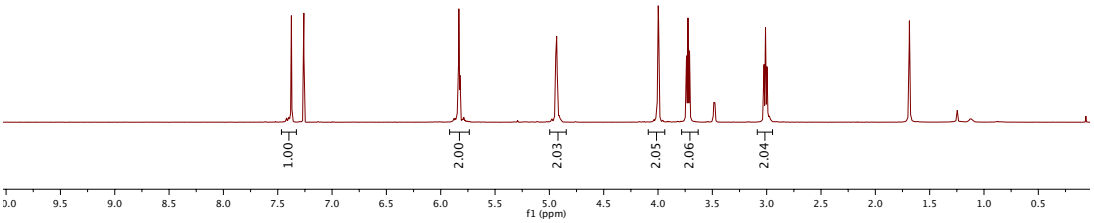

Ph
O
N
N
N
N
N
N
O
Ph

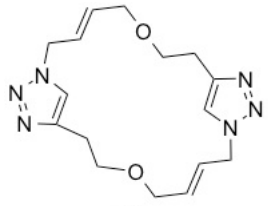
32

149.8
140.1
132.5
128.8
128.3
126.9
125.4
121.8
76.4
68.3
51.9
f1 (ppm)



35


1.00
2.00
2.03
2.05
2.06
2.04
f1 (ppm)



35

146.1
132.6
124.2
121.5
70.0
69.6
51.9
26.8
f1 (ppm)