Supplemental material for:

Expedient Synthesis of Fused Azepine Derivatives via a Sequential Rh(II)-Catalyzed Cyclopropanation / 1-Aza-Cope Rearrangement of Dienyltriazoles

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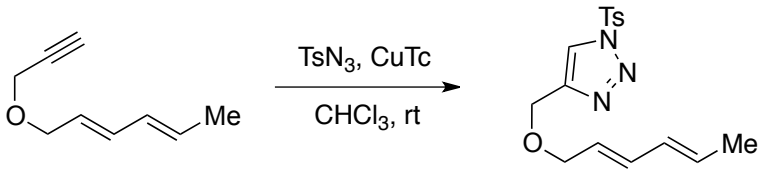
Materials and Methods.

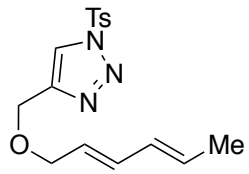
Unless stated otherwise, reactions were performed in oven-dried glassware sealed with rubber septa under a nitrogen atmosphere and were stirred with Teflon-coated magnetic stir bars. Liquid reagents and solvents were transferred via syringe using standard Schlenk techniques. Tetrahydrofuran (THF), toluene, and methanol (MeOH) were dried by passage over a column of activated alumina; dichloromethane was distilled over calcium hydride. Anhydrous chloroform was obtained in a Sure/Seal bottle from Aldrich. All other solvents and reagents were used as received unless otherwise noted. Thin layer chromatography was performed using SiliCycle silica gel 60 F-254 precoated plates (0.25 mm) and visualized by UV irradiation and anisaldehyde, CAM, potassium permanganate, or iodine stain. Sorbent silica gel (particle size 40-63 μm) was used for flash chromatography. NMR experiments were performed on Bruker spectrometers operating at 300, 400, 500 or 600 MHz for ^{1}H and 75, 100, 125, or 150 MHz for ^{13}C experiments. ^{1}H and ^{13}C chemical shifts (δ) are reported relative to the residual solvent signal. Data are reported as follows: chemical shift (multiplicity, coupling constants where applicable, number of hydrogens). Abbreviations are as follows: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublet), dt (doublet of triplet), p (pentet), hept (heptet), m (multiplet), bs (broad singlet). Only select ^{1}H and ^{13}C spectra are reported. IR spectra were recorded on a Nicolet MAGNA-IR 850 spectrometer as thin films on NaCl plates and are reported in frequency of absorption (cm^{-1}). Only selected IR absorbencies are reported. Low and high-resolution mass spectral data were obtained from the University of California, Berkeley Mass Spectral Facility, on a VG 70-Se Micromass spectrometer for FAB, and a VG Prospec Micromass spectrometer for EI. Optical rotations were measured on a Perkin-Elmer 241 polarimeter. The microwave-assisted reactions were conducted using a Biotage Initiator 2.5 reactor. $Rh_2(OAc)_4$, $Rh_2(tpa)_4$, $Rh_2(Ooct)_4$, $Rh_2(OPiv)_4$, and $Rh_2(esp)_2$ were purchased from commercial sources and used without further purification. $Rh_2(Adc)_4$ was synthesized from $Rh_2(OAc)_4$ and the corresponding carboxylic acid according to literature procedures.[1]

[1] Nelson, T. D.; Song, Z. J.; Thompson, A. S.; Zhao, M.; DeMarco, A.; Reamer, R. A.; Huntington, M. F.; Grabowski, E. J. J.; Reider, P. J. *Tetrahedron Lett.* **2000**, *41*, 1877; Wurz, R. P. Rhodium Tetrakis[tricyclo[3.3.1.13,7]decane-1-carboxylate]. In Encyclopedia of Reagents for Organic Synthesis; John Wiley & Sons, Ltd: New York, 2001.

Representative Procedure A for the Preparation of *N*-sulfonyltriazoles.



1a

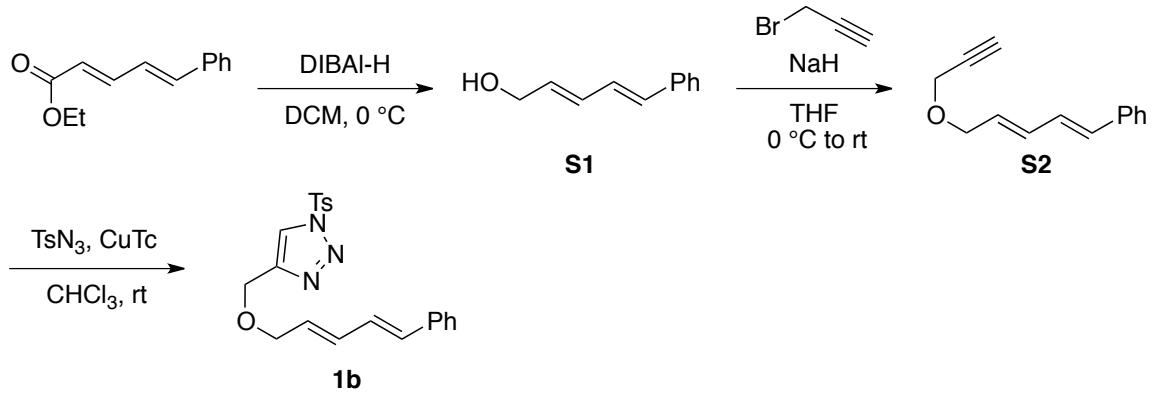


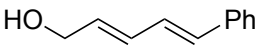
1a

4-{[(2*E*,4*E*) -hexa-2,4-dien-1-yloxy] methyl}- 1-tosyl- 1*H*- 1,2,3-triazole (1a). To a flame-dried flask under N_2 was added (2*E*,4*E*)-hexa-2,4-dien-1-yl prop-2-yn-1-yl ether[2] (160 mg, 1.2 mmol, 1.0 equiv) in chloroform (6 mL, 0.2 M). The solution was then sparged with N_2 for 15 minutes. The flask was then charged with copper (I) thiophene carboxylate (CuTc, 46 mg, 20 mol %) in a single portion, and the solution was again sparged with N_2 for an additional 5 minutes. Tosyl azide (0.22 mL, 1.3 mmol, 1.1 equiv) was then added to the reaction flask dropwise via syringe over 5 minutes. The reaction mixture was allowed to stir at ambient temperature for 2 h at which time TLC analysis indicated complete consumption of the starting material, and the reaction mixture was quenched by the addition of saturated aqueous ammonium chloride (10 mL). The biphasic mixture was stirred vigorously for 15 minutes, and then diluted with dichloromethane (5 mL). The layers were separated and the aqueous layer was extracted with dichloromethane (3 x 5 mL). The combined organic layers were dried over sodium sulfate, filtered, and concentrated *in vacuo*. The resulting residue was purified by column chromatography eluting with 4:1 hexanes:ethyl acetate to yield *N*-tosyltriazole **1a** (330 mg, 83%) as a white solid, m.p. 64-65 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.97 (d, *J* = 8.1 Hz, 2H), 7.37 (d, *J* = 8.1 Hz, 2H), 6.21 (dd, *J* = 15.3, 10.5 Hz, 1H), 6.07 - 6.01 (m, 1H), 5.76 - 5.67 (m, 1H), 5.59 (dt, *J* = 15.3, 6.4 Hz, 1H), 4.59 (s, 2H), 4.06 (d, *J* = 6.4 Hz, 2H), 2.43 (s, 3H), 1.74 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 147.3, 145.2, 134.3, 132.9, 130.7, 130.5, 130.4, 128.7, 125.5, 122.2, 71.3, 62.8, 21.8, 18.1; **IR** (thin film) ν_{max} 3150, 3020, 2915, 2855, 1660, 1594, 1448, 1393, 1215, 1196, 1178, 1091 cm^{-1}; **HRMS** (ESI^+) cal'd for $[C_{16}H_{19}N_3O_3S+Na]^+$: *m/z*, 356.1039 found 356.1045.

[2]Ni, Y.; Montgomery, J. *J. Am. Chem. Soc.* **2004**, *126*, 11162.

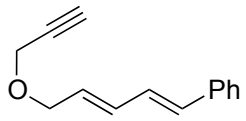
Representative Procedure B for the Preparation of *N*-sulfonyltriazoles.





S1

(2*E*,4*E*)-5-phenylpenta-2,4-dien-1-ol (S1). To a solution of ethyl-(2*E*,4*E*)-5-phenylpenta-2,4-dienoate[3] (1.1 g, 5.4 mmol, 1.0 equiv) in dichloromethane (17 mL, 0.33 M) at 0 °C was added DIBAL-H (7.1 mL of a 1.7 M solution in toluene, 12 mmol, 2.2 equiv) dropwise via syringe over 20 minutes. After holding at this temperature for 45 minutes, the reaction mixture was quenched by the slow addition of saturated aqueous sodium potassium tartrate (Rochelle's salt, 20 mL). The biphasic mixture was allowed to stir at ambient temperature for 2 h, then diluted with diethyl ether (20 mL). The layers were separated and the aqueous layer was extracted with diethyl ether (2 x 20 mL). The combined organic layers were washed with brine (20 mL), dried over sodium sulfate, filtered, and concentrated *in vacuo*. The resulting residue was purified by column chromatography eluting with 4:1 petroleum ether:ethyl acetate to give **S1** (810 mg, 93%) as a white solid, m.p. 66 - 68 °C. Spectra are consistent with those reported previously for **S1**.[4]

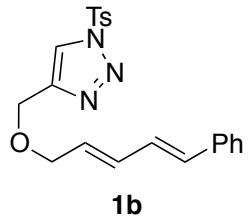


S2

(2*E*,4*E*)-5-phenylpenta-2,4-dien-1-yl prop-2-yn-1-yl ether (S2). To a solution of NaH (310 mg, 60% dispersion in mineral oil, 7.6 mmol, 1.5 equiv) in THF (10 mL, 0.5 M) at 0 °C was added alcohol **S1** (800 mg, 5.0 mmol, 1.0 equiv). After holding at this temperature for 30 minutes, propargyl bromide (0.84 mL, 80% (w/w) solution in toluene, 7.6 mmol, 1.5 equiv) was added dropwise via syringe over 5 minutes. The reaction mixture was allowed to warm to ambient temperature and stirred for 14 h. After this time, the reaction mixture was quenched by the addition of saturated aqueous ammonium chloride (10 mL) and diluted with diethyl ether (10 mL). The layers were separated and the aqueous layer was extracted with diethyl ether (3 x 10 mL). The combined organic layers were washed with brine (10 mL), dried over sodium sulfate, filtered and concentrated *in vacuo*. The resulting residue was purified by column

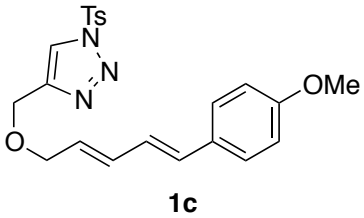
[3] Aggarwal, V. K.; Fulton, J. R.; Sheldon, C. G.; Vicente, J. D. *J. Am. Chem. Soc.* **2003**, *125*, 6034.
[4] Reddy, A. M.; Rao, V. J. *J. Org. Chem.* **1992**, *57*, 6727.

chromatography eluting with 8:1 hexanes:ethyl acetate to give dienylalkyne **S2** (670 mg, 68%) as a colorless oil. Spectra were consistent with those reported previously for **S2**.[5]



1b

1- Tosyl-4- ({[(2*E*,4*E*)-5-phenylpenta- 2,4-dien-1-yl]oxy}methyl)-1*H*-1,2,3-triazole (1b). To a flame-dried flask under N_2 was added alkyne **S2** (570 mg, 2.9 mmol, 1.0 equiv) in chloroform (14 mL, 0.2 M). The solution was then sparged with N_2 for 15 minutes. The flask was then charged with copper (I) thiophene carboxylate (CuTc, 110 mg, 20 mol %) in a single portion, and the solution was again sparged with N_2 for an additional 5 minutes. Tosyl azide (0.49 mL, 3.2 mmol, 1.1 equiv) was then added to the reaction flask dropwise via syringe over 5 minutes. The reaction mixture was allowed to stir at ambient temperature for 2 h at which time TLC analysis indicated complete consumption of the starting material, and the reaction mixture was quenched by the addition of saturated aqueous ammonium chloride (20 mL). The biphasic mixture was stirred vigorously for 15 minutes, and then diluted with dichloromethane (10 mL). The layers were separated and the aqueous layer was extracted with dichloromethane (3 x 10 mL). The combined organic layers were dried over sodium sulfate, filtered, and concentrated *in vacuo*. The resulting residue was purified by column chromatography eluting with 4:1 hexanes:ethyl acetate to yield triazole **1b** (770 mg, 68%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.99 (d, J = 8.5 Hz, 2H), 7.39 (d, J = 7.7 Hz, 2H), 7.36 (d, J = 8.2 Hz, 2H), 7.31 (t, J = 7.7 Hz, 2H), 7.23 (t, J = 7.4 Hz, 1H), 6.77 (dd, J = 15.7, 10.5 Hz, 1H), 6.56 (d, J = 15.7 Hz, 1H), 6.43 (dd, J = 15.3, 10.6 Hz, 1H), 5.87 (dt, J = 15.4, 6.3 Hz, 1H), 4.64 (s, 2H), 4.16 (d, J = 6.2 Hz, 2H), 2.42 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 147.4, 145.1, 137.0, 133.8, 133.3, 133.0, 130.4, 128.9, 128.7, 128.6, 127.9, 127.7, 126.4, 122.3, 71.2, 63.0, 21.8, 14.2; **IR** (thin film) ν_{max} 3379, 3033, 2923, 2870, 1674, 1595, 1450, 1393, 1195, 1177, 1090 cm^{-1}; **HRMS** (ESI$^+$) cal'd for $[C_{21}H_{21}N_3O_3S+Na]^+$: *m/z*, 418.1201 found 418.1199.



1c

1- Tosyl-4- ({[(2*E*,4*E*)-5-(4-methoxyphenyl) penta- 2,4-dien-1-yl]oxy}methyl)-1*H*-1,2,3-triazole (1c). Prepared from ethyl (2*E*,4*E*)-5-(4-methoxyphenyl)penta-2,4-dienoate[6] using Representative Procedure B. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.98 (d, J = 8.3 Hz, 2H), 7.36 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.8 Hz, 2H), 6.85 (d, J = 8.7 Hz, 2H), 6.64 (dd, J = 15.6, 10.4 Hz, 1H), 6.51 (d, J = 15.6 Hz, 1H), 6.40 (dd, J = 15.3, 10.4 Hz, 1H), 5.81 (dt, J = 15.1, 6.4 Hz, 1H), 4.63 (s, 2H), 4.14 (d, J = 6.4 Hz, 2H), 3.79 (s, 3H), 2.42 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 159.5, 147.4, 145.3, 134.3, 133.1, 133.0, 130.5, 129.9, 128.8, 127.8, 126.0, 122.3, 114.2, 71.4, 63.0, 55.4, 21.9; **IR** (thin film) ν_{max} 1603, 1510, 1391, 1251, 1195, 1176, 989 cm^{-1}; **HRMS** (ESI$^+$) cal'd for $[C_{22}H_{23}N_3O_4S+Na]^+$: *m/z*, 448.1301 found 448.1302.

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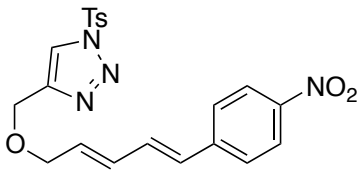
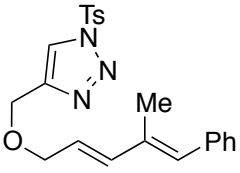
[5] Lee, S. I.; Park, S. Y.; Park, J. H.; Jung, I. G.; Choi, S. Y.; Chung, Y. K.; Lee, B. Y. *J. Org. Chem.* **2006**, *71*, 91.

[6] Dockendorff, C.; Sahli, S.; Olsen, M.; Milhau, L.; Lautens, M. *J. Am. Chem. Soc.* **2005**, *127*, 15028.



1d

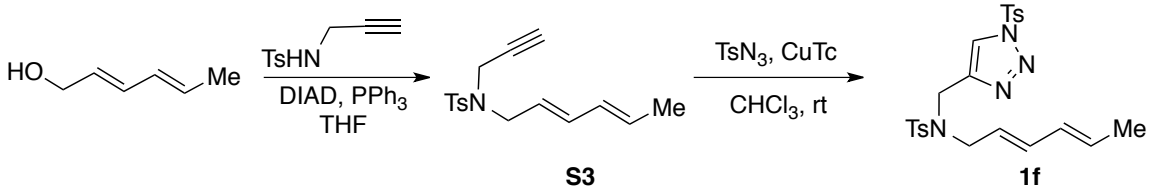
1-tosyl- 4-({[(2*E*,4*E*)-5-(4-nitrophenyl) penta-2,4-dien-1-yl]oxy}methyl)-1*H*-1,2,3-triazole (1d). Prepared from ethyl (2*E*,4*E*)-5-(4-nitrophenyl)penta-2,4-dienoate [7] using Representative Procedure B. **^{1}H NMR** (400 MHz, $CDCl_3$) δ d 8.16 (d, *J* = 8.6 Hz, 2H), 8.13 (s, 1H), 7.99 (d, *J* = 8.1 Hz, 2H), 7.50 (d, *J* = 8.6 Hz, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 6.91 (dd, *J* = 15.6, 10.6 Hz, 1H), 6.59 (d, *J* = 15.7 Hz, 1H), 6.46 (dd, *J* = 15.3, 10.5 Hz, 1H), 6.00 (dt, *J* = 15.3, 5.9 Hz, 1H), 4.66 (s, 2H), 4.19 (d, *J* = 6.0 Hz, 2H), 2.44 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.5, 146.9, 145.0, 143.7, 133.0, 132.5, 132.5, 132.5, 130.7, 130.6, 128.9, 126.9, 124.2, 122.4, 70.9, 63.3, 22.0; **IR** (thin film) ν_{max} 1592, 1511, 1391, 1340, 1195, 1179, 670, 585 cm^{-1}; **HRMS** (ESI^+) cal'd for $[C_{21}H_{20}N_4O_5S+Na]^+$: *m/z*, 463.1047 found 463.1042.



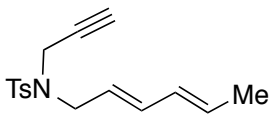
1e

1-tosyl-4- ({[(2*E*,4*E*)-4-methyl-5-phenylpenta-2,4-dien-1-yl] oxy} methyl)-1*H*-1,2,3-triazole (1e). Prepared from (2*E*,4*E*)-ethyl 4-methyl-5-phenylpenta-2,4-dienoate[8] using Representative Procedure B. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.99 (d, *J* = 8.4 Hz, 2H), 7.39-7.20 (m, 7H), 6.53 (s, 1H), 6.47 (d, *J* = 15.7 Hz, 1H), 5.84 (dt, *J* = 15.6, 6.4 Hz, 1H), 4.66 (s, 2H), 4.20 (d, *J* = 6.4 Hz, 2H), 2.43 (s, 3H), 1.99 (d, *J* = 1.3 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.4, 145.2, 138.9, 137.6, 134.9, 133.0, 132.2, 130.5, 129.2, 128.7, 128.2, 126.8, 124.2, 122.3, 71.7, 63.1, 21.9, 13.9; **IR** (thin film) ν_{max} 1594, 1391, 1195, 1178, 967, 672, 584 cm^{-1}; **HRMS** (ESI^+) cal'd for $[C_{22}H_{23}N_3O_3S+Na]^+$: *m/z*, 432.1352 found 432.1347.

Representative Procedure C for the Preparation of *N*-sulfonyltriazoles.



S3 **1f**

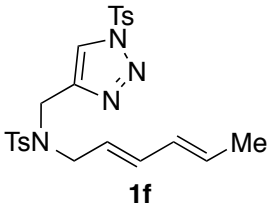


S3

***N*-((2*E*,4*E*)- hexa-2,4- dien-1-yl)- 4-methyl-*N*- (prop-2-yn-1-yl) benzenesulfonamide (S3).** *N*-Tosylpropargylamine (200 mg, 0.94 mmol) and triphenylphosphine (150 mg, 0.94 mmol) were dissolved in THF (9.4 mL, 0.1 M). (2*E*,4*E*)-hexa-2,4-dien-1-ol (92 mg, 0.94 mmol) was added, followed by DIAD (0.19 mL, 0.94 mmol). The reaction mixture was stirred for 5 h at ambient

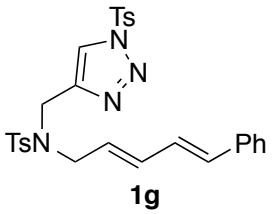
[7] Yaozeng, H.; Yanchang, S.; Jianhua, Z.; Shixiang, Z. *Synthesis* **1985**, 57.
[8] Fleming, I.; Rowley, M. *Tetrahedron* **1986,** *42,* 3181.

temperature, then concentrated *in vacuo*. The resulting residue was purified by column chromatography eluting with a gradient of 7% to 16% ethyl acetate in hexanes to give dienylalkyne **S3** (670 mg, 68%) as a white solid. Spectra were consistent with those reported previously for **S3**.[9]



1f

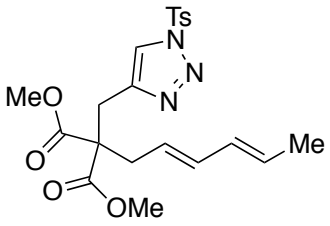
4- (((2*E*,4*E*)- hexa- 2,4-dien- 1- yloxy)methyl)-1-tosyl-1*H*-1,2,3-triazole (1f). To a flame-dried flask under N_2 was added alkyne **S3** (350 mg, 1.2 mmol, 1.0 equiv) in chloroform (6 mL, 0.2 M). The solution was then sparged with N_2 for 15 minutes. The flask was then charged with copper (I) thiophene carboxylate (CuTc, 46 mg, 20 mol %) in a single portion, and the solution was again sparged with N_2 for an additional 5 minutes. Tosyl azide (0.22 mL, 1.3 mmol, 1.1 equiv) was then added to the reaction flask dropwise via syringe over 5 minutes. The reaction mixture was allowed to stir at ambient temperature for 2 h at which time TLC analysis indicated complete consumption of the starting material, and the reaction mixture was quenched by the addition of saturated aqueous ammonium chloride (10 mL). The biphasic mixture was stirred vigorously for 15 minutes, and then diluted with dichloromethane (5 mL). The layers were separated and the aqueous layer was extracted with dichloromethane (3 x 5 mL). The combined organic layers were dried over sodium sulfate, filtered, and concentrated *in vacuo*. The resulting residue was purified twice by column chromatography eluting first with 4:1 hexanes:ethyl acetate then 1% methanol in dichloromethane to yield triazole **1f** (180 mg, 32%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.1 Hz, 2H), 7.94 (s, 1H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.25 (d, *J* = 7.9 Hz, 2H), 6.04 (dd, *J* = 15.2, 10.4 Hz, 1H), 5.88 (dd, *J* = 14.4, 11.1 Hz, 1H), 5.62 (dq, *J* = 13.9, 6.7 Hz, 1H), 5.23 (dt, *J* = 14.6, 7.0 Hz, 1H), 4.41 (s, 2H), 3.83 (d, *J* = 6.8 Hz, 2H), 2.44 (s, 3H), 2.41 (s, 3H), 1.70 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 147.4, 143.9, 143.7, 136.8, 135.7, 132.9, 131.1, 130.5, 130.1, 129.7, 128.7, 127.1, 123.1, 122.8, 49.7, 41.1, 21.8, 21.5, 18.1; **IR** (thin film) ν_{max} 3090, 3024, 2920, 2855, 2361, 2342, 1660, 1596, 1446, 1341, 1184, 1159, 1121 cm^{-1}; **HRMS** (ESI$^+$) cal'd for $[C_{23}H_{26}N_4O_4S_2+Na]^+$: *m/z*, 509.1290 found 509.1288.



1g

4-methyl-*N*-((2*E*,4*E*)-5-phenylpenta-2,4-dien-1-yl)-*N*-((1-tosyl-1*H*-1,2,3-triazol-4-yl) methyl)benzenesulfonamide (1g). Prepared from (2*E*,4*E*)-5-phenylpenta-2,4-dien-1-ol (**S1**) using Representative Procedure C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.1 Hz, 2H), 7.96 (s, 1H), 7.65 (d, *J* = 8.1 Hz, 2H), 7.39 – 7.19 (m, 9H), 6.62 (dd, *J* = 15.7, 10.3 Hz, 1H), 6.48 (d, *J* = 15.7 Hz, 1H), 6.27 (dd, *J* = 15.2, 10.3 Hz, 1H), 5.53 (dt, *J* = 14.4, 6.9 Hz, 1H), 4.46 (s, 2H), 3.94 (d, *J* = 6.9 Hz, 2H), 2.44 (s, 3H), 2.43 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.5, 144.0, 143.8, 137.0, 135.6, 133.8, 133.0, 130.6, 129.9, 128.9, 128.7, 128.0, 127.5, 127.3, 126.7, 126.6, 123.0, 49.8, 41.4, 22.0, 21.7; **IR** (thin film) ν_{max} 3026, 2923, 2854, 1596, 1392, 1343, 1195, 1180, 1159, 1091, 1038, 672, 585 cm^{-1}; **HRMS** (ESI$^+$) cal'd for $[C_{28}H_{28}N_4O_4S_{2+}Na]^+$: *m/z*, 571.1444 found 571.1438.

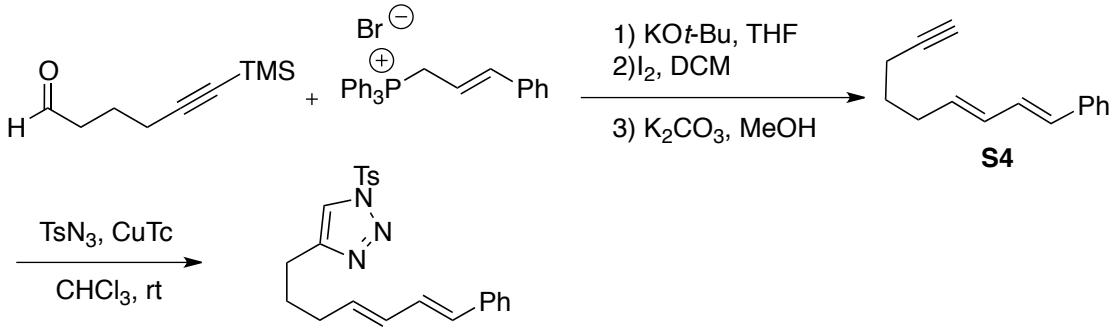
[9] DeBoef, B.; Counts, W. R.; Gilbertson, S. R. *J. Org. Chem.* **2007**, *72*, 799.



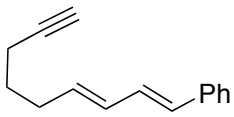
1h

Dimethyl [(2*E*,4*E*)-5-phenylpenta-2,4-dien-1-yl](*N*-tosyl-1,2,3-triazol-4-ylmethyl) propanedioate (1h). Prepared from dimethyl [(2*E*,4*E*)-5-methylpenta-2,4-dien-1-yl](prop-2-yn-1-yl)propanedioate[10] using Representative Procedure A. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.4 Hz, 2H), 7.87 (s, 1H), 7.37 (d, *J* = 8.2 Hz, 2H), 6.06 - 5.96 (m, 2H), 5.62 (dq, *J* = 13.4, 6.6 Hz, 1H), 5.35 (dt, *J* = 14.5, 7.6 Hz, 1H), 3.69 (s, 6H), 3.29 (s, 2H), 2.58 (d, *J* = 7.6 Hz, 2H), 2.44 (s, 3H), 1.73 (d, *J* = 7.0 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 170.6, 147.2, 142.7, 135.3, 133.1, 130.9, 130.4, 129.2, 128.6, 123.4, 122.4, 58.0, 52.6, 36.0, 28.7, 21.8, 18.0; **IR** (thin film) ν_{max} 3147, 3019, 2954, 2854, 1735, 1437, 1394, 1295, 1195, 1179 cm^{-1}; **HRMS** (ESI^+) cal'd for $[C_{21}H_{25}N_3O_6S+Na]^+$: *m/z*, 470.1356 found 470.1368.

Procedure for *N*-sulfonyltriazole 1i bearing a hydrocarbon tether.



S4 **1i**



S4

(1*E*,3*E*)-nona-1,3-dien-8-yn-1-ylbenzene (S4). To a flask containing potassium *t*-butoxide (150 mg, 1.3 mmol, 1.1 equiv) in diethyl ether (6 mL, 0.2 M) at ambient temperature, cinnamyltriphenylphosphonium bromide (500 mg, 1.3 mmol, 1.1 equiv) was added portionwise. After holding at this temperature for 30 minutes, the reaction mixture was cooled to 0 °C, and TMS-protected hex-5-ynal[11] (200 mg, 1.2 mmol, 1.0 equiv) dissolved in ether (1.0 mL) was added dropwise over 10 minutes. The reaction mixture was then allowed to warm to ambient temperature and stirred for 5 h. After this time, the reaction mixture was quenched by the addition of water (10 mL) and diluted with diethyl ether (10 mL). The layers were separated and the aqueous layer was extracted with diethyl ether (3 x 10 mL). The combined organic layers were washed with brine (10 mL), dried over sodium sulfate, filtered, and concentrated *in vacuo*. The resulting residue was filtered through a short silica plug eluting with pentanes to give crude trimethyl(9-phenylnona- 6,8-dien-1-yn-1-yl) silane (320 mg, quant.) as a yellow oil that was used without further purification.

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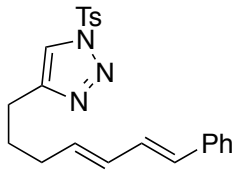
[10] Lopez-Duran, R.; Martos-Redruejo, A.; Bunuel, E.; Pardo-Rodriguez, V.; Cardenas, D. J. *Chem. Commun.*, **2013**, *49*, 10691.

[11] Harris, G. D.; Herr, R. J.; Weinreb, S. M. *J. Org. Chem.* **1993,** *58,* 5452.

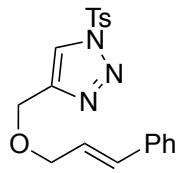
The crude diene (320 mg, 1.2 mmol, 1.0 equiv) was dissolved in dichloromethane (2.7 mL, 0.5 M), and to this solution was added iodine (15 mg, 0.065 mmol, 5.0 mol %). The reaction mixture was allowed to stir at ambient temperature for 30 min, then was quenched by the addition of sodium thiosulfate (5 mL). The biphasic mixture was vigorously stirred for 15 minutes, then the layers were separated and the aqueous layer was extracted with dichloromethane (3 x 5 mL). The combined organic layers were dried over sodium sulfate, filtered, concentrated *in vacuo* to give the crude trimethyl((6*E*,8*E*)-9-phenylnona-6,8-dien-1-yn-1-yl)silane (320 mg, quant.) as a yellow oil.

The TMS-protected alkyne (320 mg, 1.2 mmol) was dissolved in methanol (6 mL, 2.0 M) and potassium carbonate (330 mg, 2.4 mmol, 2.0 equiv) was added. The resulting mixture was allowed to stir at ambient temperature for 14 h at which time the reaction mixture was quenched by the addition of saturated aqueous ammonium chloride (5 mL) and diluted with diethyl ether (5 mL). The layers were separated and the aqueous layer was extracted with diethyl ether (3 x 5 mL). The combined organic layers were washed with brine (5 mL), dried over sodium sulfate, filtered, and concentrated *in vacuo* and passed through a short silica plug eluting with pentanes to give **S4** (185 mg, 79% over 3 steps) as a yellow oil. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.2 Hz, 2H), 7.30 (t, *J* = 7.7 Hz, 2H), 7.20 (t, *J* = 7.3 Hz, 1H), 6.75 (dd, *J* = 15.7, 10.4 Hz, 1H), 6.46 (d, *J* = 15.7 Hz, 1H), 6.24 (dd, *J* = 15.1, 10.4 Hz, 1H), 5.80 (dt, *J* = 14.7, 7.1 Hz, 1H), 2.27 (q, *J* = 7.5 Hz, 2H), 2.23 (td, *J* = 7.1, 2.6 Hz, 2H), 1.97 (t, *J* = 2.6 Hz, 1H), 1.67 (p, *J* = 7.2 Hz, 2H); **IR** (thin film) ν_{max} 3297, 3023, 2934, 2863, 2117, 1595, 1448, 1433, 1133, 989 cm^{-1}; **HRMS** (EI^+) cal'd for $[C_{15}H_{16}]^+$: *m/z*, 196.1252 found 196.1252.



1i

4-((4*E*,6*E*)-7-phenylhepta-4,6-dien-1-yl)-1-tosyl-1*H*-1,2,3-triazole (1i). Prepared from alkyne **S4** using Representative Procedure A. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.0 Hz, 2H), 7.88 (s, 1H), 7.44 - 7.34 (m, 4H), 7.30 (t, *J* = 7.1 Hz, 2H), 7.20 (t, *J* = 7.5 Hz, 1H), 6.83 - 6.69 (m, 1H), 6.45 (d, *J* = 15.7 Hz, 1H), 6.30 - 6.13 (m, 1H), 5.79 (dt, *J* = 14.6, 7.0 Hz, 1H), 2.74 (t, *J* = 7.3 Hz, 2H), 2.42 (s, 3H), 2.20 (q, *J* = 7.4 Hz, 2H), 1.87 - 1.73 (m, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 147.8, 147.1, 137.5, 134.2, 133.2, 131.4, 130.5, 130.4, 129.0, 128.5, 128.5, 127.2, 126.2, 120.4, 32.1, 28.4, 24.8, 21.8; **IR** (thin film) ν_{max} 3147, 3061, 2924, 2859, 1595, 1391, 1009 cm^{-1}; **HRMS** (ESI^+) cal'd for $[C_{22}H_{23}N_3O_2S+Na]^+$: *m/z*, 416.1403 found 416.1412.

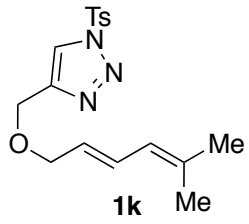


1j

(*E*)-4-((cinnamyloxy)methyl)-1-tosyl-1*H*-1,2,3-triazole (1j). Prepared from (*E*)-3-phenylprop-2-en-1-ol[12] using Representative Procedure A. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.99 (d, *J* = 8.4 Hz, 2H), 7.40-7.34 (m, 4H), 7.34-7.29 (m, 2H), 7.29-7.21 (m, 1H), 6.63 (d, *J* = 16.0 Hz, 1H), 6.28 (dt, *J* = 16.0, 6.2 Hz, 1H), 4.67 (s, 2H), 4.24 (dd, *J* = 6.2, 1.5 Hz, 2H), 2.43 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 147.4, 145.2, 136.5, 133.5, 133.1, 130.5, 128.8, 128.7, 128.0, 126.6, 125.1,

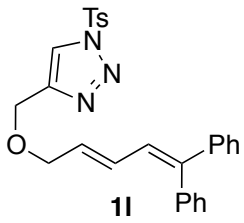
[12] Kim, H.; Lee, C. *Org. Lett.* **2002**, *4*, 4369.

122.3, 71.6, 63.1, 21.9; **IR** (thin film) ν_{max} 3146, 3029, 2922, 2857, 1595, 1393, 1306, 1196, 1179, 1091, 1010, 969, 670, 585 cm^{-1}; **HRMS** (ESI^+) cal'd for $[C_{19}H_{19}N_3O_3S+Na]^+$: *m/z*, 392.1039 found 392.1038.



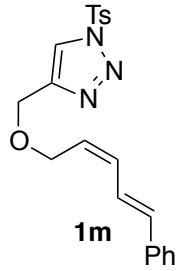
1k

(*E*)-4- (((5-methylhexa- 2,4- dien- 1-yl) oxy) methyl)- 1-tosyl-1*H*-1,2,3-triazole (1k). Prepared from (*E*)-ethyl 5-methylhexa-2,4-dienoate[13] using Representative Procedure B. (89:11 *E*:*Z* mixture of diastereomers). **^{1}H NMR** (600 MHz, $CDCl_3$, *E* isomer) δ 8.10 (s, 1H), 7.97 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 6.45 (dd, *J* = 15.0, 11.0 Hz, 1H), 5.81 (d, *J* = 10.9 Hz, 1H), 5.59 (dt, *J* = 15.0, 6.6 Hz, 1H), 4.60 (s, 2H), 4.09 (d, *J* = 6.5 Hz, 2H), 2.43 (s, 3H), 1.76 (s, 3H), 1.74 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$, *E* isomer) δ 147.4, 145.4, 137.0, 133.1, 130.8, 130.5, 128.8, 125.4, 124.2, 122.3, 71.8, 62.9, 26.1, 21.9, 18.4; **IR** (thin film) ν_{max} 2914, 2859, 1595, 1394, 1196, 1178, 1091, 1011, 963, 671, 587 cm^{-1}; **HRMS** (ESI^+) cal'd for $[C_{17}H_{21}N_3O_3S+Na]^+$: *m/z*, 370.1196 found 370.1194.



1l

(*E*)-4-(((5,5-diphenylpenta-2,4-dien-1-yl)oxy)methyl)-1-tosyl-1*H*-1,2,3-triazole (1l). Prepared from (*E*)-ethyl 5,5-diphenylpenta-2,4-dienoate[14] using Representative Procedure B. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.96 (d, *J* = 8.4 Hz, 2H), 7.47 - 7.34 (m, 6H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.29 - 7.22 (m, 4H), 7.23 - 7.17 (m, 2H), 6.70 (d, *J* = 11.0 Hz, 1H), 6.35 (dd, *J* = 15.3, 11.0 Hz, 1H), 5.93 (dt, *J* = 15.2, 6.3 Hz, 1H), 4.57 (s, 2H), 4.06 (d, *J* = 6.1 Hz, 2H), 2.40 (s, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 147.8, 145.6, 144.1, 142.4, 139.9, 133.4, 132.1, 130.9, 130.8, 130.6, 129.1, 128.7, 128.7, 128.1, 128.0, 128.0, 127.3, 122.7, 71.8, 63.5, 22.3; **IR** (thin film) ν_{max} 3378, 3151, 3057, 3029, 2923, 2867, 2248, 1705, 1666, 1595, 1395, 1195, 1179, 1091 cm^{-1}; **HRMS** (ESI^+) cal'd for $[C_{27}H_{25}N_3O_3S+Na]^+$: *m/z*, 494.1514 found 494.1510.



1m

4-((((2*Z*,4*E*)- 5-phenylpenta- 2,4-dien-1-yl) oxy) methyl)- 1-tosyl- 1*H*-1,2,3-triazole (1m). Prepared from (2*Z*,4*E*)-ethyl 5-phenylpenta-2,4-dienoate[15] using Representative Procedure B. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.98 (d, *J* = 8.8 Hz, 2H), 7.45 - 7.38 (m, 2H), 7.38 - 7.29 (m, 4H), 7.28 - 7.21 (m, 1H), 7.02 (dd, *J* = 15.4, 11.2, 1H), 6.60 (d, *J* = 15.5 Hz, 1H), 6.34 (t, *J* = 11.0 Hz, 1H), 5.62 (dt, *J* = 10.9, 6.8 Hz, 1H), 4.67 (s, 2H), 4.35 (dd, *J* = 6.9, 1.4 Hz, 2H), 2.43 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 147.4, 145.2, 137.0, 134.8, 133.1, 132.5, 130.5, 128.7, 128.0, 126.7, 123.4, 122.4, 66.8, 63.2, 21.8; **IR** (thin film) ν_{max} 3147, 3031, 2864, 1594, 1393, 1196, 1179, 1091, 1010, 979, 670, 586 cm^{-1}; **HRMS** (ESI^+) cal'd for $[C_{21}H_{21}N_3O_3S+Na]^+$: *m/z*, 418.1196 found 418.1191.

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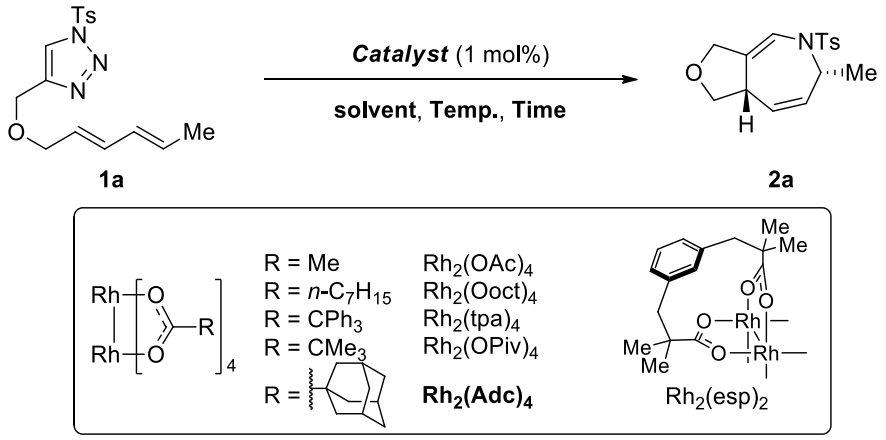
[13] Balu, N.; Thomas, J. V.; Bhat, S. V. *J. Med. Chem.* **1991**, *34*, 2821.

[14] Guthrie, R. W., et al. *J. Med. Chem.* **1989**, *32*, 1820.

[15] Thiot, C.; Schmutz, M.; Wagner, A.; Mioskowski, C. *Chem. Eur. J.* **2007**, *13*, 8971.

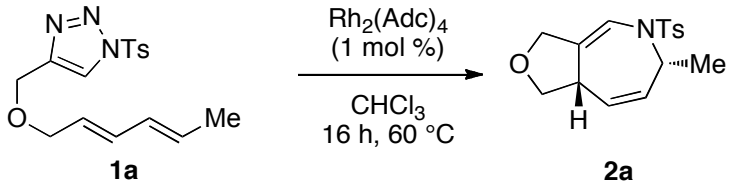
Optimization of the reaction conditions for the dihydroazepine formation



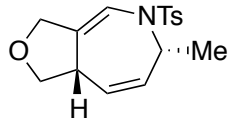
Entry	Rh_2L_4	Solvent	Temp. (°C)	time	yield 2a (%)[a]
1	$Rh_2(Ooct)_4$ (1)	$CHCl_3$	140[b]	0.25 h	54
2	$Rh_2(OAc)_4$ (1)	$CHCl_3$	140[b]	0.25 h	47
3	$Rh_2(tpa)_4$ (1)	$CHCl_3$	140[b]	0.25 h	18
4	$Rh_2(OPiv)_4$ (1)	$CHCl_3$	140[b]	0.25 h	58
5	$Rh_2(esp)_2$ (1)	$CHCl_3$	140[b]	0.25 h	66
6	$Rh_2(Adc)_4$ (1)	$CHCl_3$	140[b]	0.25 h	68
7	$Rh_2(Ooct)_4$ (1)	MeCN	140[b]	0.25 h	47
8	$Rh_2(Ooct)_4$ (1)	DME	140[b]	0.25 h	50
9	$Rh_2(Ooct)_4$ (1)	Heptane	140[b]	0.25 h	13
10	**$Rh_2(Adc)_4$ (1)**	**$CHCl_3$**	**60**	**16 h**	**74**
11	$Rh_2(Ooct)_4$ (1)	$CHCl_3$	60	16 h	57
12	$Rh_2(Ooct)_4$ (1)	TBME	60	16 h	59
13	$Rh_2(Ooct)_4$ (1)	PhH	60	16 h	56
14	$Rh_2(OPiv)_4$ (1)	$CHCl_3$	60	16 h	62
15	$Rh_2(OPiv)_4$ (1)	$CHCl_3$	23	16 h	66
16	$Rh_2(OPiv)_4$ (1)	TBME	60	16 h	63
17	$Rh_2(OPiv)_4$ (1)	1,2-DCE	60	16 h	55
18	$Rh_2(esp)_2$ (1)	$CHCl_3$	23	16 h	39

[a]Isolated yield. [b]Reaction was performed in a microwave apparatus.

Representative Procedure D for the Rh(II)-Catalyzed Cyclopropanation / 1-Aza-Cope Rearrangement of Dienyltriazoles

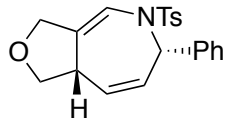


1a **2a**



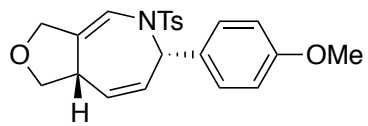
2a

6-methyl-5-tosyl-3,5,6,8a-tetrahydro-1*H*-furo[3,4-*c*]azepine (2a). A flame-dried microwave vial was charged with $Rh_2(Adc)_4$ (1.4 mg, 1.0 mol %) and *N*-tosyltriazole **1a** (50 mg, 0.15 mmol) in chloroform (0.75 mL, 0.20 M) via syringe. The resulting mixture was heated to 60 °C and held at this temperature for 16 h. After cooling to ambient temperature, silica gel was added to the reaction mixture and the solvent was removed *in vacuo*. The resulting residue was purified by column chromatography eluting with 6:1 hexanes:ethyl acetate to give **2a** (34 mg, 74% isolated yield, >95:5 dr) as a colorless oil. The diastereomeric ratio was determined by ^{1}H NMR analysis of the crude mixture. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 6.15 (d, *J* = 2.5 Hz, 1H), 5.51 (ddd, *J* = 11.5, 5.2, 2.8 Hz, 1H), 5.18 (dt, *J* = 11.6, 1.8 Hz, 1H), 4.93 - 4.75 (m, 1H), 4.50 (d, *J* = 13.4 Hz, 1H), 4.28 (dt, *J* = 13.5, 2.3 Hz, 1H), 4.11 (t, *J* = 8.4 Hz, 1H), 3.32 (dd, *J* = 10.2, 8.4 Hz, 1H), 3.08 - 2.95 (m, 1H) 2.42 (s, 3H), 1.25 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.4, 143.3, 137.9, 132.0, 129.5, 126.9, 122.2, 115.8, 74.2, 70.1, 53.2, 42.4, 21.5, 21.2; **IR** (thin film) ν_{max} 2960, 2930, 2856, 1724, 1692, 1343, 1159, 1106 cm^{-1}; **HRMS** (ESI^+) cal'd for $[C_{16}H_{19}NO_3S+Na]^+$: *m/z*, 328.0983 found 328.0981.



2b

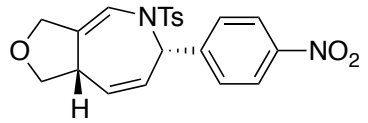
(6-phenyl-5-tosyl-3,5,6,8a-tetrahydro-1*H*-furo[3,4-*c*]azepine (2b). Prepared from *N*-sulfonyltriazole **1b** following Representative Procedure D, but the reaction was run for 0.5 h instead of 16 h. (92% isolated yield, >95:5 dr). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.8 Hz, 2H), 7.38 (d, *J* = 7.4 Hz, 2H), 7.35 - 7.28 (m, 3H), 7.26 (d, *J* = 6.3 Hz, 2H), 6.01 (t, *J* = 4.5 Hz, 1H), 5.80 (s, 1H), 5.71 (ddd, *J* = 11.0, 5.3, 2.6 Hz, 1H), 5.48 (d, *J* = 11.5 Hz, 1H), 4.41 (d, *J* = 13.7 Hz, 1H), 4.31 - 4.02 (m, 2H), 3.39 (t, *J* = 9.4 Hz, 1H), 2.87 (t, *J* = 9.4 Hz, 1H), 2.43 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 144.6, 143.3, 139.0, 138.1, 129.5, 128.6, 128.3, 128.3, 127.9, 126.9, 124.3, 116.5, 74.1, 70.1, 60.0, 42.6, 21.5; **IR** (thin film) ν_{max} 2904, 2850, 1674, 1586, 1451, 1407, 1335, 1162, 1034 cm^{-1}; **HRMS** (ESI^+) cal'd for $[C_{21}H_{21}NO_3S+Na]^+$: *m/z*, 390.1140 found 390.1138.



2c

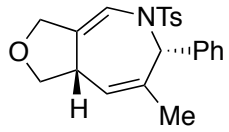
6- (4-methoxyphenyl)- 5- tosyl- 3,5,6,8a-tetrahydro-1*H*-furo[3,4-*c*]azepine (2c). Prepared from *N*-sulfonyltriazole **1c** following Representative Procedure D, but the reaction was run for 0.5 h instead of 16 h. (61% isolated yield, >95:5 dr). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.3 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 5.98-5.94 (m, 1H), 5.80-5.76 (m, 1H), 5.68 (ddd, *J* = 11.5, 5.4, 2.8 Hz, 1H), 5.46 (dt, *J* = 11.5,

1.9 Hz, 1H), 4.41 (d, *J* = 13.5 Hz, 1H), 4.20-4.10 (m, 2H), 3.80 (s, 3H), 3.38 (dd, *J* = 10.3, 8.5 Hz, 1H), 2.88 (s (br), 1H), 2.42 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 159.5, 144.6, 143.4, 138.4, 131.2, 130.0, 129.7, 129.1, 127.1, 124.2, 116.7, 113.8, 74.3, 70.3, 59.7, 55.4, 42.8, 21.7; **IR** (thin film) ν_{max} 2919, 2838, 1608, 1510, 1341, 1249, 1159, 1094, 1069, 1026, 828, 692, 580 cm^{-1}; **HRMS** (ESI$^+$) cal'd for $[C_{22}H_{23}NO_4S+Na]^+$: *m/z*, 420.1240 found 420.1239.



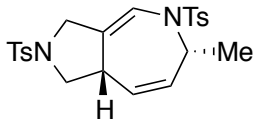
2d

6- (4-nitrophenyl)- 5-tosyl- 3,5,6,8a-tetrahydro-1*H*-furo [3,4-*c*]azepine (2d). Prepared from *N*-sulfonyltriazole **1d** following Representative Procedure D. (69% isolated yield, >95:5 dr). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.6 Hz, 2H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.57 (d, *J* = 8.6 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 6.11-6.05 (m, 1H), 5.81 (s(br), 1H), 5.71 (ddd, *J* = 11.5, 5.4, 2.8 Hz, 1H), 5.57 (d, *J* = 11.5 Hz, 1H), 4.40 (d, *J* = 13.8 Hz, 1H), 4.17-4.10 (m, 2H), 3.38 (dd, *J* = 10.2, 8.5 Hz, 1H), 2.86 (s(br), 1H), 2.43 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.7, 146.5, 145.3, 143.9, 137.8, 129.8, 129.5, 127.4, 127.0, 125.9, 123.7, 116.2, 74.1, 70.1, 59.2, 42.6, 21.7; **IR** (thin film) ν_{max} 3035, 2925, 2852, 1597, 1521, 1346, 1160, 1093, 1069, 689, 586 cm^{-1}; **HRMS** (ESI$^+$) cal'd for $[C_{21}H_{20}N_2O_5S+Na]^+$: *m/z*, 435.0985 found 435.0987.



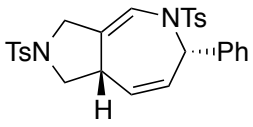
2e

7- methyl- 6- phenyl-5- tosyl- 3,5,6,8a- tetrahydro- 1*H*-f uro[3,4-*c*] azepine (2e). Prepared from *N*-sulfonyltriazole **1e** following Representative Procedure D. (63% isolated yield, >95:5 dr). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.2 Hz, 2H), 7.35 – 7.23 (m, 7H), 5.74 (d, *J* = 3.1 Hz, 1H), 5.70 – 5.65 (m, 1H), 5.26 – 5.22 (m, 1H), 4.41 (d, *J* = 13.4 Hz, 1H), 4.15 – 4.09 (m, 2H), 3.37 (dd, *J* = 10.7, 8.4 Hz, 1H), 2.86 – 2.77 (m, 1H), 2.42 (s, 3H), 1.63 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 144.0, 143.4, 138.4, 138.3, 135.0, 129.6, 129.0, 128.5, 128.1, 127.0, 120.1, 116.3, 74.5, 70.2, 63.8, 42.9, 24.4, 21.7; **IR** (thin film) ν_{max} 3028, 2922, 2848, 1598, 1493, 1453, 1342, 1162, 1102, 1089, 1068, 1043, 814, 754, 701 cm^{-1}; **HRMS** (ESI$^+$) cal'd for $[C_{22}H_{23}NO_3S+Na]^+$: *m/z*, 404.1291 found 404.1289.



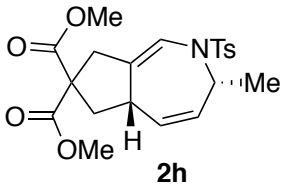
2f

6- methyl- 2,5- ditosyl- 1,2,3,5,6,8a- hexahydropyrrolo [3,4-*c*] azepine (2f). Prepared from *N*-sulfonyltriazole **1f** following Representative Procedure D, but the reaction was run for 0.5 h instead of 16 h. (72% isolated yield, >95:5 dr). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.3 Hz, 2H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 7.8 Hz, 2H), 7.25 (d, *J* = 7.8 Hz, 2H), 6.13 (s, 1H), 5.43 (ddd, *J* = 11.6, 5.3, 2.8 Hz, 1H), 5.11 (d, *J* = 11.9 Hz, 1H), 4.77 - 4.70 (bs, 1H), 4.07 (d, *J* = 14.0 Hz, 1H), 3.64 (t, *J* = 8.9 Hz, 1H), 3.58 (d, *J* = 14.1 Hz, 1H), 3.23 - 3.07 (bs, 1H), 2.57 (t, *J* = 9.7 Hz, 1H), 2.45 (s, 3H), 2.43 (s, 3H), 1.12 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 144.1, 143.6, 139.1, 137.5, 132.0, 131.8, 129.8, 129.7, 128.0, 126.8, 123.0, 118.6, 54.0, 53.0, 50.8, 40.9, 21.6, 21.5, 20.8; **IR** (thin film) ν_{max} 3463, 2978, 2928, 2872, 2251, 1669, 1597, 1344, 1162, 1092 cm^{-1}; **HRMS** (ESI$^+$) cal'd for $[C_{23}H_{26}N_2O_4S_2+Na]^+$: *m/z*, 481.1226 found 481.1236.



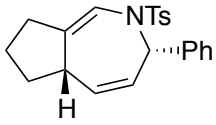
2g

6-phenyl-2,5-ditosyl-1,2,3,5,6,8a-hexahydropyrrolo[3,4-*c*]azepine (2g). Prepared from *N*-sulfonyltriazole **1g** following Representative Procedure D, but the reaction was run for 0.5 h instead of 16 h. (72% isolated yield, >95:5 dr). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.70-7.64 (m, 4H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.27-7.20 (m, 7H), 5.95-5.90 (m, 1H), 5.80 (d, *J* = 2.5 Hz, 1H), 5.65 (ddd, *J* = 11.6, 5.5, 2.8 Hz, 1H), 5.41 (dt, *J* = 11.5, 1.9 Hz, 1H), 3.98 (d, *J* = 14.2 Hz, 1H), 3.66 (t, *J* = 8.9 Hz, 1H), 3.47 (dt, *J* = 14.3, 2.4 Hz, 1H), 3.05 – 2.99 (m, 1H), 2.63 (t, *J* = 9.7 Hz, 1H), 2.47 (s, 3H), 2.44 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 144.2, 143.7, 140.6, 138.8, 137.9, 132.0, 129.9, 129.8, 128.9, 128.5, 128.4, 128.1, 128.1, 127.0, 125.2, 119.4, 59.9, 54.1, 50.9, 41.3, 21.7; **IR** (thin film) ν_{max} 3089, 3034, 2923, 2856, 1598, 1494, 1479, 1453, 1346, 1162, 1093, 1039, 815, 706, 672 cm^{-1}; **HRMS** (EI$^+$) cal'd for $[C_{28}H_{28}N_2O_4S_{2+}Na]^+$: *m/z*, 543.1383 found 543.1373.



2h

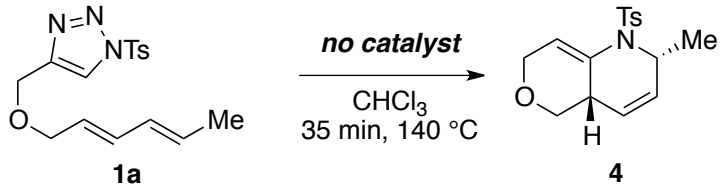
Dimethyl 3-methyl-2-tosyl-2,3,5a,6-tetrahydrocyclopenta[*c*] azepine-7,7(8*H*)-dicarboxylate (2h). Prepared from *N*-sulfonyltriazole **1h** following Representative Procedure D, but the reaction was run for 0.5 h instead of 16 h. (45% isolated yield, >95:5 dr). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 8.2 Hz, 2H), 6.14 (s, 1H), 5.40 (ddd, *J* = 11.5, 5.1, 2.9 Hz, 1H), 5.25 - 5.17 (m, 1H), 4.83 - 4.75 (m, 1H), 3.74 (s, 3H), 3.72 (s, 3H), 3.15 - 3.02 (m, 1H), 3.02 - 2.94 (m, 1H), 2.86 - 2.77 (m, 1H), 2.60 - 2.50 (m, 1H), 2.43 (s, 3H), 1.86 (dd, *J* = 12.7, 11.2 Hz, 1H), 1.24 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 171.1, 170.9, 144.0, 143.0, 130.6, 129.4, 126.8, 126.0, 118.3, 100.0, 58.3, 52.8, 52.8, 52.8, 40.9, 40.1, 38.7, 21.5, 21.2; **IR** (thin film) ν_{max} 2954, 2926, 2852, 232, 1735, 1598, 1434, 1340, 1252, 1164 cm^{-1}; **HRMS** (ESI$^+$) cal'd for $[C_{21}H_{25}NO_6S_{+}Na]^+$: *m/z*, 442.1295 found 442.1304.

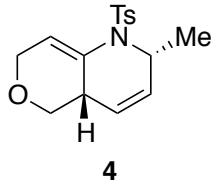


2i

3-phenyl-2-tosyl-2,3,5a,6,7,8-hexahydrocyclopenta[*c*]azepine (2i). Prepared from *N*-sulfonyltriazole **1i** following Representative Procedure D, but the reaction was run for 0.5 h instead of 16 h. (92% isolated yield, >95:5 dr). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.7 Hz, 2H), 7.36 (d, *J* = 7.4 Hz, 2H), 7.33 - 7.20 (m, 5H), 5.94 (s, 1H), 5.70 (s, 1H), 5.63 - 5.47 (m, 1H), 2.62 - 2.57 (m, 1H), 2.42 (s, 3H), 2.38 - 2.31 (m, 1H), 2.25 - 2.15 (m, 1H), 1.94 (t, *J* = 8.4 Hz, 1H), 1.76 - 1.66 (m, 1H), 1.66 - 1.54 (bs, 1H), 1.44 - 1.31 (m, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 149.5, 142.9, 139.5, 138.5, 129.9, 129.2, 128.7, 128.1, 127.6, 127.0, 126.5, 117.0, 59.8, 42.0, 34.8, 31.6, 24.8, 21.5; **IR** (thin film) ν_{max} 3029, 2955, 2867, 1665, 1598, 1451, 1337, 1161, 1094 cm^{-1}; **HRMS** (ESI$^+$) cal'd for $[C_{22}H_{23}NO_2S+Na]^+$: *m/z*, 388.1347 found 388.1343.

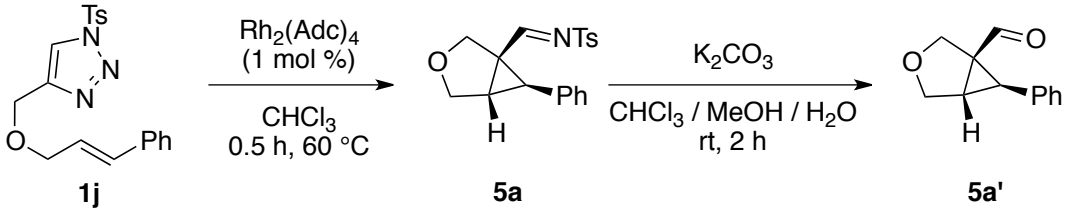
Procedure for the Synthesis of 4 via a thermal non-catalyzed process.

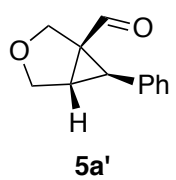




2-methyl- 1- [(4-methylphenyl) sulfonyl]- 1,4a,5,7- tetrahydro- 2*H*-pyrano[4,3-*b*]pyridine (4). A flame-dried 2 mL microwave vial was charged with **1a** (50 mg, 0.15 mmol, 1.0 equiv), the vial was sealed and backfilled with N_2. Chloroform (0.8 mL, 0.2 M) was added, and the vial was heated at 140 °C in the microwave for 35 minutes. The mixture was allowed to cool to room temperature and concentrated to dryness, and the product was purified by silica-gel chromatography using 1% diethyl ether in dichloromethane as eluent, to afford pure bicyclic compound **4** (23 mg, 50% yield) as a white crystalline solid, m.p. 128-129 °C. It is noteworthy that none of the dihydroazepine **2a** was observed in the crude mixture under these conditions. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 16.7 Hz, 2H), 6.03 (s (br), 1H), 5.62 (ddd, *J* = 10.3, 4.1, 2.6 Hz, 1H), 5.17 (d, *J* = 10.3 Hz, 1H), 4.69-4.62 (m, 1H), 4.35 (dt, *J* = 16.9, 3.1 Hz, 1H), 4.25 (ddd, *J* = 16.9, 4.1, 1.9 Hz, 1H), 3.90 (dd, *J* = 10.8, 5.5 Hz, 1H), 3.05 (t, *J* = 10.7 Hz, 1H), 2.51 (s (br, 1H), 2.40 (s, 3H), 1.32 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 143.4, 137.7, 130.2, 129.7, 129.7, 127.3, 125.6, 121.8, 68.9, 66.1, 52.7, 33.5, 22.9, 21.7; **IR** (thin film) ν_{max} 3031, 2970, 2926, 2851, 1675, 1599, 1458, 1342, 1165, 1136, 1101, 1036, 976, 763, 675, 568, 548 cm^{-1}; **HRMS** (ESI$^+$) cal'd for $[C_{16}H_{19}NO_3S+Na]^+$: *m/z*, 328.0978 found 328.0979.

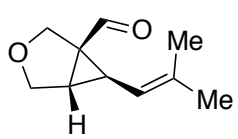
Representative Procedure E for the Synthesis and Hydrolysis of Cyclopropanecarboximines from *N*-sulfonyltriazoles





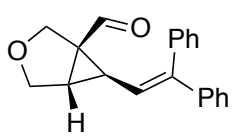
6-phenyl-3-oxabicyclo[3.1.0]hexane-1-carbaldehyde (5a'). A flame-dried microwave vial was charged with $Rh_2(Adc)_4$ (1.4 mg, 1.0 mol %) and *N*-tosyltriazole **1j** (55 mg, 0.15 mmol, 1.0 equiv) in chloroform (0.75 mL, 0.20 M) via syringe. The resulting mixture was heated to 60 °C for 0.5 h. After cooling to ambient temperature, an equal volume of methanol (0.75 mL), water (a few drops), and anhydrous potassium carbonate (41 mg, 0.30 mmol, 2.0 equiv) were added to the reaction mixture, and the resulting

suspension was stirred vigorously for 2 h at which time TLC analysis indicated complete hydrolysis of imine **5a**. Solvents were removed *in vacuo*. The residue was re-suspended in dichloromethane (5 mL) and dried over sodium sulfate, filtered and concentrated *in vacuo*. The resulting residue was purified by column chromatography eluting with 6:1 hexanes:ethyl acetate to give **5a'** (51% isolated yield, >95:5 dr, 66% NMR yield, >95:5 dr for imine **5a**) as a colorless oil. Diastereomeric ratio was determined by ^{1}H NMR analysis of the crude mixture. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.95 (s, 1H), 7.37 - 7.29 (m, 4H), 7.30 - 7.24 (m, 1H), 4.21 (d, *J* = 9.1 Hz, 1H), 4.08 (d, *J* = 8.7 Hz, 1H), 4.03 (d, *J* = 9.1 Hz, 1H), 3.90 (dd, *J* = 8.8, 3.1 Hz, 1H), 2.99 (dd, *J* = 5.6, 3.0 Hz, 1H), 2.93 (d, *J* = 5.6 Hz, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 198.3, 134.0, 129.0, 128.9, 127.6, 68.9, 68.2, 46.9, 33.5, 32.0; **IR** (thin film) ν_{max} 2930, 2863, 1692, 1371, 1239, 1199, 1072, 1058, 1027, 909, 795, 733, 698 cm^{-1}; **HRMS** (EI$^+$) cal'd for $[C_{12}H_{12}O_2]^+$: *m/z*, 188.0837 found 188.0837.



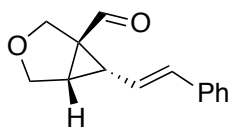
5b'

6-(2-methylprop-1-en-1-yl)-3-oxabicyclo[3.1.0]hexane-1-carbalde hyde (5b'). Prepared from *N*-sulfonyltriazole **1k** (*E:Z* = 89:11) following Representative Procedure E. (49% isolated yield, >95:5 dr, 67% NMR yield, 88:12 dr for imine **5b**). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.35 (s, 1H), 5.21 (d, *J* = 8.0 Hz, 1H), 4.13 (d, *J* = 9.0 Hz, 1H), 3.93 (d, *J* = 8.8 Hz, 1H), 3.89 (d, *J* = 9.0 Hz, 1H), 3.76 (d, *J* = 8.9, 1H), 2.47-2.41 (m, 1H), 2.32-2.25 (m, 1H), 1.73 (s, 3H), 1.70 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 198.7, 137.5, 118.1, 68.8, 68.0, 46.9, 35.8, 29.4, 25.6, 18.7; **IR** (thin film) ν_{max} 2931, 2873, 1693, 1381, 1238, 1200, 1075, 1015, 903, 704, 626 cm^{-1}; **HRMS** (EI$^+$) cal'd for $[C_{10}H_{14}O_2]^+$: *m/z*, 166.0994 found 166.0992.



5c'

6-(2,2-diphenylvinyl)- 3- oxabicyclo[3.1.0]hexane-1-carbaldehyde (5c'). Prepared from *N*-sulfonyltriazole **1l** following Representative Procedure E. (64% isolated yield, >95:5 dr, 82% NMR yield, >95:5 dr for imine **5c**). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.56 (s, 1H), 7.38 (t, *J* = 7.4 Hz, 2H), 7.34 (d, *J* = 7.3 Hz, 1H), 7.31 - 7.25 (m, 3H), 7.21 (t, *J* = 6.3 Hz, 4H), 6.09 (d, *J* = 9.1 Hz, 1H), 4.15 (d, *J* = 9.1 Hz, 1H), 3.88 (d, *J* = 8.8 Hz, 1H), 3.83 (d, *J* = 9.1 Hz, 1H), 3.77 (dd, *J* = 8.9, 2.9 Hz, 1H), 2.63 (dd, *J* = 5.4, 2.9 Hz, 1H), 2.33 (dd, *J* = 9.2, 5.3 Hz, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 197.7, 145.4, 141.8, 139.1, 129.9, 128.4, 128.2, 127.7, 127.6, 127.5, 122.4, 68.6, 67.7, 48.5, 37.1, 31.7; **IR** (thin film) ν_{max} 3053, 3030, 2960, 2928, 2863, 2745, 1693, 1494, 1444, 1374, 1205, 1068, 1018 cm^{-1}; **HRMS** (EI$^+$) cal'd for $[C_{20}H_{18}O_2]^+$: *m/z*, 290. 1307 found 290.1303.

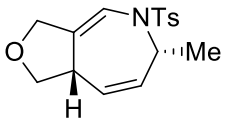


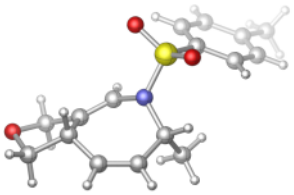
5d'

6-((*E*)-styryl)-3-oxabicyclo[3.1.0]hexane-1-carbaldehyde (5d'). Prepared from *N*-sulfonyltriazole **1m** following Representative Procedure E. (61% isolated yield, >95:5 dr, 70% NMR yield, >95:5 dr for imine **5d**). **^{1}H NMR** (600 MHz, $CDCl_3$) δ9.24 (s, 1H), 7.41-7.34 (m, 2H), 7.35-7.27 (m, 2H), 7.26-7.20 (m, 1H), 6.73 (d, *J* = 15.9 Hz, 1H), 6.23 (dd, *J* = 15.9, 9.2 Hz, 1H), 4.43 (d, *J* = 9.6 Hz, 1H), 4.12-4.03 (m, 3H), 2.74 (t, *J* = 8.8 Hz, 1H), 2.55 (ddd, *J* = 8.5, 3.1, 1.2 Hz, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 196.8, 137.0, 135.3, 128.7, 127.7, 126.3, 120.9, 67.8, 66.4,

48.3, 33.8, 32.4; **IR** (thin film) ν_{max} 2924, 2874, 1703, 1693, 1493, 1451, 1203, 1114, 1075, 1041, 1023, 966, 910, 755, 696 cm^{-1}; **HRMS** (EI^+) cal'd for $[C_{14}H_{14}O_2]^+$: *m/z*, 214.0994 found 214.0992.

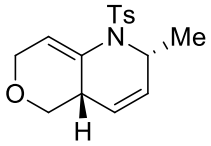
X-Ray Data of compound 2a:

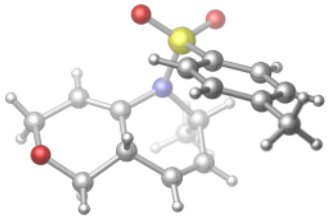




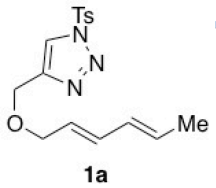
X-ray ID	sarpong55	
Empirical formula	C16 H19 N O3 S	
Formula weight	305.38	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	P b c a	
Unit cell dimensions	a = 14.1109(14) Å	α= 90°.
	b = 8.0225(8) Å	β= 90°.
	c = 27.064(3) Å	γ = 90°.
Volume	3063.8(5) $Å^3$	
Z	8	
Density (calculated)	1.324 Mg/m^3	
Absorption coefficient	1.960 mm^{-1}	
F(000)	1296	
Crystal size	0.120 x 0.050 x 0.050 mm^3	
Crystal color/habit	colorless rod	
Theta range for data collection	3.266 to 68.391°.	
Index ranges	-14<=h<=16, -8<=k<=9, -32<=l<=32	
Reflections collected	50557	
Independent reflections	2806 [R(int) = 0.0294]	
Completeness to theta = 67.000°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.864 and 0.774	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2806 / 0 / 192	
Goodness-of-fit on F^2	1.059	
Final R indices [I>2sigma(I)]	R1 = 0.0364, wR2 = 0.0960	
R indices (all data)	R1 = 0.0368, wR2 = 0.0963	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.406 and -0.441 $e.Å^{-3}$	

X-Ray Data of compound **4**:

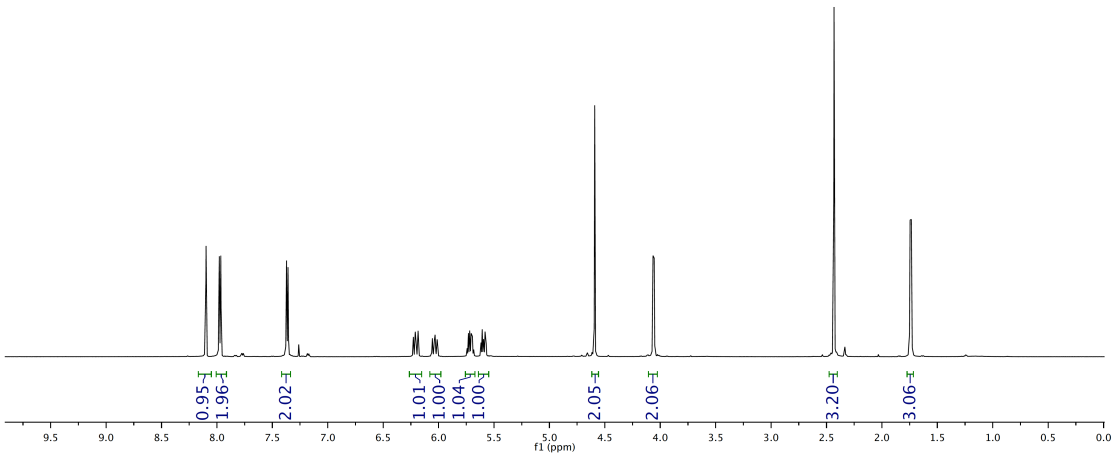




X-ray ID	sarpong57	
Empirical formula	C16 H19 N O3 S	
Formula weight	305.38	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 7.3521(5) Å	α= 90°.
	b = 8.0929(5) Å	β= 94.599(3)°.
	c = 25.1517(17) Å	γ = 90°.
Volume	1491.70(17) Å^3	
Z	4	
Density (calculated)	1.360 Mg/m^3	
Absorption coefficient	2.013 mm^{-1}	
F(000)	648	
Crystal size	0.100 x 0.100 x 0.020 mm^3	
Crystal color/habit	colorless blade	
Theta range for data collection	3.526 to 68.323°.	
Index ranges	-8<=h<=8, -9<=k<=7, -30<=l<=30	
Reflections collected	26265	
Independent reflections	2724 [R(int) = 0.0263]	
Completeness to theta = 67.000°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.929 and 0.847	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2724 / 0 / 192	
Goodness-of-fit on F^2	1.041	
Final R indices [I>2sigma(I)]	R1 = 0.0352, wR2 = 0.0938	
R indices (all data)	R1 = 0.0366, wR2 = 0.0950	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.441 and -0.375 e.Å^{-3}	


Ts
N
N
N
O
Me

1a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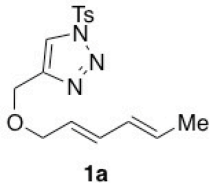
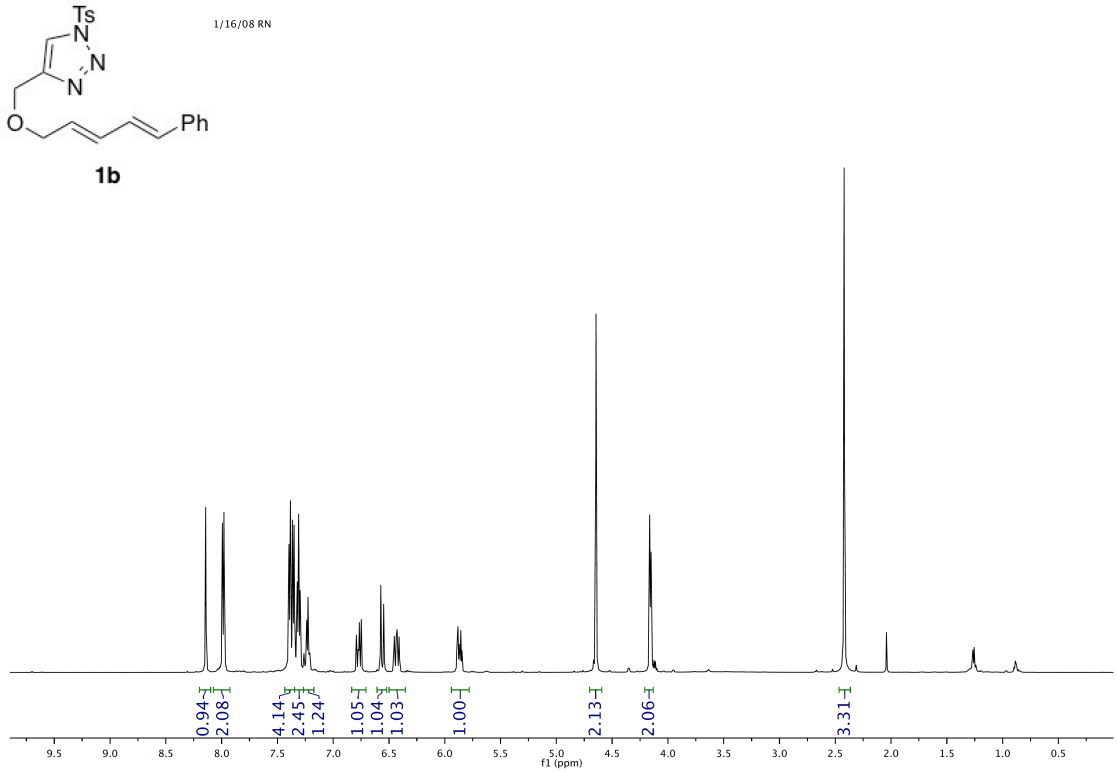
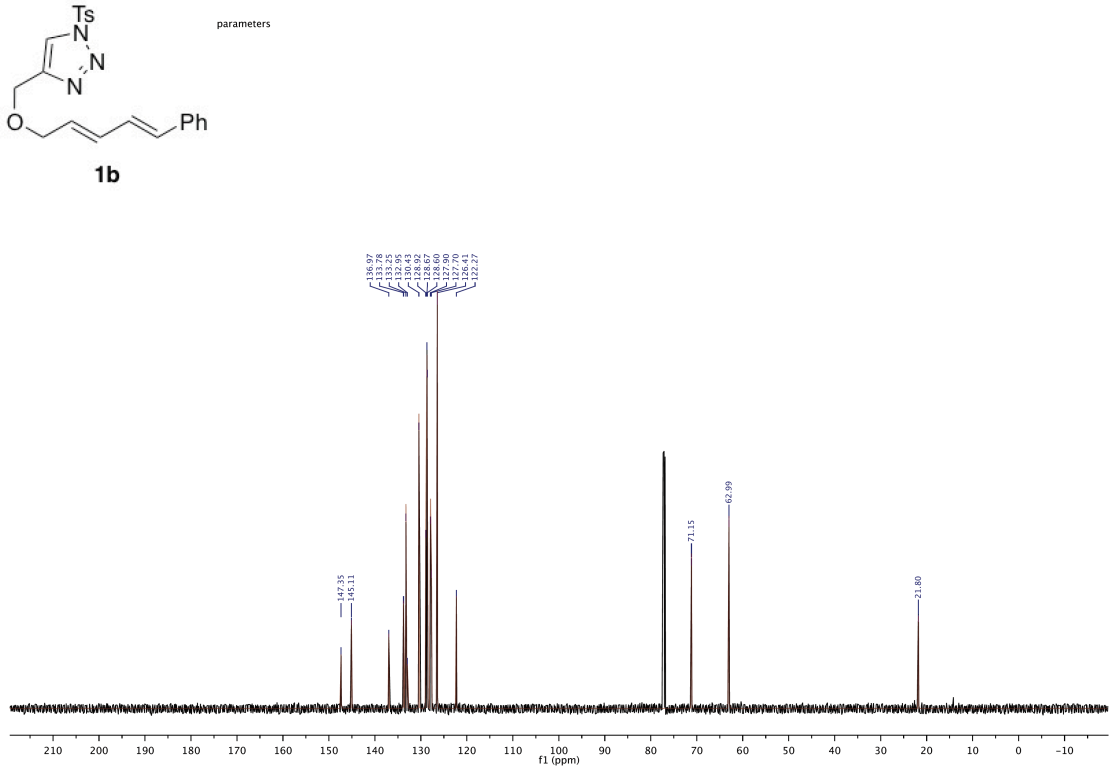
1.00
1.04
1.00
2.05
2.06
3.20
3.06
f1 (ppm)

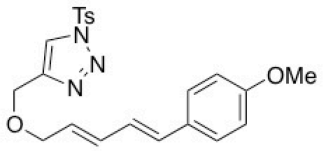

Ts
N
N
N
O
Me

1a

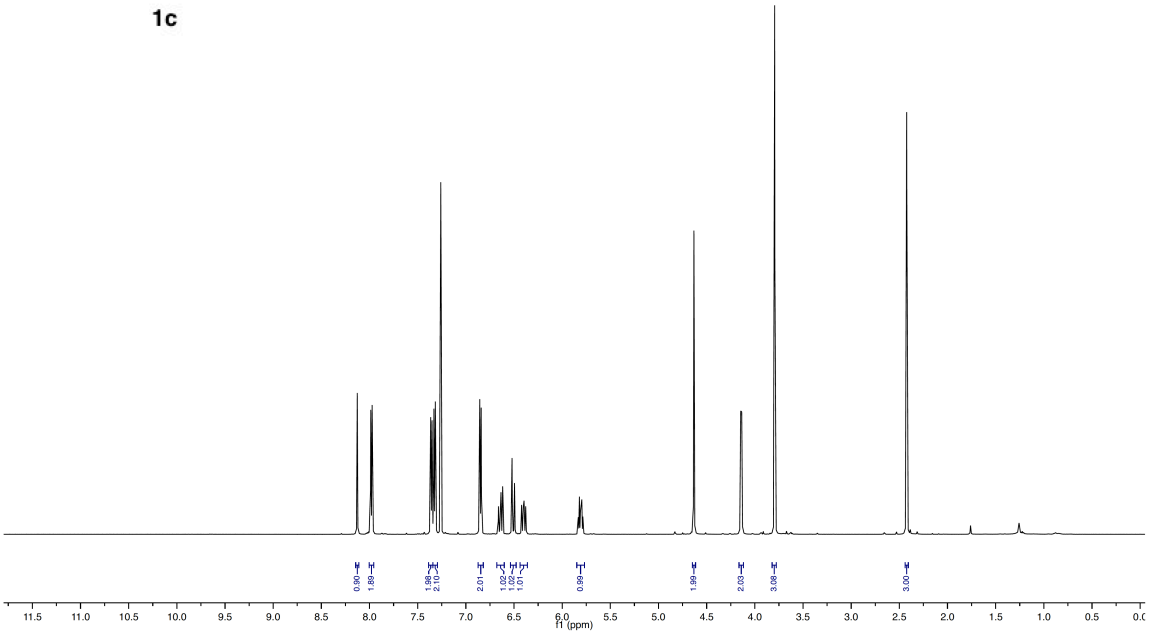
134.26
132.93
130.41
130.51
130.41
128.67
128.46
128.40
122.19
147.33
145.20
71.32
62.77
21.81
18.11
f1 (ppm)


Ts
N
N
N
O
Ph
1b
1/16/08 RN
0.94
2.08
4.14
2.45
1.24
1.05
1.04
1.03
1.00
2.13
2.06
3.31
f1 (ppm)


Ts
N
N
N
O
Ph
1b
parameters
136.97
133.78
133.25
132.96
130.43
128.92
128.62
128.60
127.90
127.70
126.41
122.27
147.35
145.11
71.15
62.99
21.80
f1 (ppm)


Ts
N
N
N
O
OMe

1c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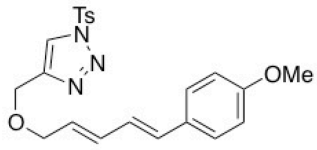
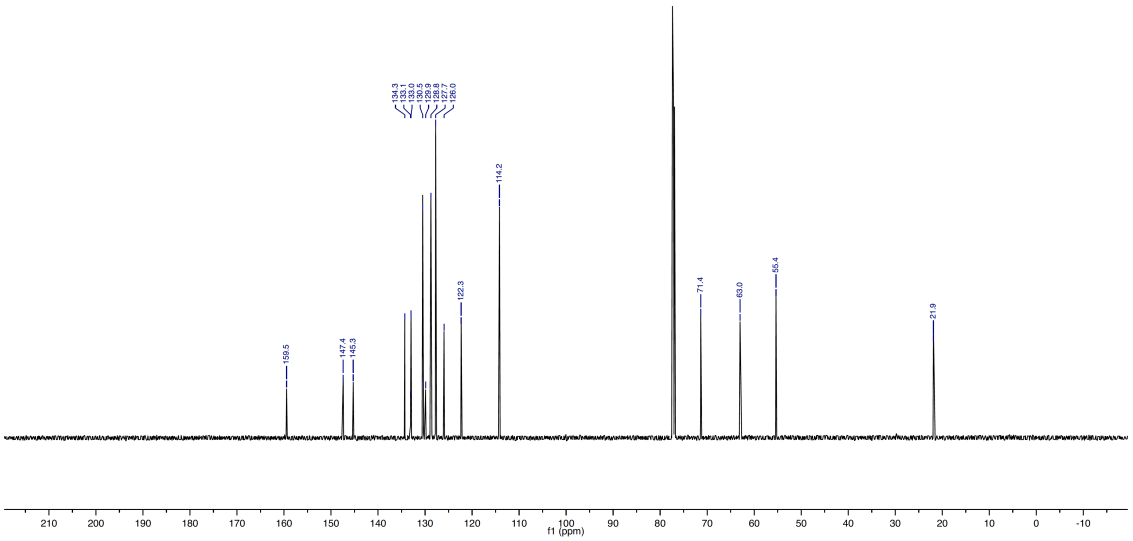
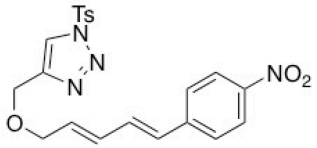
1.85
1.98
2.10
2.01
1.02
1.00
1.01
0.99
1.99
2.03
3.08
3.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

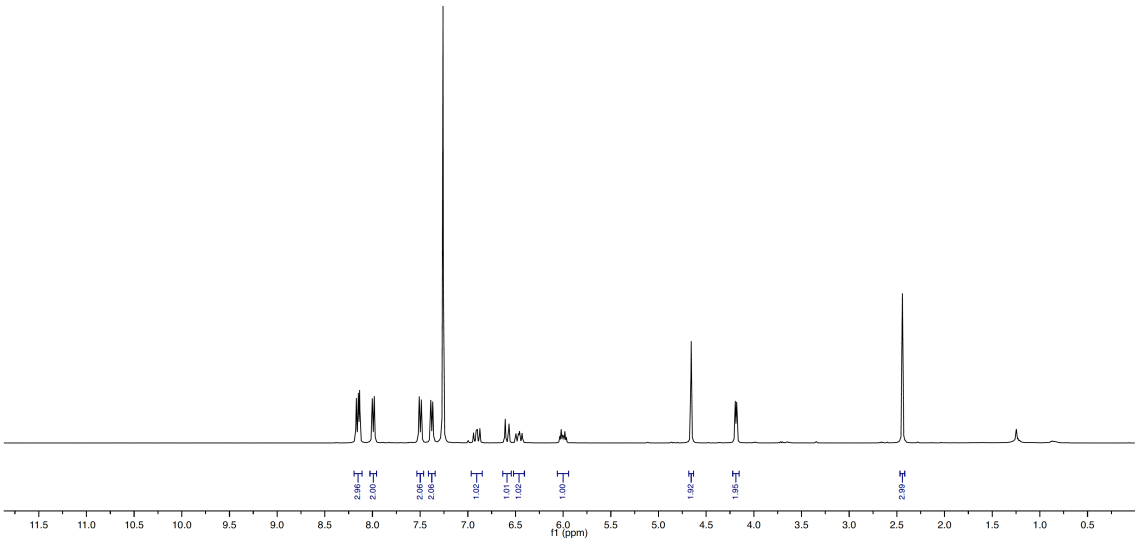

Ts
N
N
N
O
OMe

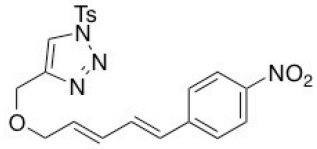
1c


134.3
133.1
133.0
129.9
128.8
127.7
126.0
159.5
147.4
145.3
122.3
114.2
71.4
63.0
55.4
21.9
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

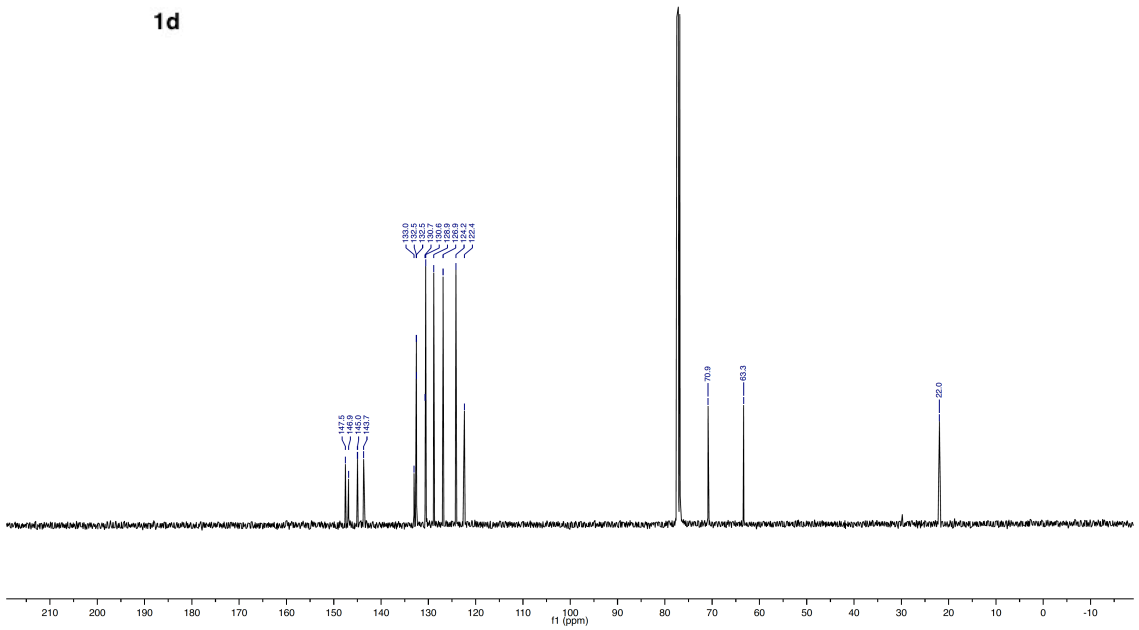

Ts
N
N
N
O
NO2

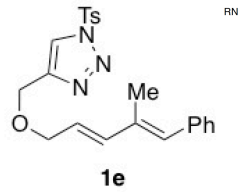
1d


2.96
2.00
2.06
2.06
1.02
1.01
1.02
1.00
1.92
1.95
2.99
f1 (ppm)


Ts
N
N
N
O
NO2

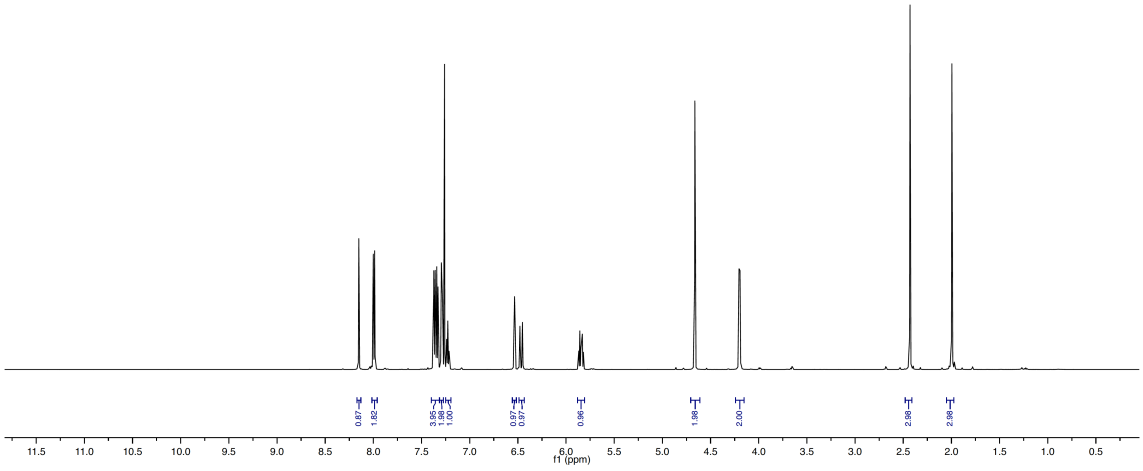
1d


133.0
132.5
132.0
130.7
130.6
128.9
126.9
124.2
122.4
147.5
146.9
145.0
143.7
70.9
63.3
22.0
f1 (ppm)


Ts
N
N
N
Me
O
Ph

1e

RN


0.87
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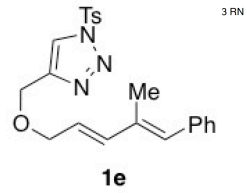
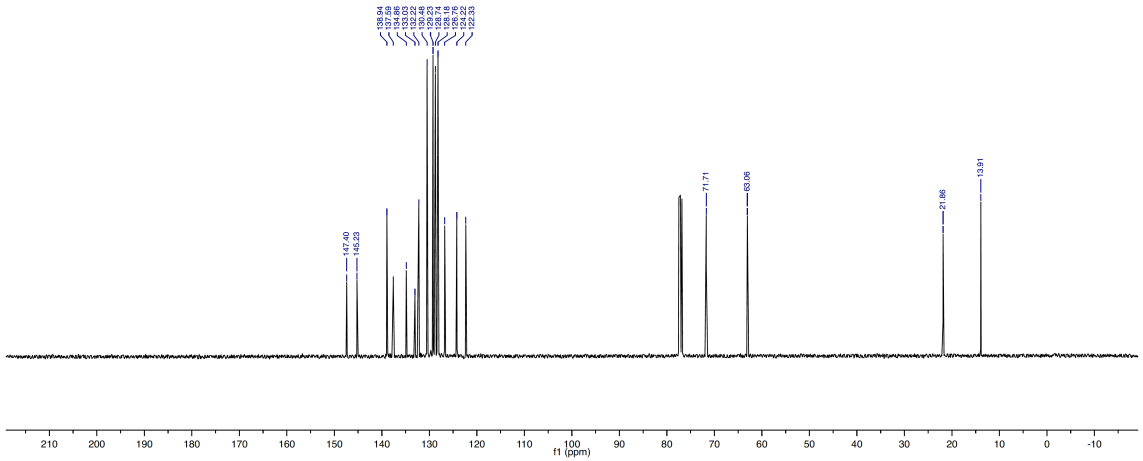
3.85
1.00
1.00
0.97
0.97
0.96
1.98
2.00
2.98
2.98
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


Ts
N
N
N
Me
O
Ph

1e

3 RN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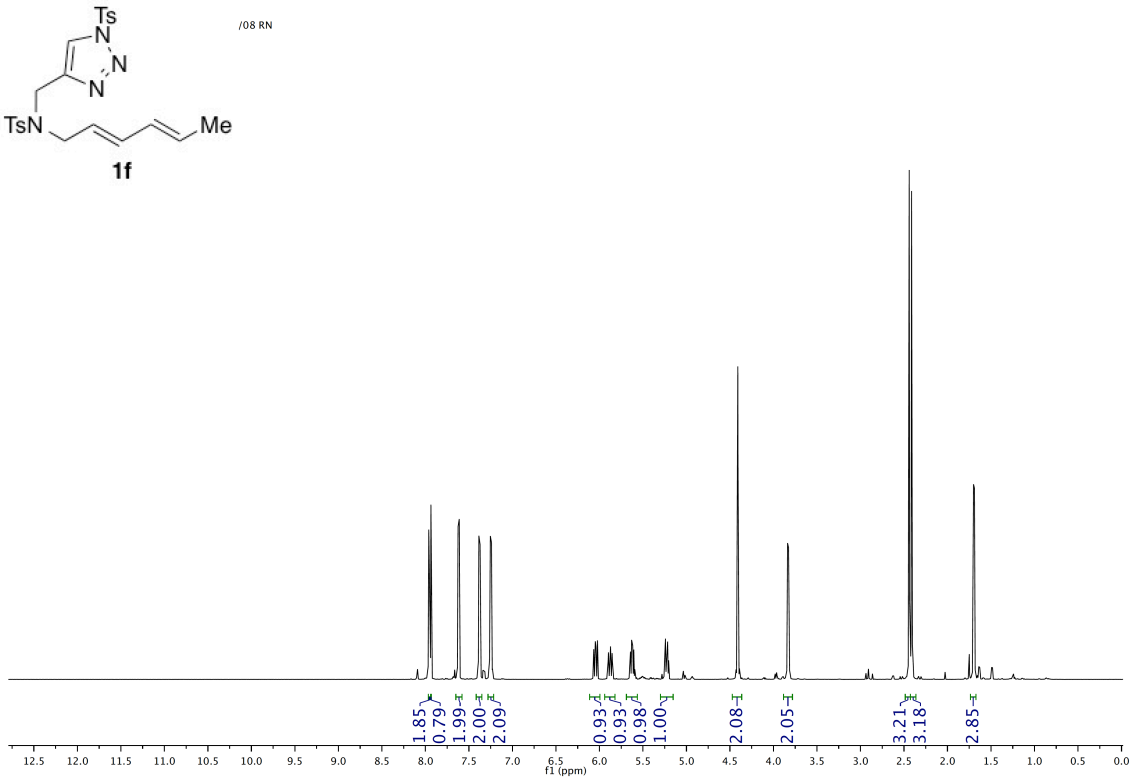
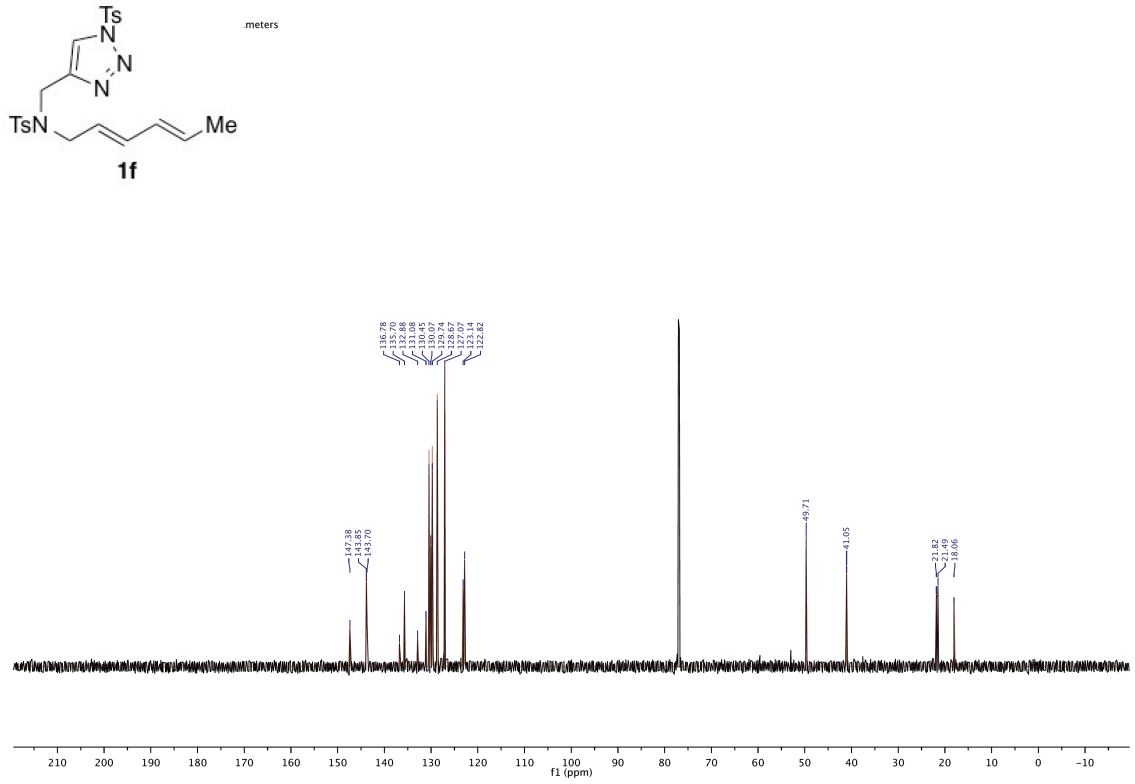
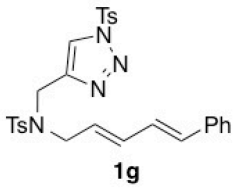
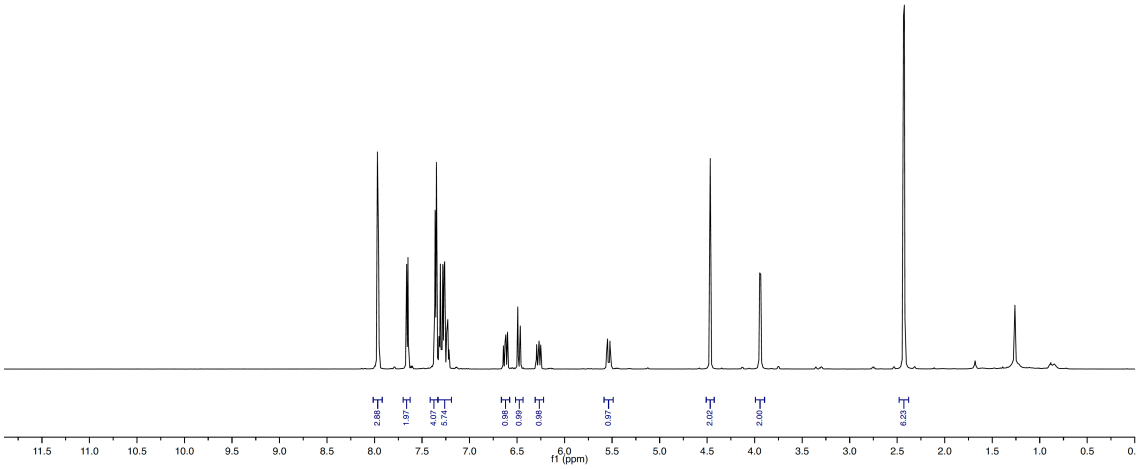
134.65
133.03
132.70
130.48
129.23
128.74
128.18
126.75
124.22
122.33
147.40
145.23
71.71
63.06
21.86
13.91
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

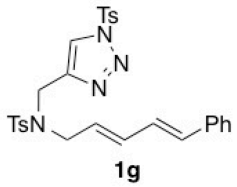

Ts
N
N
N
TsN
Me
1f
/08 RN
1.85
0.79
1.99
2.00
2.09
0.93
0.93
0.98
1.00
2.08
2.05
3.21
3.18
2.85
f1 (ppm)


Ts
N
N
N
TsN
Me
1f
.meters
136.78
134.70
132.88
131.08
130.45
130.07
129.74
128.67
127.07
123.14
122.82
147.38
143.85
143.70
69.71
41.05
21.82
21.49
18.06
f1 (ppm)

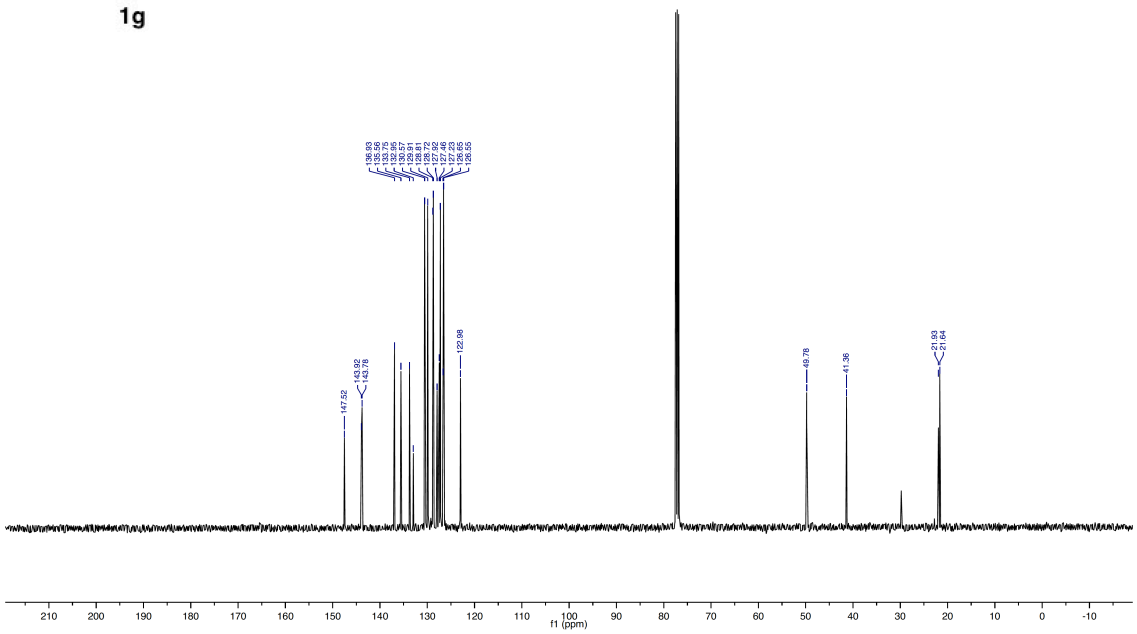

Ts
N
N
N
TsN
Ph

1g


2.88
1.97
4.07
5.74
0.98
0.99
0.98
0.97
2.02
2.00
6.23
f1 (ppm)


Ts
N
N
N
TsN
Ph

1g


147.52
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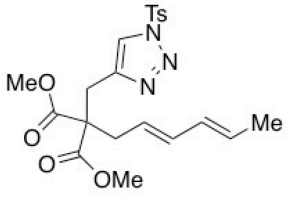
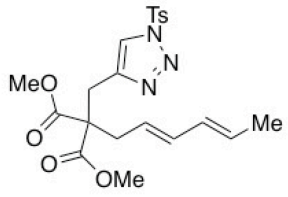
143.78
122.98
49.78
41.36
21.93
21.64
f1 (ppm)


Ts
N
N
N
MeO
O
O
OMe
Me

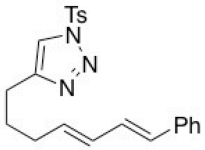
1h

2.04
0.96
2.09
2.11
0.97
1.00
6.50
2.21
1.98
3.49
3.20
f1 (ppm)


Ts
N
N
N
MeO
O
O
OMe
Me

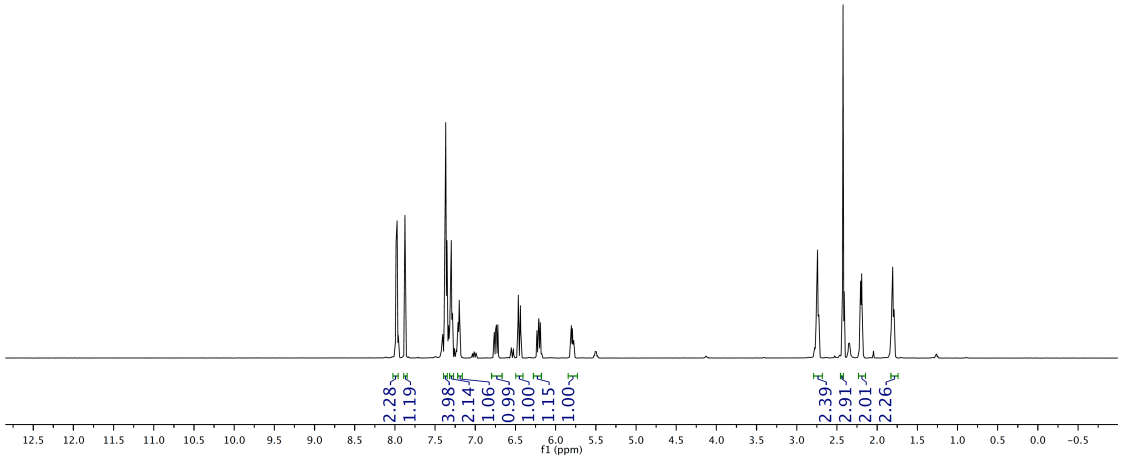
1h

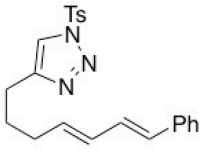
170.55
147.18
142.69
136.27
133.10
130.93
130.35
129.21
128.55
123.42
122.41
57.99
52.62
36.01
28.73
21.78
17.98
f1 (ppm)



1i

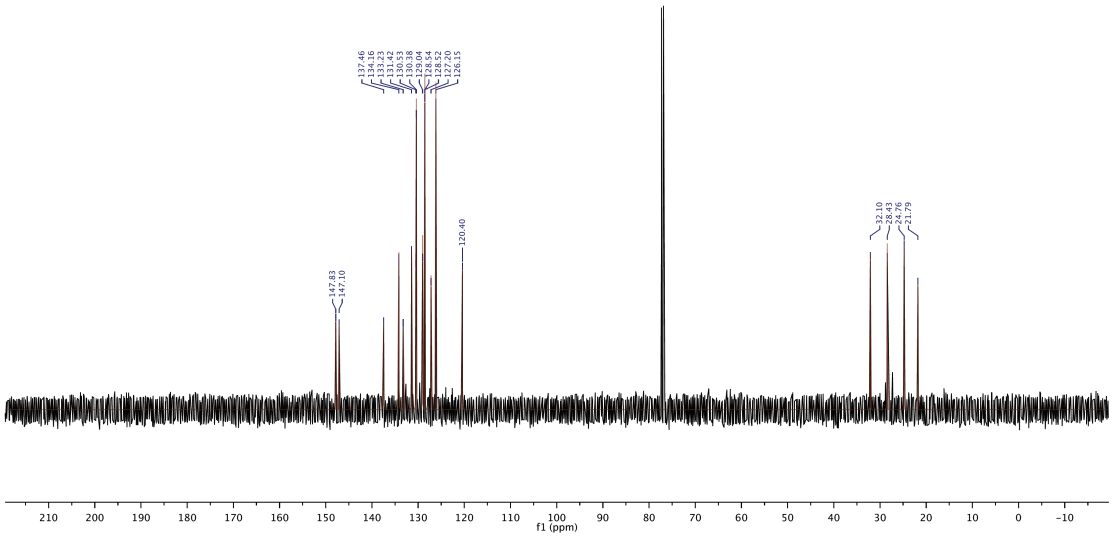
11/16/08 RN

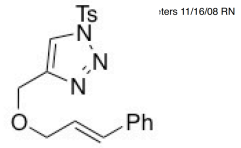




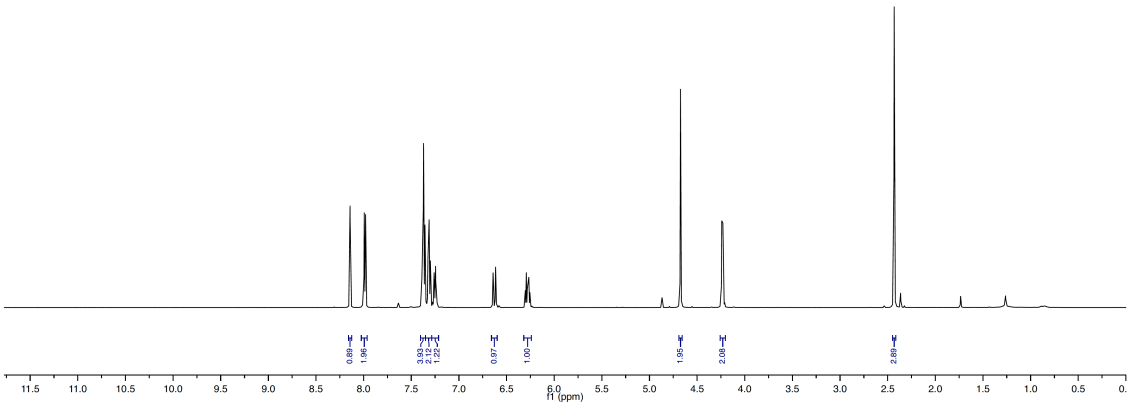
1i

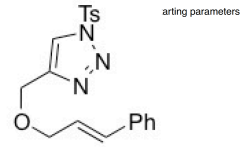
ıg parameters



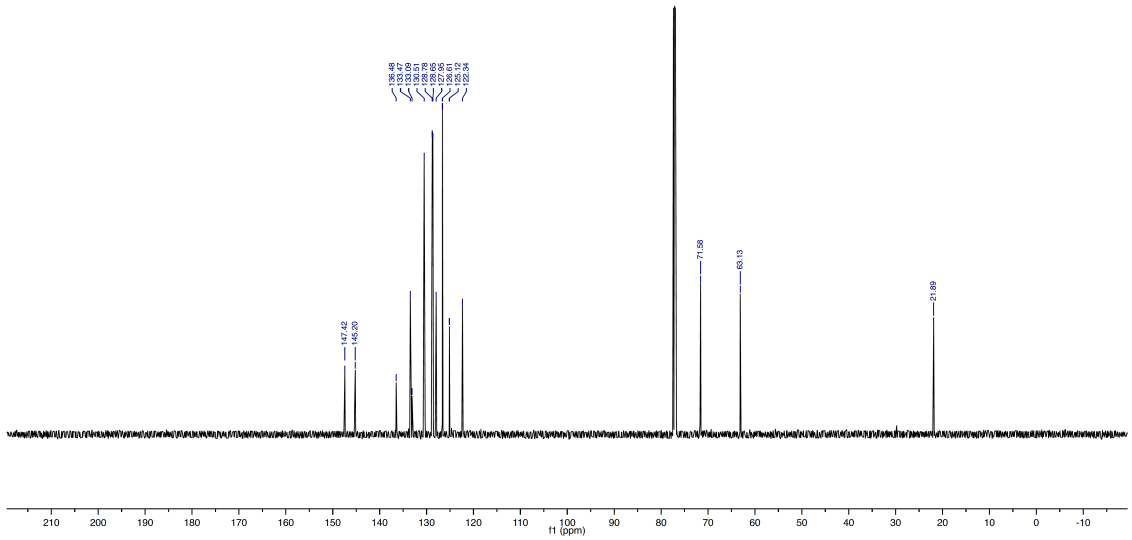

Ts
N
N
N
O
Ph

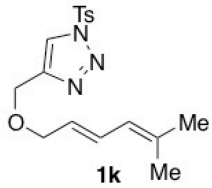
1j


0.89
1.98
3.93
2.12
1.22
0.97
1.00
1.95
2.08
2.89
f1 (ppm)


Ts
N
N
N
O
Ph

1j

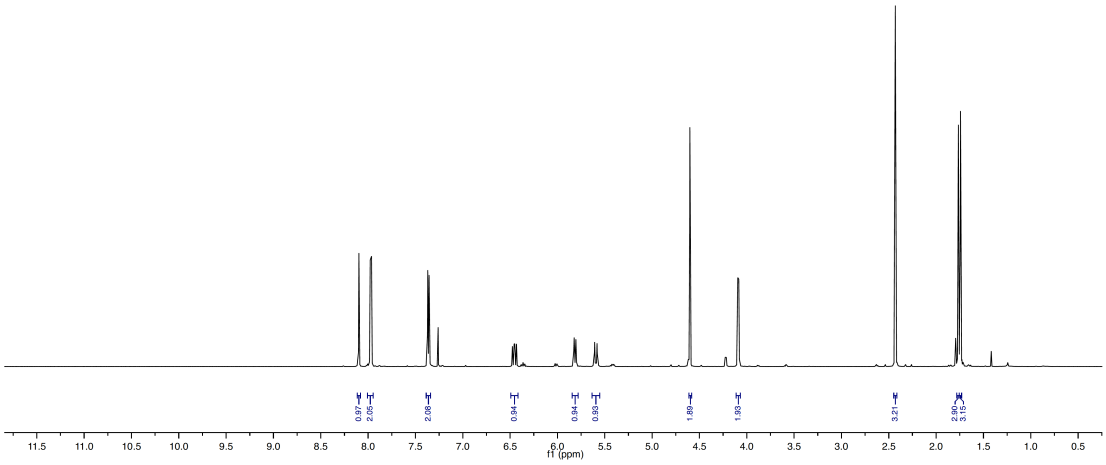

136.48
133.47
131.09
130.51
128.78
128.65
127.95
126.61
125.12
122.34
147.42
145.20
71.58
63.13
21.89
f1 (ppm)

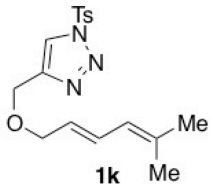


1k

(89:11 *E*:*Z*)

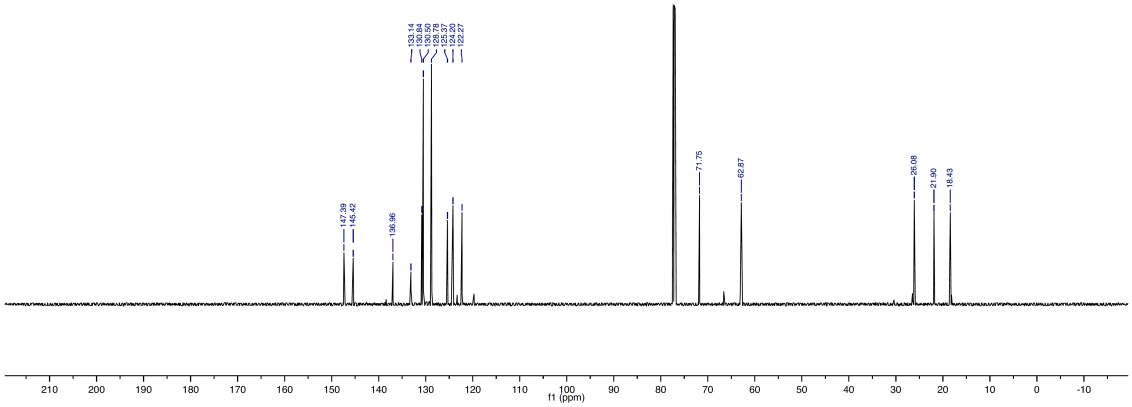
16/08 RN

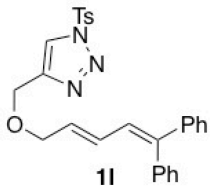




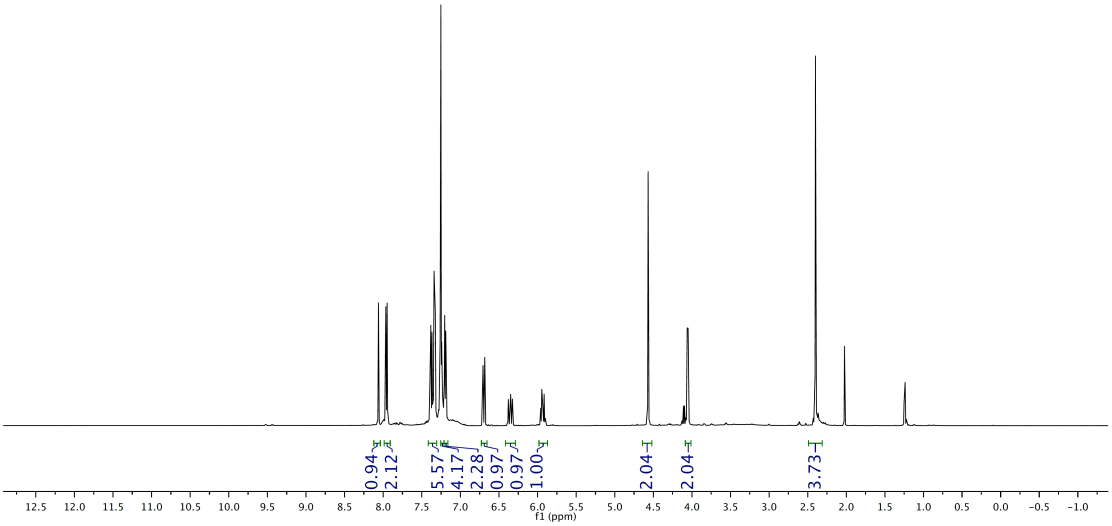
1k

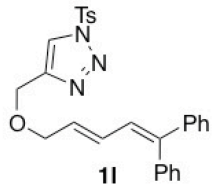
(89:11 *E*:*Z*)



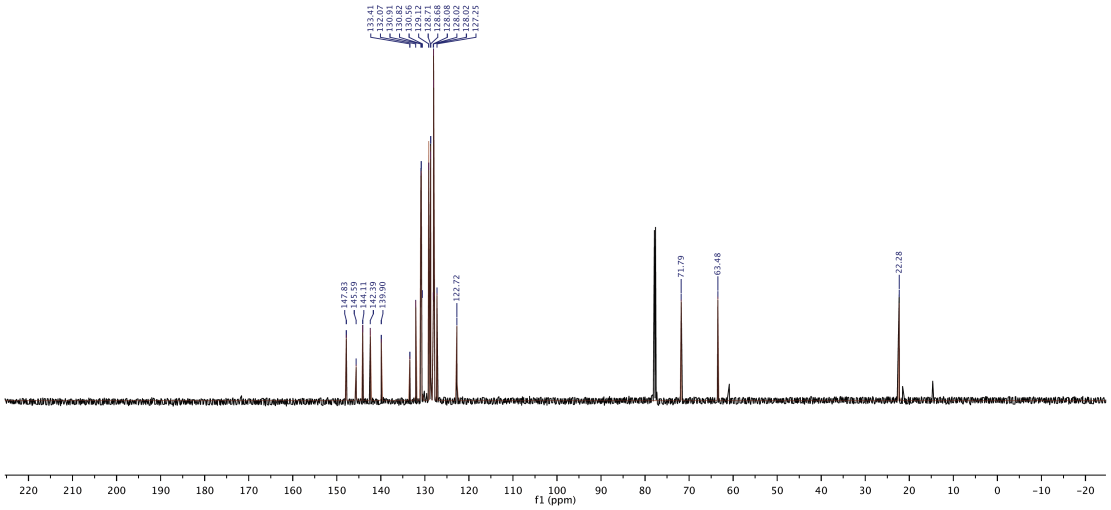

Ts
N
N
N
O
Ph
Ph

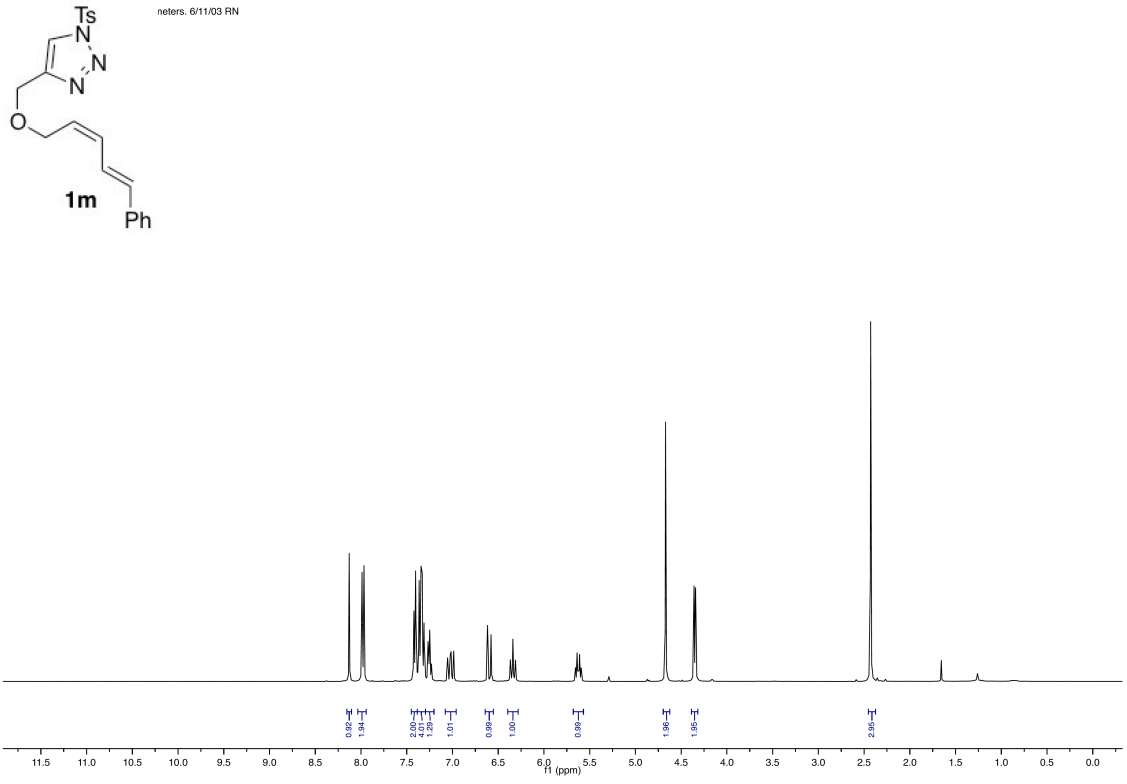
1l

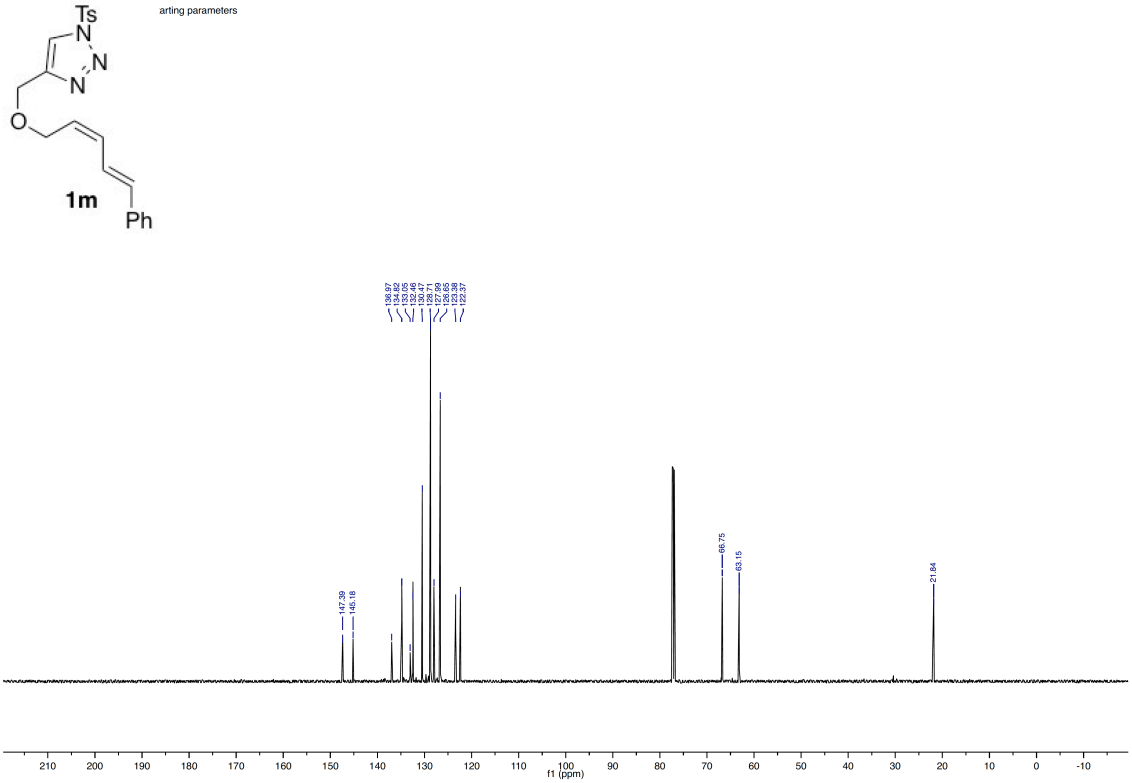

0.94
2.12
5.57
4.17
2.28
0.97
0.97
1.00
2.04
2.04
3.73
f1 (ppm)

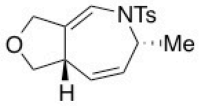

Ts
N
N
N
O
Ph
Ph

1l

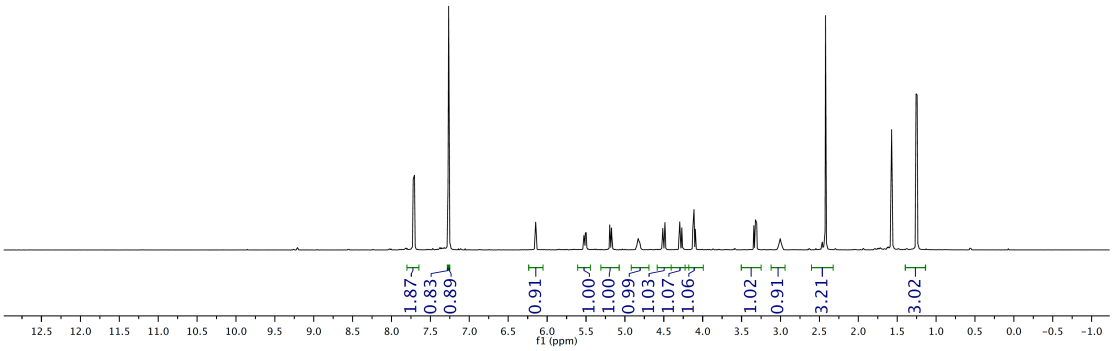

147.83
145.50
144.11
142.39
139.90
122.72
71.79
63.48
22.28
f1 (ppm)

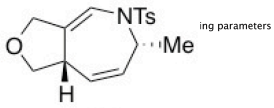

neters. 6/11/03 RN
Ts
N
N
N
O
1m
Ph
0.92
1.94
2.00
4.01
1.89
1.01
0.99
1.00
0.89
1.98
1.95
2.95
f1 (ppm)


arting parameters
Ts
N
N
N
O
1m
Ph
136.97
134.92
134.46
132.46
132.17
128.71
127.69
127.56
123.38
122.37
147.39
145.18
66.75
63.15
21.84
f1 (ppm)



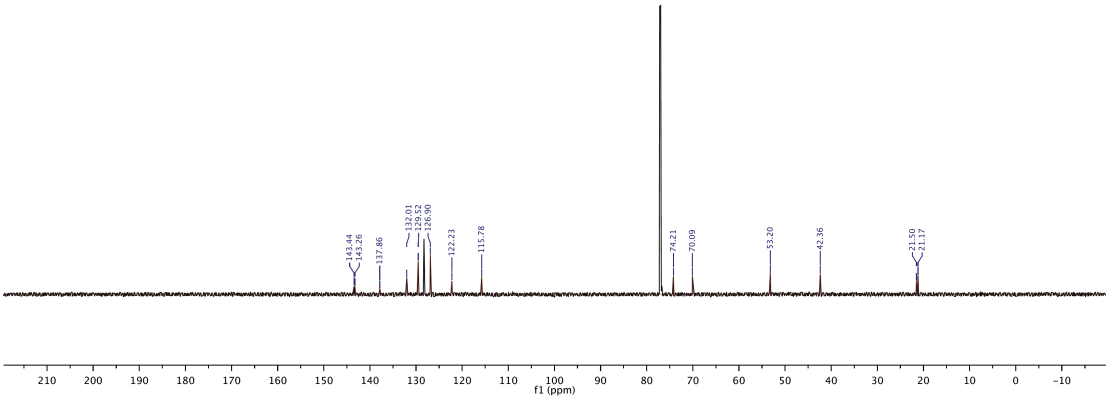
2a

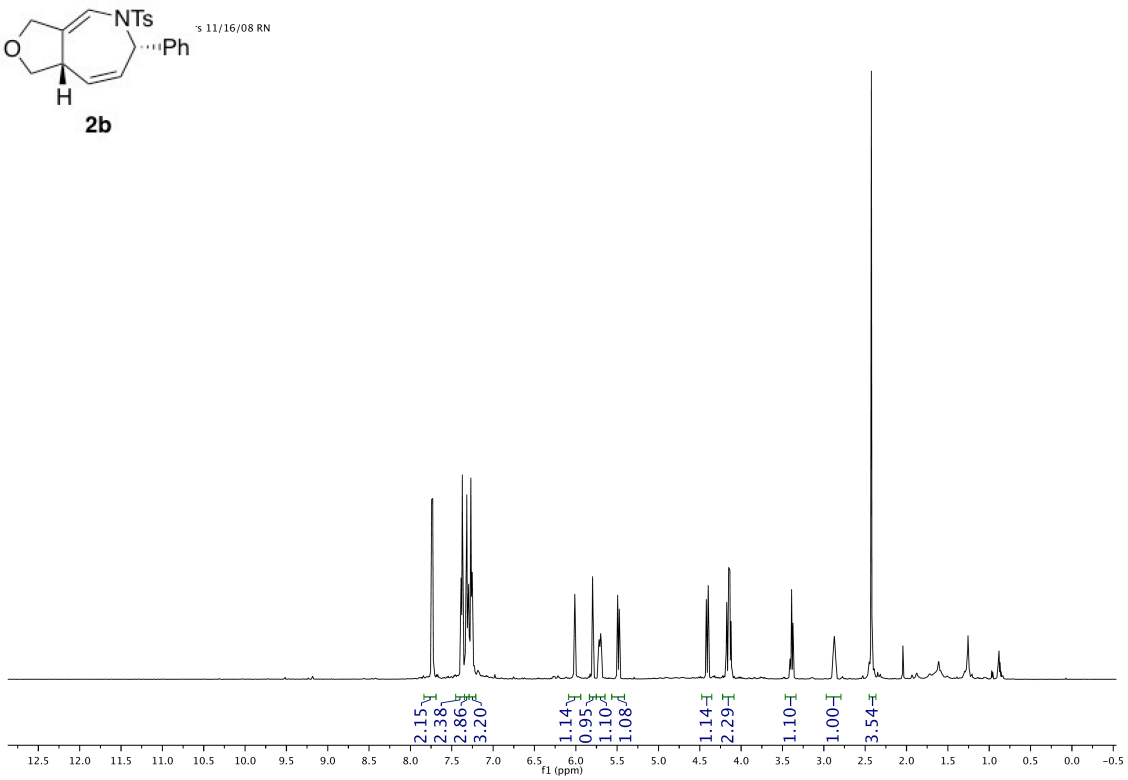


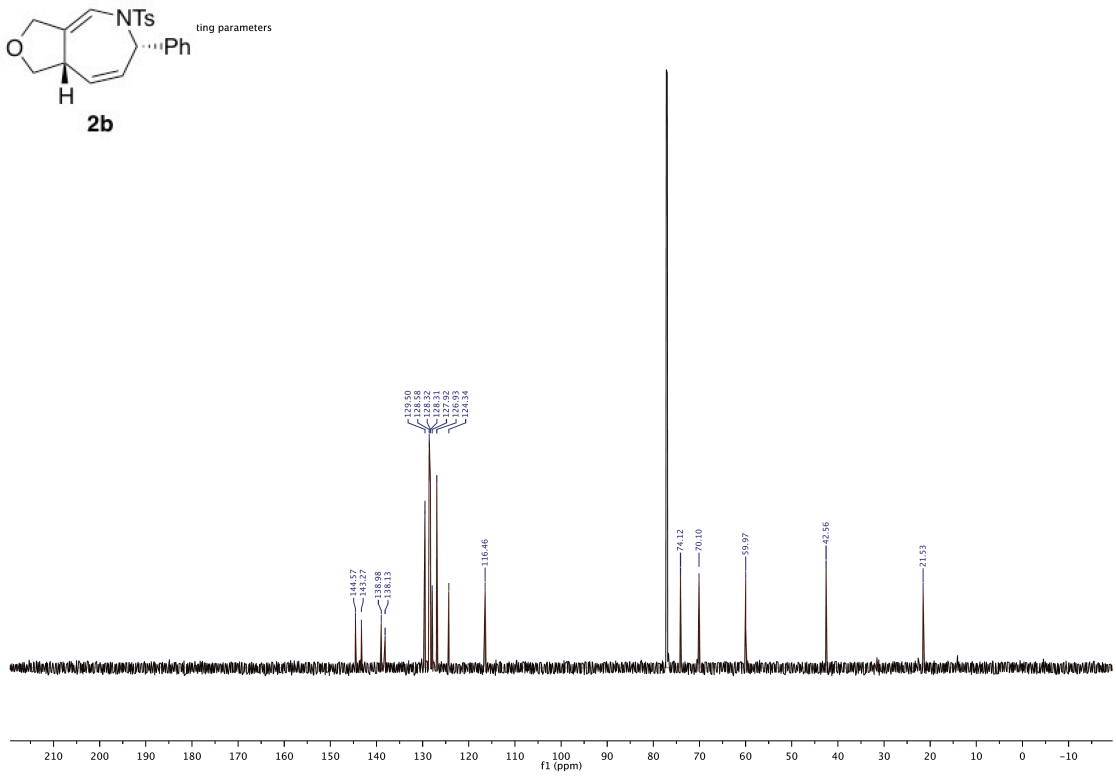


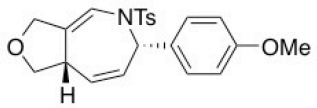
ing parameters

2a

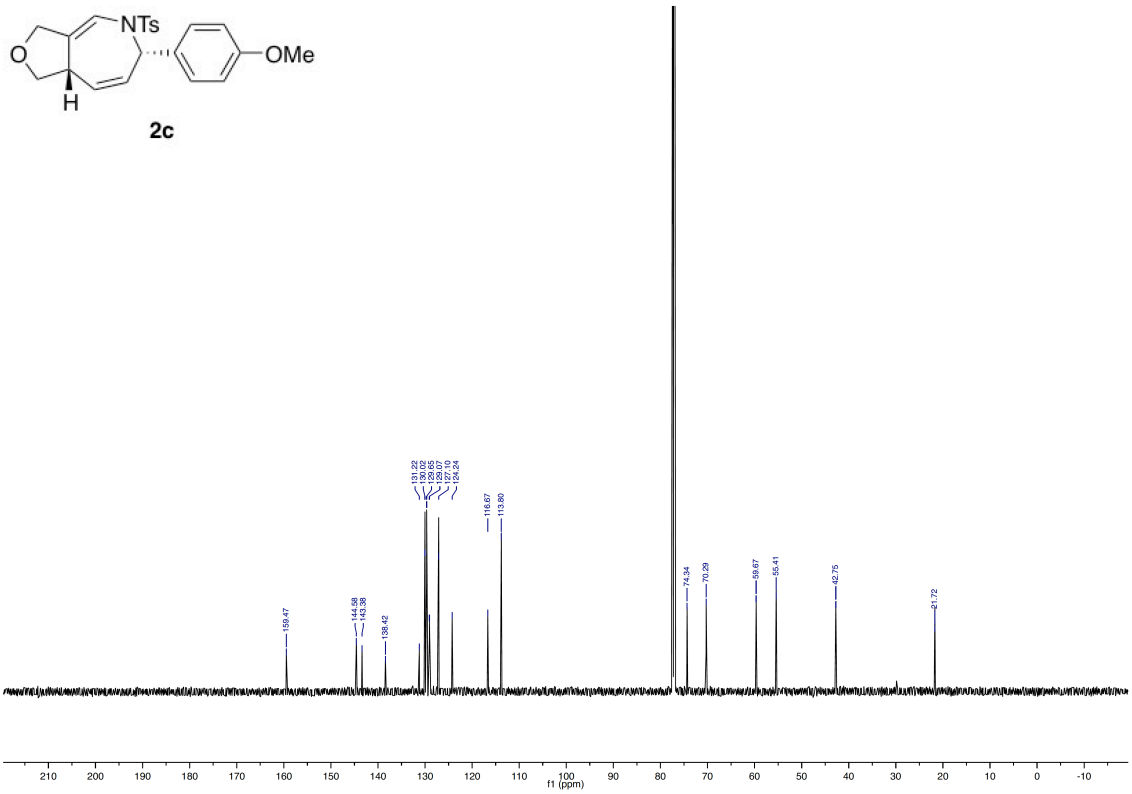



NTs
Ph
O
H
2b
2.15
2.38
2.86
3.20
1.14
0.95
1.10
1.08
1.14
2.29
1.10
1.00
3.54
f1 (ppm)


NTs
Ph
O
H
2b
144.57
143.27
138.98
138.13
129.50
128.56
128.32
128.31
127.73
126.95
124.34
116.46
74.12
70.10
59.97
42.56
21.53
f1 (ppm)

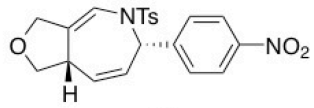

NTs
O
OMe
H

2c

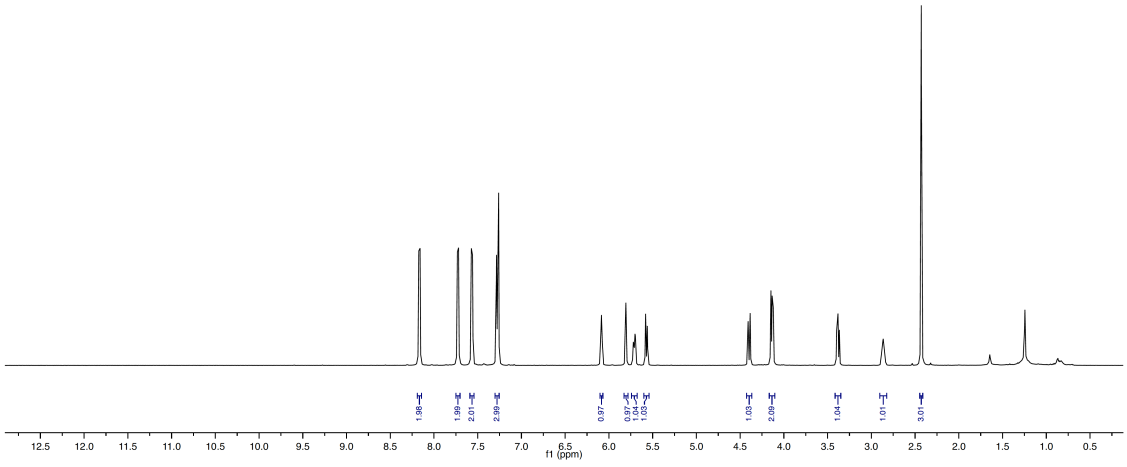

159.47
144.58
143.36
138.42
131.22
130.63
130.55
129.07
127.93
124.24
116.67
113.80
74.34
70.29
59.67
55.41
42.75
21.72
f1 (ppm)

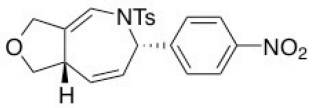
NTs
O
OMe
H

2c

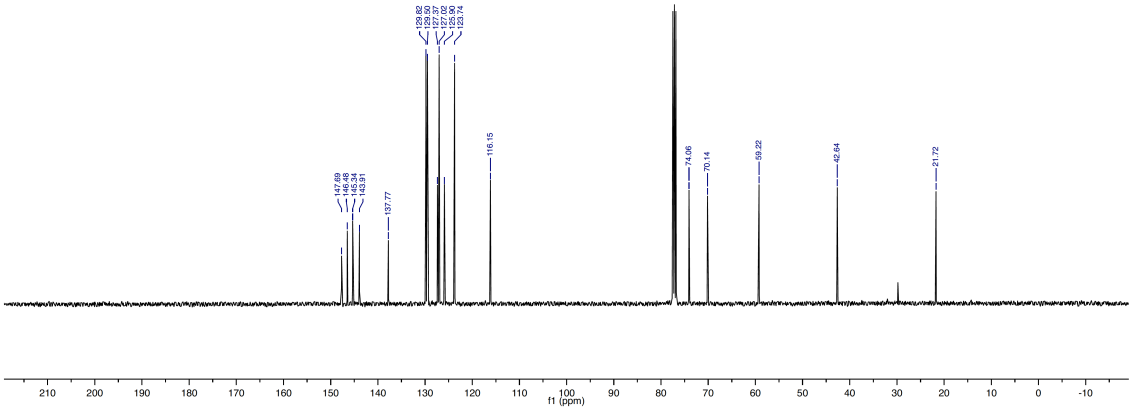

NTs
O
H
NO2

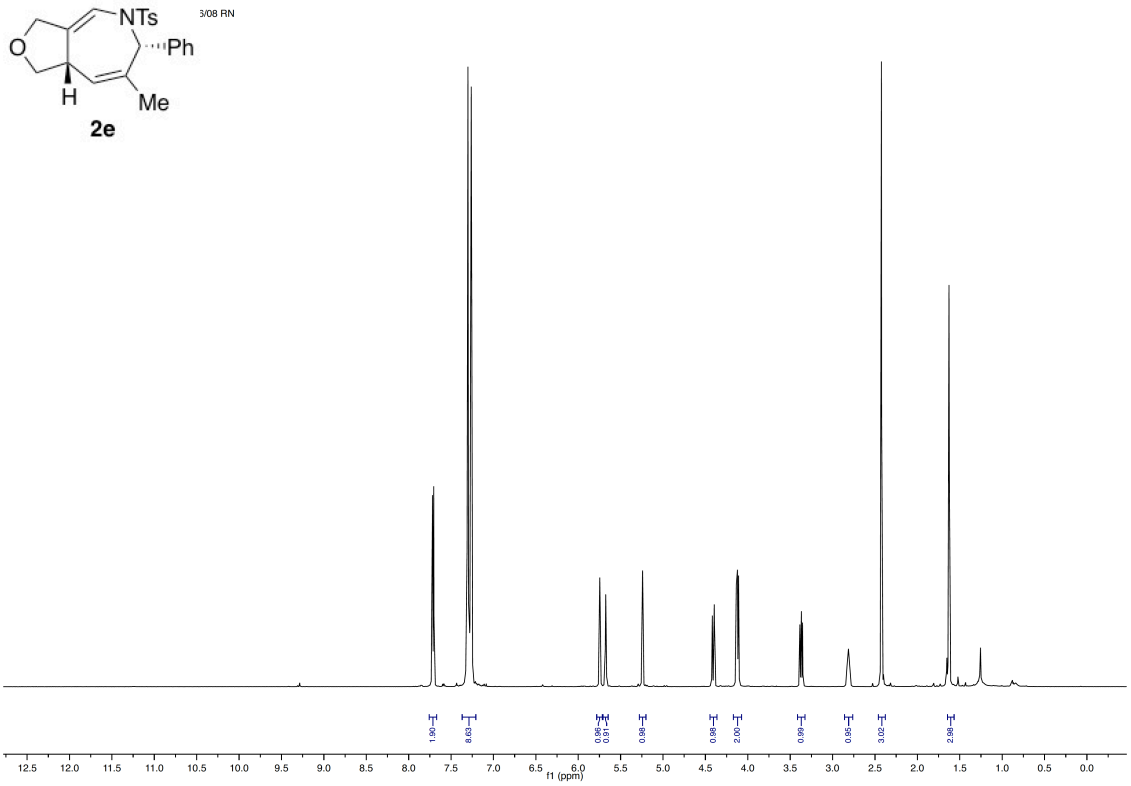
2d

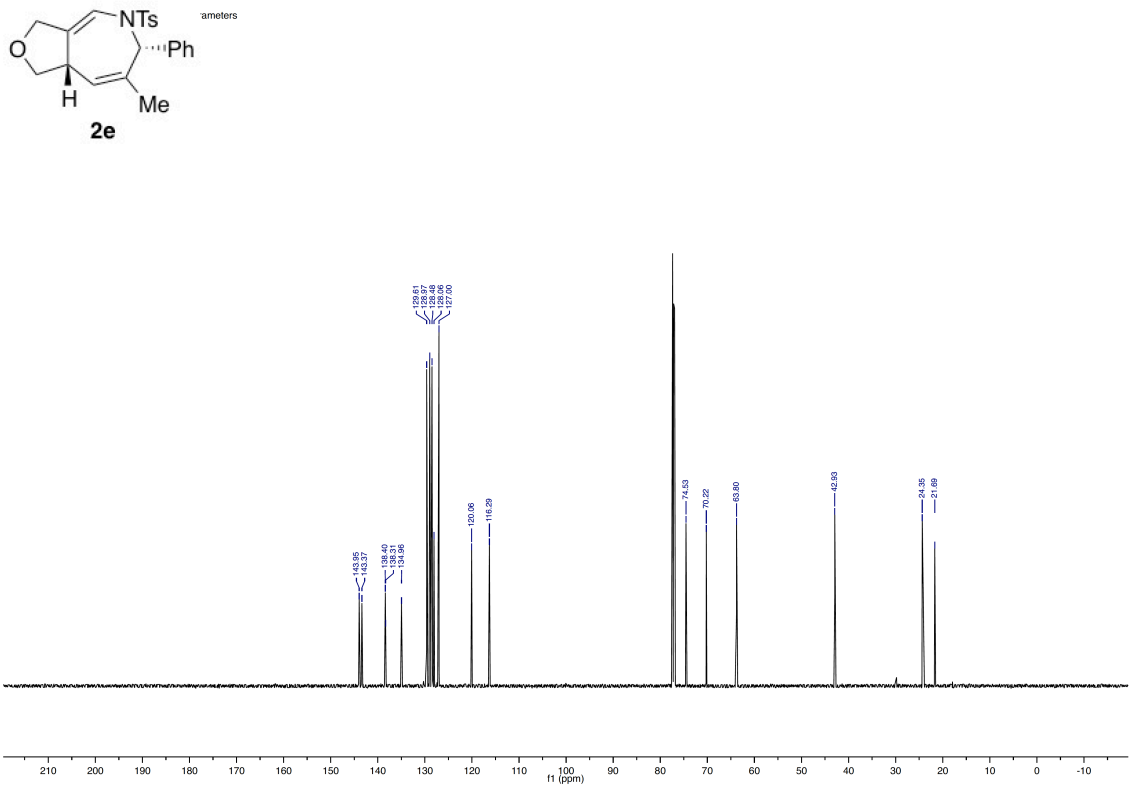

1.98
1.99
2.01
2.99
0.97
0.97
1.04
1.08
1.03
2.09
1.04
1.01
3.01
f1 (ppm)

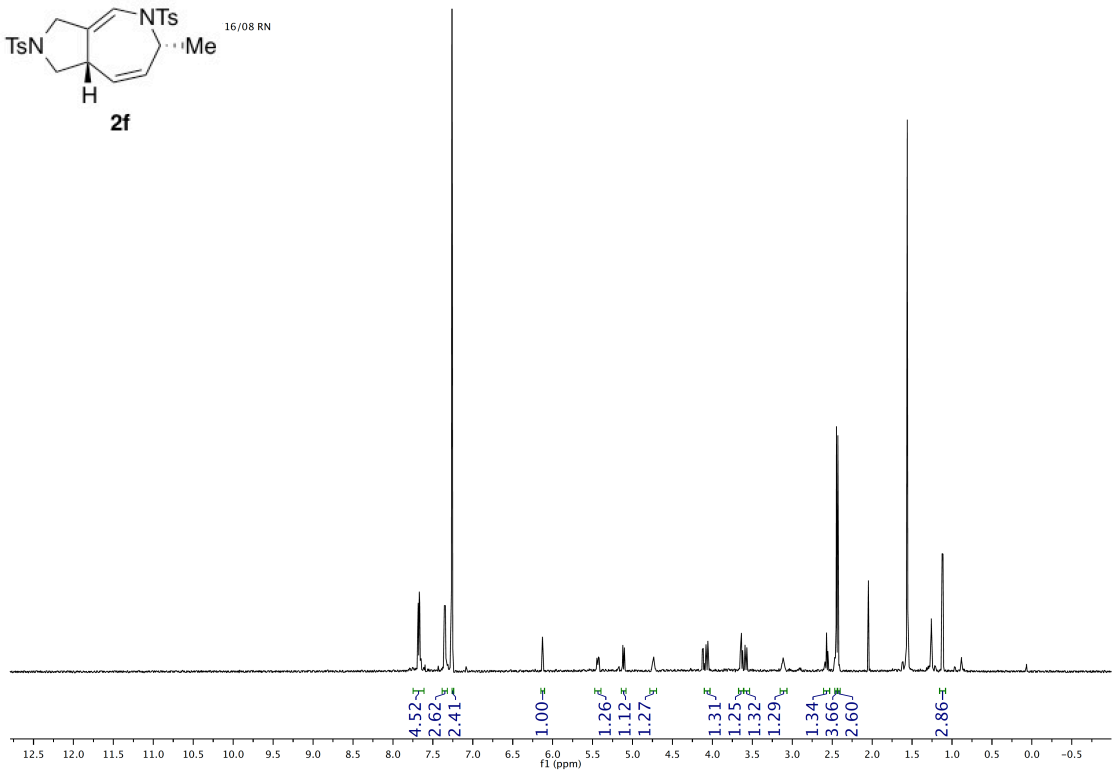

NTs
O
H
NO2

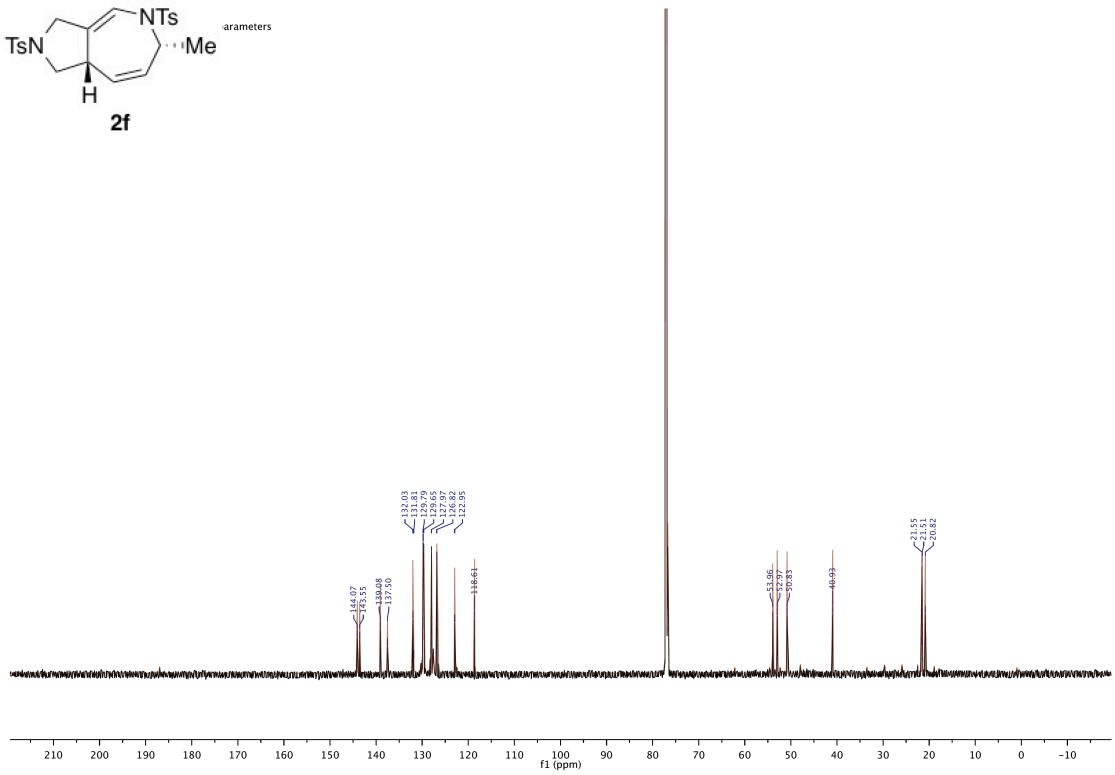
2d

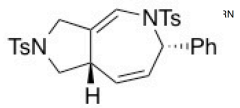

129.82
129.50
127.77
127.02
125.60
123.74
147.69
146.48
145.41
143.91
137.77
116.15
74.06
70.14
59.22
42.64
21.72
f1 (ppm)


NTs
Ph
Me
H
O
2e
3/08 RN
f1 (ppm)

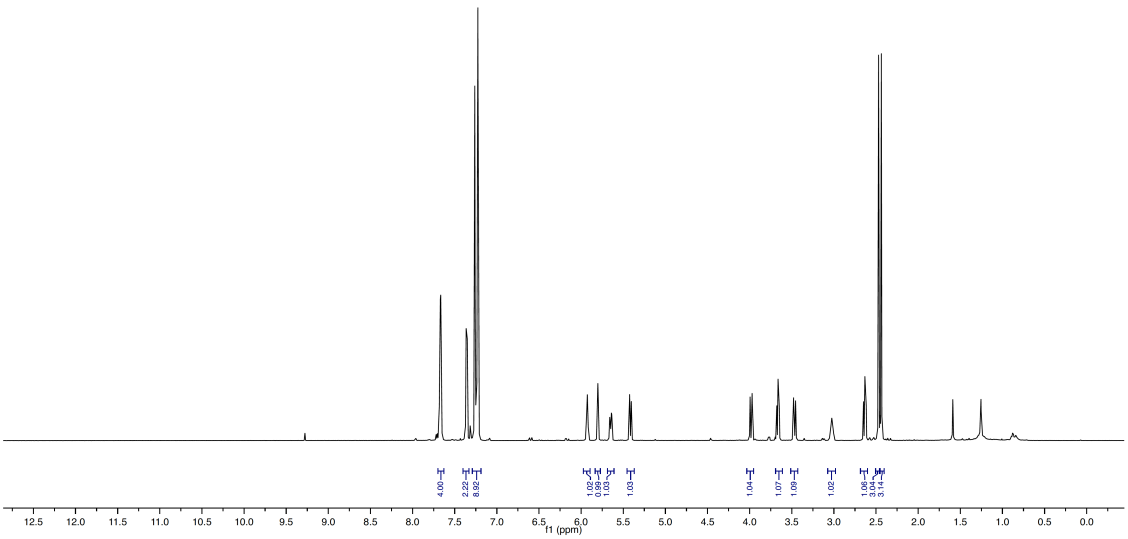

NTs
Ph
Me
H
O
2e
ameters
143.95
143.37
138.40
138.31
134.96
129.61
128.97
128.68
128.06
127.00
120.06
116.29
74.53
70.22
63.80
42.93
24.35
21.69
f1 (ppm)

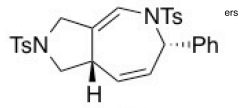

NTs
TsN
Me
H
16/08 RN
2f
4.52
2.62
2.41
1.00
1.26
1.12
1.27
1.31
1.25
1.32
1.29
1.34
3.66
2.60
2.86
f1 (ppm)


NTs
TsN
Me
H
arameters
2f
144.07
143.55
137.03
131.81
129.79
129.07
127.97
126.82
122.95
118.61
53.96
52.97
50.83
40.93
21.55
21.51
20.82
f1 (ppm)

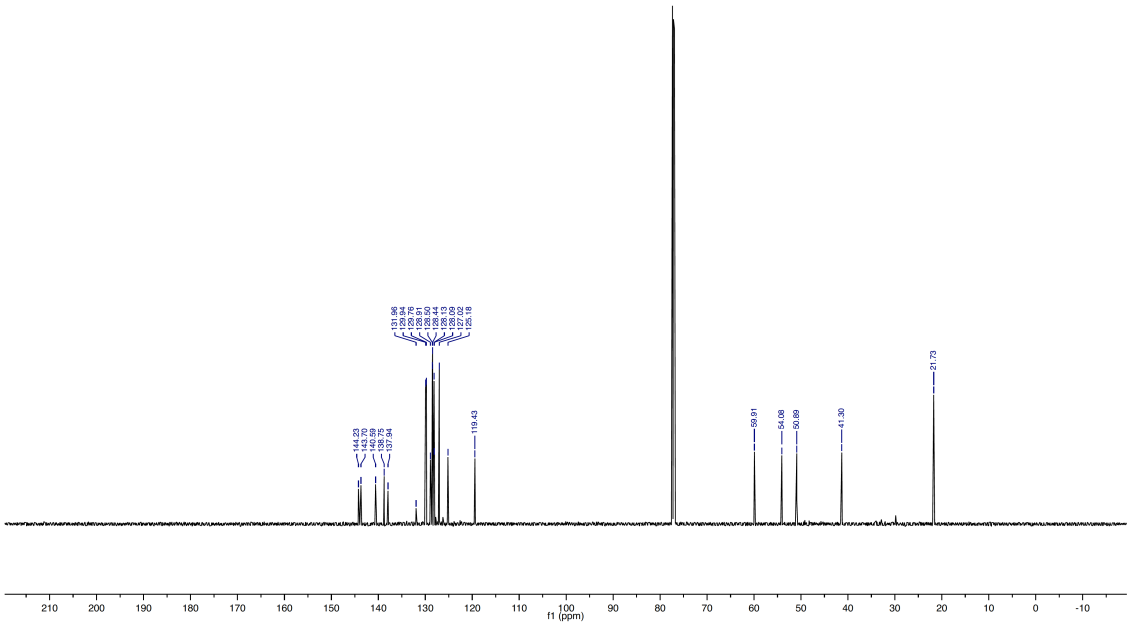

NTs
TsN
Ph
H

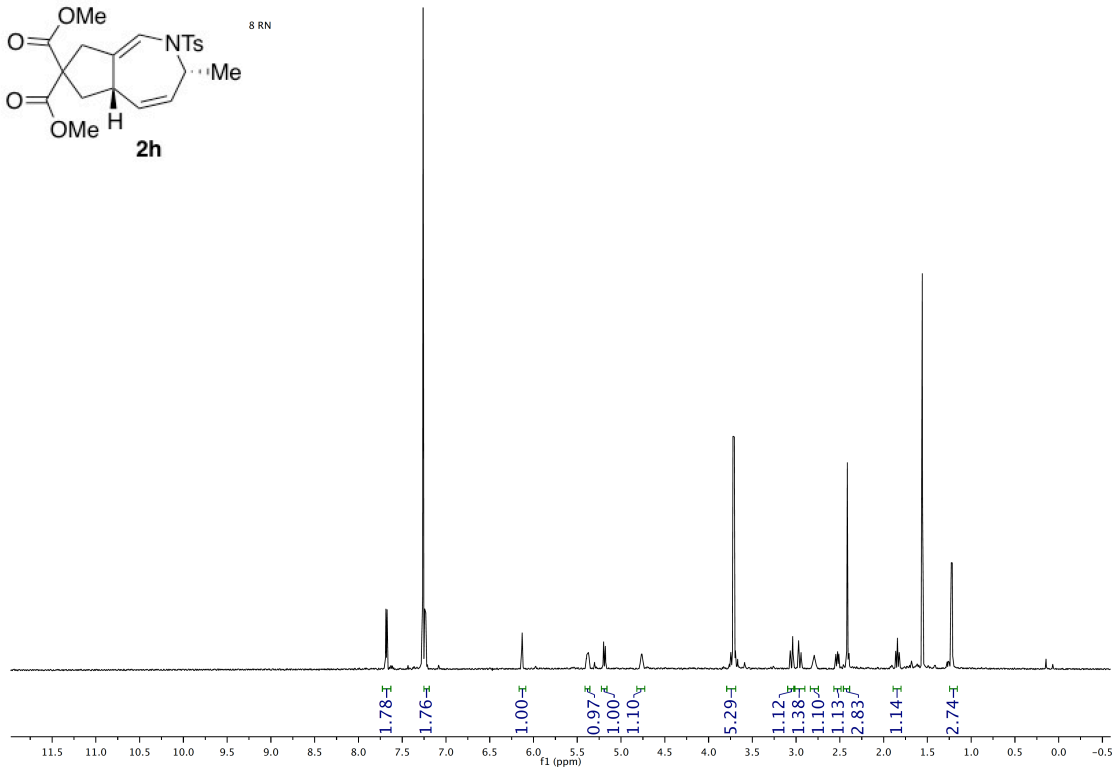
2g

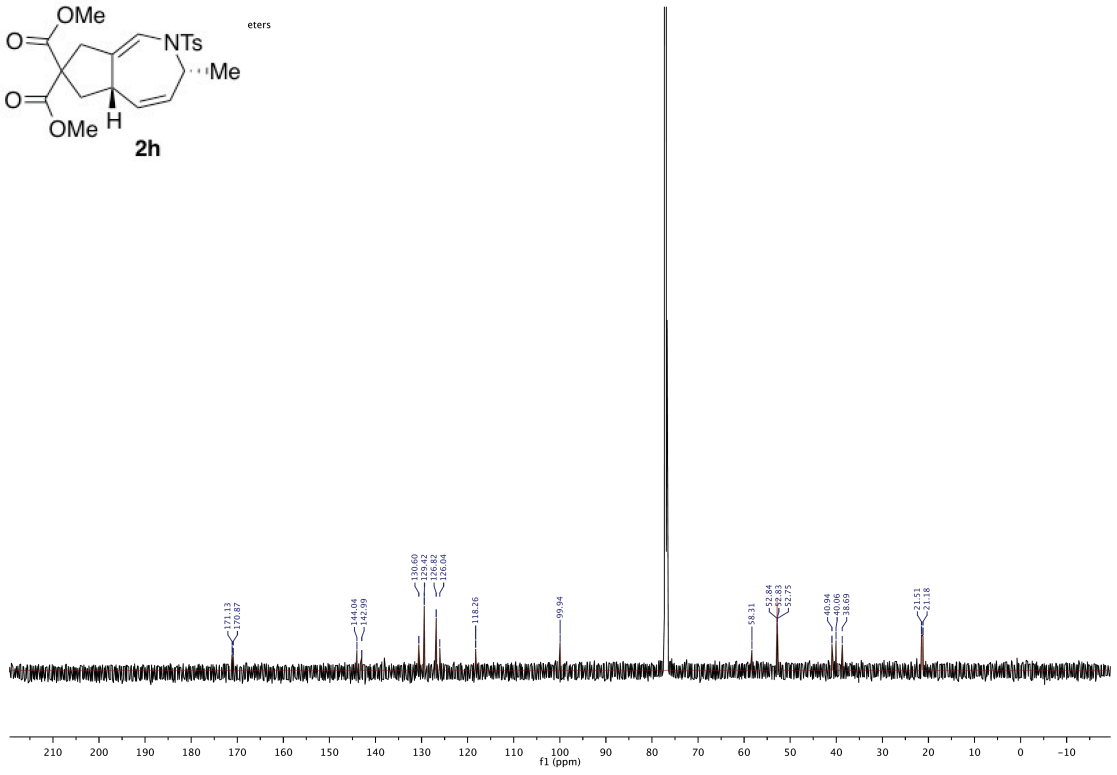

4.00
2.22
6.62
1.02
0.99
1.03
1.03
1.04
1.07
1.09
1.02
1.06
3.04
3.14
f1 (ppm)

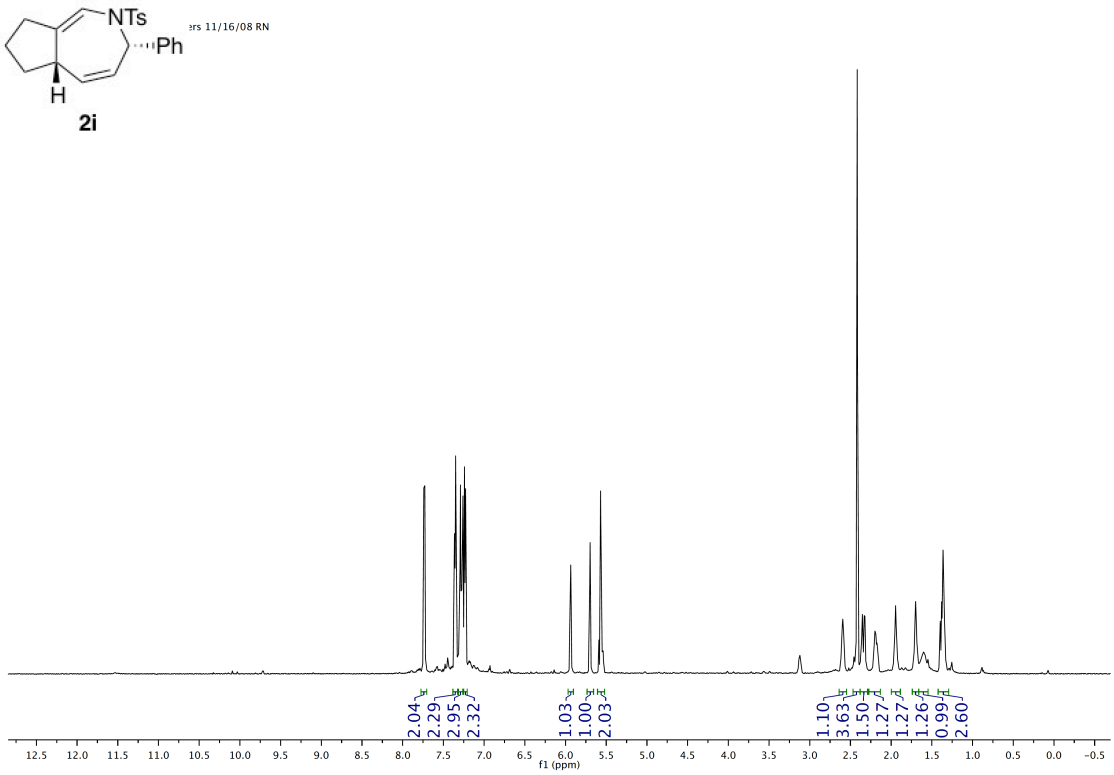

NTs
TsN
Ph
H

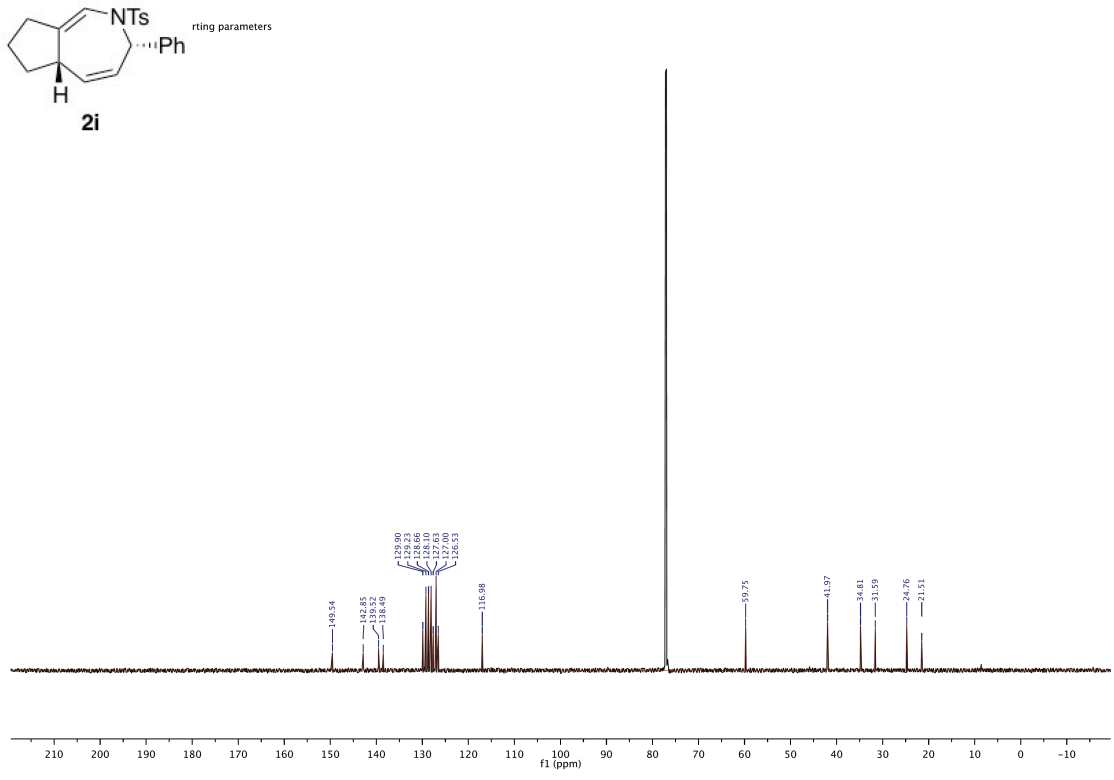
2g

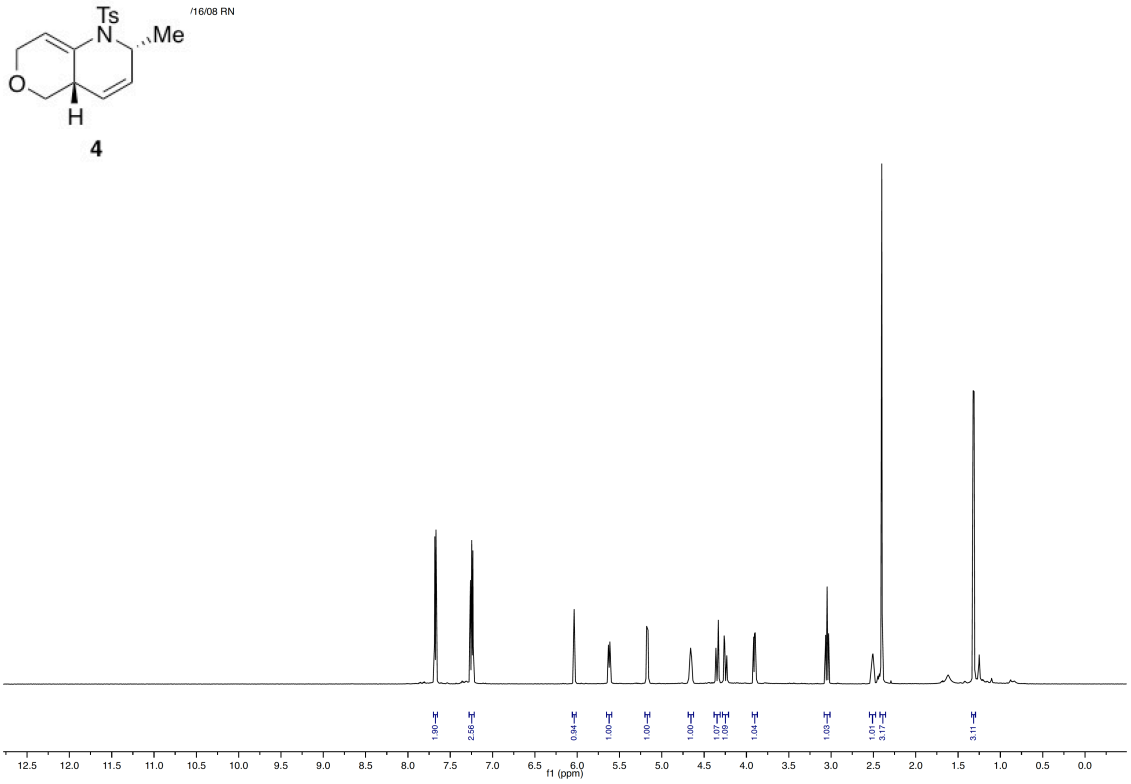

131.96
129.94
129.76
128.51
128.50
128.44
128.13
128.09
127.62
125.18
144.23
143.70
140.59
138.73
137.94
119.43
59.91
54.08
50.89
41.30
21.73
f1 (ppm)

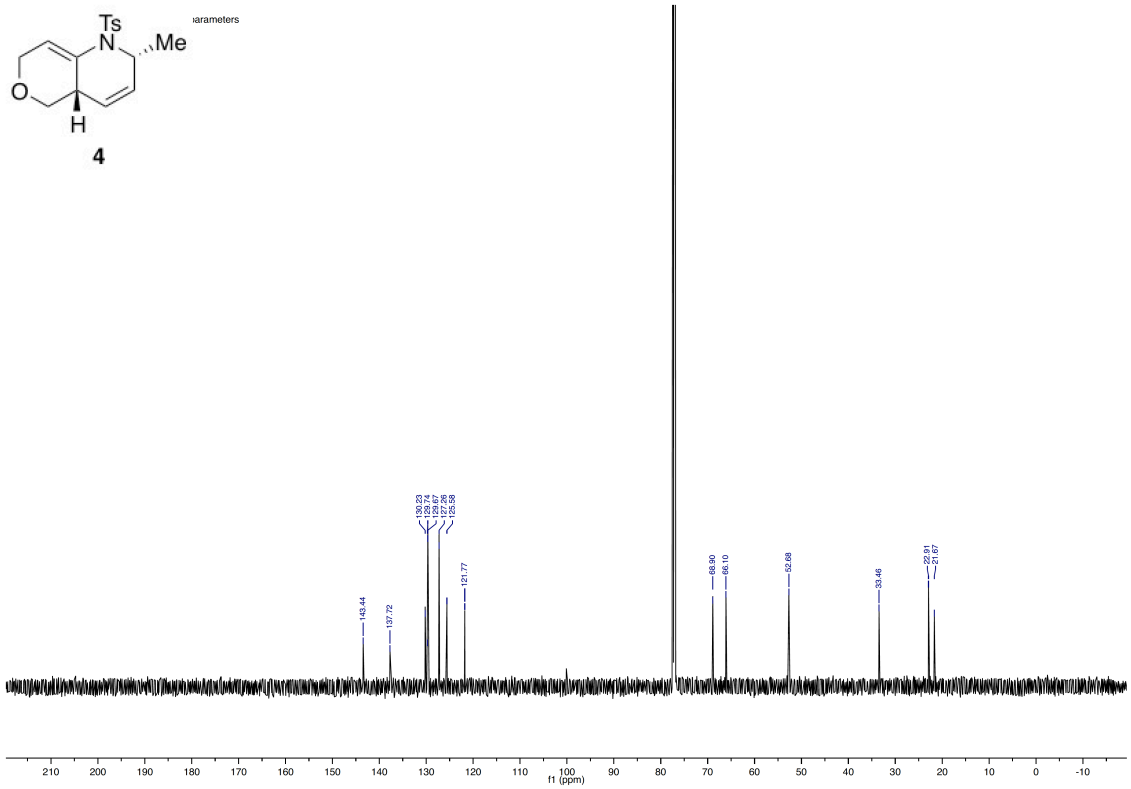

OMe
O
NTs
Me
O
OMe
H
2h
8 RN
1.78
1.76
1.00
0.97
1.00
1.10
5.29
1.12
1.38
1.10
1.13
2.83
1.14
2.74
f1 (ppm)

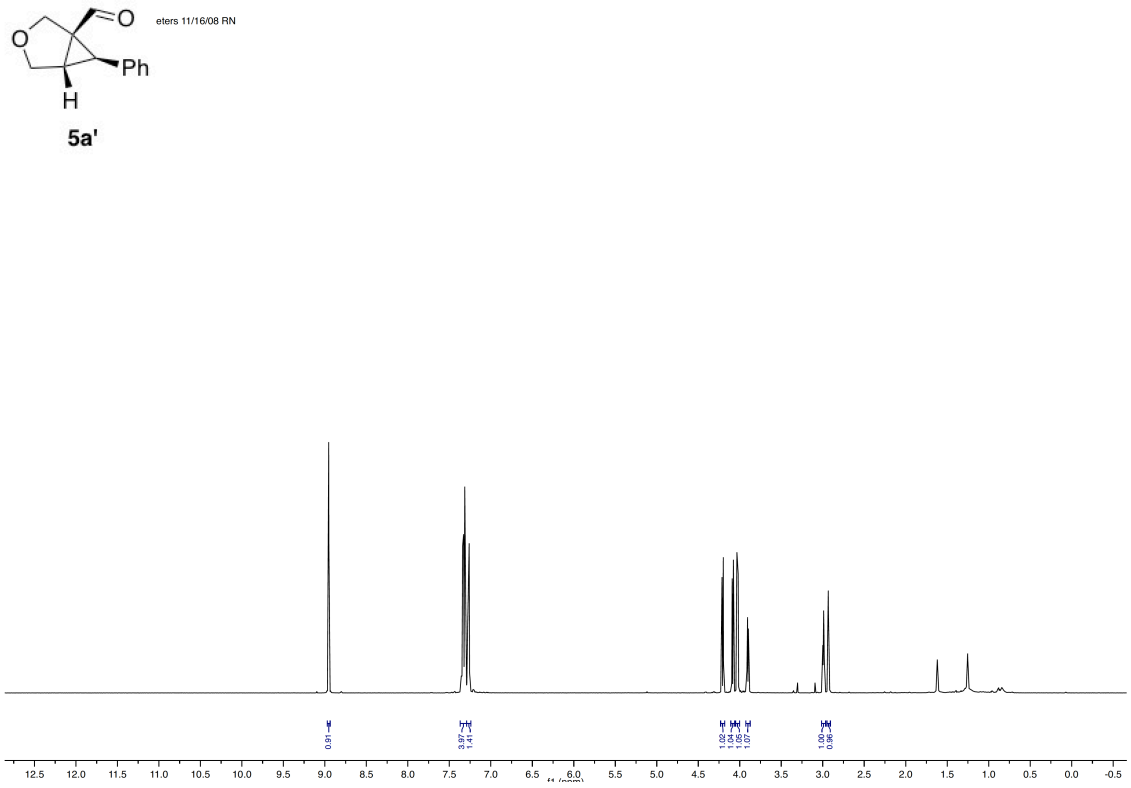

OMe
O
NTs
Me
O
OMe
H
2h
eters
171.13
170.87
144.04
142.99
130.60
129.42
126.82
126.04
118.26
99.94
58.31
52.84
52.83
52.75
40.94
40.66
38.69
21.51
21.18
f1 (ppm)

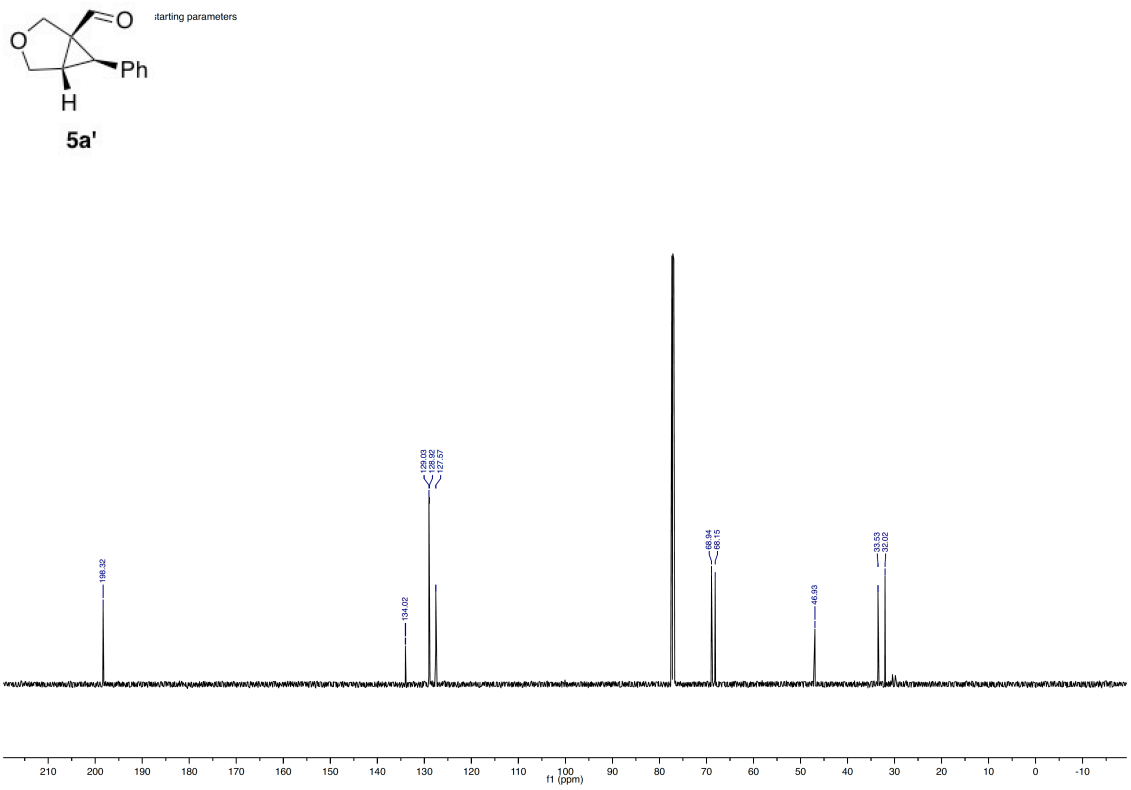

NTs
Ph
H
2i
ers 11/16/08 RN
2.04
2.29
2.95
2.32
1.03
1.00
2.03
1.10
3.63
1.50
1.27
1.27
1.26
0.99
2.60
f1 (ppm)

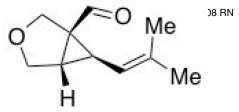

NTs
Ph
H
2i
rting parameters
149.54
142.85
139.22
138.49
129.90
129.23
128.66
128.10
127.63
127.00
126.93
116.98
59.75
41.97
34.81
31.59
24.76
21.51
f1 (ppm)


Ts
N
Me
O
H
4
/16/08 RN
1.90
2.56
0.94
1.00
1.00
1.00
1.07
1.09
1.04
1.03
1.01
3.17
3.11
f1 (ppm)

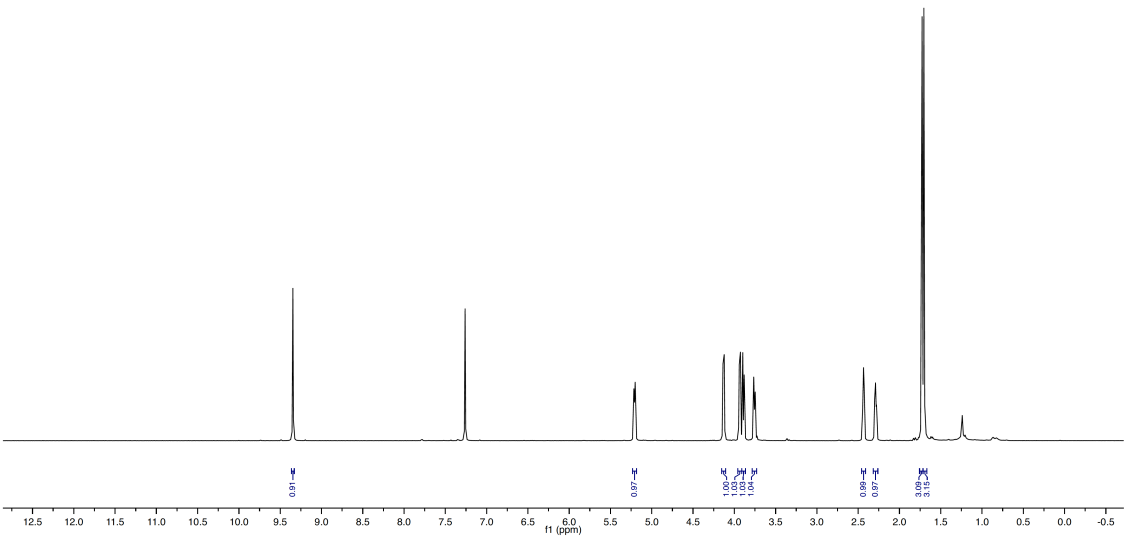

Ts
N
Me
O
H
4
arameters
130.23
129.74
128.67
127.26
125.58
143.44
137.72
121.77
68.90
66.10
52.68
33.46
28.91
21.67
f1 (ppm)

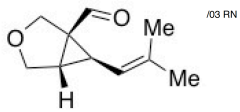

eters 11/16/08 RN
O
O
Ph
H
5a'
0.91
3.97
1.41
1.02
1.04
1.05
1.07
1.00
0.96
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5


tarting parameters
O
O
Ph
H
5a'
198.32
134.02
129.03
128.92
127.57
68.94
68.15
46.93
33.53
32.02
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

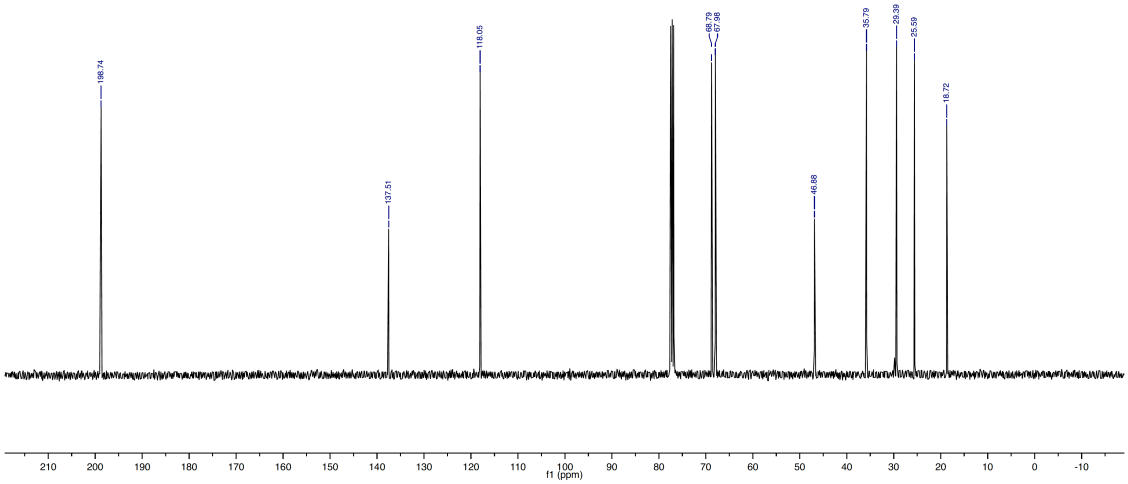

O
Me
Me
H

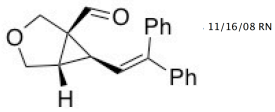
5b'


0.91
0.97
1.00
1.03
1.04
0.99
0.97
3.03
3.15
f1 (ppm)


O
Me
Me
H

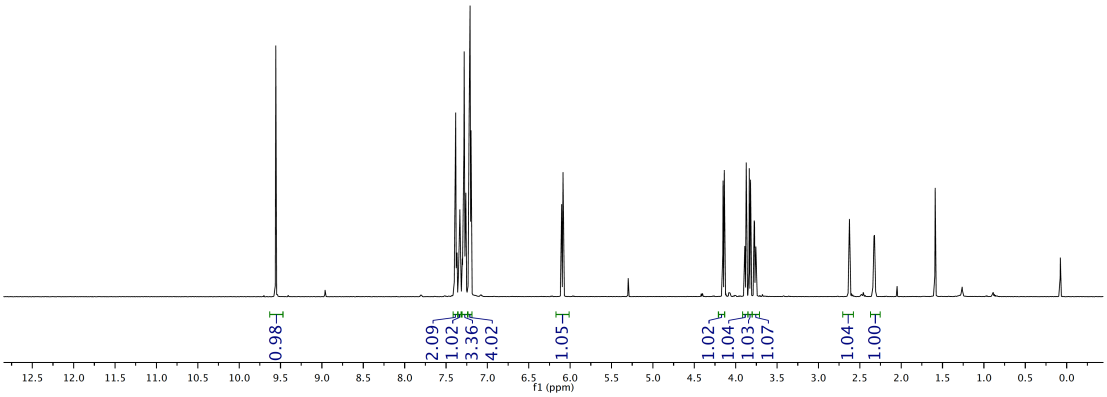
5b'

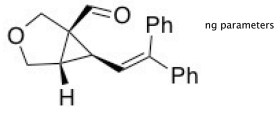

198.74
137.51
118.05
68.79
67.98
46.88
35.79
29.39
25.59
18.72
f1 (ppm)



11/16/08 RN

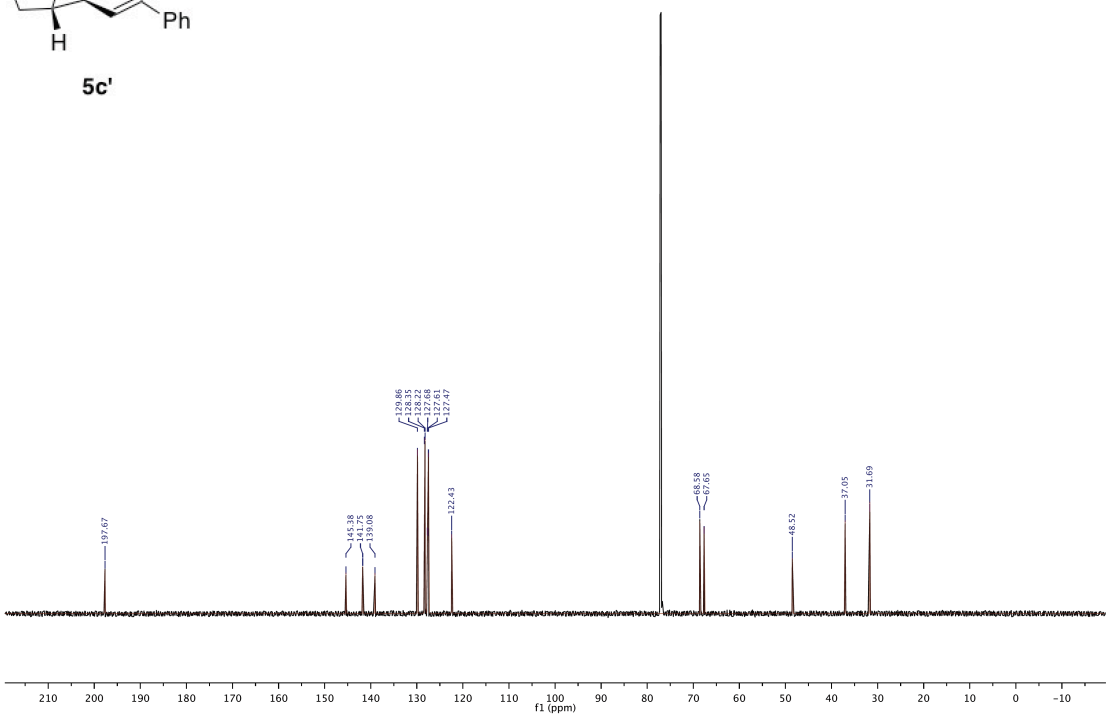
5c'

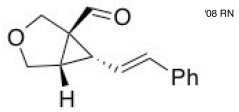




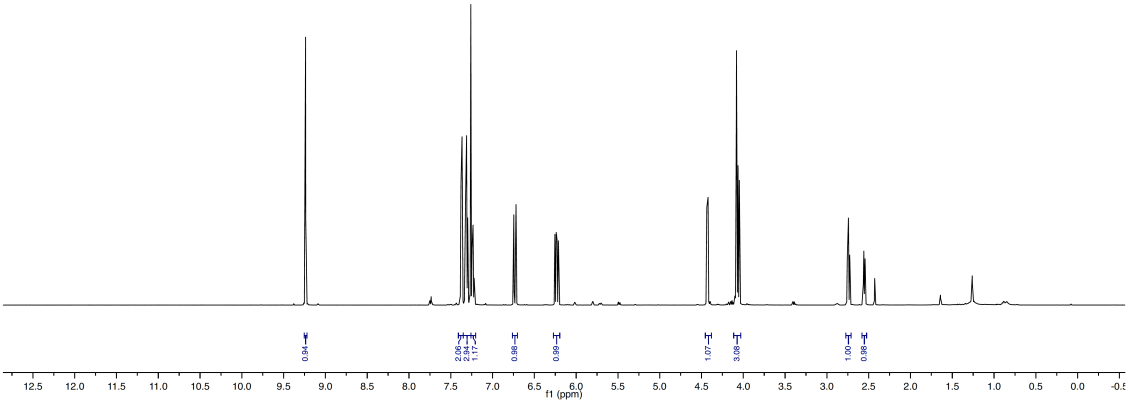
ng parameters

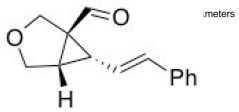
5c'



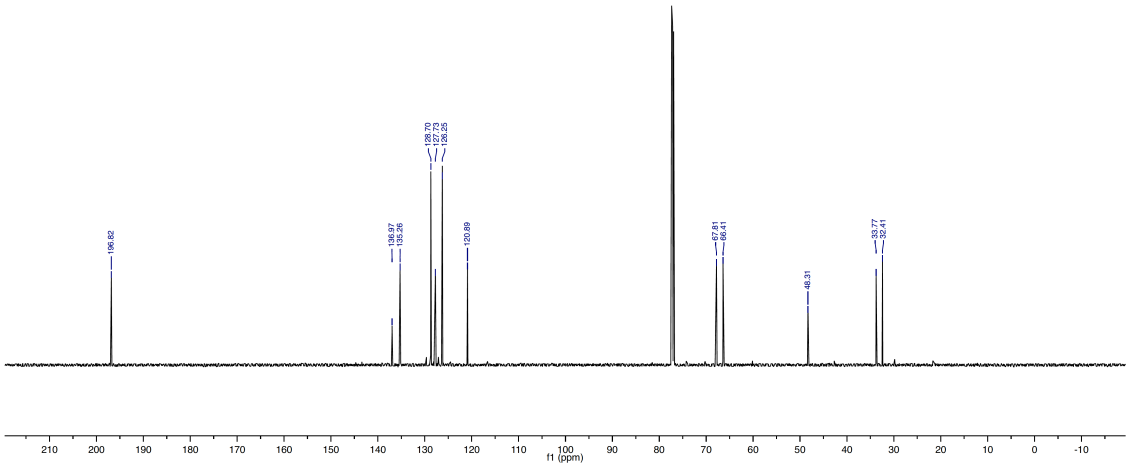

O
O
Ph
H

5d'


0.94
2.06
2.94
1.17
0.98
0.99
1.07
3.08
1.00
0.98
f1 (ppm)


O
O
Ph
H

5d'


196.82
136.97
135.26
129.70
128.73
126.93
120.89
67.81
66.41
48.31
33.77
32.41
f1 (ppm)