SUPPORTING INFORMATION

Synthetic Studies and Mechanistic Insight in Nickel-Catalyzed [4+2+1] Cycloadditions

Yike Ni and John Montgomery*

Department of Chemistry, Wayne State University, Detroit, MI 48202-3489 and Department of Chemistry, University of Michigan, 930 N. University, Ann Arbor, MI 48109-1055

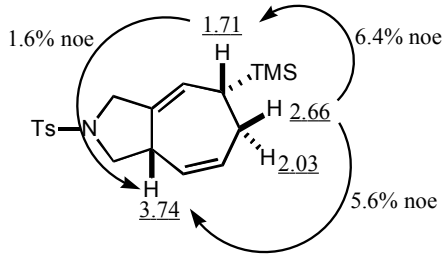
jmontg@umich.edu

Unless otherwise noted, reagents were commercially available and were used without purification. Tetrahydrofuran (THF) was treated under nitrogen using a solvent purification system (Innovative Technology, Inc., Model # SPS-400-3). $Ni(COD)_2$ (Strem Chemicals, Inc., used as received) was stored and weighed in an inert atmosphere glovebox. All reactions were conducted in flame-dried glassware under a nitrogen or argon atmosphere. ^1H and ^{13}C spectra were obtained in $CDCl_3$ at rt, unless otherwise noted, on a Varian Mercury 400 or Varian Unity 500 MHz instrument. Chemical shifts of ^1H NMR spectra were recorded in parts per million (ppm) on the δ scale from an internal standard of residual chloroform (7.27 ppm). Chemical shifts of ^{13}C NMR spectra were recorded in ppm from the central peak of $CDCl_3$ (77.0 ppm) on the δ scale. High resolution mass spectra (HRMS) were obtained on a Kratos MS 80 mass spectrometer by

the Central Instrumentation Facility, Department of Chemistry, Wayne State University, Detroit, Michigan.

General procedure for the $Ni(COD)_2$ catalyzed cycloadditions:

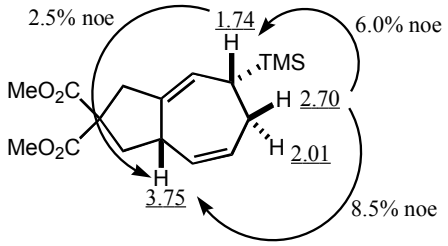
To a premixed THF solution of enyne or dienyne (1 equiv, 0.1 M) and $TMSCHN_2$ (2 equiv) was added a THF solution of $Ni(COD)_2$ (10 mol%) at 60 °C. The resulting brown solution was stirred at 60 °C for 10 – 30 minutes and allowed to cool to rt. The solvent was removed by rotary evaporation and the residue was absorbed onto silica gel. Flash column chromatography provided the bicyclic products.



2a

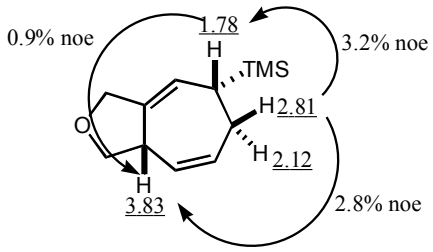
2-(Toluene-4-sulfonyl)-7-trimethylsilanyl-1,2,3,3a,6,7-hexahydro-cyclohepta[*c*]-pyrrole (2a). General procedure was followed using 138 mg (0.5 mmol) of dienyne **1a**, 0.5 mL (1.0 mmol, 2.0 M in Et_2O) of $TMSCHN_2$, 15 mg (0.05 mmol) of $Ni(COD)_2$ to afford 124 mg (68%, > 95 : 5 as judged by GC analysis on the crude reaction mixture) of product **2a**. ^1H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, J = 8.5 Hz, 2H), 7.32 (d, J = 8.5 Hz, 2H), 5.75 (dtd, J = 11.0, 6.5, 2.5 Hz, 1H), 5.50 (d, J = 5.0 Hz, 1H), 5.39 (d, J = 10.5 Hz, 1H), 3.97 (d, J = 13.0 Hz, 1H), 3.73 (m, 2H), 3.62 (d, J = 13.0 Hz, 1H), 2.75 (m, 1H), 2.66 (m, 1H), 2.43 (s, 3H), 2.03 (dt, J = 15.0, 7.0 Hz, 1H), 1.71 (m, 1H), -0.06 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.8, 134.7, 132.9, 131.9, 129.9, 129.8, 128.1, 124.4,

54.6, 53.9, 40.5, 28.0, 27.4, 21.8, -1.8; IR (film) 2952, 2844, 1598, 1456, 1348, 1248, 1164 cm^{-1}; HRMS (EI) m/e calcd for $C_{19}H_{26}NO_2SiS$ 360.1454, found 360.1459 $(M-H)^+$.



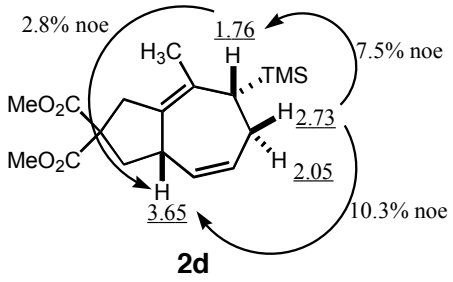
2b

7-Trimethylsilanyl-3,3a,6,7-tetrahydro-1*H*-azulene-2,2-dicarboxylic acid dimethyl ester (2b). General procedure was followed using 50 mg (0.2 mmol) of dienyne **1b**, 0.2 mL (0.4 mmol, 2.0 M in Et_2O) of $TMSCHN_2$, 6 mg (0.02 mmol) of $Ni(COD)_2$ to afford 49 mg (76%, 13 : 1 as judged by GC analysis on the crude reaction mixture) of product **2b**. ^1H NMR (500 MHz, $CDCl_3$) δ 5.70 (dtd, *J* = 10.5, 6.5, 2.0 Hz, 1H), 5.55 (dt, *J* = 10.0, 2.0 Hz, 1H), 5.50 (m, 1H), 3.75 (m, 1H), 3.73 (s, 3H), 3.71 (s, 3H), 2.98 (d, *J* = 16.0 Hz, 1H), 2.91 (dq, *J* = 16.0, 2.5 Hz, 1H), 2.70 (m, 1H), 2.60 (ddd, *J* = 12.5, 8.5, 1.0 Hz, 1H), 2.05 (dd, *J* = 12.5, 11.0 Hz, 1H), 2.01 (m, 1H), 1.74 (m, 1H), -0.01 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.5, 172.2, 138.7, 134.0, 130.6, 123.7, 58.6, 53.0, 52.9, 42.1, 41.6, 39.7, 27.7, 27.3, -1.9; IR (film) 2952, 2844, 1736, 1434, 1249 cm^{-1}; HRMS (EI) m/e calcd for $C_{17}H_{26}O_4Si$ 322.1600, found 322.1599 (M^+).



2c

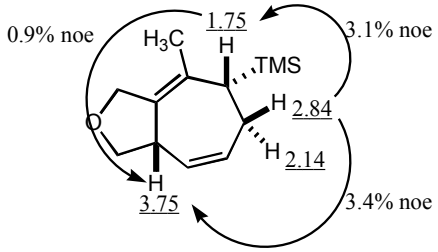
Trimethyl-(3,5,6,8a-tetrahydro-1*H*-cyclohepta[*c*]furan-5-yl)-silane (2c). General procedure was followed using 62 mg (0.5 mmol) of dienyne **1c**, 0.5 mL (1.0 mmol, 2.0 M in Et_2O) of $TMSCHN_2$, 15 mg (0.05 mmol) of $Ni(COD)_2$ to afford 75 mg (65%, 10 : 1 as judged by NMR analysis on the purified sample) of inseparable isomers of product **2c**. ^1H NMR (500 MHz, $CDCl_3$) δ 5.82 (dtd, *J* = 10.5, 6.5, 3.0 Hz, 1H), 5.52 (dt, *J* = 10.5, 2.5 Hz, 1H), 5.51 (m, 1H), 4.39 (dq, *J* = 12.5, 2.0 Hz, 1H), 4.25 (dq, *J* = 12.2, 2.0 Hz, 1H), 4.20 (t, *J* = 8.0 Hz, 1H), 3.83 (m, 1H), 3.47 (dd, *J* = 10.0, 8.0 Hz, 1H), 2.81 (m, 1H), 2.12 (dt, *J* = 14.5, 6.8 Hz, 1H), 1.78 (m, 1H), 0.02 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.7, 131.8, 129.9, 120.7, 74.7, 73.1, 41.4, 27.7, 27.6, -1.8; IR (film) 2952, 2843, 1652, 1449, 1248 cm^{-1}; HRMS (EI) m/e calcd for $C_{12}H_{20}OSi$ 208.1283, found 208.1288 (M^+).



2d

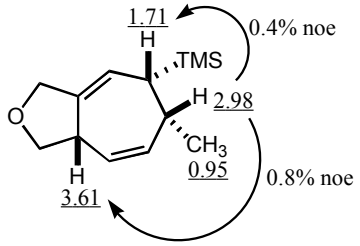
8-Methyl-7-trimethylsilanyl-3,3a,6,7-tetrahydro-1*H*-azulene-2,2-dicarboxylic acid dimethyl ester (2d). General procedure was followed using 125 mg (0.5 mmol) of dienyne **1d**, 0.5 mL (1.0 mmol, 2.0 M in Et_2O) of $TMSCHN_2$, 15 mg (0.05 mmol) of $Ni(COD)_2$ to afford 131 mg (78%, > 95 : 5 as judged by NMR analysis on the purified sample) of **2d**. ^1H NMR (500 MHz, $CDCl_3$) δ 5.77 (dtd, *J* = 9.5, 6.5, 2.5 Hz, 1H), 5.58

(dt, *J* = 10.0, 2.2 Hz, 1H), 3.73 (s, 3H), 3.71 (s, 3H), 3.65 (m, 1H), 3.01 (d, *J* = 17.0 Hz, 1H), 2.84 (dd, *J* = 16.5, 1.5 Hz, 1H), 2.73 (m, 1H), 2.57 (ddd, *J* = 13.0, 8.0, 1.5 Hz, 1H), 2.05 (dt, *J* = 15.0, 6.5 Hz, 1H), 1.98 (t, *J* = 12.5 Hz, 1H), 1.76 (m, 1H), 1.60 (s, 3H), 0.02 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.6, 172.5, 134.1, 131.0, 130.9, 130.2, 58.1, 52.9, 52.8, 41.8, 40.5, 40.1, 34.1, 28.4, 22.9, 0.04; IR (film) 2952, 2845, 1735, 1434, 1249 cm^{-1}; HRMS (EI) m/e calcd for $C_{18}H_{28}O_4Si$ 336.1757, found 336.1754 (M^+).



2e

Trimethyl-(4-methyl-3,5,6,8a-tetrahydro-1*H*-cyclohepta[*c*]furan-5-yl)-silane (2e). General procedure was followed using 136 mg (1.0 mmol) of dienyne **1e**, 1.0 mL (2.0 mmol, 2.0 M in Et_2O) of $TMSCHN_2$, 28 mg (0.1 mmol) of $Ni(COD)_2$ to afford 135 mg (62%, 16 : 1 as judged by NMR analysis on the purified sample) of inseparable isomers of product **2e**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.89 (dtd, *J* = 10.0, 6.8, 2.8 Hz, 1H), 5.56 (dt, *J* = 10.4, 2.4 Hz, 1H), 4.44 (d, *J* = 12.8 Hz, 1H), 4.30 (d, *J* = 12.0 Hz, 1H), 4.17 (t, *J* = 7.8 Hz, 1H), 3.75 (m, 1H), 3.43 (dd, *J* = 10.8, 7.8 Hz, 1H), 2.84 (m, 1H), 2.14 (dt, *J* = 13.6, 6.8 Hz, 1H), 1.75 (m, 1H), 1.54 (s, 3H), 0.05 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.0, 130.3, 130.1, 128.7, 74.8, 72.2, 41.7, 33.7, 28.7, 22.4, 0.1; IR (film) 2951, 2839, 1653, 1247 cm^{-1}; HRMS (EI) m/e calcd for $C_{13}H_{22}OSi$ 222.1440, found 222.1443 (M^+).

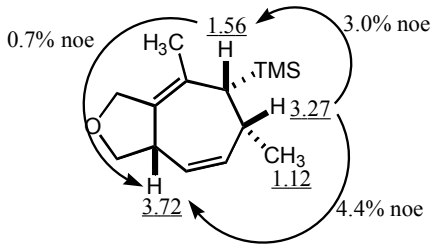


2f

Trimethyl-(6-methyl-3,5,6,8a-tetrahydro-1*H*-cyclohepta[*c*]furan-5-yl)-silane (2f). General procedure was followed using 70 mg (0.5 mmol) of dienyne **1f**, 0.5 mL (1.0 mmol, 2.0 M in Et_2O) of $TMSCHN_2$, 15 mg (0.05 mmol) of $Ni(COD)_2$ to afford 50 mg (45%, 4 : 1 as judged by GC analysis on the crude reaction mixture) of inseparable isomers of product **2f** (note: Two conformers of the major isomer of **2f** interconvert slowly on the NMR time scale. Signals for the major isomer begin to sharpen at 55 ºC in C_6D_6). ^{1}H NMR (500 MHz, C_6D_6, VT = 55 ºC) δ 5.45 (ddd, *J* = 10.0, 6.0, 2.8 Hz, 1H), 5.36 (m, 1H), 5.20 (d, *J* = 10.0 Hz, 1H), 4.35 (d, *J* = 12.5 Hz, 1H), 4.17 (dd, *J* = 12.5, 2.0 Hz, 1H), 4.03 (t, *J* = 8.5 Hz, 1H), 3.61 (m, 1H), 3.34 (dd, *J* = 10.5, 7.5 Hz, 1H), 2.98 (br s, 1H), 1.71 (br s, 1H), 0.95 (d, *J* = 7.0 Hz, 3H), -0.01 (s, 9H); ^{13}C NMR (125 MHz, C_6D_6, 55 ºC, complete listing for both isomers) δ 138.8, 136.1, 126.7, 120.1, 74.8, 74.3, 73.0, 72.6, 44.6, 41.9, 35.8, 34.7, 34.1, 29.9, 24.2, 20.6, -0.3, -1.4;

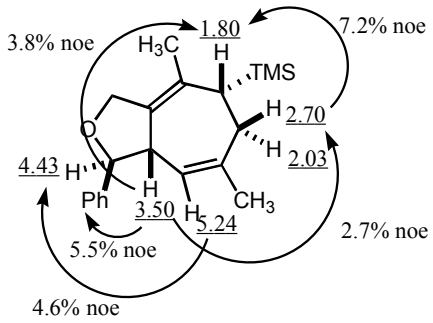
^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC) δ 5.60 (ddd, *J* = 10.0, 6.0, 3.0 Hz, 1H), 5.52 (m, 1H), 5.39 (m, 1H), 4.40 (d, *J* = 12.0 Hz, 1H), 4.25 (dd, *J* = 12.0, 2.0 Hz, 1H), 4.20 (t, *J* = 8.2 Hz, 1H), 3.78 (m, 1H), 3.44 (dd, *J* = 10.5, 8.0 Hz, 1H), 3.14 (br m, 1H), 1.83 (br m, 1H), 1.07 (d, *J* = 8.0 Hz, 3H), 0.04 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, complete listing for both isomers) δ 139.4, 138.6, 136.8, 126.4, 125.4, 121.1, 119.9, 75.0, 74.6, 73.2, 73.0, 44.0, 41.7, 36.0, 34.8, 33.8, 29.9, 24.3, 21.1, 0.1, -1.0; IR (film) 2953, 2844,

1653, 1457, 1248 cm^{-1}; HRMS (EI) m/e calcd for $C_{12}H_{19}OSi$ 207.1205, found 207. 1201 $(M\text{-}CH_3)^+$.



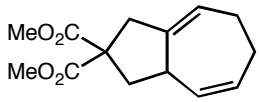
2g

(4,6-Dimethyl-3,5,6,8a-tetrahydro-1*H*-cyclohepta[*c*]furan-5-yl)-trimethyl-silane (2g). General procedure was followed using 150 mg (1.0 mmol) of dienyne **1g**, 1.0 mL (2.0 mmol, 2.0 M in Et_2O) of $TMSCHN_2$, 28 mg (0.1 mmol) of $Ni(COD)_2$ to afford 115 mg (49%, > 95 : 5 as judged by NMR analysis on the purified sample) of product **2g** (note: Two conformers of **2g** interconvert very slowly on the NMR time scale, and sharp signals in the ^1H NMR for both conformers are noted at 25 ºC in $CDCl_3$. The signals broaden and approach coalescence at 75 ºC in C_6D_6). Major conformer: ^1H NMR (500 MHz, $CDCl_3$, 25 ºC) δ 5.74 (ddd, *J* = 9.5, 7.0, 3.0 Hz, 1H), 5.45 (d, *J* = 9.5 Hz, 1H), 4.43 (d, *J* = 12.0 Hz, 1H), 4.30 (d, *J* = 12.0 Hz, 1H), 4.16 (t, *J* = 8.0 Hz, 1H), 3.72 (m, 1H), 3.42 (dd, *J* = 12.5, 7.5 Hz, 1H), 3.27 (m, 1H), 1.56 (m, 1H), 1.53 (s, 3H), 1.12 (d, *J* = 7.5 Hz, 3H), 0.06 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC) δ 139.4, 129.8, 128.1, 125.9, 74.2, 72.2, 42.8, 42.6, 36.1, 23.4, 21.6, 2.0; Minor conformer: ^1H NMR (500 MHz, $CDCl_3$) δ 5.54 (m, 1H), 5.19 (d, *J* = 10.5 Hz, 1H), 4.36 (d, *J* = 12.5 Hz, 1H), 4.28 (m, 1H), 4.21 (t, *J* = 8.2 Hz, 1H), 3.70 (m, 1H), 3.45 (d, *J* = 8.5 Hz, 1H), 2.51 (m, 1H), 2.46 (m, 1H), 1.70 (s, 3H), 1.00 (d, *J* = 7.5 Hz, 3H), 0.10 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.4, 138.8, 127.1, 125.6, 75.9, 70.7, 41.9, 38.1, 33.2, 21.9, 18.6, 0.0; IR (film) 2955, 2836, 1652, 1457, 1248 cm^{-1}; HRMS (EI) m/e calcd for $C_{14}H_{24}OSi$ 236.1596, found 236.1592 (M^+).



2h

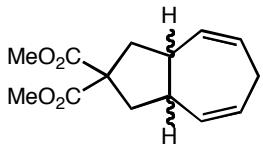
(4,7-Dimethyl-1-phenyl-3,5,6,8a-tetrahydro-1*H*-cyclohepta[*c*]furan-5-yl)-trimethyl-silane (2h). General procedure was followed using 140 mg (0.6 mmol) of dienyne **1h**, 0.6 mL (1.2 mmol, 2.0 M in Et_2O) of $TMSCHN_2$, 18 mg (0.06 mmol) of $Ni(COD)_2$ to afford 138 mg (74%, > 95 : 5 as judged by NMR analysis on the purified sample) of product **2h**. ^1H NMR (500 MHz, $CDCl_3$) δ 7.44 - 7.28 (m, 5H), 5.24 (d, *J* = 1.5 Hz, 1H), 4.65 (d, *J* = 12.5 Hz, 1H), 4.44 (dd, *J* = 12.5, 1.5 Hz, 1H), 4.43 (d, *J* = 10.0 Hz, 1H), 3.50 (d, *J* = 9.0 Hz, 1H), 2.70 (d, *J* = 15.0 Hz, 1H), 2.03 (dd, *J* = 15.0, 7.0 Hz, 1H), 1.80 (m, 1H), 1.72 (s, 3H), 1.62 (s, 3H), 0.10 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.6, 139.3, 133.6, 128.6, 128.3, 128.2, 127.2, 122.8, 88.0, 71.6, 49.8, 33.8, 33.6, 26.3, 21.6, -0.2; IR (film) 2950, 2846, 1683, 1454, 1248 cm^{-1}; HRMS (EI) m/e calcd for $C_{19}H_{25}OSi$ 297.1675, found 297. 1679 $(M\text{-}CH_3)^+$.



3

3,3a,6,7-Tetrahydro-1*H*-azulene-2,2-dicarboxylic acid dimethyl ester (3). To a 3 mL THF solution of **2b** (46 mg, 0.14 mmol) was added TBAF (0.3 ml, 1.0 M in THF) at rt. The resulting brown solution was warmed to 60 °C and stirred for 30 minutes. The solvent was removed by rotary evaporation and the residue was absorbed onto silica gel.

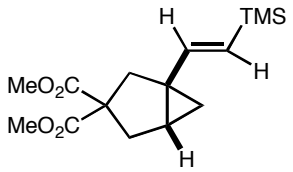
Flash column chromatography on silica gel (Hexane : Ethyl ether = 10 : 1) afforded **3** (29 mg, 82%) as a light oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.68 (m, 1H), 5.63 (m, 1H), 5.49 (d, *J* = 10.5 Hz, 1H), 3.73 (s, 3H), 3.71 (s, 3H), 3.67 (m, 1H), 3.00 – 2.89 (m, 2H), 2.65 (ddd, *J* = 13.0, 8.0, 1.5 Hz, 1H), 2.38 – 2.28 (m, 2H), 2.09 – 2.02 (m, 2H), 2.01 (dd, *J* = 12.8, 10.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.3, 172.1, 142.6, 132.2, 130.4, 122.5, 58.8, 53.0, 52.9, 41.7, 41.5, 39.8, 26.4, 25.9; IR (film) 2955, 2843, 1734, 1653, 1435, 1250 cm^{-1}; HRMS (EI) m/e calcd for $C_{14}H_{18}O_4$ 250.1205, found 250.1205 (M^+).



4

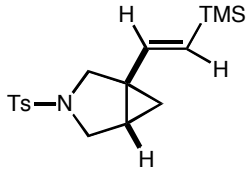
3,3a,6,8a-Tetrahydro-1*H*-azulene-2,2-dicarboxylic acid dimethyl ester (4). To a 3 mL CH_2Cl_2 solution of **2b** (26 mg, 0.08 mmol) was added BF_3·2HOAc complex (35 μL, 0.24 mmol) at 0 °C. The resulting orange solution was allowed to warm to rt and stirred for 20 minutes. The reaction mixture was diluted with 5 mL ethyl ether and quenched with saturated $NaHCO_3$. Extraction with ethyl ether (3 x 10 mL) and chromatographic purification on silica gel (Hexane : Ethyl ether = 10 : 1) afforded **4** (16 mg, 80%) as a light oil (d.r. = 3 : 1, *cis* : *trans*). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.71 – 5.65 (m, $2H_{maj}$ + $2H_{min}$), 5.57 – 5.53 (dt, *J* = 11.0, 4.5 Hz, $2H_{min}$), 5.47 (d, *J* = 10.5 Hz, $2H_{maj}$), 3.72 (s, $6H_{maj}$ + $6H_{min}$), 2.99 – 2.88 (m, $3H_{maj}$ + $2H_{min}$), 2.70 (dd, *J* = 13.0, 7.0 Hz, $2H_{min}$), 2.61 – 2.53 (m, $1H_{maj}$ + $2H_{min}$), 2.37 (dd, *J* = 13.5, 7.0 Hz, $2H_{maj}$), 2.31 (dd, *J* = 13.0, 6.5 Hz, $2H_{maj}$), 1.93 (t, *J* = 12.2 Hz, $2H_{min}$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.7, 173.3, 173.1, 132.0, 131.7, 129.5, 127.3, 58.0, 53.1, 53.0, 52.9, 44.2, 42.7, 41.4, 40.8, 29.9, 27.9; IR (film)

2953, 1733, 1652, 1435, 1249 cm^{-1}; HRMS (EI) m/e calcd for $C_{14}H_{18}O_4$ 250.1205, found 250.1202 (M^+).



14a

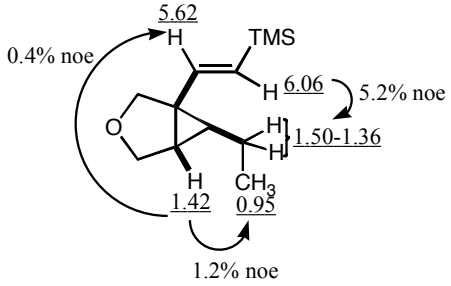
(*E*)-dimethyl 1-(2-(trimethylsilyl)vinyl)bicyclo[3.1.0]hexane-3,3-dicarboxylate (14a). General procedure was followed using 106 mg (0.5 mmol) of enyne **13a**, 0.5 mL (1.0 mmol, 2.0 M in diethyl ether) of $TMSCHN_2$, 15 mg (0.05 mmol) of $Ni(COD)_2$ to afford 108 mg (72%) of product **14a** exclusively as the *E* isomer. ^1H NMR (400 MHz, $CDCl_3$) δ 5.72 (d, *J* = 18.4 Hz, 1H), 5.60 (d, *J* = 19.6 Hz, 1H), 3.71 (s, 3H), 3.69 (s, 3H), 2.65 – 2.55 (m, 3H), 2.48 (dd, *J* = 14.0, 4.8 Hz, 1H), 1.41 (dt, *J* = 8.0, 5.2 Hz, 1H), 0.72 (t, *J* = 6.8 Hz, 1H), 0.54 (t, *J* = 5.2 Hz, 1H), 0.03 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.4, 172.5, 149.7, 125.6, 59.3, 53.2, 53.1, 37.3, 35.9, 33.5, 26.8, 17.8, -0.9; IR (film) 2954, 1736, 1610, 1435, 1248 cm^{-1}; HRMS (EI) m/e calcd for $C_{15}H_{24}O_4Si$ 296.1444, found 296.1444 (M^+).



14b

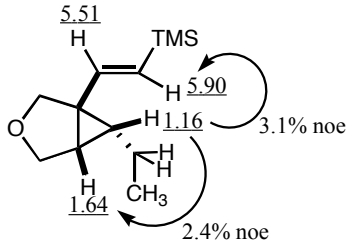
3-Tosyl-1-(2-(trimethylsilyl)vinyl)-3-aza-bicyclo[3.1.0]hexane (14b). General procedure was followed using 50 mg (0.2 mmol) of enyne **13b**, 0.2 mL (0.4 mmol, 2.0 M in Hexane) of $TMSCHN_2$, 6 mg (0.02 mmol) of $Ni(COD)_2$ to afford 40 mg (60%) of product **14b** as a mixture of *E* / *Z* = 10 : 1 isomers.[1] For *E*-isomer: ^1H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 9.0 Hz, 2H), 7.34 (d, *J* = 8.5 Hz, 2H), 5.68 (d, *J* = 19.0 Hz, 1H),

5.52 (d, *J* = 19.0 Hz, 1H), 3.54 (d, *J* = 9.0 Hz, 1H), 3.53 (d, *J* = 9.0 Hz, 1H), 3.18 (d, *J* = 9.5 Hz, 1H), 3.09 (dd, *J* = 9.3, 4.0 Hz, 1H), 2.44 (s, 3H), 1.46 (quint, *J* = 4.0 Hz, 1H), 0.93 (t, *J* = 5.2 Hz, 1H), 0.86 (m, 1H), 0.01 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.9, 143.7, 133.7, 129.9, 127.8, 127.6, 51.0, 49.9, 32.1, 25.1, 21.8, 16.1, -1.1; IR (film) 2953, 1614, 1348, 1166 cm^{-1}; HRMS (EI) m/e calcd for $C_{17}H_{25}NO_2SSi$ 335.1375, found 335.1377 (M^+).



14c

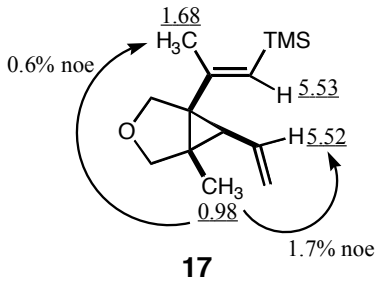
((*E*)-2-((1*R*, 5*S*, 6*S*)-6-ethyl-3-oxa-bicyclo[3.1.0]hexan-1-yl)vinyl)trimethylsilane (14c). General procedure was followed using 50 mg (0.4 mmol) of enyne **13c**, 0.4 mL (0.8 mmol, 2.0 M in diethyl ether) of $TMSCHN_2$, 12 mg (0.04 mmol) of $Ni(COD)_2$ to afford 30 mg (36%) of product **14c** as an exclusive *E* isomer (d.r. > 95 : 5 as judged by NMR analysis on the purified sample). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.06 (d, *J* = 19.6 Hz, 1H), 5.62 (d, *J* = 18.8 Hz, 1H), 3.87 (d, *J* = 8.4 Hz, 1H), 3.82 (d, *J* = 8.4 Hz, 1H), 3.80 (d, *J* = 8.4 Hz, 1H), 3.73 (dd, *J* = 8.0, 2.4 Hz, 1H), 1.50 – 1.36 (m, 3H), 1.03 (m, 1H), 0.95 (t, *J* = 7.5 Hz, 3H), 0.06 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 129.5, 71.5, 70.0, 37.2, 32.0, 29.4, 21.3, 14.0, -0.9; IR (film) 2958, 1605, 1456, 1248 cm^{-1}; HRMS (EI) m/e calcd for $C_{12}H_{22}OSi$ 210.1440, found 210.1441 (M^+).



E / *Z* = 9 : 1

14d

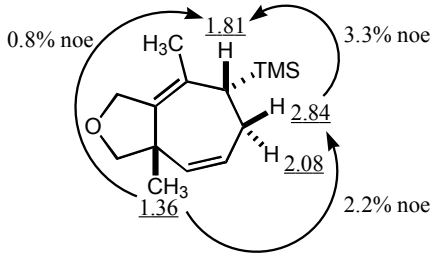
((*E*)-2-((1*R*, 5*S* , 6*R*)-6-ethyl-3-oxa-bicyclo[3.1.0]hexan-1-yl)vinyl)trimethylsilane (14d). General procedure was followed using 100 mg (0.8 mmol) of enyne **13d**, 2.0 mL (4.0 mmol, 2.0 M in diethyl ether) of $TMSCHN_2$, 22 mg (0.08 mmol) of $Ni(COD)_2$ to afford 42 mg (25%) of product **14d** as a mixture of *E* / *Z* = 9 : 1 isomers (d.r. > 95 : 5 as judged by NMR analysis on the purified sample). ^1H NMR (400 MHz, $CDCl_3$) δ 5.90 (d, *J* = 18.8 Hz, 1H), 5.51 (d, *J* = 18.8 Hz, 1H), 4.08 (d, *J* = 8.4 Hz, 1H), 3.97 (dd, *J* = 8.4, 3.6 Hz, 1H), 3.82 (d, *J* = 8.8 Hz, 1H), 3.81 (d, *J* = 8.0 Hz, 1H), 1.64 (dd, *J* = 8.2, 4.2 Hz, 1H), 1.55 – 1.45 (m, 2H), 1.16 (q, *J* = 7.2 Hz, 1H), 1.00 (t, *J* = 7.6 Hz, 3H), 0.04 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.6, 126.4, 69.4, 68.2, 37.9, 31.2, 30.6, 15.1, 14.7, -0.9; IR (film) 2957, 1608, 1456, 1248 cm^{-1}; HRMS (EI) m/e calcd for $C_{12}H_{22}OSi$ 210.1440, found 210.1440 (M^+).



17

Trimethyl((*E*)-2-((1*R*, 5*S*, 6*S*)-5-methyl-6-vinyl-3-oxa-bicyclo[3.1.0]hexan-1-yl)prop-1-enyl)silane (17). General procedure was followed using 170 mg (1.1 mmol) of dienyne **16**, 1.2 mL (2.4 mmol, 2.0 M in diethyl ether) of $TMSCHN_2$, 35 mg (0.12 mmol) of

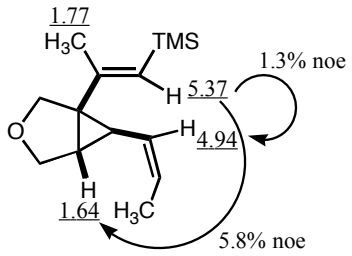
$Ni(COD)_2$ to afford 120 mg (48%) of product **17** as an exclusive *E* isomer (d.r. = 9 : 1 as judged by NMR analysis on the purified sample). ^1H NMR (500 MHz, C_6D_6) δ 5.52 - 5.53 (m, 2H), 5.11 (dd, *J* = 17.0, 2.0 Hz, 1H), 4.97 (dd, *J* = 10.5, 2.0 Hz, 1H), 3.90 (d, *J* = 7.5 Hz, 1H), 3.72 (d, *J* = 8.0 Hz, 1H), 3.64 (d, *J* = 8.5 Hz, 1H), 3.44 (d, *J* = 8.0 Hz, 1H), 1.81 (d, *J* = 10.5 Hz, 1H), 1.68 (s, 3H), 0.98 (s, 3H), 0.10 (s, 9H); ^{13}C NMR (125 MHz, C_6D_6) δ 148.8, 135.4, 131.3, 114.6, 76.2, 75.2, 46.5, 34.4, 31.7, 21.4, 10.6, -0.0; IR (film) 2954, 1636, 1614, 1248 cm^{-1}; HRMS (EI) m/e calcd for $C_{14}H_{24}OSi$ 236.1596, found 236.1601 (M^+).



19

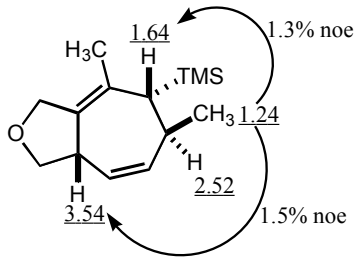
((3a*E*, 5*R* , 7*Z* , 8a*S*)-4,8a-dimethyl-3,5,6,8a-tetrahydro-1*H*-cyclohepta[*c*]furan-5-yl)trimethylsilane (19). General procedure was followed using 75 mg (0.5 mmol) of dienyne **16**, 1.25 mL (2.5 mmol, 2.0 M in diethyl ether) of $TMSCHN_2$, 15 mg (0.05 mmol) of $Ni(COD)_2$ to afford 62 mg (52%) of product **19** (d.r. > 95 : 5 as judged by NMR analysis on the purified sample). From thermolysis of divinylcyclopropane: A 1 mL toluene solution of **17** (18 mg, 0.07 mmol) was stirred at 105 ºC for 12 hrs to afford 11 mg (60%) of product **19** (d.r. > 95 : 5 as judged by NMR analysis on the purified sample). ^1H NMR (500 MHz, $CDCl_3$) δ 5.80 (ddd, *J* = 11.0, 7.5, 6.0 Hz, 1H), 5.57 (dd, *J* = 10.3, 2.2 Hz, 1H), 4.48 (d, *J* = 12.5 Hz, 1H), 4.37 (d, *J* = 12.5 Hz, 1H), 3.66 (d, *J* = 7.0 Hz, 1H), 3.50 (d, *J* = 7.0 Hz, 1H), 2.86 (m, 1H), 2.09 (ddd, *J* = 14.5, 7.5, 5.5 Hz, 1H), 1.81 (m, 1H), 1.54 (s, 3H), 1.36 (s, 3H), 0.04 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ

134.5, 133.6, 130.1, 128.6, 80.9, 72.6, 46.3, 35.3, 28.2, 26.4, 22.8, 0.1; IR (film) 2960, 1669, 1456, 1248, 1054 cm^{-1}; HRMS (EI) m/e calcd for $C_{14}H_{24}OSi$ 236.1596, found 236.1597 (M^+).



21

Trimethyl((*E*)-2-((1*R* , 5*S* , 6*S*)-6-((*Z*)-prop-1-enyl)-3-oxa-bicyclo[3.1.0]hexan-1-yl)prop-1-enyl)silane (21). General procedure was followed using 40 mg (0.26 mmol) of dienyne **20**, 0.3 mL (0.52 mmol, 2.0 M in Et_2O) of $TMSCHN_2$, 8 mg (0.026 mmol) of $Ni(COD)_2$ to afford 42 mg (69%) of **21** (d.r. > 95 : 5 as judged by NMR analysis on the purified sample). ^1H NMR (400 MHz, $CDCl_3$) δ 5.43 (m, 1H), 5.37 (s, 1H), 4.94 (t, *J* = 10.4 Hz, 1H), 3.97 (d, *J* = 8.0 Hz, 1H), 3.93 (d, *J* = 8.0 Hz, 1H), 3.84 (dd, *J* = 8.0, 2.4 Hz, 1H), 3.63 (d, *J* = 7.6 Hz, 1H), 1.85 (dd, *J* = 9.6, 4.0 Hz, 1H), 1.77 (s, 3H), 1.70 (dd, *J* = 6.4, 1.6 Hz, 3H), 1.64 (t, *J* = 3.2 Hz, 1H), 0.11 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.2, 127.9, 127.3, 124.0, 73.8, 70.6, 45.4, 30.8, 24.4, 22.1, 13.5, 0.2; IR (film) 2956, 1616, 1248 cm^{-1}; HRMS (EI) m/e calcd for $C_{14}H_{24}OSi$ 236.1596, found 236.1594 (M^+).



23

((3a*E*, 5*R*, 6S, 7*Z*, 8a*S*)-4,6-dimethyl-3,5,6,8a-tetrahydro-1*H*-cyclohepta[*c*]furan-5-yl)trimethylsilane (23). General procedure was followed using 60 mg (0.4 mmol) of dienyne **20**, 0.4 mL (0.8 mmol, 2.0 M in diethyl ether) of $TMSCHN_2$, 12 mg (0.04 mmol) of $Ni(COD)_2$ to afford 56 mg (60%) of product **23** (d.r. > 95 : 5 as judged by NMR analysis on the purified sample). From thermolysis of divinylcyclopropane: A 1 mL toluene solution of **21** (16 mg, 0.06 mmol) was stirred at 105 ºC for 11 hrs to afford 12 mg (75%) of product **23** (d.r. > 95 : 5 as judged by NMR analysis on the purified sample). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.92 (ddd, *J* = 10.5, 8.5, 3.5 Hz, 1H), 5.44 (dd, *J* = 10.5, 2.0 Hz, 1H), 4.46 (dq, *J* = 12.5, 1.5 Hz, 1H), 4.37 (d, *J* = 12.5 Hz, 1H), 4.11 (t, *J* = 7.5 Hz, 1H), 3.54 (m, 1H), 3.39 (dd, *J* = 12.5, 7.5 Hz, 1H), 2.52 (m, 1H), 1.64 (m, 1H), 1.56 (m, 3H), 1.24 (d, *J* = 7.0 Hz, 3H), 0.03 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.5, 127.1, 126.8, 126.2, 74.2, 72.2, 43.7, 42.4, 34.6, 23.8, 19.3, 0.0; IR (film) 2954, 1653, 1456, 1246, 1055 cm^{-1}; HRMS (EI) m/e calcd for $C_{14}H_{24}OSi$ 236.1596, found 236.1591 (M^+).

Preparation of starting substrates

Starting materials **1b**,[2] **1c** and **1f**,[3] **1d**,[4] **1e**,[5] **1g,**[6] **13a**,[7] **13b**,[8] **13c** and **13d**,[9] were prepared using literature procedures with minor modifications. **1a**, **1h**, **16**, and **20** were prepared and characterized as described below.

4-Methyl-*N*-penta-2,4-dienyl-*N*-prop-2-ynyl-benzenesulfonamide (1a). To a 28 mL THF suspension of NaH (96 mg, 2.4 mmol, 60%) and tetrabutylammonium iodide (75 mg, 0.2 mmol) was added a 2 mL THF solution of 4-methyl-*N*-prop-2-ynyl-benzenesulfonamide (420 mg, 2 mmol) at 0 ºC. The resulting mixture was allowed to warm to rt and stirred at rt for 1 h, then a 2 mL THF solution of 5-chloro-penta-1,3-diene (248 mg, 2.4 mmol) was added dropwise. The final solution was stirred at rt overnight. The reaction mixture was quenched with saturated NH_4Cl. Standard extraction and column chromatography provided 480 mg (87%) of **1a** as a light oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 6.30 (dt, *J* = 16.5, 10.0 Hz, 1H), 6.21 (dd, *J* = 15.0, 10.5 Hz, 1H), 5.56 (dt, *J* = 14.5, 7.0 Hz, 1H), 5.20 (d, *J* = 16.0 Hz, 1H), 5.11 (d, *J* = 10.5 Hz, 1H), 4.07 (d, *J* = 2.5 Hz, 2H), 3.85 (d, *J* = 6.5 Hz, 2H), 2.42 (s, 3H), 2.01 (t, *J* = 2.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.8, 136.2, 136.0, 135.8, 129.7, 128.0, 127.1, 118.7, 76.7, 74.0, 48.2, 36.0, 21.8. IR (film) 3291, 2922, 2121, 1599 cm^{-1}; HRMS (EI) m/e calcd for $C_{15}H_{17}NO_2S$ 275.0980, found 275.0980 (M^+).

1b: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.24 (dt, *J* = 16.5, 10.0 Hz, 1H), 6.13 (dd, *J* = 15.0, 10.0 Hz, 1H), 5.45 (dt, *J* = 15.5, 7.5 Hz, 1H), 5.11 (d, *J* = 16.5 Hz, 1H), 5.00 (d, *J* = 10.5 Hz, 1H), 3.71 (s, 6H), 2.80 (d, *J* = 8.0 Hz, 2H), 2.76 (d, *J* = 2.5 Hz, 2H), 2.01 (t, *J* = 2.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.3, 136.7, 135.9, 127.2, 117.1, 78.9, 71.8, 57.3, 53.0, 35.6, 23.0.

1c: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.35 (m, 1H), 6.29 (m, 1H), 5.76 (dt, *J* = 14.5, 6.5 Hz, 1H), 5.23 (m, 1H), 5.12 (m, 1H), 4.15 (d, *J* = 2.5 Hz, 2H), 4.11 (d, *J* = 7.0 Hz, 2H), 2.44 (t, *J* = 2.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.4, 134.4, 129.2, 118.3, 79.9, 74.7, 69.9, 57.2.

1d: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.26 (dt, *J* = 17.5, 10.5 Hz, 1H), 6.12 (dd, *J* = 15.5, 10.5 Hz, 1H), 5.48 (dt, *J* = 15.0, 7.5 Hz, 1H), 5.13 (d, *J* = 16.5 Hz, 1H), 5.01 (d, *J* = 10.0 Hz, 1H), 3.72 (s, 6H), 2.80 (d, *J* = 7.5 Hz, 2H), 2.72 (q, *J* = 2.5 Hz, 2H), 1.75 (t, *J* = 2.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.7, 136.8, 135.6, 127.7, 116.8, 79.2, 73.4, 57.7, 52.9, 35.7, 23.4, 3.7.

1e: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.34 (m, 1H), 6.27 (m, 1H), 5.76 (dt, *J* = 15.5, 6.2 Hz, 1H), 5.21 (m, 1H), 5.10 (m, 1H), 4.09 (q, *J* = 2.5 Hz, 2H), 4.07 (dd, *J* = 6.5, 1.5 Hz, 2H), 1.85 (t, *J* = 2.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.5, 134.0, 129.6, 118.0, 82.8, 75.3, 69.8, 57.9, 3.8.

1f: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.20 (dd, *J* = 15.0, 10.5 Hz, 1H), 6.03 (ddq, *J* = 15.0, 10.5, 1.5 Hz, 1H), 5.71 (dq, *J* = 15.0, 6.9 Hz, 1H), 5.57 (dt, *J* = 15.3, 6.6 Hz, 1H), 4.10 (d, *J* = 2.4 Hz, 2H), 4.05 (d, *J* = 6.6 Hz, 2H), 2.40 (t, *J* = 2.4 Hz, 1H), 1.73 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.4, 130.9, 130.7, 125.8, 80.0, 74.6, 70.2, 56.9, 18.3.

1g: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.20 (dd, *J* = 15.5, 10.5 Hz, 1H), 6.03 (dd, *J* = 15.6, 10.5 Hz, 1H), 5.69 (dq, *J* = 15.2, 6.5 Hz, 1H), 5.59 (dt, *J* = 15.2, 6.4 Hz, 1H), 4.06 (q, *J* = 2.4 Hz, 2H), 4.03 (d, *J* = 6.4 Hz, 2H), 1.84 (t, *J* = 2.0 Hz, 3H), 1.74 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.1, 131.0, 130.5, 126.2, 82.6, 75.4, 70.1, 57.6, 18.4, 3.9.

(1-But-2-ynyloxy-4-methyl-penta-2,4-dienyl)-benzene (1h). The Wipf procedure[10] was followed to prepare the alcohol **A** (4-methyl-1-phenyl-penta-2,4-dien-1-ol). The procedure of making **1a** was followed using NaH (96 mg, 2.4 mmol), tetrabutylammonium iodide (75 mg, 0.2 mmol), alcohol **A** (350 mg, 2 mmol), 1-bromo-2-butyne (210 μL, 2.4 mmol) to afford 360 mg (80%) of product **1h** as a light oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.25 (m, 5H), 6.37 (d, *J* = 15.5 Hz, 1H), 5.76 (dd, *J* = 15.0, 7.0 Hz, 1H), 5.06 (d, *J* = 7.5 Hz, 1H), 5.00 (s, 2H), 4.12 (dq, *J* = 15.0, 2.5 Hz, 1H), 4.06 (dq, *J* = 15.0, 2.5 Hz, 1H), 1.87 (t, *J* = 2.5 Hz, 3H), 1.84 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.6, 140.9, 135.2, 129.9, 128.7, 128.0, 127.3, 117.6, 82.6, 81.1, 75.4, 56.2, 18.8, 3.9; IR (film) 2919, 2855, 2222, 1609, 1452 cm^{-1}; HRMS (EI) m/e calcd for $C_{15}H_{15}O$ 211.1123, found 211.1124 $(M\text{-}CH_3)^+$.

13a: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.60 (m, 1H), 5.17 (m, 1H), 5.11 (m, 1H), 3.72 (s, 6H), 2.78 (m, 4H), 2.01 (t, *J* = 2.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.3, 131.8, 120.2, 78.9, 71.7, 57.0, 53.0, 36.7, 22.9.

13b: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 5.75 – 5.66 (m, 1H), 5.27 (d, *J* = 17.0 Hz, 1H), 5.22 (d, *J* = 10.5 Hz, 1H), 4.07 (d, *J* = 2.5 Hz, 2H), 3.81 (d, *J* = 6.0 Hz, 2H), 2.40 (s, 3H), 2.00 (t, *J* = 2.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.8, 136.2, 132.1, 129.7, 128.0, 120.2, 76.6, 74.0, 49.2, 36.0, 21.8.

13c: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.79 (dtt, *J* = 15.5, 6.5, 1.5 Hz, 1H), 5.53 (dtt, *J* = 15.5, 6.5, 1.5 Hz, 1H), 4.12 (d, *J* = 2.0 Hz, 2H), 4.01 (dq, *J* = 7.0, 1.0 Hz, 2H), 2.41 (t, *J* = 2.5 Hz, 1H), 2.10 – 2.03 (m, 2H), 1.00 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.7, 124.5, 80.1, 74.4, 70.6, 56.9, 25.5, 13.5.

13d: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.63 (dtt, *J* = 10.5, 7.5, 1.5 Hz, 1H), 5.48 (dtt, *J* = 11.0, 6.5, 1.5 Hz, 1H), 4.13 – 4.11 (m, 4H), 2.42 (t, *J* = 2.5 Hz, 1H), 2.14 – 2.07 (m, 2H), 0.98 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.7, 124.6, 80.1, 74.4, 65.2, 57.1, 21.1, 14.4.

(*E*)-4-((But-2-ynyloxy)methyl)penta-1,3-diene (16). To a 20 mL CH_2Cl_2 solution of carbethoxyethylidene-(triphenylphosphorane) (2.7 g, 7 mmol)) was added dropwise acrolein (0.47 mL, 7 mmol)) at rt. After stirring at rt for 1 h, the reaction mixture was warmed to 38 ºC over 2 h. Most of the solvent was removed by rotary evaporation. The residue was diluted with pentane and then filtered. Condensation and column chromatography (pentane : ethyl ether = 20 : 1) afforded (*E*)-ethyl 2-methylpenta-2,4-dienoate (900 mg, 92%) as a colorless oil. To an 80 mL Et_2O solution of (*E*)-ethyl 2-methylpenta-2,4-dienoate (1.8 g, 12.8 mmol) was added quickly DIBAL-H (38.4 mL,

38.4 mmol, 1.0 M in hexane) at -78 °C. After stirring 5 min at -78 °C, the reaction was quenched with 6 mL saturated NH_4Cl solution and stirred for another 10 min, followed by addition of Et_2O/H_2O and 10 g sodium potassium tartrate. Then the reaction mixture was allowed to warm to rt and stir until it became clear solution. Standard extraction and column chromatography (hexane : ethyl ether = 3 : 1) provided 1.04 g (83%) of (*E*)-2-methylpenta-2,4-dien-1-ol as a light oil. The procedure for preparing **1a** was then followed using (*E*)-2-methylpenta-2,4-dien-1-ol (1.0 g, 10.2 mmol), 1-bromo-2-butyne (1.1 mL, 12.5 mmol), NaH (0.5 g, 12.5 mmol), TBAI (0.37 g, 1 mmol) to generate compound **16** (1.5 g, 99%) as a light oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.57 (dt, *J* = 17.0, 10.5 Hz, 1H), 6.06 (d, *J* = 10.5 Hz, 1H), 5.19 (d, *J* = 17.0 Hz, 1H), 5.10 (d, *J* = 10.0 Hz, 1H), 4.04 (q, *J* = 2.0 Hz, 2H), 3.96 (s, 2H), 1.84 (t, *J* = 2.0 Hz, 3H), 1.77 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 134.9, 132.7, 128.0, 117.4, 82.5, 75.4, 75.2, 57.7, 14.6, 3.8.

(20). To a mixture of *cis*-1-bromo-propene (0.85 mL, 10 mmol) and $Pd(PPh_3)_4$ (20 mg, 0.015 mmol) in 10 mL pyrrolidine was added propargyl alcohol (0.87 mL, 15 mmol) at rt. The resulting mixture was refluxed at 98 °C for 2 h, cooled to rt and then quenched with saturated NH_4Cl solution. Standard extraction and column chromatography (hexane : ethyl ether = 2 : 1) provided 420 mg (45%) of alcohol (*Z*)-hex-4-en-2-yn-1-ol as a light oil. To a suspension of $LiAlH_4$ (190 mg, 5 mmol) in 16 mL Et_2O was added a 4 mL ethyl ether solution of (*Z*)-hex-4-en-2-yn-1-ol (384 mg, 4 mmol) at rt. The resulting mixture was refluxed for 7 h, cooled to 0 °C and then quenched with saturated NH_4Cl solution. Standard extraction and column chromatography (hexane : ethyl ether = 2 : 1) provided 386 mg (98%) of alcohol (2*E*,4*Z*)-hexa-2,4-dien-1-ol as a light oil. The procedure for

preparing **1a** was then followed using (2*E*,4*Z*)-hexa-2,4-dien-1-ol (285 mg, 2.9 mmol), 1-bromo-2-butyne (0.3 mL, 3.6 mmol), NaH (138 mg, 3.6 mmol), TBAI (111 mg, 0.3 mmol) to generate compound **20** (390 mg, 85%) as a light oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.56 (ddd, *J* = 15.5, 11.0, 1.0 Hz, 1H), 6.00 (td, *J* = 10.5, 1.5 Hz, 1H), 5.70 (dt, *J* = 15.0, 6.2 Hz, 1H), 5.51 (m, 1H), 4.10 – 4.07 (m, 4H), 1.84 (t, *J* = 2.0 Hz, 3H), 1.74 (dd, *J* = 7.5, 1.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 128.8, 128.7, 128.5, 127.3, 82.7, 75.4, 70.2, 57.8, 13.6, 3.8.

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YN-IV-86B

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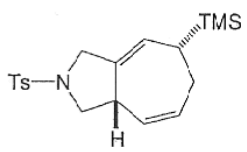

29

Unity 500 spectrometer

YN-IV-152

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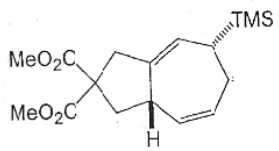

2b

Unity 500 spectrometer

YN-IV-102

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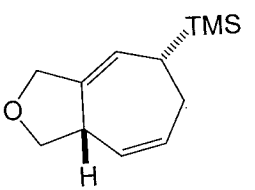

2c

YN-IV-114

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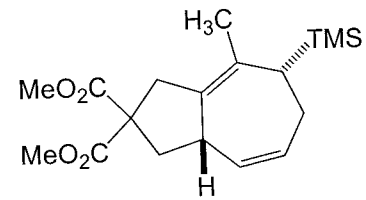

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Mercury 400 spectrometer

YN-IV-126

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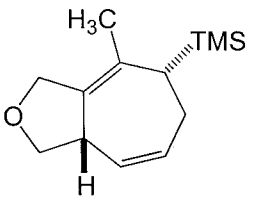

2e

YN-IV-130-C6D6-TEMP=55c-MAY2104

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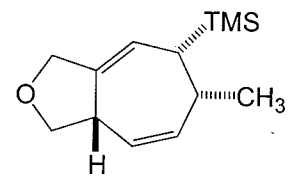

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YN-IV-132

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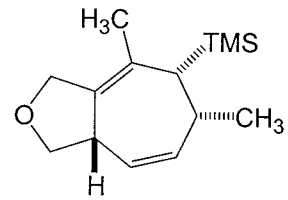

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Unity 500 spectrometer

YN-IV-137

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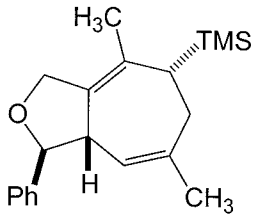

2h

Unity 500 spectrometer

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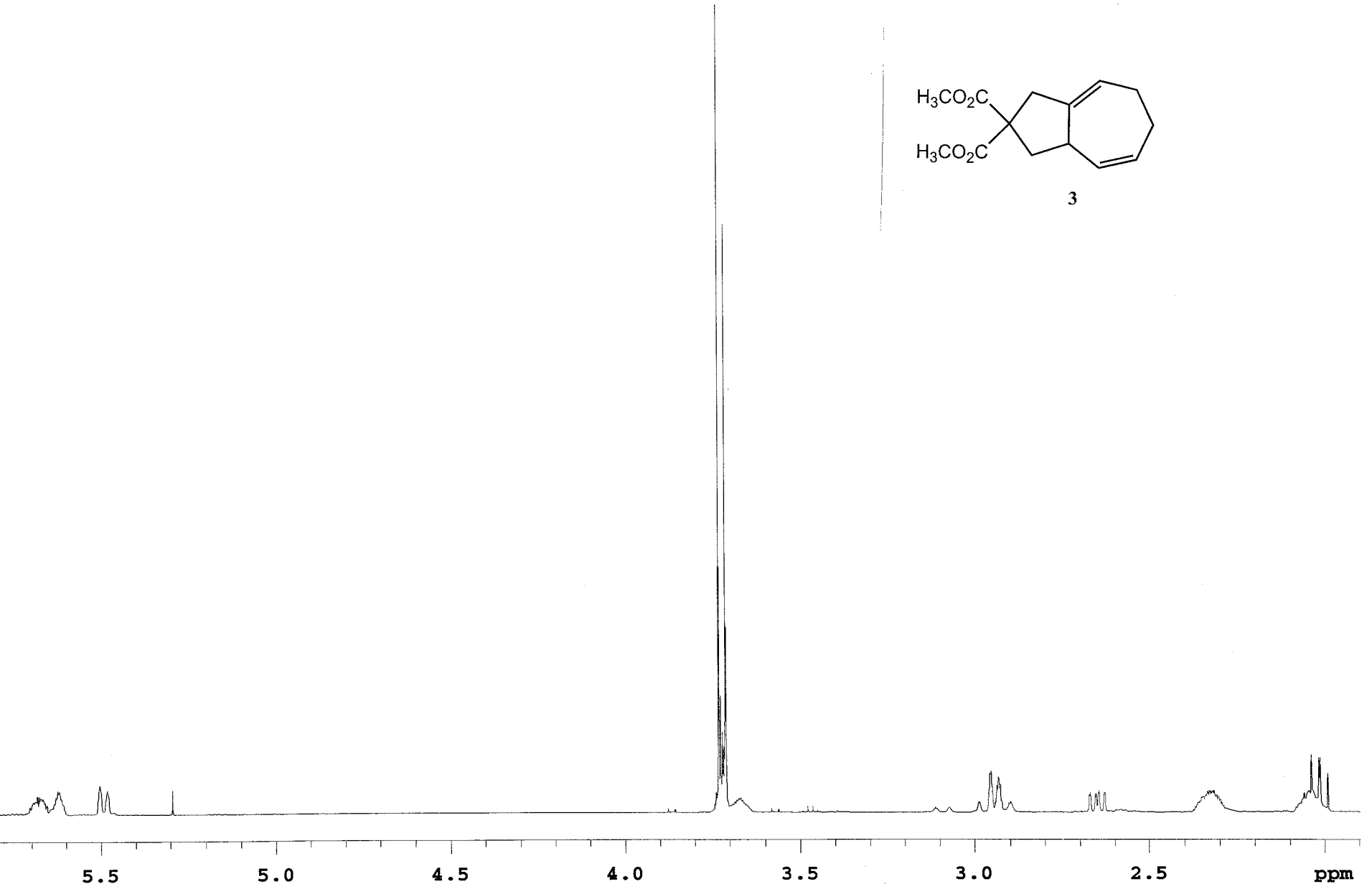

3

Unity 500 spectrometer

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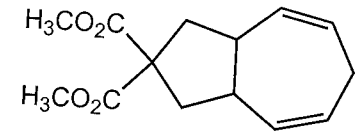

4

YN-IV-197

Mercury 400 spectrometer

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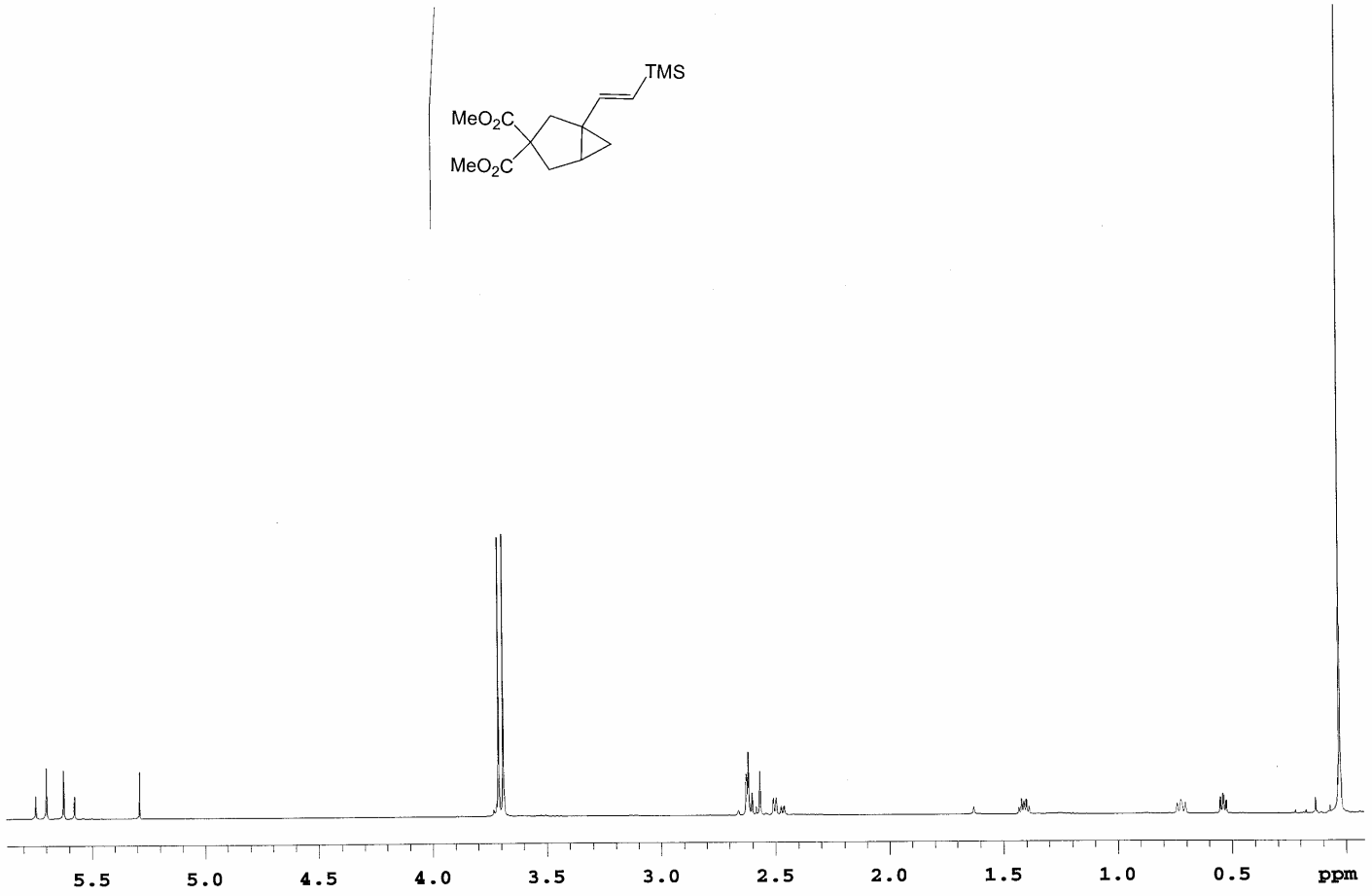

YN-III-278

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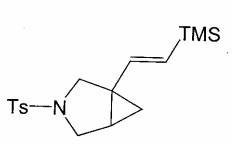

YN-IV-198

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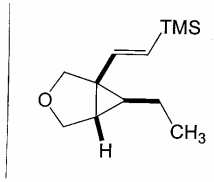

YN-IV-200

Mercury 400 spectrometer

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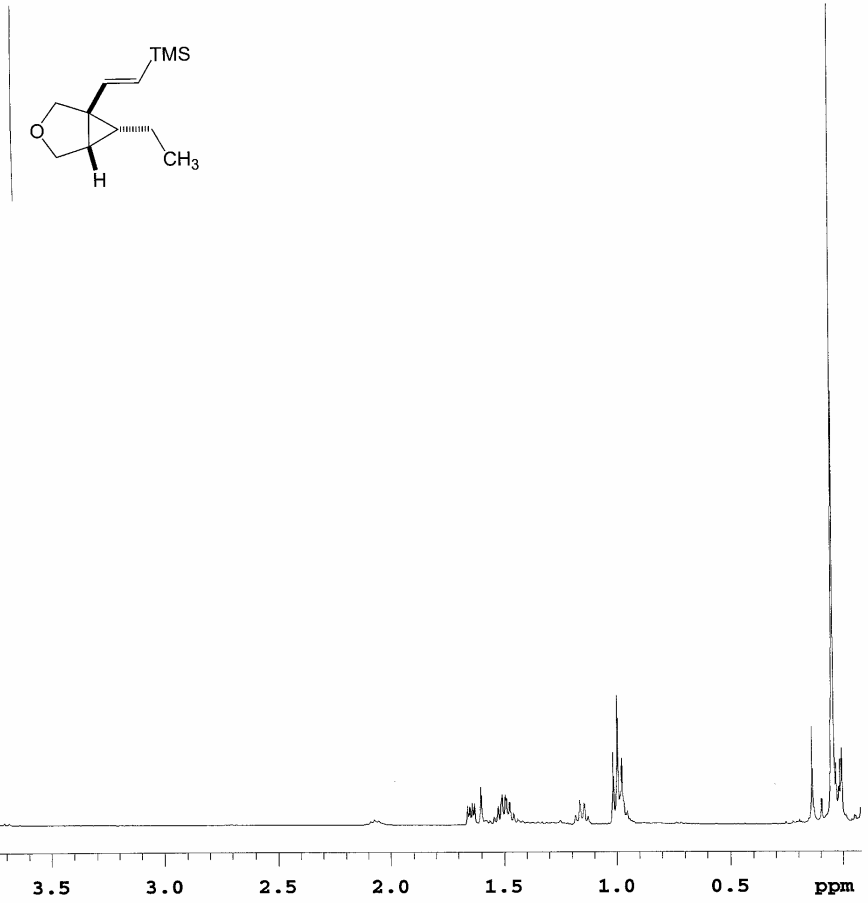

YN-IV-181-C6D6

Unity 500 spectrometer

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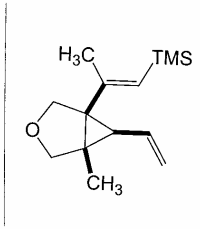

YN-IV-146B-PROTON

Pulse Sequence: s2pul

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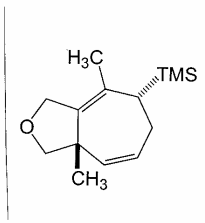

YN-IV-189

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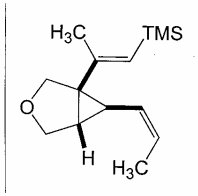

YN-IV-191

Unity 500 spectrometer

Pulse Sequence: s2pul