Supporting Information

Re(I)-Catalyzed Hydropropargylation of Silyl Enol Ethers Utilizing Dynamic Interconversion of Vinylidene-Alkenylmetal Intermediates via 1,5-Hydride Transfer

Nobuharu Iwasawa,* Shoya Watanabe, Akane Ario, Hideyuki Sogo

Department of Chemistry, School of Science, Tokyo Institute of Technology,
O-okayama, Meguro-ku, Tokyo 152-8551, Japan

1. General

All reactions were performed under nitrogen atmosphere. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL ECX-500 (500 MHz for ^{1}H and 125 MHz for ^{13}C) or ECZ-500 (500 MHz for ^{1}H and 125 MHz for ^{13}C) or ECS-400 (400 MHz for ^{1}H and 100 MHz for ^{13}C) spectrometer using $CDCl_3$ (^{13}C, δ = 77.0) as internal standards. IR spectra were recorded on an FT/IR-460 plus (JASCO Co., Ltd.). High-resolution mass analyses (FD^+) were performed on a JEOL JMS-T100 GCV mass spectrometer. Single crystals were immersed in immersion oil on micromount and transferred to a Rigaku Varimax with Saturn system equipped with a Rigaku GNNP low temperature device. Gel permeation chromatography (GPC) was performed using LC-918 series (Japan Analytical Industry Co., Ltd.). Silica Gel 60 (Kanto Chemical Co., Inc.) was used for flash column chromatography. Merck Aluminium Oxide 90 (active neutral) was used for alumina flash column chromatography. Merck Kieselgel 60 F_{254} (0.25 mm thickness, coated on glass 20 x 20 cm^2) plate was used for analytical thin layer chromatography (TLC), and Wakogel B-5F coated on glass (20 x 20 cm^2) in a thickness of 0.9 mm was used for preparative TLC.

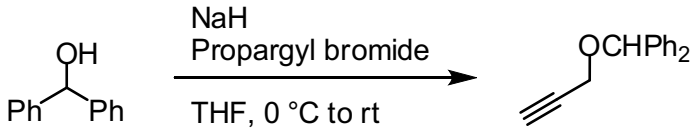
2. Reagents

Reagents were used as received without further purification, unless otherwise noted. TIPSOTf and triethylamine were purified by distillation over CaH_2. THF, Et_2O, and toluene were purified by solvent purification system of Glass-Contour. Dehydrated 1,4-dioxane was purchased from Kanto Chemical Co., Inc. and was dried over molecular sieves. Dehydrated dichloromethane was purchased from Kanto Chemical Co., Inc. and other solvents were distilled according to the standard procedures and stored over molecular sieves. $ReI(CO)_5$ was prepared according to literature procedure[1] and was recrystallized from acetone/hexane.

3. Experimental Procedure and Physical Data

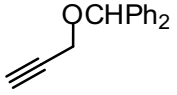
・Intermolecular hydropropargylation reaction

Synthesis of propargyl ether 1.



1

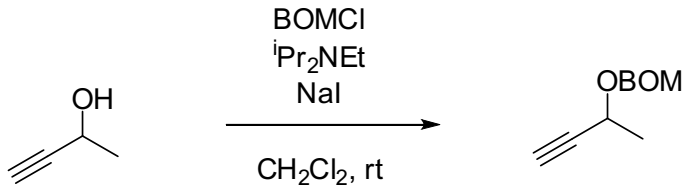
To a THF suspension (30 ml) of sodium hydride (60%, 1.4 g, 36 mmol, 1.2 equiv.) was added a THF solution (30 ml) of benzhydrol (5.5 g, 30 mmol, 1.0 equiv.) at 0 °C and the mixture was stirred at the same temperature for 30 min. Tetrabutylammonium iodide (550 mg, 1.5 mmol, 5 mol%) and propargyl bromide (2.7 ml, 36 mmol, 1.2 equiv.) were added slowly to the reaction mixture at 0 °C and the resulting mixture was stirred at room temperature for 5 h. The reaction mixture was quenched with sat. aqueous NH_4Cl and the aqueous layer was extracted with ethyl acetate three times. The combined organic layer was washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure. The crude material was purified by silica-gel flash column chromatography (ethyl acetate/hexane = 1/19) to give propargyl ether **1** as a yellow oil in 94% yield (6.3 g, 28 mmol).



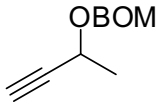
1

IR (neat) 3290, 3061, 3029, 2116, 1600, 1494, 1451, 1068, 1027, 742, 700 cm^{-1};
^{1}H NMR ($CDCl_3$, 500 MHz) δ = 2.49 (t, J = 2.8 Hz, 1H), 4.20 (d, J = 2.8 Hz, 2H), 5.72 (s, 1H), 7.29-7.43 (m, 10H);
^{13}C NMR ($CDCl_3$, 125 MHz) δ = 55.7, 74.5, 79.7, 81.6, 127.2, 127.6, 128.4, 141.1
HRMS (FD^+): m/z calcd for $[M]^+$ $[C_{16}H_{14}O]^+$ 222.1045, found 222.1046.

Synthesis of BOM ether of 3-butyn-2-ol

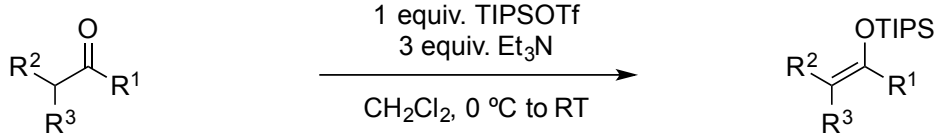


To a dichloromethane solution (5 ml) of NaI (15 mg, 0.10 mmol, 5.0 mol%), 3-butyn-2-ol (0.16 ml, 2.0 mmol, 1.0 equiv.), and *N,N*-diisopropylethylamine (0.69 ml, 4.0 mmol, 2.0 equiv.) was added benzyl chloromethyl ether (0.33 ml, 2.4 mmol, 1.2 equiv.) at room temperature, and the mixture was stirred at the same temperature for 8 h. The reaction mixture was quenched with water and the aqueous layer was extracted with diethyl ether three times. The combined organic layer was washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure. The crude material was purified by silica-gel flash column chromatography (ethyl acetate/hexane = 1/9) and GPC (AcOEt) to give BOM ether of 3-butyn-2-ol as a colorless oil in 39% yield (150 mg, 0.79 mmol).



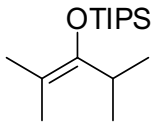
IR (neat) 3292, 2890, 2112, 1452,1378, 1176, 1038, 740, 664;
^{1}H NMR ($CDCl_3$, 500 MHz) δ = 1.46 (d, *J* = 6.5 Hz, 3H), 2.42 (d, *J* = 2.5 Hz, 1H), 4.52 (dq, *J* = 6.5, 2.0 Hz, 1H), 4.60 (d, *J* = 12.0 Hz, 1H), 4.67 (d, *J* = 12.5 Hz, 1H), 4.79 (d, *J* = 7.0 Hz, 1H), 5.02 (d, *J* = 7.0 Hz, 1H), 7.28-7.37 (m, 5H);
^{13}C NMR ($CDCl_3$, 125 MHz) δ = 21.9, 61.4, 69.8, 72.9, 83.3, 92.3, 127.7, 127.9, 128.4, 137.7;
HRMS (FD^+): m/z calcd for $[M]^+$ $[C_{12}H_{14}O_2]^+$ 190.09938, found 190.09888.

General procedure for the synthesis of silyl enol ethers 2a, 2c, 2i, 2k, 2n, and 2o.



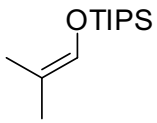
To a mixture of ketone (1.0 equiv.) and Et_3N (3.0 equiv.) in CH_2Cl_2 (0.5 M) was added TIPSOTf (1.0 equiv.) at 0 ºC. After the mixture was stirred at room temperature overnight, the reaction was quenched with sat. aqueous $NaHCO_3$, and the organic materials were extracted with Et_2O three times. The combined organic extracts were washed with brine and dried over anhydrous magnesium sulfate. After the filtration of the drying agent, the filtrate was evaporated, and the crude product was purified by flash column chromatography (hexane) using neutral alumina containing 5% H_2O to give the corresponding silyl enol ether.

2b[2], **2d**[3], **2e**[3], **2f**[4], **2g**[3], **2h**[5], **2j**[3], and **2l**[4] were reported in the literature.



2a

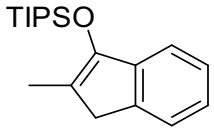
a colorless oil (413 mg, 1.53 mmol, 76%).
IR (neat) 2964, 2946, 2894, 2868, 1667, 1466, 1387, 1362, 1264, 1207, 1169, 1077, 883, 679 cm^{-1};
^{1}H NMR ($CDCl_3$, 500 MHz) δ = 1.06 (d, *J* = 7.7 Hz, 6H), 1.10 (d, *J* = 7.7 Hz, 18H), 1.12-1.25 (m, 3H), 1.58 (s, 3H), 1.61 (s, 3H), 2.71 (septet, *J* = 7.7 Hz, 1H);
^{13}C NMR ($CDCl_3$, 125 MHz) δ =14.1, 18.3, 18.8, 19.2, 20.5, 31.0, 104.9, 149.7;
HRMS (FD^+): m/z calcd for $[M]^+$ $[C_{16}H_{34}OSi]^+$ 270.2379, found 270.2373.



2c

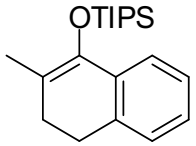
a colorless oil (668 mg, 2.92 mmol, 75%).

IR (neat) 2945, 2893, 2868, 2724, 1684, 1464, 1385, 1179, 994, 882, 815, 686 cm^{-1};
^{1}H NMR ($CDCl_3$, 500 MHz) δ = 1.07 (d, *J* = 6.9 Hz, 18H), 1.09-1.22 (m, 3H), 1.52 (s, 3H), 1.61 (s, 3H), 6.11-6.14 (m, 1H);
^{13}C NMR ($CDCl_3$, 125 MHz) δ = 12.0, 14.7, 17.8, 19.3, 112.4, 134.0;
HRMS (FD^+): m/z calcd for $[M]^+$ $[C_{13}H_{28}OSi]^+$ 228.1909, found 228.1907.



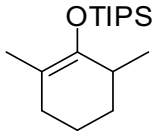
2i

a colorless oil (381 mg, 1.26 mmol, 95%).
IR (neat) 3070, 3046, 3024, 2945, 2892, 2867, 1634, 1464, 1385, 1359, 1176, 996, 883, 860, 685 cm^{-1};
^{1}H NMR ($CDCl_3$, 500 MHz) δ = 1.14 (d, *J* = 7.2 Hz, 18H), 1.23-1.34 (m, 3H), 2.01 (s, 3H), 3.16 (s, 2H), 7.11 (dt, *J* = 1.2, 7.2 Hz, 1H), 7.21-7.31 (m, 3H);
^{13}C NMR ($CDCl_3$, 125 MHz) δ = 12.5, 13.6, 18.0, 38.5, 117.2, 118.4, 123.2, 123.9, 125.9, 140.8, 143.0, 148.2;
HRMS (FD^+): m/z calcd for $[M]^+$ $[C_{19}H_{30}OSi]^+$ 302.2066, found 302.2071.



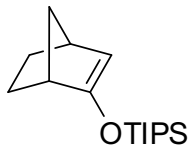
2k

a colorless oil (643 mg, 2.03 mmol, 97%).
IR (neat) 3067, 3023, 2941, 2891, 2865, 1647, 1462, 1299, 1186, 1152, 1089, 884, 794, 663 cm^{-1};
^{1}H NMR ($CDCl_3$, 500 MHz) δ = 1.10 (d, *J* = 7.5 Hz, 18H), 1.18-1.28 (m, 3H), 1.85 (s, 3H), 2.21 (t, *J* = 7.8 Hz, 2H), 2.69 (t, *J* = 7.8 Hz, 2H), 7.05-7.11 (m, 2H), 7.13-7.19 (m, 1H), 7.39 (d, *J* = 7.8 Hz, 1H);
^{13}C NMR ($CDCl_3$, 125 MHz) δ = 13.8, 17.4, 18.0, 28.2, 29.5, 116.0, 121.2, 125.9, 126.0, 126.5, 134.9, 135.9, 143.6;
HRMS (FD^+): m/z calcd for $[M]^+$ $[C_{20}H_{32}OSi]^+$ 316.2222, found 316.2227.



2n

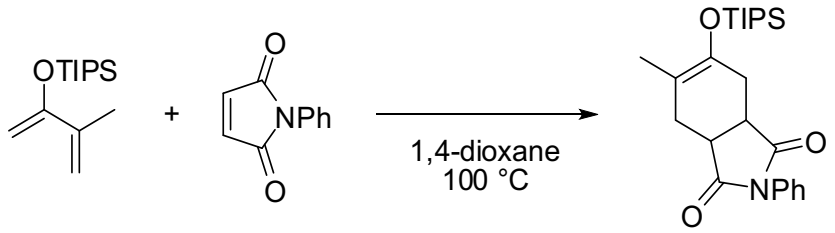
a colorless oil (423 mg, 1.50 mmol, 75%).
IR (neat) 2930, 2867, 1680, 1465, 1380, 1345, 1242, 1176, 1070, 997, 921, 884, 791, 678 cm^{-1};
^{1}H NMR ($CDCl_3$, 500 MHz) δ = 1.05-1.21 (m, 24H), 1.40-1.52 (m, 2H), 1.56-1.67 (m, 1H), 1.59 (s, 3H), 1.67-1.78 (m, 1H), 1.84-2.01 (m, 2H), 2.18 (br s, 1H);
^{13}C NMR ($CDCl_3$, 125 MHz) δ = 13.4, 17.1, 18.09, 18.14, 18.9, 19.3, 30.9, 31.4, 33.9, 110.5, 147.8;
HRMS (FD^+): m/z calcd for $[M]^+$ $[C_{17}H_{34}OSi]^+$ 282.2379, found 282.2375.



2o

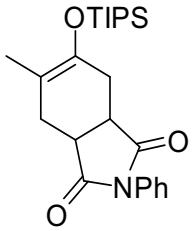
a colorless oil (455 mg, 1.71 mmol, 85%).
IR (neat) 3078, 2961, 2946, 2893, 2868, 1612, 1468, 1334, 1231, 1147, 1110, 896, 883, 808, 687 cm^{-1};
^{1}H NMR ($CDCl_3$, 500 MHz) δ = 1.00-1.10 (m, 19H), 1.11-1.22 (m, 4H), 1.26-1.34 (m, 1H), 1.44-1.49 (m, 1H), 1.59-1.73 (m, 2H), 2.54-2.58 (m, 1H), 2.72-2.76 (m, 1H), 4.63 (d, *J* = 3.2 Hz, 1H);
^{13}C NMR ($CDCl_3$, 125 MHz) δ = 12.5, 17.87, 17.90, 24.7, 27.8, 40.9, 45.8, 47.0, 104.5, 161.6;
HRMS (FD^+): m/z calcd for $[M]^+$ $[C_{16}H_{30}OSi]^+$ 266.2066, found 266.2072.

Synthesis of silyl enol ether 2m.



2m

A 1,4-dioxane solution (1.5 ml) of 2-triisopropylsiloxy-3-methyl-1,3-butadiene[6] (242 mg, 1.0 mmol, 1.0 equiv.) and N-phenylmaleimide (208 mg, 1.2 mmol, 1.2 equiv.) was heated for 17 h at 100 ºC. The reaction mixture was concentrated under reduced pressure in vacuo. The crude product was purified by silica gel column chromatography (ethyl acetate : hexane = 25 : 75) to give the silyl enol ether **2m** in 76% yield (314 mg, 0.759 mmol) as a white solid.

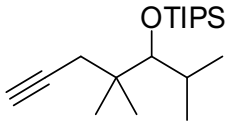


2m

IR (neat) 2944, 2868, 1713, 1679, 1598, 1498, 1461, 1379, 1196, 882, 689 cm^{-1};
^{1}H NMR ($CDCl_3$, 500 MHz) δ = 1.05-1.10 (m, 18H), 1.10-1.22 (m, 3H), 1.69 (s, 3H), 2.40 (dd, *J* = 6.9, 14.9 Hz, 1H), 2.49-2.58 (m, 2H), 2.65 (dd, *J* = 2.3, 15.5 Hz, 1H), 3.16 (ddd, *J* = 3.5, 6.9, 9.2 Hz, 1H), 3.28 (ddd, *J* = 2.9, 8.0, 9.2 Hz, 1H), 7.22-7.26 (m, 2H), 7.34-7.40 (m, 1H), 7.42-7.48 (m, 2H);
^{13}C NMR ($CDCl_3$, 125 MHz) δ = 13.1, 16.3, 17.92, 17.94, 29.5, 29.8, 39.4, 40.5, 108.7, 126.3, 128.4, 129.0, 132.1, 142.8, 178.7, 179.0;
HRMS (FD^+): m/z calcd for $[M]^+$ $[C_{24}H_{35}NO_3Si]^+$ 413.2386, found 413.2391.

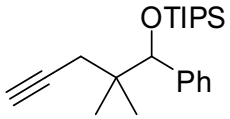
General procedure for hydropropargylation of silyl enol ethers.

A mixture of $ReI(CO)_5$ (1.7 mg, 0.0038 mmol, 3.1 mol%), propargyl ether **1** (0.15 mmol, 1.25 equiv.), and silyl enol ether (0.12 mmol, 1.0 equiv.) in 1,4-dioxane (1.5 mL) was stirred for 10 h at 100 ºC. The reaction mixture was quenched with TMEDA (0.2 ml) and the reaction mixture was concentrated under reduced pressure in vacuo. The crude product was purified by preparative TLC or silica gel column chromatography to give the product.



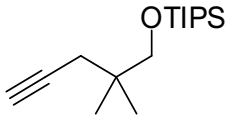
3a

The crude product was purified by silica gel column chromatography (hexane) to give the title compound **3a** as a colorless oil in 85% yield (32.0 mg, 0.103 mmol).
IR (neat) 3313, 2965, 2946, 2892, 2869, 2117, 1466, 1388, 1366, 1119, 1056, 883, 812, 676 cm^{-1};
^{1}H NMR ($CDCl_3$, 500 MHz) δ = 0.94 (d, *J* = 6.9 Hz, 3H), 1.00-1.05 (m, 9H), 1.09-1.17 (m, 21H), 1.93-2.02 (m, 2H), 2.19 (dd, *J* = 2.9, 16.6 Hz, 1H), 2.25 (dd, *J* = 2.6, 16.6 Hz, 1H), 3.64 (d, *J* = 2.0 Hz, 1H);
^{13}C NMR ($CDCl_3$, 125 MHz) δ = 13.8, 18.2, 18.62, 18.64, 22.9, 23.7, 24.1, 29.8, 30.8, 39.9, 70.0, 82.96, 83.02;
HRMS (FD^+): m/z calcd for $[M-^iPr]^+$ $[C_{16}H_{31}OSi]^+$ 267.2144, found 267.2148.



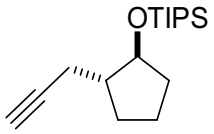
3b

$ReI(CO)_5$ (3.4 mg, 0.0075 mmol, 5.0 mol%), propargyl ether **1** (67.1 mg, 0.30 mmol, 2.0 equiv.), and silyl enol ether **2b** (45.5 mg, 0.15 mmol, 1.0 equiv.) were used. The crude product was purified by silica gel column chromatography (CH_2Cl_2 : hexane = 3 : 97) to give the title compound **3b** as a colorless oil in 96% yield (49.6 mg, 0.144 mmol).
IR (neat) 3311, 3063, 3030, 2944, 2867, 2116, 1603, 1464, 1385, 1247, 1198, 1096, 1064, 882, 822, 705, 680, 633 cm^{-1};
^1H NMR ($CDCl_3$, 500 MHz) δ = 0.90 (s, 3H), 0.97 (s, 21H), 1.04 (s, 3H), 2.02 (t, *J* = 3.0 Hz, 1H), 2.08 (dd, *J* = 3.0, 17.0 Hz, 1H), 2.25 (dd, *J* = 3.0, 17.0 Hz, 1H), 4.72 (s, 1H), 7.20-7.36 (m, 5H);
^{13}C NMR ($CDCl_3$, 125 MHz) δ = 12.8, 18.1, 22.7, 23.1, 29.0, 39.6, 70.4, 81.0, 82.9, 127.17, 127.19, 128.2, 141.9;
HRMS (FD^+): m/z calcd for $[M]^+$ $[C_{22}H_{36}OSi]^+$ 344.2535, found 344.2544.



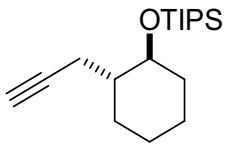
3c

The crude product was purified by silica gel column chromatography (hexane) to give the title compound **3c** as a colorless oil in 62% yield (20.1 mg, 0.075 mmol).
IR (neat) 3313, 2945, 2867, 2724, 2118, 1467, 1389, 1251, 1105, 999, 882, 809, 683 cm^{-1};
^1H NMR ($CDCl_3$, 500 MHz) δ = 0.96 (s, 6H), 1.03-1.11 (m, 21H), 1.94 (t, *J* = 2.9 Hz, 1H), 2.17 (d, *J* = 2.9 Hz, 2H), 3.44 (s, 2H);
^{13}C NMR ($CDCl_3$, 125 MHz) δ = 12.0, 18.0, 18.1, 23.7, 28.1, 36.0, 69.5, 70.9, 82.8;
HRMS (FD^+): m/z calcd for $[M+H]^+$ $[C_{16}H_{33}OSi]^+$ 269.2301, found 269.2294.

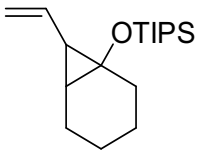


3d

The crude product was purified by silica gel column chromatography (CH_2Cl_2 : hexane = 3 : 97) to give the title compound (a single isomer) as a colorless oil containing unidentified product (ca. 6%, likely a mixture of vinylcyclopropanes) in 86% yield (29.0 mg, 0.103 mmol). The stereochemistry of the product was determined by comparing spectral data of the desilylated compound with literature values.[7]
IR (neat) 3313, 2959, 2944, 2893, 2867, 2119, 1464, 1383, 1368, 1247, 1123, 1053, 882, 680, 634 cm^{-1};
^1H NMR ($CDCl_3$, 500 MHz) δ = 1.06 (s, 21H), 1.34-1.43 (m, 1H), 1.53-1.63 (m, 2H), 1.69-1.79 (m, 1H), 1.79-1.88 (m, 1H), 1.88-2.03 (m, 3H), 2.16 (ddd, *J* = 3.0, 7.0, 16.5 Hz, 1H), 2.29 (ddd, *J* = 3.0, 6.0, 16.5 Hz, 1H), 4.03 (q, *J* = 5.5 Hz, 1H);
^{13}C NMR ($CDCl_3$, 125 MHz) δ = 12.3, 18.07, 18.10, 21.4, 21.6, 28.2, 34.6, 47.0, 68.7, 77.8, 83.3;
HRMS (FD^+): m/z calcd for $[M+H]^+$ $[C_{17}H_{33}OSi]^+$ 281.2301, found 281.2308.

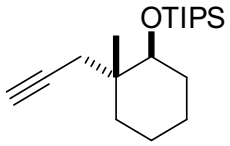


3e

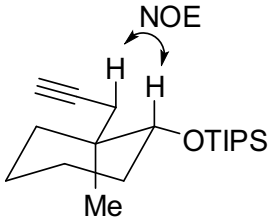


4e

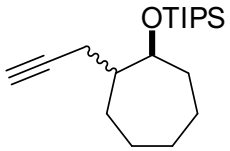
The crude product was purified by silica gel column chromatography (CH_2Cl_2 : hexane = 3 : 97) to give the title compound **3e** as a colorless oil containing a trace amount of vinylcyclopropane **4e** in 87% yield (30.8 mg, 0.105 mmol). Diastereomer ratio of **3e** was determined by ^1H-NMR (d.r. = 91 : 9). The stereochemistry of the major isomer was determined by comparing spectral data of the desilylated compound with literature values.[8]
IR (neat) 3313, 2939, 2866, 2118, 1464, 1385, 1367, 1247, 1102, 883, 678 cm^{-1};
^1H NMR ($CDCl_3$, 500 MHz) δ = 1.02-1.13 (m, 21H), 1.13-1.80 (m, 7H), 1.87-1.99 (m, 3H), 2.09-2.17 (m, 0.09H), 2.25 (ddd, *J* = 2.5, 7.5, 16.5 Hz, 0.91H), 2.33-2.40 (m, 0.09H), 2.53 (ddd, *J* = 3.0, 4.0, 16.5 Hz, 0.91H), 3.51 (dt, *J* = 4.0, 9.5 Hz, 0.91H), 4.06-4.11 (m, 0.09H);
^{13}C NMR ($CDCl_3$, 125 MHz) δ = 12.9, 18.2, 18.3, 21.7, 24.7, 25.1, 29.6, 35.6, 44.4, 69.2, 74.1, 83.5;
HRMS (FD^+): m/z calcd for $[M+H]^+$ $[C_{18}H_{35}OSi]^+$ 295.2457, found 295.2463.



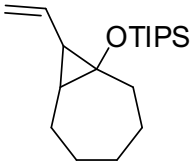
3f



The crude product was purified by silica gel column chromatography (CH_2Cl_2 : hexane = 3 : 97) to give the title compound as a colorless oil in 90% yield (33.3 mg, 0.108 mmol) as a single isomer. The stereochemistry of the product was determined by the coupling constant of C*H*-OTIPS (3.68 ppm, dd, *J* = 4.5, 11.5 Hz) and NOE as shown above.
IR (neat) 3313, 2940, 2867, 2116, 1463, 1383, 1244, 1105, 882, 676, 636 cm^{-1};
^{1}H NMR ($CDCl_3$, 500 MHz) δ = 0.94 (s, 3H), 1.07 (s, 21H), 1.16-1.29 (m, 1H), 1.29-1.62 (m, 5H), 1.63-1.76 (m, 2H), 1.97 (t, *J* = 3.0 Hz, 1H), 2.27 (d, *J* = 2.0 Hz, 2H), 3.68 (dd, *J* = 4.5, 11.5 Hz, 1H);
^{13}C NMR ($CDCl_3$, 125 MHz) δ = 13.0, 17.0, 18.27, 18.33, 21.2, 24.7, 30.6, 31.2, 35.1, 39.3, 70.2, 75.6, 82.7;
HRMS (FD^+): m/z calcd for $[M-^iPr]^+$ $[C_{16}H_{29}OSi]^+$ 265.1988, found 265.1982.



3g

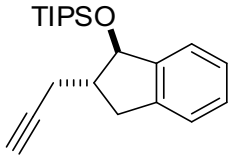


4g

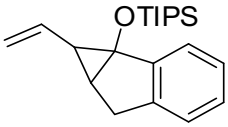
The crude product was purified by silica gel column chromatography (CH_2Cl_2 : hexane = 3 : 97) to give the title compound **3g** as a colorless oil containing a trace amount of vinylcyclopropane **4g** in 88% yield (32.5 mg, 0.105 mmol). Diastereomer ratio of **3g** was determined by ^{1}H-NMR (d.r. = 67 : 33). These compounds were separated by GPC (AcOEt). The stereochemistry of the major isomer was determined by comparing spectral data of the compound **S1** with literature values (see page S11).

3g-major (a colorless oil)
IR (neat) 3313, 2929, 2866, 2117, 1463, 1384, 1365, 1246, 1101, 1065, 882, 677 cm^{-1};
^{1}H NMR ($CDCl_3$, 500 MHz) δ = 1.07 (s, 21H), 1.32-1.53 (m, 4H), 1.61-1.83 (m, 7H), 1.92 (t, *J* = 2.7 Hz, 1H), 2.24 (ddd, *J* = 2.6, 7.8, 16.6 Hz, 1H), 2.39 (ddd, *J* = 2.6, 7.2, 16.6 Hz, 1H), 3.81 (dt, *J* = 2.6, 7.2 Hz, 1H);
^{13}C NMR ($CDCl_3$, 125 MHz) δ = 12.8, 18.2, 18.3, 21.6, 23.4, 26.0, 28.6, 35.2, 46.6, 68.8, 75.8, 83.9;
HRMS (FD^+): m/z calcd for $[M+H]^+$ $[C_{19}H_{37}OSi]^+$ 309.2614, found 309.2614.

3g-minor (a colorless oil)
IR (neat) 3312, 2940, 2866, 2118, 1462, 1383, 1366, 1246, 1090, 882, 678 cm^{-1};
^{1}H NMR ($CDCl_3$, 500 MHz) δ = 1.07 (s, 21H), 1.38-1.59 (m, 5H), 1.59-1.80 (m, 5H), 1.81-1.89 (m, 1H), 1.93 (t, *J* = 2.6 Hz, 1H), 2.13 (ddd, *J* = 2.6, 8.9, 16.6 Hz, 1H), 2.42 (ddd, *J* = 2.6, 6.3, 16.6 Hz, 1H), 4.12-4.17 (m, 1H);
^{13}C NMR ($CDCl_3$, 125 MHz) δ = 12.8, 18.2, 18.3, 21.8, 22.9, 25.4, 27.2, 27.8, 35.9, 44.6, 68.5, 73.6, 84.9;
HRMS (FD^+): m/z calcd for $[M+H]^+$ $[C_{19}H_{37}OSi]^+$ 309.2614, found 309.2614.



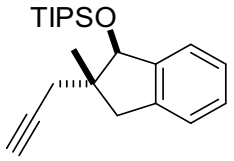
3h



4h

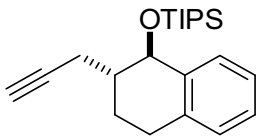
The crude product was purified by preparative TLC (TLC plate was deactivated by treatment with hexane containing 0.5% Et_3N before use, CH_2Cl_2 : hexane = 20 : 80) to give the title compound **3h** as a single isomer along with vinylcyclopropane **4h** (**3h** : **4h** = 88 : 12) as a colorless oil in 78% yield (30.6 mg, 0.093 mmol). The ratio of these compounds was determined by ^{1}H-NMR. C*H*=CH_2 of **4h**: 5.82 (dt, *J* = 9.8, 16.9 Hz) and C*H*=CH_2 of the other isomer of **4h**: 4.68-4.76 (m). The stereochemistry of the product was determined by X-ray crystal structure analysis of the desilylated compound **S2** (see page S11).
IR (neat) 3311, 3072, 3027, 2944, 2893, 2866, 2119, 1462, 1123, 1089, 1065, 882, 743, 679 cm^{-1};

^{1}H NMR ($CDCl_3$, 500 MHz) δ = 1.09-1.24 (m, 21H), 2.00 (t, J = 2.6 Hz, 1H), 2.34-2.47 (m, 2H), 2.47-2.56 (m, 1H), 2.75 (dd, J = 6.6, 15.8 Hz, 1H), 3.17 (dd, J = 7.5, 15.8 Hz, 1H), 5.19 (d, J = 5.2 Hz, 1H), 7.18-7.25 (m, 3H), 7.33-7.39 (m, 1H);
^{13}C NMR ($CDCl_3$, 125 MHz) δ = 12.9, 18.3, 21.2, 35.0, 48.4, 70.2, 80.2, 82.5, 124.7, 124.9, 126.5, 127.9, 141.6, 144.8;
HRMS (FD$^+$): m/z calcd for $[M]^+$ $[C_{21}H_{32}OSi]^+$ 328.2222, found 328.2229.

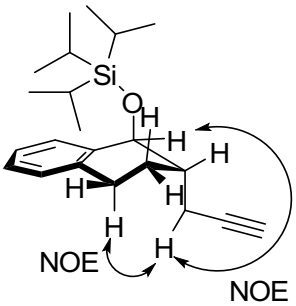


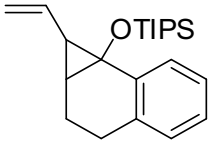
3i

The crude product was purified by preparative TLC (TLC plate was deactivated by treatment with hexane containing 0.5% Et_3N before use, CH_2Cl_2 : hexane = 10 : 90) to give the title compound as a colorless oil in 86% yield (35.1 mg, 0.102 mmol) as a single isomer. The stereochemistry of the product was determined by X-ray crystal structure analysis of the desilylated compound **S3** (see page S12).
IR (neat) 3311, 3072, 3026, 2961, 2944, 2895, 2867, 2118, 1462, 1135, 1106, 1091, 1066, 882, 837, 739, 678, 635 cm^{-1};
^{1}H NMR ($CDCl_3$, 500 MHz) δ = 1.03 (s, 3H), 1.09 (d, J = 6.6 Hz, 9H), 1.13 (d, J = 6.6 Hz, 9H), 1.13-1.23 (m, 3H), 2.05 (t, J = 2.6 Hz, 1H), 2.29 (dd, J = 2.6, 16.9 Hz, 1H), 2.37 (dd, J = 2.6, 16.9 Hz, 1H), 2.71 (d, J = 15.5 Hz, 1H), 2.93 (d, J = 15.5 Hz, 1H), 5.21 (s, 1H), 7.14-7.21 (m, 3H), 7.30-7.35 (m, 1H);
^{13}C NMR ($CDCl_3$, 125 MHz) δ = 13.3, 18.3, 18.4, 19.9, 28.2, 41.8, 49.0, 71.2, 81.0, 82.4, 124.6, 125.0, 126.2, 127.5, 140.9, 144.8;
HRMS (FD$^+$): m/z calcd for $[M+H]^+$ $[C_{22}H_{35}OSi]^+$ 343.2457, found 343.2466.



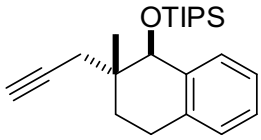
3j



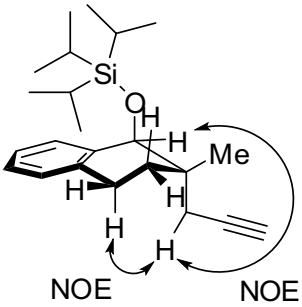


4j

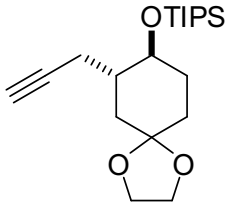
The crude product was purified by silica gel column chromatography (CH_2Cl_2 : hexane = 3 : 97) to give the title compound **3j** as a single isomer along with vinylcyclopropane **4j** (**3j** : **4j** = 90 : 10) as a colorless oil in 89% yield (36.7 mg, 0.107 mmol). The ratio of these compounds was determined by ^{1}H-NMR. C*H*=CH_2 of **4j**: 5.90 (dt, J = 9.2, 17.5 Hz). The stereochemistry of the product was determined by NOE as shown above.
IR (neat) 3311, 3019, 2941, 2892, 2866, 2118, 1458, 1362, 1247, 1085, 1061, 881, 741, 677, 634 cm^{-1};
^{1}H NMR ($CDCl_3$, 500 MHz) δ = 1.02 (d, J = 6.9 Hz, 9H), 1.05-1.18 (m, 12H), 1.69-1.77 (m, 1H), 1.97 (t, J = 2.6 Hz, 1H), 2.05 (dd, J = 2.6, 7.7 Hz, 2H), 2.26-2.41 (m, 2H), 2.68 (ddd, J = 6.4, 10.5, 17.2 Hz, 1H), 2.82 (ddd, J = 3.5, 6.6, 17.2 Hz, 1H), 4.77 (d, J = 3.2 Hz, 1H), 7.08 (d, J = 7.2 Hz, 1H), 7.11-7.20 (m, 2H), 7.23-7.27 (m, 1H);
^{13}C NMR ($CDCl_3$, 125 MHz) δ = 12.8, 18.2, 18.3, 19.9, 21.4, 24.5, 39.8, 69.3, 71.9, 82.9, 125.6, 127.5, 128.8, 130.6, 136.4, 136.8;
HRMS (FD$^+$): m/z calcd for $[M+H]^+$ $[C_{22}H_{35}OSi]^+$ 343.2457, found 343.2449.



3k

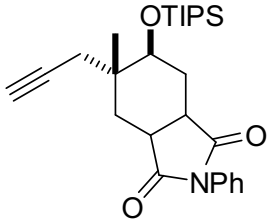


The crude product was purified by preparative TLC (TLC plate was deactivated by treatment with hexane containing 0.5% Et_3N before use, CH_2Cl_2 : hexane = 10 : 90) to give the title compound as a colorless oil in 91% yield (38.9 mg, 0.109 mmol) as a single isomer. The stereochemistry of the product was determined by NOE as shown above.
IR (neat) 3310, 3064, 3021, 2943, 2891, 2866, 2117, 1459, 1384, 1375, 1243, 1085, 1065, 883, 819, 681, 634 cm^{-1};
^{1}H NMR ($CDCl_3$, 500 MHz) δ = 0.84-0.91 (m, 9H), 1.03-1.06 (m, 12H), 1.22 (s, 3H), 1.60 (ddd, *J* = 3.5, 7.5, 13.5 Hz, 1H), 1.91 (dd, *J* = 3.3, 15.9 Hz, 1H), 1.95-2.01 (m, 2H), 2.11 (ddd, *J* = 7.8, 9.5, 13.5 Hz, 1H), 2.67-2.76 (m, 1H), 2.90 (ddd, *J* = 3.5, 7.8, 17.8 Hz, 1H), 4.57 (s, 1H), 7.06-7.13 (m, 2H), 7.18 (dt, *J* = 1.2, 7.5 Hz, 1H), 7.23 (d, *J* = 7.8 Hz, 1H);
^{13}C NMR ($CDCl_3$, 125 MHz) δ = 13.4, 18.1, 18.5, 23.4, 25.6, 26.9, 27.7, 38.1, 70.1, 76.3, 81.8, 125.3, 127.6, 128.7, 129.8, 136.3, 138.0;
HRMS (FD^+): m/z calcd for $[M+H]^+$ $[C_{23}H_{37}OSi]^+$ 357.2614, found 357.2615.



3l

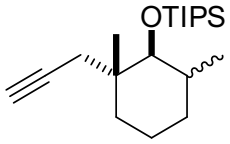
$ReI(CO)_5$ (3.4 mg, 0.0075 mmol, 5.0 mol%), propargyl ether **1** (67.1 mg, 0.30 mmol, 2.0 equiv.), and silyl enol ether **2l** (47.0 mg, 0.15 mmol, 1.0 equiv.) were used. The crude product was purified by silica gel column chromatography (ethyl acetate : hexane = 2.5 : 97.5) to give the title compound as a colorless oil in 89% yield (47.1 mg, 0.134 mmol). Diastereomer ratio was determined by ^{1}H-NMR (d.r. = 82 : 18). The stereochemistry of the product was determined by the coupling constant of C*H*-OTIPS (3.67 ppm, dt, *J* = 4.0, 9.0 Hz) and by comparing the coupling pattern of C*H*-OTIPS with that of compound **3e**.
IR (neat) 3310, 2944, 2866, 2116, 1634, 1463, 1380, 1253, 1108, 1064, 881, 680, 639 cm^{-1};
^{1}H NMR ($CDCl_3$, 500 MHz) δ = 1.05-1.10 (m, 21H), 1.49-1.74 (m, 3H), 1.75-1.83 (m, 1H), 1.83-2.01 (m, 4H), 2.14 (ddd, *J* = 3.0, 7.5, 17.5 Hz, 0.18H), 2.29-2.47 (m, 1.82H) 3.67 (dt, *J* = 4.0, 9.0 Hz, 0.82H), 3.89-4.00 (m, 4H), 4.15 (brs, 0.18H);
^{13}C NMR ($CDCl_3$, 125 MHz)
Major isomer δ = 12.8, 18.2, 21.4, 31.7, 32.5, 36.9, 41.5, 64.2, 64.4, 69.8, 72.2, 82.7, 108.4;
Minor isomer δ = 12.8, 18.2, 21.6, 29.3, 31.0, 34.8, 40.8, 64.2, 64.3, 68.0, 69.2, 83.6, 108.9;
HRMS (FD^+): m/z calcd for $[M]^+$ $[C_{20}H_{36}O_3Si]^+$ 352.2434, found 352.2439.



3m

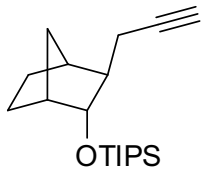
$ReI(CO)_5$ (3.4 mg, 0.0075 mmol, 5.0 mol%), propargyl ether **1** (67.1 mg, 0.30 mmol, 2.0 equiv.), and silyl enol ether **2m** (61.7 mg, 0.15 mmol, 1.0 equiv.) were used. The crude product was purified by silica gel column chromatography (ethyl acetate : hexane = 15 : 85) to give the title compound as a yellow oil in 88% yield (59.9 mg, 0.132 mmol). Two diastereomers were obtained in 93 : 7 ratio and the ratio was determined by integration of C*H*-OTIPS signal at δ = 3.96 and 3.76. From the result of the related product **3f**, the stereochemistry of the hydropropargylated product moiety was assumed to be *trans* as shown in **3m**, and two diastereomers were thought to be isomers concerning the succinimide moiety. However, the relative stereochemistry could not be determined.
IR (neat) 3308, 2943, 2891, 2866, 2114, 2017, 1920, 1844, 1715, 1598, 1501, 1459, 1379, 1186, 1110, 881, 752, 681 cm^{-1};
^{1}H NMR ($CDCl_3$, 500 MHz) δ = 0.99 (s, 3H), 1.02-1.15 (m, 21H), 1.89-1.99 (m, 2H), 2.06 (t, *J* = 2.9 Hz, 1H), 2.16-2.24 (m, 2H), 2.25 (dd, *J* = 2.3, 13.8 Hz, 1H), 2.34 (dd, *J* = 2.9, 16.7 Hz, 1H), 2.96-3.12 (m, 2H), 3.96 (dd, *J* = 4.0, 9.2 Hz, 1H), 7.27-7.31 (m, 2H), 7.35-7.41 (m, 1H), 7.43-7.50 (m, 2H);
^{13}C NMR ($CDCl_3$, 125 MHz) δ = 12.9, 18.3, 19.8, 28.9, 29.4, 31.1, 37.6, 38.2, 38.6, 71.4, 71.9, 81.0, 126.3, 128.4, 129.1, 132.0, 177.7, 178.3;

HRMS (FD$^+$): m/z calcd for [M]$^+$ [$C_{27}H_{39}NO_3Si$]$^+$ 453.2699, found 453.2702.

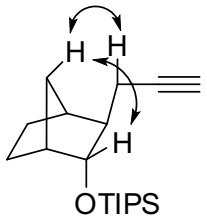


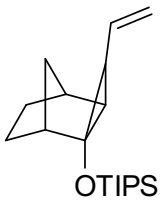
3n

The crude product was purified by silica gel column chromatography (CH_2Cl_2 : hexane = 3 : 97) to give the title compound as a colorless oil in 86% yield (33.1 mg, 0.103 mmol). Two diastereomers were obtained in 80 : 20 ratio, which were thought to be isomers concerning the methyl group at C-6.
IR (neat) 3312, 2944, 2929, 2867, 2116, 1459, 1385, 1253, 1107, 1013, 883, 787, 677, 636 cm^{-1};
^{1}H NMR ($CDCl_3$, 500 MHz) δ = 0.94-0.98 (m, 6H), 1.06-1.15 (m, 22H), 1.27-1.46 (m, 3H), 1.56-1.70 (m, 3H), 1.98 (t, *J* = 2.9 Hz, 1H), 2.12 (dd, *J* = 2.9, 16.6 Hz, 0.2H), 2.20 (dd, *J* = 2.3, 16.1 Hz, 0.8H), 2.28 (dd, *J* = 2.9, 16.0 Hz, 0.8H), 2.33 (dd, *J* = 2.9, 16.6 Hz, 0.2H), 3.30 (d, *J* = 9.8 Hz, 0.8H), 3.76 (d, *J* = 3.5 Hz, 0.2H);
^{13}C NMR ($CDCl_3$, 125 MHz)
Major isomer δ = 14.2, 17.2, 18.6, 20.4, 21.0, 31.3, 34.5, 35.4, 36.1, 39.9, 70.5, 82.6, 82.8;
Minor isomer δ = 13.8, 17.7, 18.51, 18.54, 20.0, 23.4, 28.7, 28.9, 32.9, 33.4, 39.2, 70.4, 78.2, 82.3;
HRMS (FD$^+$): m/z calcd for [M-^{i}Pr]$^+$ [$C_{17}H_{31}OSi$]$^+$ 279.2144, found 279.2148.



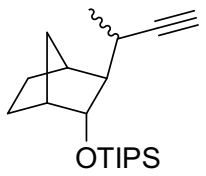
3o



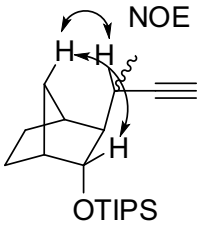


4o

The crude product was purified by silica gel column chromatography (CH_2Cl_2 : hexane = 3 : 97) to give the title compound **3o** (a single isomer) containing vinylcyclopropane **4o** (**3o** : **4o** = 95 : 5) as a colorless oil in 86% yield (31.5 mg, 0.103 mmol). The ratio of these compounds was determined by ^{1}H-NMR. C*H*=CH_2 of **4o**: 5.60 (dt, *J* = 10.0, 17.2 Hz). The stereochemistry of the product was determined by NOE as shown above.
IR (neat) 3313, 2946, 2890, 2868, 2119, 1367, 1237, 1105, 1067, 882, 832, 633 cm^{-1};
^{1}H NMR ($CDCl_3$, 500 MHz) δ = 1.05 (s, 21H), 1.15-1.21 (m, 1H), 1.24-1.37 (m, 3H), 1.44-1.50 (m, 1H), 1.54-1.63 (m, 1H) 1.92 (t, *J* = 2.6 Hz, 1H), 1.93-2.00 (m, 1H), 2.03 (ddd, *J* = 2.6, 10.6, 16.6 Hz, 1H), 2.16 (brd, *J* = 2.7 Hz, 1H), 2.21 (brs, 1H), 2.32 (ddd, *J* = 2.6, 4.3, 16.6 Hz, 1H), 3.72 (t, *J* = 3.3 Hz, 1H);
^{13}C NMR ($CDCl_3$, 125 MHz) δ = 12.3, 18.1, 19.7, 23.3, 30.0, 34.2, 41.1, 43.8, 51.0, 68.2, 79.7, 84.0;
HRMS (FD$^+$): m/z calcd for [M+H]$^+$ [$C_{19}H_{35}OSi$]$^+$ 307.2457, found 307.2454.



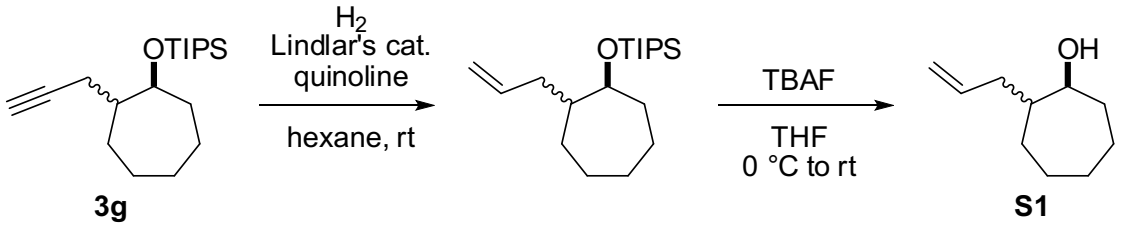
3p



BOM ether of 3-butyn-2-ol was used instead of propargyl ether **1**. The yield was determined by ^{1}H-NMR analysis of the crude product using 1,1,2,2-tetrachloroethane as the internal standard (45%) because the product cannot be purified completely by preparative TLC (hexane). Two diastereomers were obtained in 83 : 17 ratio, which were thought to be isomers concerning the methyl group. The ratio was determined by integration of C*H*-OTIPS signal at δ = 3.96 and 4.14.The stereochemistry of the two contiguous stereogenic centers on the bicyclo[2.2.1]heptane ring of the major isomer of **3p** was determined by NOE as shown above. Spectra of the major isomer of **3p** were shown below.
IR (neat) 3310, 2949, 2869, 2721, 2112, 1462, 1244, 1125, 1100, 883, 847, 632 cm^{-1};
^{1}H NMR ($CDCl_3$, 500 MHz) δ = 1.06 (s, 21H), 1.11-1.16 (m, 2H), 1.21-1.35 (m, 5H), 1.52-1.61 (m, 1H), 1.72 (dt, *J* = 10.5, 1.5 Hz, 1H), 1.88-1.96 (m, 1H), 2.03 (d, *J* = 3.0 Hz, 1H), 2.21 (br s, 1H), 2.25 (br d, *J* = 4.0 Hz, 1H), 2.41-2.49 (m, 1H), 3.96 (dt, *J* = 4.5, 1.0 Hz, 1H);

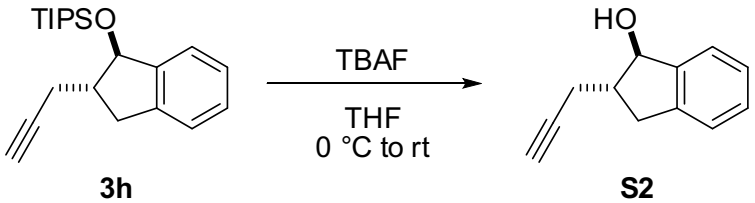
^{13}C NMR ($CDCl_3$, 125 MHz) δ = 12.5, 18.1, 18.2, 20.0, 20.1, 29.1, 31.2, 34.7, 39.3, 43.4, 56.4, 69.2, 79.4, 88.3;
HRMS (FD$^+$): m/z calcd for $[M+H]^+$ $[C_{20}H_{37}OSi]^+$ 321.26137, found 321.26116.

Determination of the stereochemistry of 3g-major, 3h, and 3i

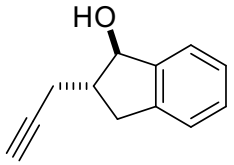


A mixture of Lindlar's cat. (300 mg), **3g** (463 mg, 1.5 mmol, 1.0 equiv.), and quinoline (375 µl, 3.15 mmol, 2.1 equiv.) in hexane (9 ml) was stirred under H_2 atmosphere (balloon) for 30 min at room temperature. The reaction mixture was filtered through Celite pad and concentrated under reduced pressure. The crude material was filtered through silica gel column chromatography (hexane) to remove quinoline. The obtained product (407 mg, ca. 1.3 mmol) was used for the next reaction without further purification.

To a THF solution (5 ml) of the crude material was added TBAF (1 M THF solution, 1.8 ml, 1.8 mmol, 1.4 equiv.) slowly at 0 ºC, and the mixture was stirred at room temperature for 4 h. The reaction mixture was quenched with sat. aqueous NH_4Cl and the aqueous layer was extracted with diethyl ether three times. The combined organic layer was washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure. The crude material was purified by silica gel column chromatography (ethyl acetate : hexane = 20 : 80) to give **S1** as a colorless oil in 56% yield (130 mg, 0.84 mmol). Spectral data of the major diastereomer of **S1** were in good agreement with literature values.[9]

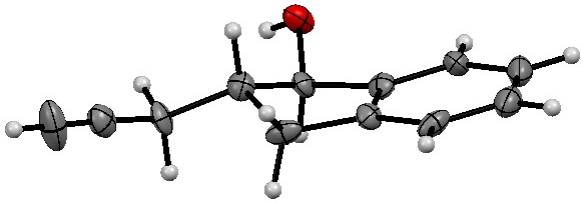


To a THF solution (8 ml) of **3h** (259 mg, 0.79 mmol, 1.0 equiv.) was added TBAF (1 M THF solution, 1.2 ml, 1.2 mmol, 1.5 equiv.) slowly at 0 ºC, and the mixture was stirred at room temperature for 1 h. The reaction mixture was quenched with sat. aqueous NH_4Cl and the aqueous layer was extracted with diethyl ether three times. The combined organic layer was washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure. The crude material was purified by silica gel column chromatography (ethyl acetate : hexane = 25 : 75) to give **S2** as a pale yellow solid in 65% yield (88.6 mg, 0.51 mmol).

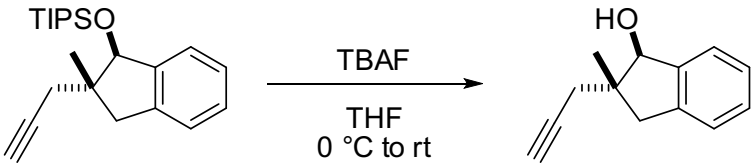


S2

IR (neat) 3295, 3072, 3025, 2909, 2849, 2116, 1607, 1460, 1323, 1206, 1059, 747, 637 cm^{-1};
^{1}H NMR ($CDCl_3$, 500 MHz) δ = 2.03-2.07 (m, 2H), 2.39-2.49 (m, 1H), 2.49-2.61 (m, 2H), 2.72 (dd, J = 8.6, 15.5 Hz, 1H), 3.14 (dd, J = 8.0, 15.5 Hz, 1H), 5.05 (t, J = 6.9 Hz, 1H), 7.19-7.29 (m, 3H), 7.36-7.42 (m, 1H);
^{13}C NMR ($CDCl_3$, 125 MHz) δ = 21.3, 35.2, 48.9, 70.2, 80.1, 82.5, 123.9, 124.7, 126.9, 128.2, 141.1, 144.2;
HRMS (FD$^+$): m/z calcd for $[M]^+$ $[C_{12}H_{12}O]^+$ 172.0888, found 172.0884.

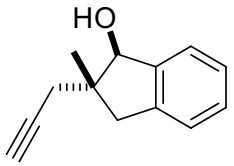


ORTEP of **S2**



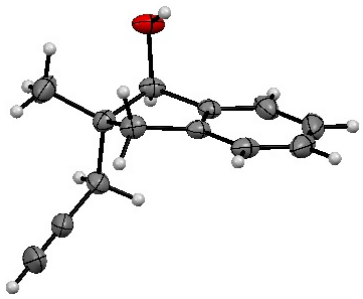
3i **S3**

To a THF solution (8 ml) of **3i** (548 mg, 1.60 mmol, 1.0 equiv.) was added TBAF (1 M THF solution, 2.4 ml, 2.4 mmol, 1.5 equiv.) slowly at 0 °C, and the mixture was stirred at room temperature for 1 h. The reaction mixture was quenched with sat. aqueous NH_4Cl and the aqueous layer was extracted with diethyl ether three times. The combined organic layer was washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure. The crude material was purified by silica gel column chromatography (ethyl acetate : hexane = 16 : 84) to give **S3** as a white solid in 59% yield (175 mg, 0.94 mmol).



S3

IR (neat) 3297, 3073, 3026, 2964, 2901, 2846, 2116, 1609, 1460, 1377, 1297, 1208, 1177, 1054, 741, 638 cm^{-1};
^{1}H NMR ($CDCl_3$, 500 MHz) δ = 1.11 (s, 3H), 1.83 (d, *J* = 7.5 Hz, 1H), 2.08 (t, *J* = 2.9 Hz, 1H), 2.38 (dd, *J* = 2.3, 16.6 Hz, 1H), 2.43 (dd, *J* = 2.3, 16.6 Hz, 1H), 2.75 (d, *J* = 15.5 Hz, 1H), 2.92 (d, *J* = 15.5 Hz, 1H), 5.01 (d, *J* = 7.5 Hz, 1H), 7.17-7.26 (m, 3H), 7.35-7.40 (m, 1H);
^{13}C NMR ($CDCl_3$, 125 MHz) δ = 19.2, 28.8, 42.5, 47.5, 70.9, 81.1, 82.2, 124.3, 125.0, 126.7, 128.1, 140.6, 143.6;
HRMS (FD^+): m/z calcd for $[M]^+$ $[C_{13}H_{14}O]^+$ 186.1045, found 186.1042.



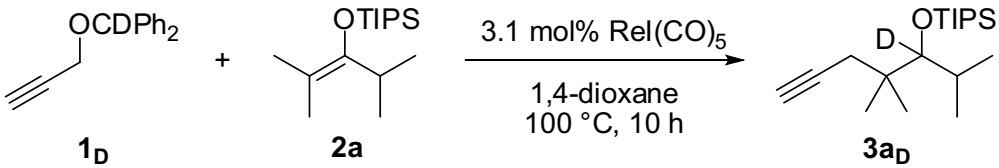
ORTEP of **S3**

・Mechanistic studies

Deuterium-labelling experiment

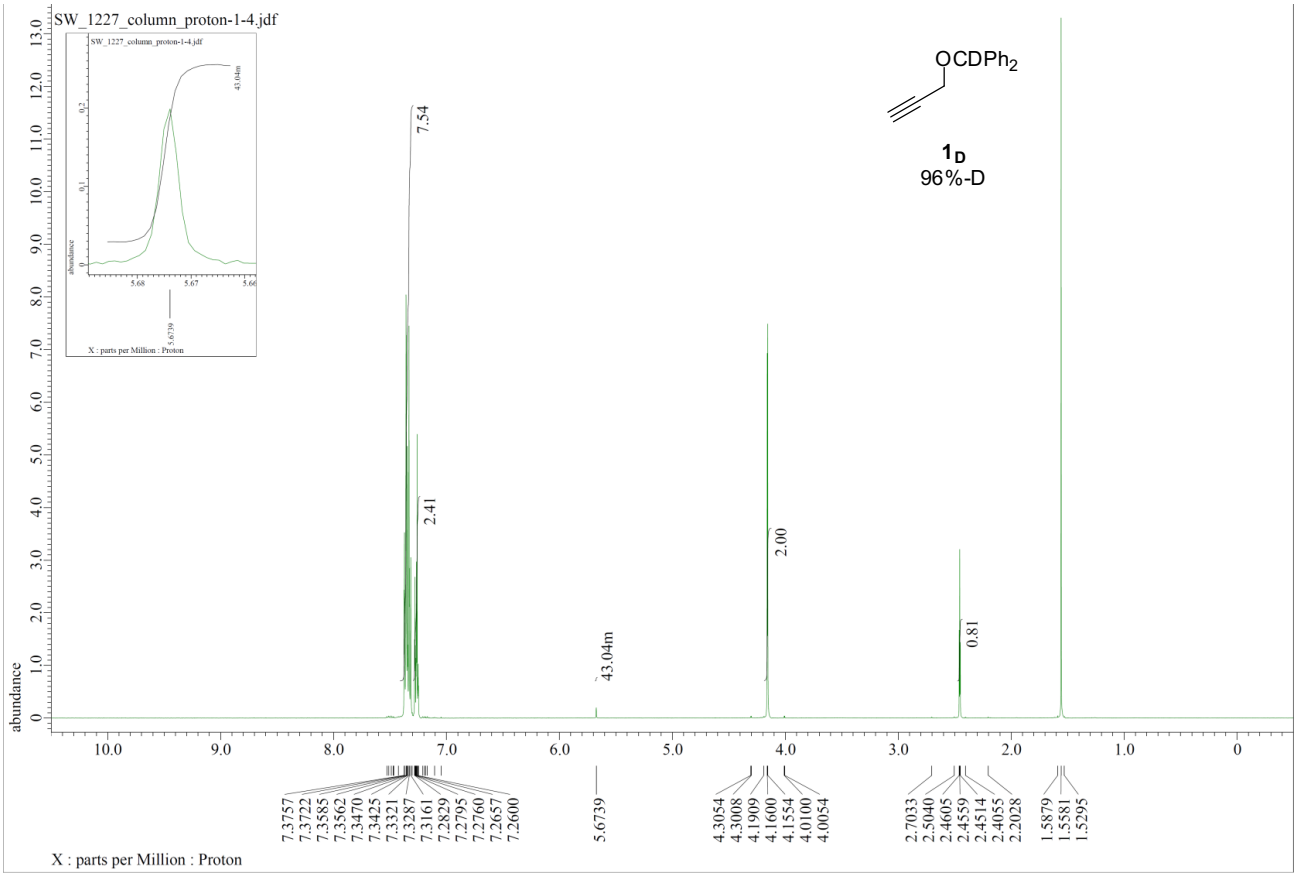
Propargyl ether $\mathbf{1_D}$ (96%-D) was synthesized according to the same procedure for the preparation of **1** (see page S2) by using deuterated benzhydrol, which was prepared by the reduction of benzophenone with sodium borodeuteride. Degree of deuteration was determined by integration of ^{1}H-NMR (δ = 5.67 vs 4.16).

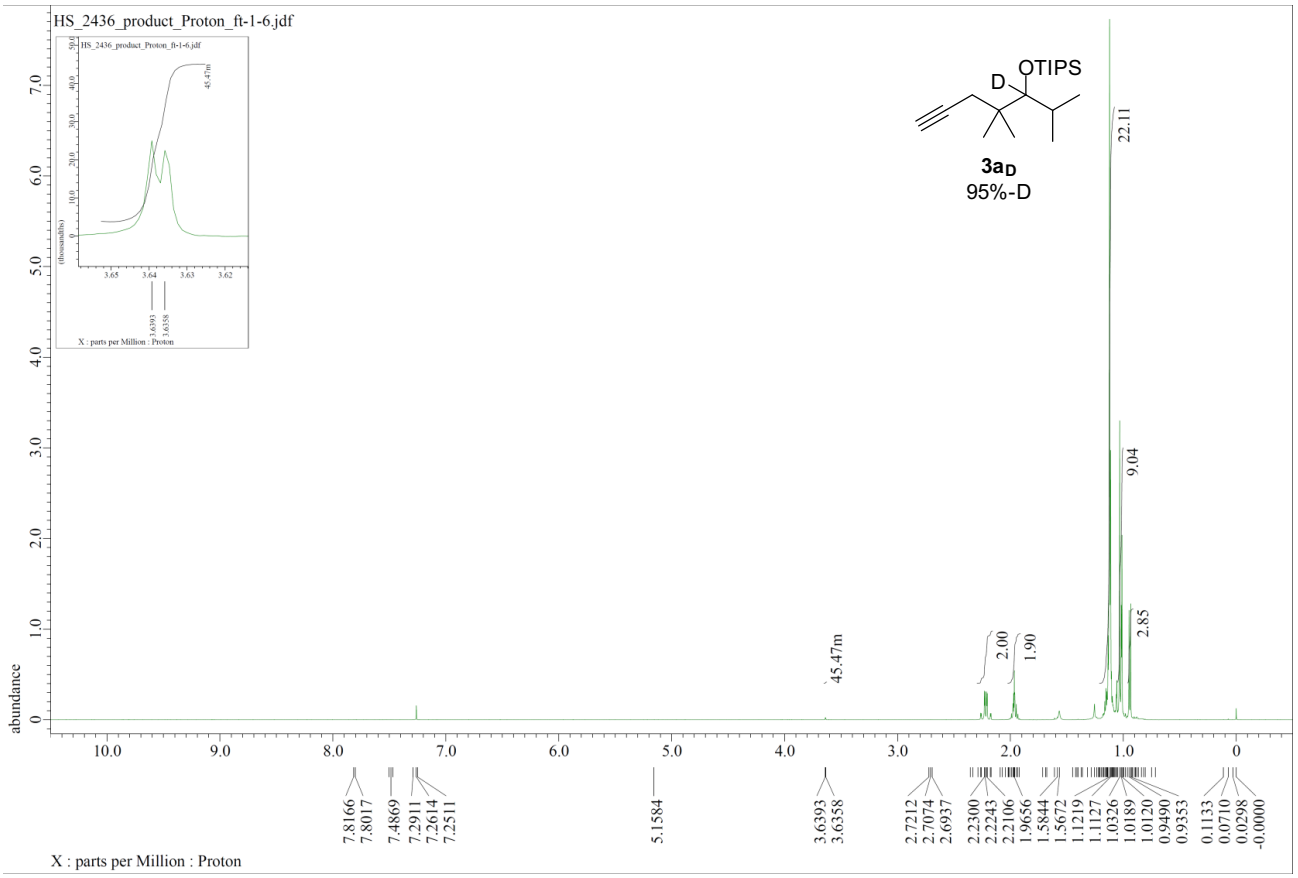
Propargyl ether $\mathbf{1_D}$**'** (>98%-D) was synthesized by the deuteration of propargyl ether **1** by treatment of **1** with ^{n}BuLi followed by addition of D_2O. Degree of deuteration was determined by integration of ^{1}H-NMR (δ = 2.45 vs 4.16).

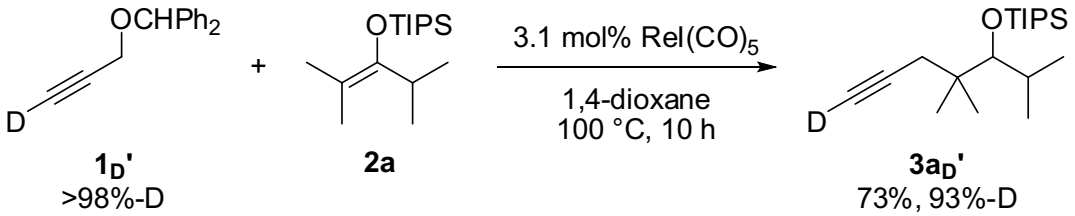


$\mathbf{1_D}$ 96%-D **2a** $\mathbf{3a_D}$ 87%, 95%-D

A mixture of $ReI(CO)_5$ (1.7 mg, 0.0038 mmol, 3.1 mol%), propargyl ether $\mathbf{1_D}$ (33.8 mg, 0.15 mmol, 1.25 equiv.), and silyl enol ether **2a** (32.5 mg, 0.12 mmol, 1.0 equiv.) in 1,4-dioxane (1.5 mL) was stirred for 10 h at 100 ºC. The reaction mixture was quenched with TMEDA (0.2 ml) and the mixture was concentrated under reduced pressure in vacuo. The crude product was purified by silica gel column chromatography (hexane) to give silyl ether $\mathbf{3a_D}$ in 87% yield (32.5 mg, 0.104 mmol). Degree of deuteration was determined to be 95% by integration of ^{1}H-NMR (δ = 3.64 vs 2.22).

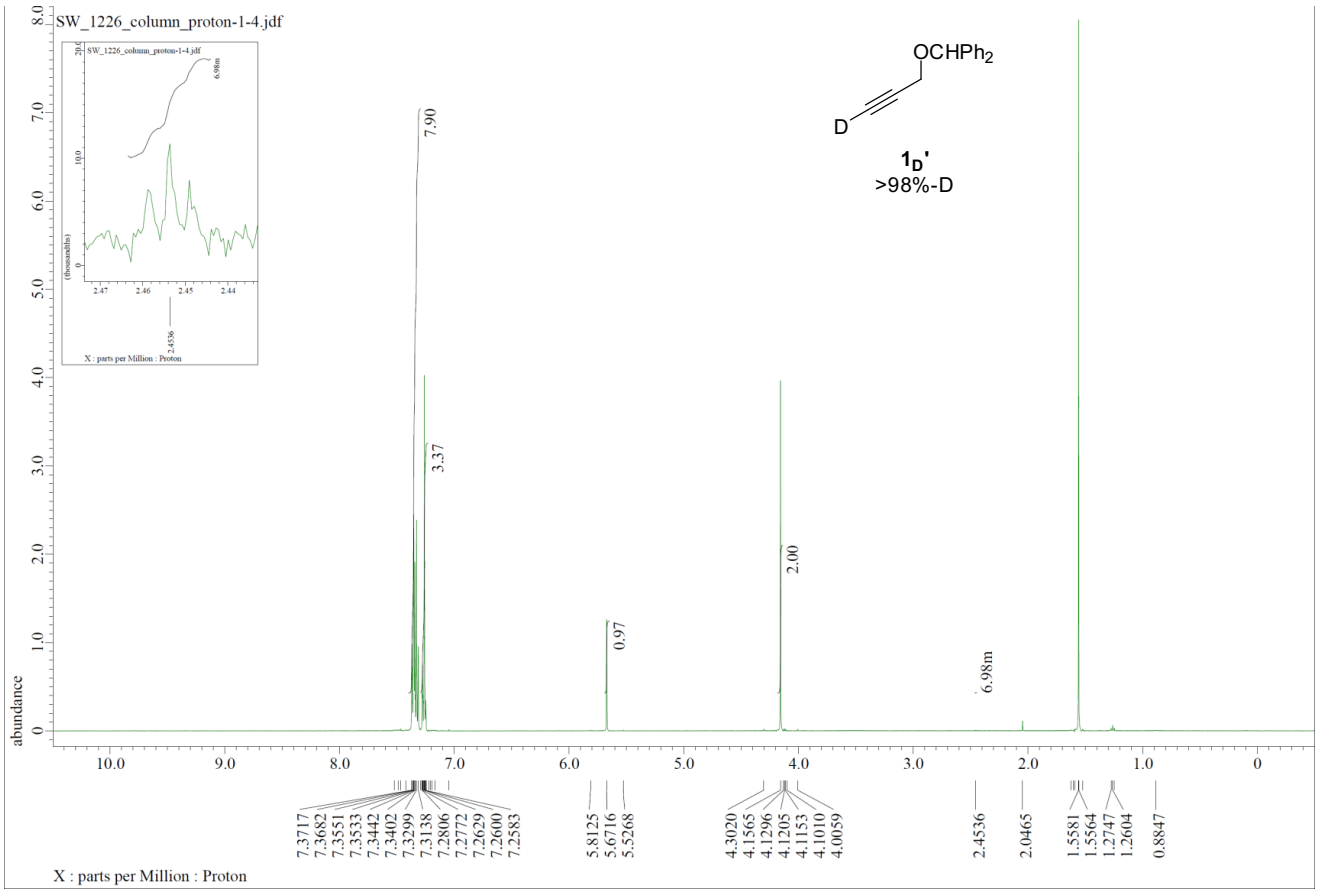

SW_1227_column_proton-1-4.jdf
OCDPh2
1D
96%-D
7.54
2.41
2.00
0.81
43.04m
abundance
X : parts per Million : Proton

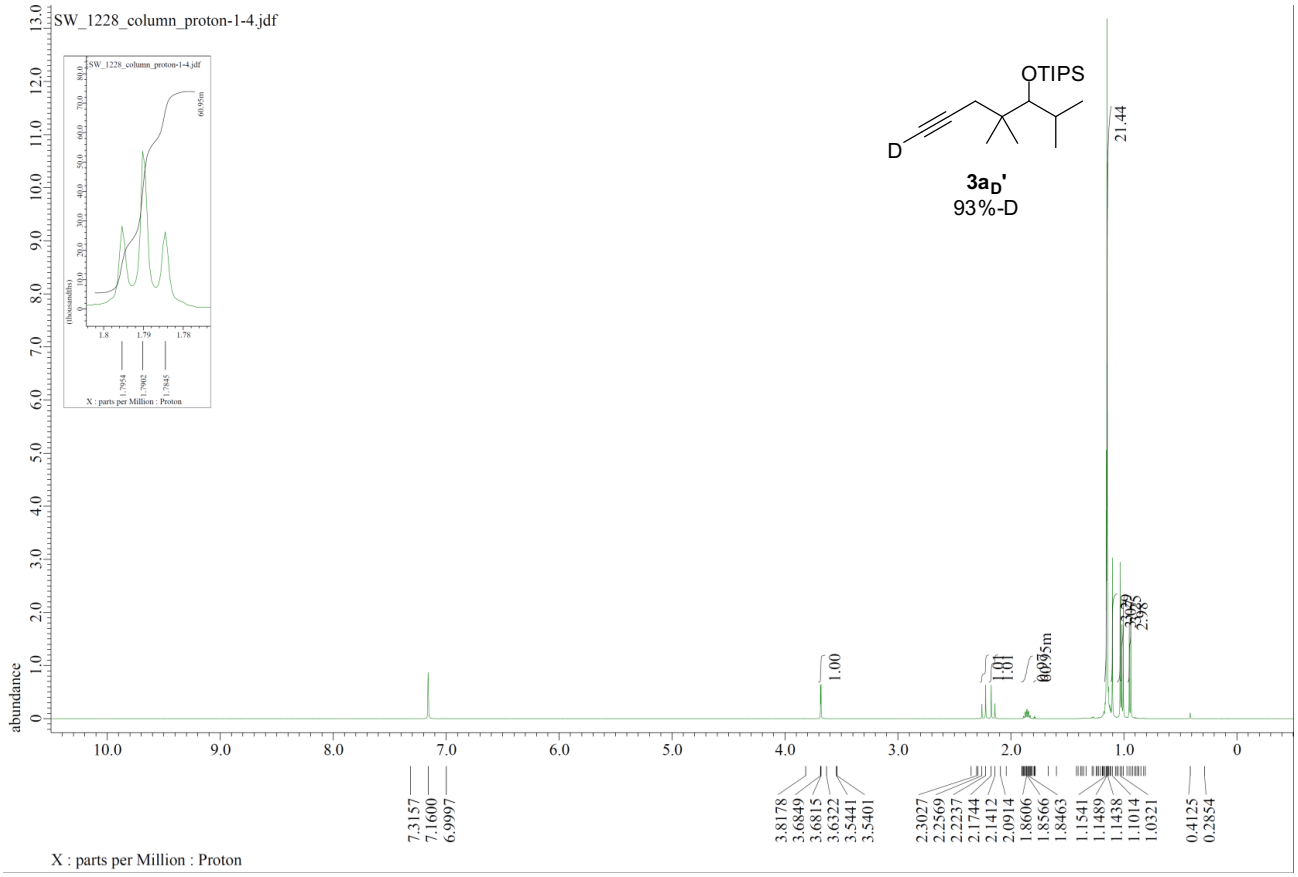

HS_2436_product_Proton_ft-1-6.jdf
D
OTIPS
3aD
95%-D
22.11
9.04
2.85
2.00
1.90
45.47m
abundance
X : parts per Million : Proton

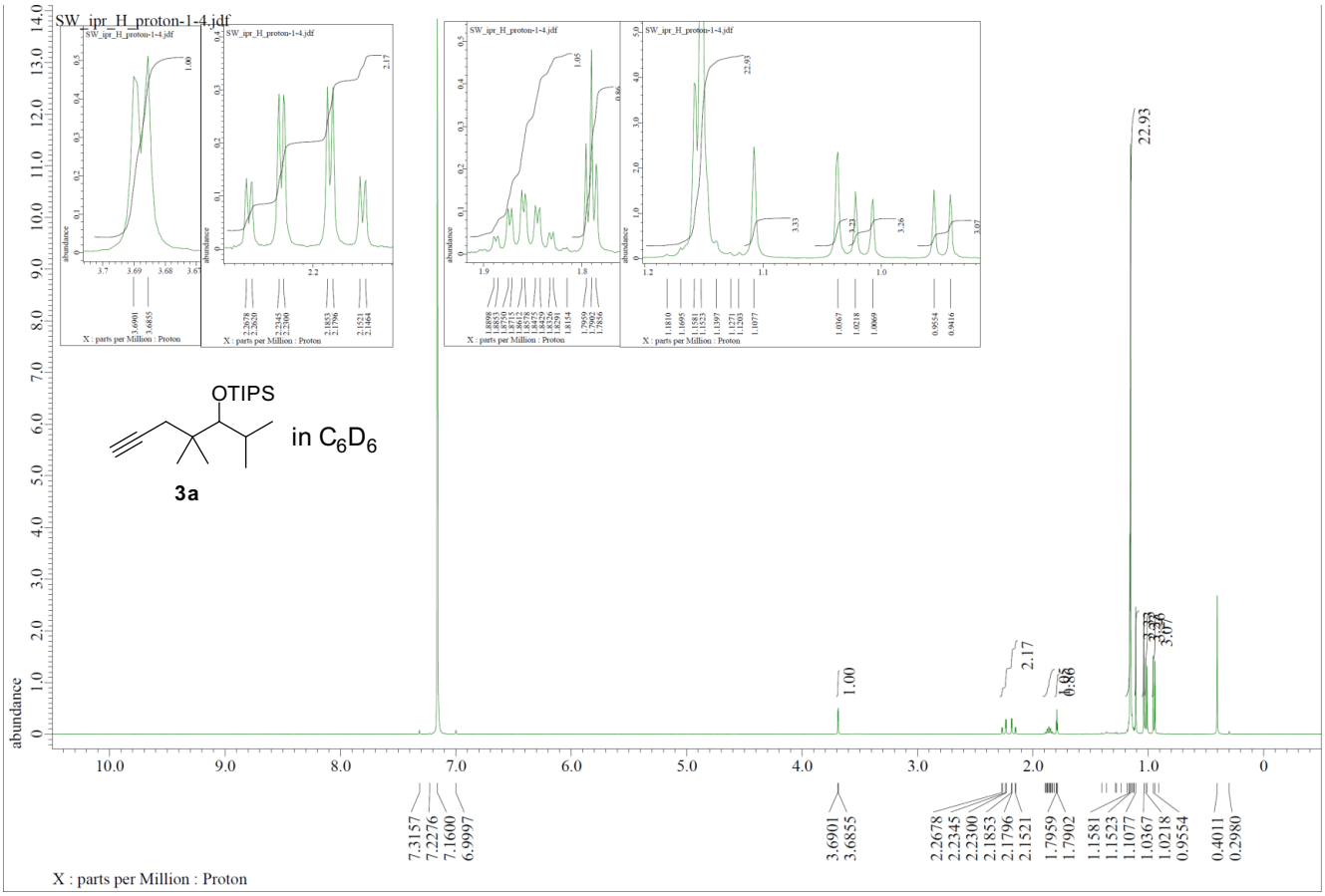


A mixture of $ReI(CO)_5$ (1.7 mg, 0.0038 mmol, 3.1 mol%), propargyl ether **1$_D$'** (33.5 mg, 0.15 mmol, 1.25 equiv.), and silyl enol ether **2a** (32.5 mg, 0.12 mmol, 1.0 equiv.) in 1,4-dioxane (1.5 mL) was stirred for 10 h at 100 ºC. The reaction mixture was quenched with TMEDA (0.2 ml) and the mixture was concentrated under reduced pressure in vacuo. The crude product was purified by silica gel column chromatography (hexane) to give silyl ether **3a$_D$'** in 73% yield (27.3 mg, 0.088 mmol). Degree of deuteration was determined to be 93% by integration of ^{1}H-NMR (δ = 1.79 vs 3.68)Loss of deuterium (ca. 5%) probably occurred during the reaction by exchange with a small amount of H_2O in the solvent. C_6D_6 was used as a deuterated solvent to determine the deuteration ratio of **3a$_D$'**. Chemical shifts of **3a** in C_6D_6 was shown below.

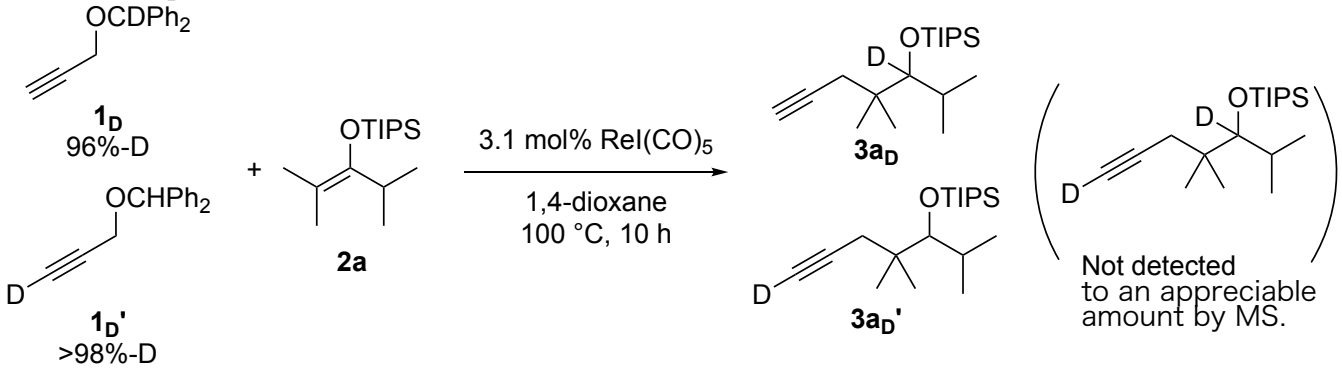
^{1}H NMR (C_6D_6, 500 MHz) δ = 0.95 (d, *J* = 7.2 Hz, 3H), 1.01 (d, *J* = 6.9 Hz, 3H), 1.04 (s, 3H), 1.11 (s, 3H), 1.13-1.18 (m, 21H), 1.79 (t, *J* = 2.6 Hz, 1H), 1.82-1.90 (m, 1H), 2.17 (dd, *J* = 16.3, 2.3 Hz, 1H), 2.25 (dd, *J* = 16.6, 2.6 Hz, 1H), 3.69 (d, *J* = 2.0 Hz, 1H)




SW_1228_column_proton-1-4.jdf
OTIPS
D
3aD'
93%-D
21.44
1.00
abundance
X : parts per Million : Proton


SW_ipr_H_proton-1-4.jdf
OTIPS
in C6D6
3a
22.93
1.00
2.17
abundance
X : parts per Million : Proton

Cross-over experiment

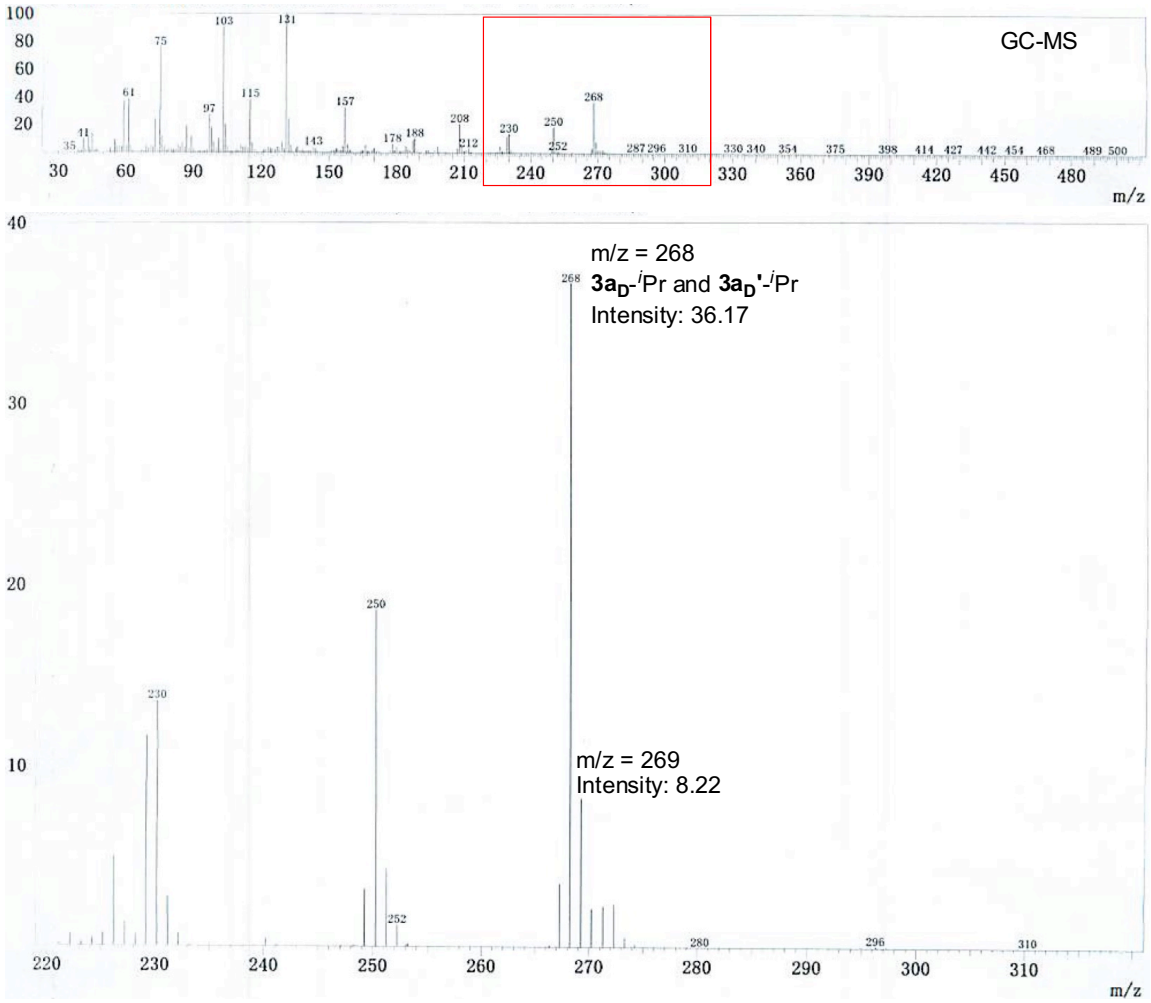


A mixture of $ReI(CO)_5$ (1.7 mg, 0.0038 mmol, 3.1 mol%), propargyl ether **1D** (16.7 mg, 0.075 mmol, 0.50 equiv.), propargyl ether **1D'** (16.6 mg, 0.075 mmol, 0.50 equiv.), and silyl enol ether **2a** (40.6 mg, 0.15 mmol, 1.0 equiv.) in 1,4-dioxane (1.5 mL) was stirred for 10 h at 100 ºC. The reaction mixture was quenched with TMEDA (0.2 ml) and the mixture was concentrated under reduced pressure in vacuo. The crude material was filtered through silica gel column chromatography (hexane) to afford a mixture of silyl ethers **3aD**, **3aD'** and unreacted silyl enol ether **2a**. The yield of the product was estimated by integration of ^{1}H NMR to be 53%, and the ratio of **3aD** and **3aD'** was about 6 : 4. The isotope ratio was determined by GC-MS.

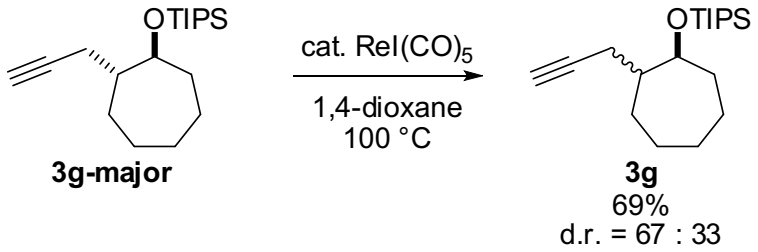
A theoretical isotope ratio was calculated by following formula: $\%(M+1) = (1.1 \times C_n)+(5.1 \times Si_n) = (1.1 \times 16)+(5.1) = 22.7\%$.

An actual isotope ratio was determined by comparing intensity of m/z = 268 (**3aD**-^{i}Pr and **3aD'**-^{i}Pr) with m/z = 269: $100 \times 8.22/36.17 = 22.73\%$, which coincided with the theoretical value.

This result suggested that di-deuterated product was not formed to an appreciable amount and hydride transfer occurred in an intramolecular manner.

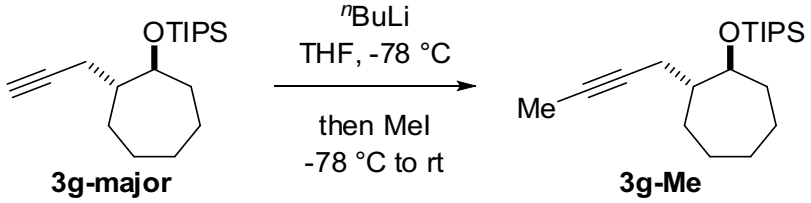


Isomerization of 3g

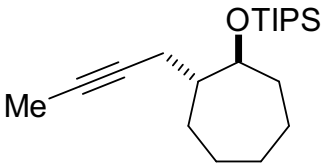


A mixture of $ReI(CO)_5$ (1.0 mg, 0.0022 mmol, 20 mol%) and **3g-major** (0.011 mmol, 1.25 equiv.) in 1,4-dioxane (0.75 mL) was stirred for 13 h at 100 ºC. The reaction mixture was quenched with TMEDA (0.2 ml) and the reaction mixture was concentrated under reduced pressure in vacuo. The crude product was purified by silica gel column chromatography to give **3g** as a colorless oil in 69% yield (2.4 mg, 0.0078 mmol). Diastereomer ratio was determined by ^{1}H-NMR (d.r. = 67 : 33).

Isomerization of 3g-Me

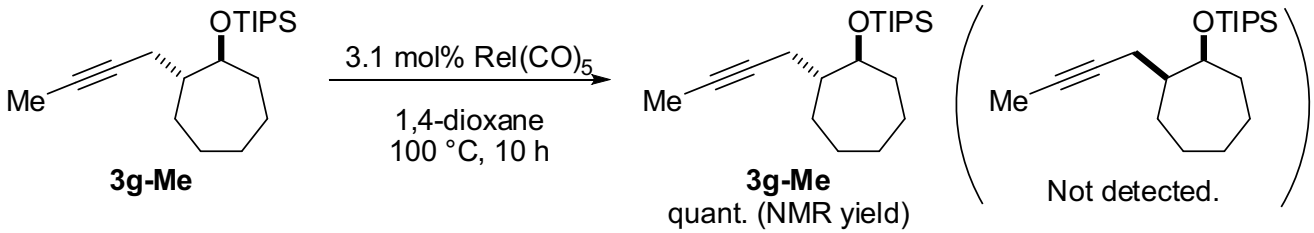


To a THF solution (6 ml) of **3g-major** (90.3 mg, 0.29 mmol, 1.0 equiv.) was added ^{n}BuLi (1.6 M THF solution, 280 µl, 0.44 mmol, 1.5 equiv.) at -78 ºC and the mixture was stirred at the same temperature for 3 h. MeI (36 µl, 0.59 mmol, 2.0 equiv.) was added slowly to the reaction mixture at -78 ºC and the resulting mixture was gradually warmed up to room temperature over 4 h with stirring. The reaction mixture was quenched with sat. aqueous NH_4Cl and the aqueous layer was extracted with diethyl ether three times. The combined organic layer was washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure. The crude mixture was purified by silica gel column chromatography (hexane) to give **3g-Me** as a colorless oil in 71% yield (63.2 mg, 0.21 mmol).



3g-Me

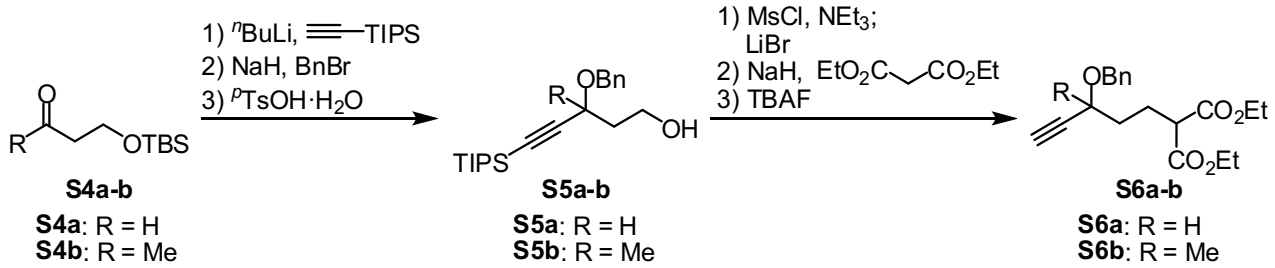
IR (neat) 2926, 2865, 2236, 1462, 1384, 1248, 1098, 1064, 998, 884, 677 cm^{-1};
^{1}H NMR ($CDCl_3$, 500 MHz) δ = 1.07 (s, 21H), 1.23-1.54 (m, 4H), 1.60-1.82 (m, 7H), 1.77 (t, J = 2.9 Hz, 3H), 2.10-2.19 (m, 1H), 2.23-2.32 (m, 1H), 3.83 (dt, J = 6.3, 2.9 Hz, 1H);
^{13}C NMR ($CDCl_3$, 125 MHz) δ = 3.49, 12.8, 18.2, 18.3, 21.5, 23.7, 25.7, 28.8, 28.9, 34.9, 46.9, 75.6, 76.0, 78.4;
HRMS (FD$^+$): m/z calcd for $[M+H]^+$ $[C_{20}H_{39}OSi]^+$ 323.2770, found 323.2774.



A mixture of $ReI(CO)_5$ (1.1 mg, 0.0025 mmol, 2.5 mol%) and **3g-Me** (32.5 mg, 0.10 mmol, 1.25 equiv.) in 1,4-dioxane (1.0 mL) was stirred for 10 h at 100 ºC. The reaction mixture was quenched with TMEDA (0.2 ml) and the reaction mixture was concentrated under reduced pressure in vacuo. The starting material was recovered without change in nearly quantitative yield as judged by ^{1}H-NMR analysis of the crude product using 1,1,2,2-tetrachloroethane as the internal standard.

・Intramolecular hydropropargylation reaction

Synthesis of substrate.



S4a[10] and **S4b** [11] were prepared according to the reported procedures.

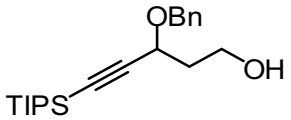
Synthesis of alcohol S5a and S5b.

Typical procedure was described for preparation of S5a.

To a THF solution (30 ml) of triisopropylsilylacetylene (12 ml, 53 mmol, 1.1 equiv.) was added ^{n}BuLi (1.6 M THF solution, 33 ml, 53 mmol, 1.1 equiv.) at -78 °C and the mixture was stirred at the same temperature for 30 min. A THF solution (18 ml) of aldehyde **S4a** (9.0 g, 48 mmol, 1.0 equiv.) was added slowly to the reaction mixture at -78 °C and the resulting mixture was gradually warmed up to room temperature over 2 h with stirring. The reaction mixture was quenched with water and the aqueous layer was extracted with ethyl acetate three times. The combined organic layer was washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure. The crude alcohol was used for the next reaction without further purification.

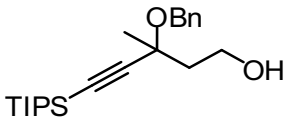
To a THF suspension (100 ml) of sodium hydride (60%, 2.5 g, 62 mmol, 1.3 equiv.) was added a THF solution (20 ml) of crude alcohol at 0 °C and the mixture was stirred at the same temperature for 30 min. Benzyl bromide (6.8 ml, 58 mmol, 1.2 equiv.) was added slowly to the reaction mixture at 0 °C and the resulting mixture was stirred at room temperature for 16 h. The reaction mixture was quenched with sat. aqueous NH_4Cl and the aqueous layer was extracted with ethyl acetate three times. The combined organic layer was washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure. The crude propargyl ether was used for the next reaction without further purification.

To an acetone (152 ml) and water (8 ml) solution of crude propargyl ether was added *p*-toluenesulfonic acid monohydrate (3.7 g, 19 mmol, 0.4 equiv.) and the solution was stirred at room temperature for 4 h. Pyridine (1.6 ml, 19 mmol, 0.4 equiv.) was added to the reaction mixture and the solvent was removed under reduced pressure. The residue was dissolved in ethyl acetate, which was washed with brine. The organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude material was purified by silica gel column chromatography (ethyl acetate : hexane = 25 : 75) to give alcohol **S5a** as a yellow oil in 61% yield (in 3 steps, 10 g, 29 mmol).



S5a

Spectral data were in good agreement with literature values.[12]



S5b

S4b (10 g, 50 mmol) was used. a yellow oil (12 g, 33 mmol, 66% yield in 3 steps).
IR (neat) 3437, 3032, 2943, 2892, 2865, 2163, 1462, 1381, 1054, 882, 736, 676 cm^{-1};

^{1}H NMR ($CDCl_3$, 500 MHz) δ = 1.11 (s, 21H), 1.59 (s, 3H), 2.00 (ddd, *J* = 3.5, 6.0, 14.5 Hz, 1H), 2.11 (ddd, *J* = 4.0, 8.5, 14.5 Hz, 1 H), 2.94 (br s, 1H), 3.80-3.88 (m, 1H), 4.06-4.14 (m, 1H), 4.58 (d, *J* = 10.5 Hz, 1H), 4.82 (d, *J* = 11.0 Hz, 1H), 7.26-7.38 (m, 5H);
^{13}C NMR ($CDCl_3$, 125 MHz) δ = 11.0, 18.5, 26.8, 44.2, 60.1, 66.6, 75.1, 87.4, 107.9, 127.6, 127.8, 128.2, 138.3;
HRMS (FD$^+$): m/z calcd for $[M+H]^+$ $[C_{22}H_{37}O_2Si]^+$ 361.2563, found. 361.2565

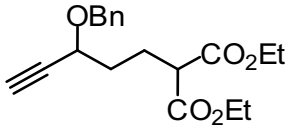
Synthesis of malonate S6a and S6b.

Typical procedure was described for preparation of S6a.

To a DMF solution (145 ml) of alcohol **S5a** (10 g, 29 mmol, 1.0 equiv.) and *N,N*-diisopropylethylamine (8.6 ml, 49 mmol, 1.7 equiv.) was added methanesulfonyl chloride (3.4 ml, 44 mmol, 1.5 equiv.) slowly at 0 °C, and the mixture was stirred at room temperature overnight. To the reaction mixture was added lithium bromide (13 g, 145 mmol, 5.0 equiv.) and the mixture was stirred at 70 °C for 7 h. The reaction mixture was quenched with water and the aqueous layer was extracted with diethyl ether three times. The combined organic layer was washed with water and brine and dried over $MgSO_4$. The solvent was removed under reduced pressure. The crude alkyl bromide was used for the next reaction without further purification.

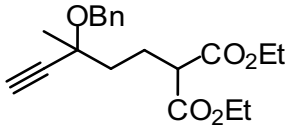
To a DMF suspension (84 ml) of sodium hydride (60%, 1.1 g, 27 mmol, 1.1 equiv.) was slowly added a DMF solution (20 ml) of diethyl malonate (4.4 g, 27 mmol, 1.1 equiv.) at 0 °C and the mixture was stirred at room temperature for 30 min. A DMF solution (20 ml) of the crude alkyl bromide and tetrabutylammonium iodide (2.7 g, 7,4 mmol, 30 mol%) was added to the reaction mixture and the resulting mixture was stirred at 120 °C for 8 h. The reaction mixture was quenched with sat. aqueous NH_4Cl and the aqueous layer was extracted with diethyl ether three times. The combined organic layer was washed with water and brine and dried over $MgSO_4$. The solvent was removed under reduced pressure. The crude malonate was used for the next reaction without further purification.

To a THF solution (49 ml) of the crude malonate was added TBAF (1 M THF solution, 30 ml, 30 mmol, 1.2 equiv.) slowly at 0 °C, and the mixture was stirred at room temperature for 1 h. The reaction mixture was quenched with sat. aqueous NH_4Cl and the aqueous layer was extracted with ethyl acetate three times. The combined organic layer was washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure. The crude material was purified by silica gel column chromatography (ethyl acetate : hexane = 10 : 90) to give malonate **S6a** as a yellow oil in 65% yield (in 3 steps, 6.3 g, 19 mmol).



S6a

IR (neat) 3278, 2981, 2938, 2870, 2112, 1731, 1453, 1370, 1301, 1253, 1157, 1095, 1027, 859, 699 cm^{-1};
^{1}H NMR ($CDCl_3$, 500 MHz) δ = 1.25 (t, *J* = 7.5 Hz, 3H), 1.26 (t, *J* = 6.9 Hz, 3H), 1.74-1.90 (m, 2H), 2.02-2.16 (m, 2H), 2.49 (d, *J* = 1.7 Hz, 1H), 3.35 (t, *J* = 7.5 Hz, 1H), 4.11(dt, *J* = 1.8, 6.3 Hz, 1H), 4.13-4.26 (m, 4H), 4.49 (d, *J* = 12.1 Hz, 1H), 4.80 (d, *J* = 11.5 Hz, 1H), 7.26-7.39 (m, 5H);
^{13}C NMR ($CDCl_3$, 125 MHz) δ = 14.1, 24.5, 33.1, 51.5, 61.4, 67.8, 70.5, 74.4, 82.1, 127.7, 128.0, 128.4, 137.6, 169.2;
HRMS (FD$^+$): m/z calcd for $[M]^+$ $[C_{19}H_{24}O_5]^+$ 332.1624, found. 332.1617

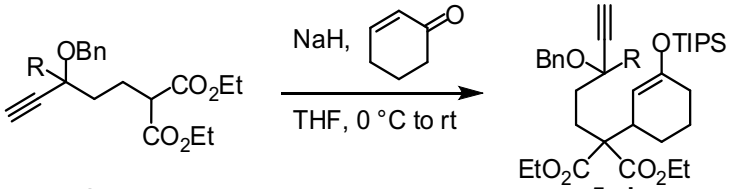


S6b

S5b (12 g, 33 mmol) was used. a yellow oil (5.4 g, 16 mmol, 48% yield in 3 steps).
IR (neat) 3277, 3064, 3032, 2982, 2937, 2871, 2108, 1731, 1452, 1371, 1179, 1055, 737, 697 cm^{-1};
^{1}H NMR ($CDCl_3$, 500 MHz) δ = 1.26 (t, *J* = 7.5 Hz, 6H), 1.52 (s, 3H), 1.75-1.88 (m, 2H), 2.08-2.23 (m, 2H), 2.52 (s, 1H), 3.36 (t, *J* = 7.5 Hz, 1H), 4.13-4.26 (m, 4H), 4.58 (d, *J* = 10.9 Hz, 1H), 4.67 (d, *J* = 11.5 Hz, 1H), 7.23-7.29 (m, 1H), 7.30-7.38 (m, 4H);
^{13}C NMR ($CDCl_3$, 125 MHz) δ = 14.1, 23.7, 26.2, 39.0, 51.8, 61.3, 66.2, 73.1, 73.9, 84.5, 127.3, 127.6, 128.3, 138.8, 169.3;
HRMS (FD$^+$): m/z calcd for $[M]^+$ $[C_{20}H_{26}O_5]^+$ 346.1780, found. 346.1779

Synthesis of 5a and 5b.

Typical procedure was described for preparation of 5a.

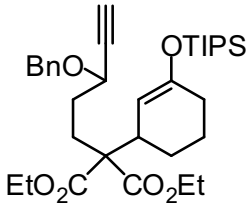


S6a-b
S6a: R = H
S6b: R = Me

5a-b
5a: R = H
5b: R = Me

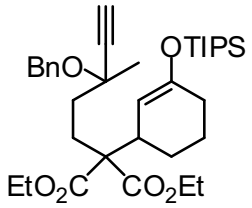
Solution 1: To a THF suspension (3 ml) of sodium hydride (60%, 60 mg, 1.5 mmol, 1.5 equiv.) was added a THF solution (2 ml) of malonate **S6a** (365 mg, 1.1 mmol, 1.1 equiv.) at 0 °C and the mixture was stirred at the same temperature for 45 min.

Solution 2: To a THF solution (5 ml) of cyclohexenone (100 µl, 1.0 mmol, 1.0 equiv.) was added TIPSOTf (300 µl, 1.1 mmol, 1.1 equiv.) slowly at 0 °C and the mixture was stirred at the same temperature for 30 min. Solution 1 was added slowly to solution 2 with syringe at 0 °C and the mixture was stirred at room temperature for 3.5 h. The reaction mixture was quenched with sat. aqueous $NaHCO_3$ and the aqueous layer was extracted with ethyl acetate three times. The combined organic layer was washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure. The crude material was purified by silica gel column chromatography (ethyl acetate : hexane = 5 : 95) to give the silyl enol ether **5a** as a yellow oil in 72% yield (422 mg, 0.72 mmol).



5a

Diastereomer ratio was determined by ^{1}H-NMR (d.r. = ca.50 : 50).
IR (neat) 3304, 3063, 3032, 2942, 2867, 2759, 2112, 1726, 1663, 1461, 1370, 1194, 1096, 883, 739, 685 cm^{-1};
^{1}H NMR ($CDCl_3$, 500 MHz) δ = 1.06 (d, *J* = 6.5 Hz, 18H), 1.09-1.21 (m, 3H), 1.21-1.26 (m, 6H), 1.26-1.34 (m, 1H), 1.49-1.60 (m, 1H), 1.68-1.86 (m, 4H), 1.90-2.18 (m, 4H), 2.46 (d, *J* = 2.5 Hz, 0.5H), 2.47 (d, *J* = 2.5 Hz, 0.5H), 2.92-2.99 (m, 1H), 4.03-4.09 (m, 1H), 4.10-4.21 (m, 4H), 4.50 (d, *J* = 11.5 Hz, 1H), 4.78 (d, *J* = 12.0 Hz, 0.5H), 4.79 (d, *J* = 12.0 Hz, 0.5 H), 4.89 (br s, 1H), 7.26-7.37 (m, 5H);
^{13}C NMR ($CDCl_3$, 125 MHz) δ = 12.4, 14.02, 14.04, 17.9, 22.5, 24.1, 28.2, 29.5, 30.8, 30.9, 39.47, 39.51, 60.7, 60.78, 60.82, 68.4, 70.28, 70.30, 74.06, 74.12, 82.25, 82.27, 104.1, 127.6, 127.8, 128.3, 137.7, 151.9, 170.78, 170.80;
HRMS (FD$^+$): m/z calcd for $[M+H]^+$ $[C_{34}H_{53}O_6Si]^+$ 585.3611, found 585.3613

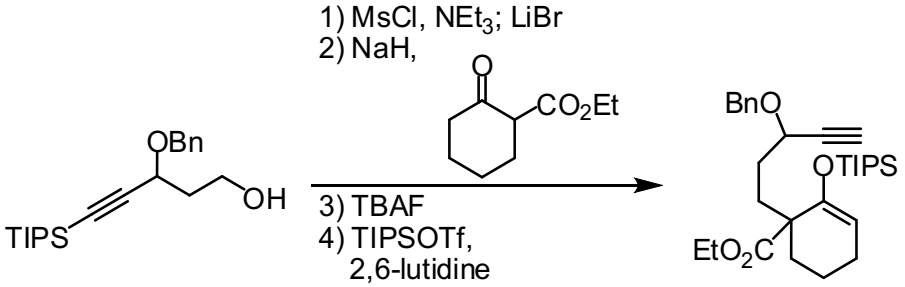


5b

a yellow oil (467 mg, 0.78 mmol, 78% yield). Diastereomer ratio was determined by ^{1}H-NMR (d.r. = ca.50 : 50).
IR (neat) 3305, 3064, 3031, 2942, 2867, 2726, 2108, 1727, 1663, 1462, 1370, 1197, 1065, 914, 883, 736, 686 cm^{-1};
^{1}H NMR ($CDCl_3$, 500 MHz) δ = 1.05 (d, *J* = 7.5 Hz, 18H), 1.09-1.20 (m, 3H), 1.20-1.26 (m, 6H), 1.26-1.36 (m, 1H), 1.50 (s, 3H), 1.51-1.60 (m, 1H), 1.69 (dt, *J* = 4.5, 13.0 Hz, 0.5H), 1.74-1.86 (m, 3.5H), 1.94 (br dd, *J* = 5.5, 17.0 Hz, 1H), 2.02-2.17 (m, 2.5H), 2.21 (dt, *J* = 4.5, 13.5 Hz, 0.5H), 2.485 (s, 0.5H), 2.489 (s, 0.5H), 2.91-2.98 (m, 1H), 4.10-

4.26 (m, 4H), 4.59 (d, J = 11.0 Hz, 1H), 4.65 (d, J = 11.0 Hz, 1H), 4.91 (br s, 1H), 7.22-7.28 (m, 1H), 7.29-7.36 (m, 4H);
^{13}C NMR ($CDCl_3$, 125 MHz) δ = 12.4, 14.1, 18.0, 22.5, 24.1, 24.2, 26.1, 26.2, 27.4, 27.5, 29.6, 36.2, 36.3, 39.3, 39.4, 60.7, 60.79, 60.83, 66.0, 73.19, 73.23, 73.6, 73.7, 84.7, 84.8, 104.1, 104.3, 127.2, 127.5, 128.2, 138.9, 151.86, 151.92, 170.9;
HRMS (FD^+): m/z calcd for $[M+H]^+$ $[C_{35}H_{55}O_6Si]^+$ 599.3768, found 599.3776

Synthesis of 5c.



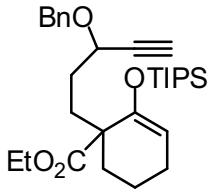
S5a **5c**

To a DMF solution (20 ml) of alcohol **S5a** (1.4 g, 4.0 mmol, 1.0 equiv.) and *N,N*-diisopropylethylamine (1.2 ml, 6.8 mmol, 1.7 equiv.) was added methanesulfonyl chloride (0.46 ml, 6.0 mmol, 1.5 equiv.) slowly at 0 ºC, and the mixture was stirred at room temperature overnight. To the reaction mixture was added lithium bromide (1.7 g, 20 mmol, 5.0 equiv.) and the mixture was stirred at 70 ºC for 7 h. The reaction mixture was quenched with water and the aqueous layer was extracted with diethyl ether three times. The combined organic layer was washed with water and brine and dried over $MgSO_4$. The solvent was removed under reduced pressure. The crude alkyl bromide was used for the next reaction without further purification.

To a DMF solution (10 ml) of sodium hydride (60%, 180 mg, 4.4 mmol, 1.1 equiv.) was added a DMF solution (10 ml) of ethyl 2-oxocyclohexanecarboxylate (0.70 ml, 4.4 mmol, 1.1 equiv.) at 0 ºC and the mixture was stirred at room temperature for 30 min. A DMF solution (10 ml) of the crude alkyl bromide and tetrabutylammonium iodide (440 mg, 1,2 mmol, 30 mol%) was added to the reaction mixture and the resulting mixture was stirred at 120 ºC for 10 h. The reaction mixture was quenched with sat. aqueous NH_4Cl and the aqueous layer was extracted with diethyl ether three times. The combined organic layer was washed with water and brine and dried over $MgSO_4$. The solvent was removed under reduced pressure. The crude β-keto ester was used for the next reaction without further purification.

To a THF solution (8 ml) of the crude β-keto ester was added TBAF (1 M THF solution, 4.8 ml, 4.8 mmol, 1.2 equiv.) slowly at 0 ºC, and the mixture was stirred at room temperature for 1 h. The reaction mixture was quenched with sat. aqueous NH_4Cl and the aqueous layer was extracted with ethyl acetate three times. The combined organic layer was washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure. The crude material was filtered through silica gel column chromatography (ethyl acetate/hexane = 1/9), and the obtained material was used for the next reaction without further purification.

To a dichloromethane solution (40 ml) of the crude material and 2,6-lutidine (4.6 ml, 40 mmol, 10 equiv.) was added TIPSOTf (1.6 ml, 6.0 mmol, 1.5 equiv.) slowly at 0 ºC, and the mixture was stirred at room temperature for 24 h. The reaction mixture was quenched with sat. aqueous $NaHCO_3$ and the aqueous layer was extracted with dichloromethane three times. The combined organic layer was dried over $MgSO_4$. The solvent was removed under reduced pressure. The crude material was purified by silica gel column chromatography (ethyl acetate : hexane = 10 : 90) to give silyl enol ether **5c** as a yellow oil in 23% yield (in 4 steps, 460 mg, 0.92 mmol).

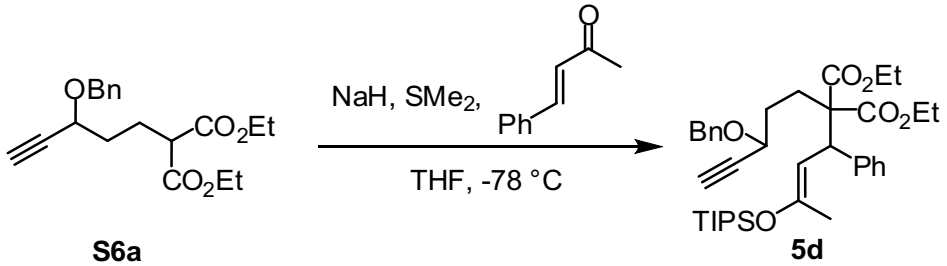


5c

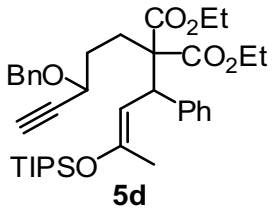
Diastereomer ratio was determined by ^{1}H-NMR (d.r. = 58 : 42).
IR (neat) 3306, 3032, 2943, 2867, 2759, 2720, 2111, 1728, 1662, 1460, 1188, 927, 882, 738, 684 cm^{-1};
^{1}H NMR ($CDCl_3$, 500 MHz) δ = 1.02-1.10 (m, 18H), 1.12-1.20 (m, 3H), 1.23 (t, J = 7.0 Hz, 3H), 1.50-1.71 (m, 3H), 1.73-2.09 (m, 7H), 2.44 (d, J = 2.0 Hz, 0.42H), 2.46 (d, J = 2.0 Hz, 0.58H), 4.00-4.10 (m, 2H), 4.11-4.19 (m, 1H), 4.50 (d, J = 11.5 Hz, 0.42H), 4.51 (d, J = 12.0 Hz, 0.58H), 4.78 (d, J = 12.0 Hz, 0.58H), 4.80 (d, J = 12.0 Hz, 0.42H), 4.83-4.87 (m, 1H), 7.26-7.30 (m, 1H), 7.30-7.38 (m, 4H);

^{13}C NMR ($CDCl_3$, 125 MHz) δ = 12.8, 14.2, 18.1, 18.2, 19.2, 23.9, 30.7, 30.81, 30.83, 31.7, 31.8, 50.3, 60.4, 68.9, 69.0, 70.35, 70.38, 73.8, 73.9, 82.8, 103.2, 127.6, 127.9, 128.0, 128.3, 137.9, 138.0, 149.8, 175.5;
HRMS (FD^+): m/z calcd for $[M]^+$ $[C_{30}H_{46}O_4Si]^+$ 498.3165, found 498.3169

Synthesis of 5d.



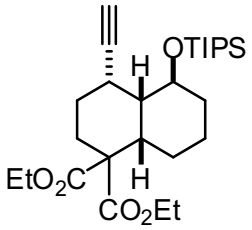
Solution 1: To a THF suspension (3 ml) of sodium hydride (60%, 80 mg, 2.0 mmol, 2.0 equiv.) was added a THF solution (2 ml) of **S6a** (500 mg, 1.5 mmol, 1.5 equiv.) at 0 °C and the mixture was stirred at the same temperature for 45 min.
Solution 2: To a THF solution (5 ml) of benzalacetone (150 mg, 1.0 mmol, 1.0 equiv.) was added TIPSOTf (400 µl, 1.5 mmol, 1.5 equiv.) and dimethyl sulfide (220 µl, 3.0 mmol, 3 equiv.) slowly at -78 °C and the mixture was stirred at the same temperature for 30 min. Solution 1 was added slowly to solution 2 with syringe at -78 °C and the mixture was stirred at the same temperature for 5 h. The reaction mixture was quenched with sat. aqueous $NaHCO_3$ and the aqueous layer was extracted with ethyl acetate three times. The combined organic layer was washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure. The crude material was purified by silica gel column chromatography (ethyl acetate : hexane = 5 : 95) and GPC (AcOEt) to give silyl enol ether **5d** as a yellow oil in 42% yield (260 mg, 0.42 mmol).



Diastereomer ratio was determined by ^{1}H-NMR (d.r. = 50 : 50)
IR (neat) 3285, 3087, 3063, 3030, 2944, 2867, 2758, 2112, 1728, 1659, 1458, 1384, 1194, 1030, 883, 699 cm^{-1};
^{1}H NMR ($CDCl_3$, 500 MHz) δ = 1.04 (d, *J* = 7.5 Hz, 9H), 1.06 (d, *J* = 7.5 Hz, 9H), 1.13-1.25 (m, 9H), 1.61-2.10 (m, 4H), 1.757 (d, *J* = 1.0 Hz, 1.5H), 1.763 (d, *J* = 0.5 Hz, 1.5H), 2.44 (d, *J* = 2.0 Hz, 0.5H), 2.46 (d, *J* = 2.5 Hz, 0.5H), 3.94-4.03 (m, 2H), 4.06-4.25 (m, 4H), 4.476 (d, *J* = 11.5 Hz, 0.5H), 4.481 (d, *J* = 12.0 Hz, 0.5H), 4.76 (d, *J* = 12.0 Hz, 0.5H), 4.77 (d, *J* = 12.0 Hz, 0.5H), 5.38-5.43 (m, 1H), 7.13-7.25 (m, 5H), 7.26-7.38 (m, 5H);
^{13}C NMR ($CDCl_3$, 125 MHz) δ = 12.5, 13.9, 17.9, 18.0, 31.1, 31.21, 31.23, 49.2, 49.3, 60.87, 60.92, 62.1, 62.2, 68.2, 68.3, 70.2, 73.9, 74.1, 82.2, 82.3, 105.58, 105.61, 126.5, 127.6, 127.8, 127.86, 127.89, 128.3, 129.0, 129.1, 137.72, 137.74, 140.8, 150.0, 170.1, 170.2, 170.48, 170.53;
HRMS (FD^+): m/z calcd for $[M+H]^+$ $[C_{38}H_{55}O_6Si]^+$ 635.3768, found 635.3762

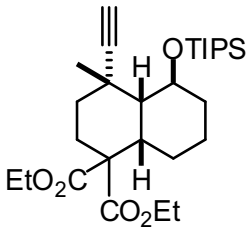
General procedure for intramolecular hydropropargylation

A mixture of $ReI(CO)_5$ (2.3 mg, 0.005 mmol, 5 mol%) and silyl enol ether (0.10 mmol) in 1,4-dioxane (1.0 ml) was stirred for 5 h at 100 °C. The reaction mixture was quenched with TMEDA (0.2 ml) and concentrated under reduced pressure in vacuo. The crude material was purified by silica gel column chromatography (ethyl acetate : hexane = 5 : 95) to give the product.



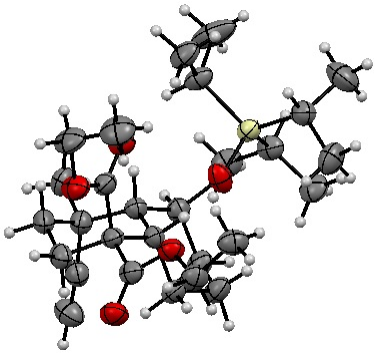
6a

a white solid. (38.2 mg, 0.080 mmol, 80%). Diastereomer ratio was determined by ^{1}H-NMR (d.r. = 88 : 12). The stereochemistry of the product was determined by NOE of the desilylated compound **S7** (see page S18).
IR (neat) 3306, 2940, 2866, 2109, 1734, 1462, 1234, 1096, 1035, 882, 680 cm^{-1};
^{1}H NMR ($CDCl_3$, 500 MHz) δ = 0.90-1.16 (m, 22H), 1.21 (t, *J* = 7.5 Hz, 3H), 1.23 (t, *J* = 7.5 Hz, 3H), 1.26-1.66 (m, 3H), 1.72-2.00 (m, 3H), 2.02-2.50 (m, 4H), 2.04 (d, *J* = 2.5 Hz, 0.12H), 2.14 (d, *J* = 2.5 Hz, 0.88H), 2.65 (br s, 1H), 2.89 (dt, *J* = 4.0, 14.0 Hz, 0.88H) 2.94-3.01 (m, 0.12H), 3.94 (d, *J* = 2.0 Hz, 0.88H), 4.06-4.26 (m, 4H), 4.45 (br s, 0.12H);
^{13}C NMR ($CDCl_3$, 125 MHz)
Major isomer δ = 12.3, 14.0, 14.1, 18.1, 18.2, 20.4, 23.0, 23.6, 27.7, 29.2, 29.5, 35.1, 42.3, 59.0, 60.96, 60.98, 71.4, 72.3, 88.5, 170.9, 171.3;
Minor isomer δ = 12.3, 14.0, 14.1, 18.1, 18.2, 19.7, 25.7, 26.8, 28.1, 29.9, 34.0, 44.5, 58.7, 61.08, 61.13, 68.5, 69.9, 86.5, 170.3, 171.0;
HRMS (FD$^+$): m/z calcd for $[M+H]^+$ $[C_{27}H_{47}O_5Si]^+$ 479.3193, found 479.3192

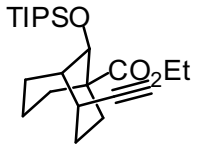


6b

a white solid. (34.3 mg, 0.070 mmol, 70%). The stereochemistry of the product was determined by X-ray crystal structure analysis.
IR (neat) 3305, 2866, 2103, 1734, 1462, 1237, 1147, 1038, 882, 680 cm^{-1};
^{1}H NMR ($CDCl_3$, 500 MHz) δ = 0.89-0.96 (m, 1H), 1.04-1.30 (m, 31H), 1.45-1.59 (m, 2H), 1.72-1.86 (m, 2H), 1.96-2.13 (m, 3H), 2.22 (s, 1H), 2.33-2.45 (m, 2H), 2.94 (dt, *J* = 13.7, 3.5 Hz, 1H) 4.06-4.24 (m, 4H), 4.27 (br d, *J* = 1.7 Hz, 1H);
^{13}C NMR ($CDCl_3$, 125 MHz) δ = 12.3, 14.0, 14.1, 18.1, 18.2, 20.0, 23.0, 24.2, 28.8, 30.7, 31.7, 34.9, 39.0, 48.6, 59.2, 60.87, 60.93, 67.4, 72.6, 91.6, 170.8, 171.3;
HRMS (FD$^+$): m/z calcd for $[M+H]^+$ $[C_{28}H_{49}O_5Si]^+$ 493.3349, found 493.3358



ORTEP of **6b**



6c

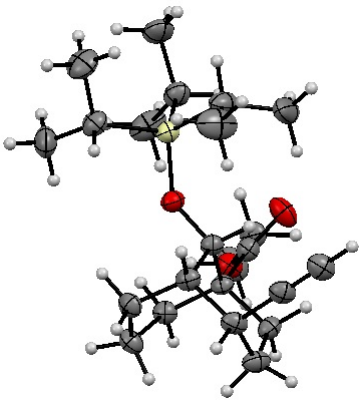
a white solid (32.1 mg, 0.082 mmol, 82%). The stereochemistry of the product was determined by X-ray crystal structure analysis.

IR (neat) 3309, 2942, 2866, 2111, 1728, 1462, 1239, 1102, 884, 803, 677 cm^{-1};

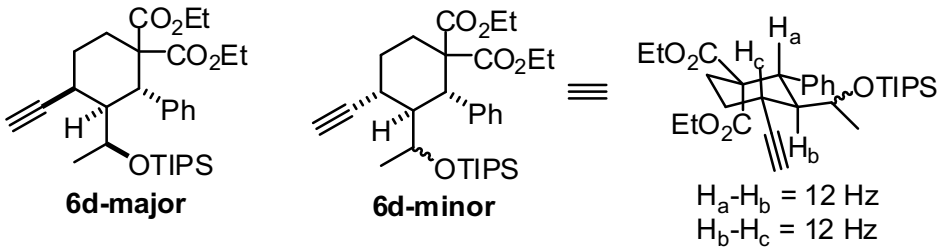
^{1}H NMR ($CDCl_3$, 500 MHz) δ = 1.01-1.10 (m, 21H), 1.25 (t, *J* = 7.5 Hz, 3H), 1.32-1.38 (m, 1H), 1.56-1.84 (m, 5H), 2.03-2.16 (m, 3H), 2.13 (d, *J* = 2.5 Hz, 1H), 2.20-2.30 (m, 2H), 2.90 (br d, *J* = 6.0 Hz, 1H), 4.00 (dq, *J* = 7.0, 11.0 Hz, 1H), 4.17 (dq, *J* = 7.0, 11.0 Hz, 1H), 4.73 (d, *J* = 3.5 Hz, 1H);

^{13}C NMR ($CDCl_3$, 125 MHz) δ = 12.8, 14.0, 18.17, 18.21, 20.3, 23.6, 25.5, 26.3, 32.3, 33.2, 39.9, 47.3, 60.3, 69.2, 70.1, 87.8, 177.0;

HRMS (FD^+): m/z calcd for $[M-^iPr]^+$ $[C_{20}H_{33}O_3Si]^+$ 349.2199, found 349.2194



ORTEP of **6c**



6d-major: a white solid. **6d-minor**: a colorless oil. (32.6 mg, 0.062 mmol, 62%). Diastereomer ratio was determined by ^{1}H-NMR (d.r. = 84 : 16). These compounds were separated by GPC (AcOEt). The stereochemistry of **6d-major** was determined by X-ray crystal structure analysis. The stereochemistry of the three contiguous stereogenic centers on the cyclohexane ring of **6d-minor** was proposed by the coupling constant as shown above and the stereochemistry of OTIPS group on the side chain was not determined.

6d-major

IR (neat) 3309, 2941, 2866, 2111, 1725, 1464, 1368, 1254, 1154, 1064, 884, 679 cm^{-1};

^{1}H NMR ($CDCl_3$, 400 MHz) δ = 0.73-0.88 (m, 3H), 0.89-1.00 (m, 21H), 1.09 (t, *J* = 6.8 Hz, 3H), 1.14 (d, *J* = 6.4 Hz, 3H), 1.80-1.93 (m, 2H), 2.08, (d, *J* = 2.4 Hz, 1H), 2.19 (dt, *J* = 13.6, 2.4 Hz, 1H), 2.54-2.69 (m, 2H), 3.11-3.19 (m, 1H), 3.66 (d, *J* = 12.4 Hz, 1H), 3.76 (dq, *J* = 10.8, 7.2 Hz, 1H), 3.91-4.03 (m, 2H), 4.03-4.13 (m, 2H), 7.09-7.22 (m, 3H), 7.38 (br s, 2H);

^{13}C NMR ($CDCl_3$, 125 MHz) δ = 12.9, 13.5, 13.8, 18.2, 18.4, 22.0, 27.1, 29.0, 30.0, 44.9, 47.6, 60.3, 60.7, 61.0, 68.0, 71.7, 86.0, 126.5, 127.2, 129.9 (br), 132.3 (br), 138.7, 171.0, 171.7;

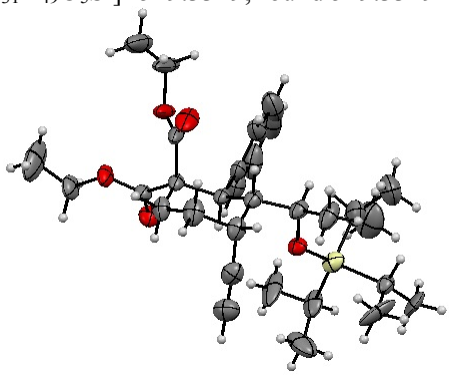
HRMS (FD^+): m/z calcd for $[M+H]^+$ $[C_{31}H_{49}O_5Si]^+$ 529.3349, found 529.3362

6d-minor

IR (neat) 3309, 2942, 2865, 2113, 1726, 1458, 1367, 1261, 1160, 1063, 884, 703 cm^{-1};

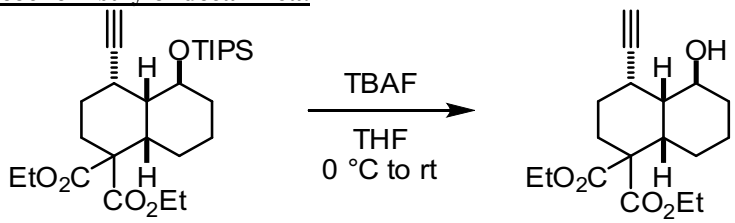
^{1}H NMR ($CDCl_3$, 400 MHz) δ = 0.71 (d, *J* = 6.4 Hz, 3H), 0.83 (t, *J* = 7.2 Hz, 3H), 0.99-1.09 (m, 21H), 1.19 (t, *J* = 6.8 Hz, 3H), 1.60-1.74 (m, 1H), 1.97-2.12 (m, 2H), 2.05 (d, *J* = 2.4 Hz, 1H), 2.25-2.36 (m, 1H), 2.56-2.66 (m, 1H), 2.79 (t,

J = 12.0 Hz, 1H), 3.06 (d, J = 12.0 Hz, 1H), 3.62 (dq, J = 10.8, 7.2 Hz, 1H), 3.85 (dq, J = 10.8, 7.2 Hz, 1H), 4.15 (q, J = 6.8 Hz, 2H), 4.31 (q, J = 6.4 Hz, 1H), 7.10-7.22 (m, 3H), 7.50 (br, 2H);
^{13}C NMR ($CDCl_3$, 125 MHz) δ = 12.6, 13.4, 14.0, 18.2, 18.3, 22.4, 28.7, 31.8, 33.5, 47.7, 50.5, 60.6, 60.7, 61.0, 69.4, 70.0, 87.9, 126.8, 127.4, 130.4 (br), 131.9 (br), 140.1, 170.6, 171.6;
HRMS (FD$^+$): m/z calcd for $[M+H]^+$ $[C_{31}H_{49}O_5Si]^+$ 529.3349, found 529.3349



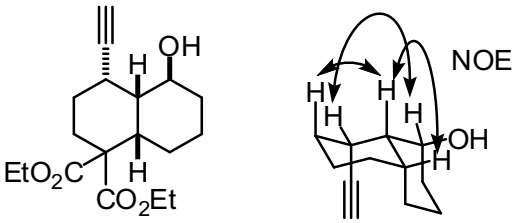
ORTEP of **6d-major**

Determination of the stereochemistry of decalin 6a.



6a **S7**

To a THF solution (3 ml) of **6a** (92 mg, 0.19 mmol, 1.0 equiv.) was added TBAF (1 M THF solution, 960 µl, 0.96 mmol, 5.0 equiv.) slowly at 0 °C, and the mixture was stirred at room temperature for 24 h. The reaction mixture was quenched with sat. aqueous NH_4Cl and the aqueous layer was extracted with ethyl acetate three times. The combined organic layer was washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure. The crude material was purified by silica gel column chromatography (ethyl acetate : hexane = 50 : 50) and GPC (AcOEt) to give major diastereomer of **S7** as a yellow oil in 30% yield (18 mg, 0.057 mmol). The stereochemistry of the product was determined by NOE as shown below.



IR (neat) 3526, 3284, 2932, 2868, 2106, 1729, 1449, 1238, 1176, 626 cm^{-1};
^{1}H NMR ($CDCl_3$, 500 MHz) δ = 0.95-1.05 (m, 1H), 1.225 (t, J = 7.2 Hz, 3H), 1.228 (t, J = 7.2 Hz, 3H), 1.36-1.45 (m, 1H), 1.54-1.79 (m, 3H), 1.88 (dq, J = 13.8, 2.7 Hz, 1H), 2.01 (dq, J = 4.0, 13.2 Hz, 1H), 2.01 (br d, J = 14.5 Hz, 1H), 2.15 (d, J = 2.9 Hz, 1H), 2.24 (br s, 1H), 2.41 (dt, J = 3.0, 14.5 Hz, 1H), 2.46-2.56 (m, 1H), 2.73 (br s, 1H), 2.83 (dt, J = 13.5, 4.0 Hz, 1H), 3.92 (br d, J = 2.0 Hz, 1H), 4.09-4.26 (m, 4H);
^{13}C NMR ($CDCl_3$, 125 MHz) δ = 14.0, 14.1, 20.3, 22.8, 23.2, 27.6, 27.9, 29.3, 35.2, 41.6, 58.6, 61.1, 61.3, 70.9, 72.5, 87.9, 170.9, 171.1;
HRMS (FD$^+$): m/z calcd for $[M]^+$ $[C_{18}H_{26}O_5]^+$ 322.1780, found 322.1786

4. Reference

(1) Darst, K. P.; Lukehart, C. M. *J. Organometal. Chem.* **1979**, *171*, 65.

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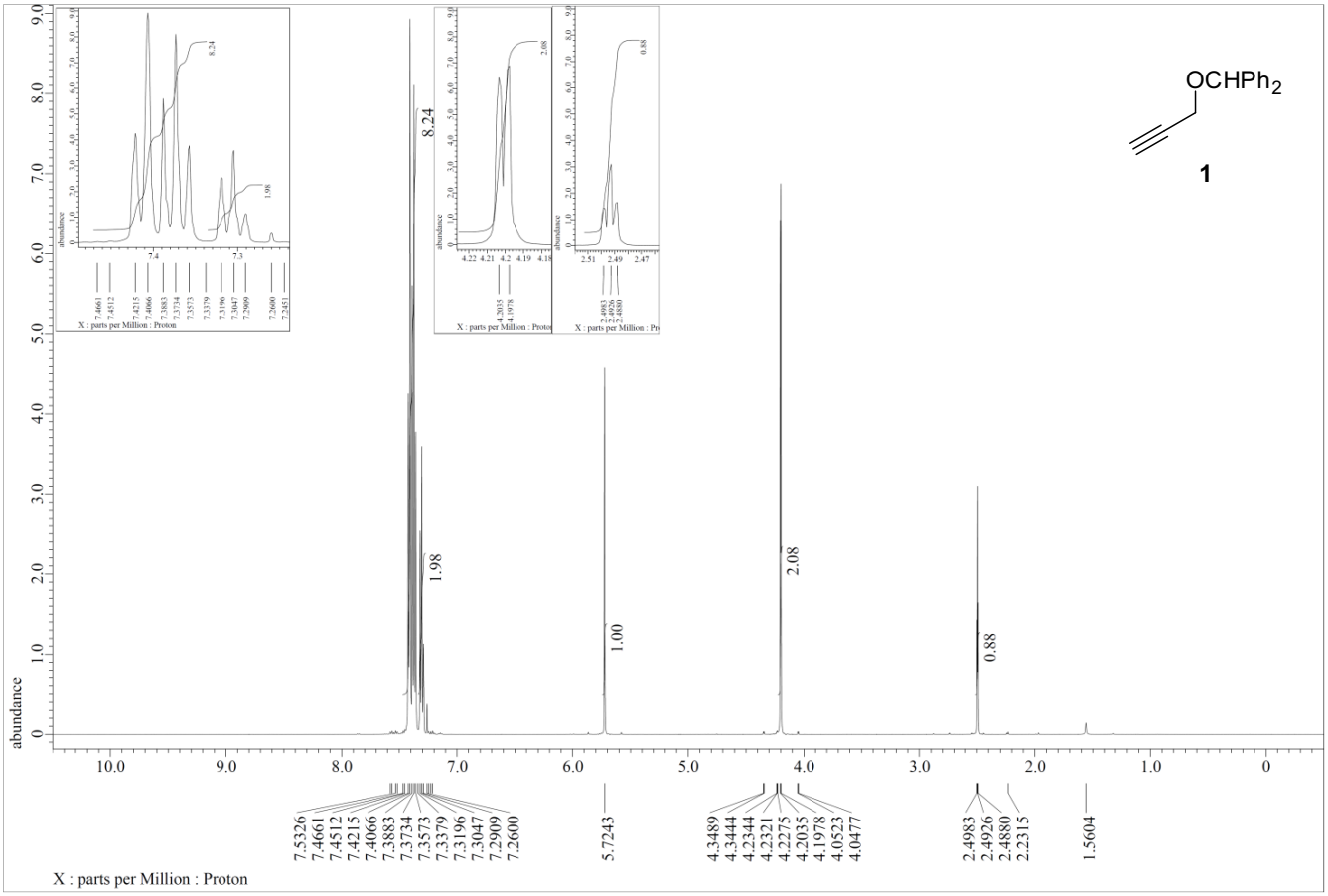
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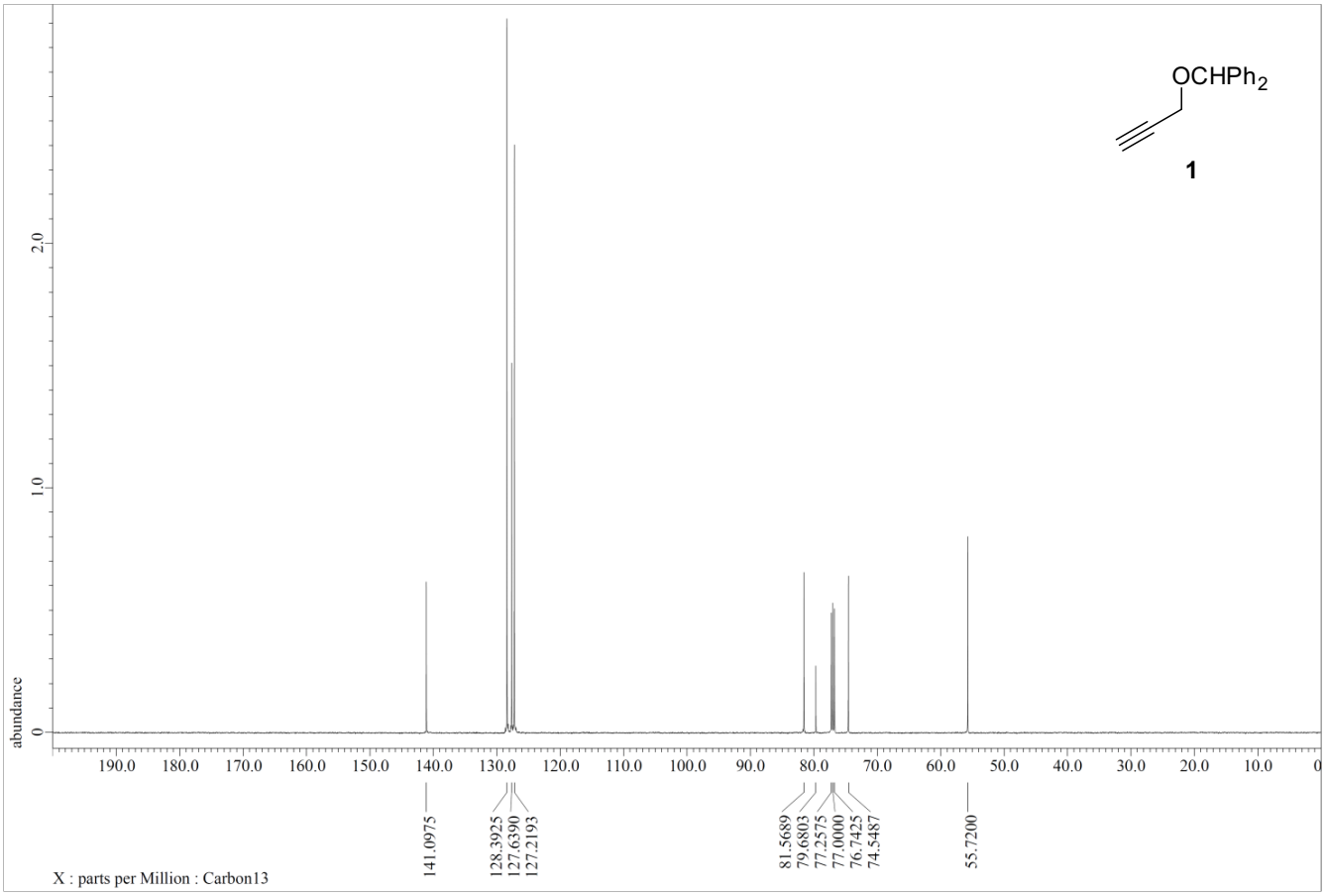
1.98
1.00
2.08
0.88
7.5326
7.4661
7.4512
7.4215
7.4066
7.3883
7.3734
7.3573
7.3379
7.3196
7.3047
7.2909
7.2600
5.7243
4.3489
4.3344
4.2344
4.2321
4.2275
4.2035
4.1978
4.0523
4.0477
2.4983
2.4926
2.4880
2.2315
1.5604
X : parts per Million : Proton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abundance
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128.3925
127.6390
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81.5689
79.6803
77.2575
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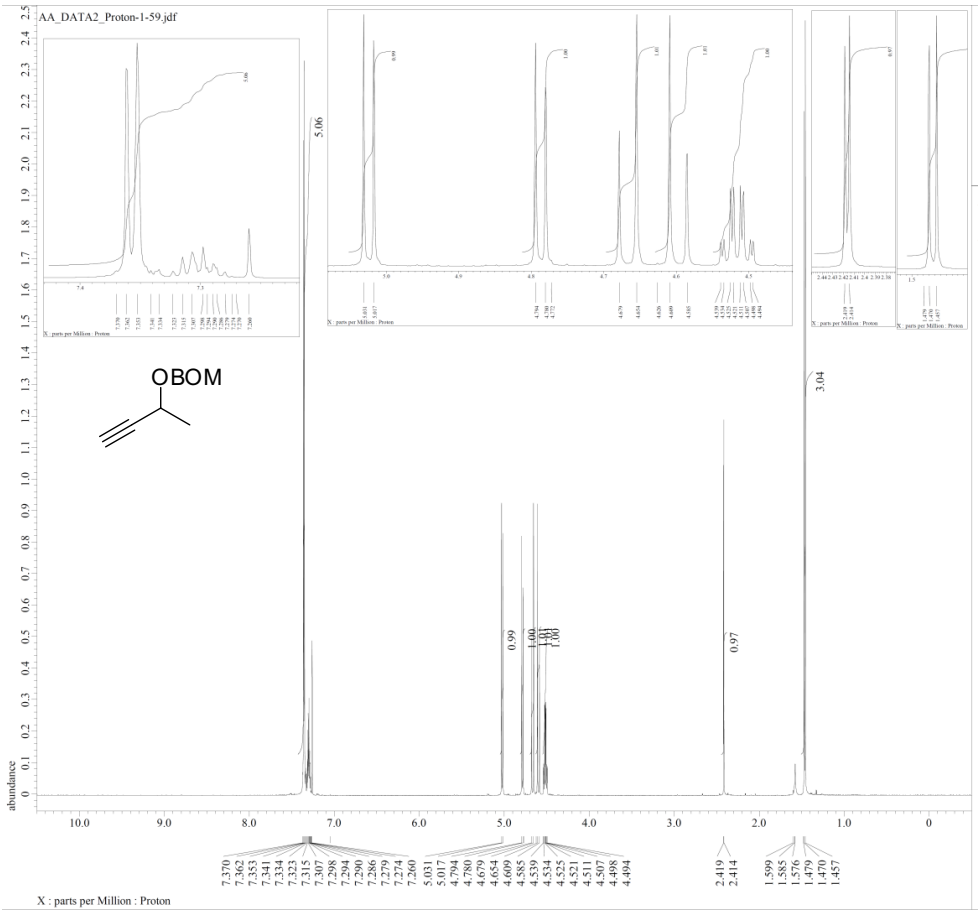
76.7425
74.5487
55.7200
X : parts per Million : Carbon13

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zerofill( 1 )
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machinephase
ppm

以下に由来:: AA_DATA2_Proton-1-1.jdf
```

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Revision_Time           = 17-MAY-2018 14:32:43

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Dim_Title               = Proton
Dim_Units               = [ppm]
Dimensions              = X
Spectrometer            = JNM-ECZ500R/S1

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X_Acq_Duration          = 1.76422912[s]
X_Domain                = 1H
X_Freq                  = 495.13191398[MHz]
X_Offset                = 5[ppm]
X_Points                = 16384
X_Prescans              = 1
X_Resolution            = 0.5668198[Hz]
X_Sweep                 = 9.28677563[kHz]
X_Sweep_Clipped         = 7.42942051[kHz]
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Irr_Freq                = 495.13191398[MHz]
Irr_Offset              = 5[ppm]
Tri_Domain              = Proton
Tri_Freq                = 495.13191398[MHz]
Tri_Offset              = 5[ppm]
Clipped                 = FALSE
Scans                   = 16
Total_Scans             = 16

Relaxation_Delay        = 5[s]
Recvr_Gain              = 56
Temp_Get                = 21.7[dC]
X_90_Width              = 11.53[us]
X_Acq_Time              = 1.76422912[s]
X_Angle                 = 45[deg]
X_Atn                   = 3.3[db]
X_Pulse                 = 5.765[us]
Irr_Mode                = Off
Tri_Mode                = Off
Dante_Loop              = 500
Dante_Presat            = FALSE
Decimation_Rate         = 0
Initial_Wait            = 1[s]
Phase                   = (0, 90, 270, 180, 180
Presat_Time             = 5[s]
Presat_Time_Flag        = FALSE
Relaxation_Delay_Calc   = 0[s]
Relaxation_Delay_Temp   = 5[s]
Repetition_Time         = 6.76422912[s]
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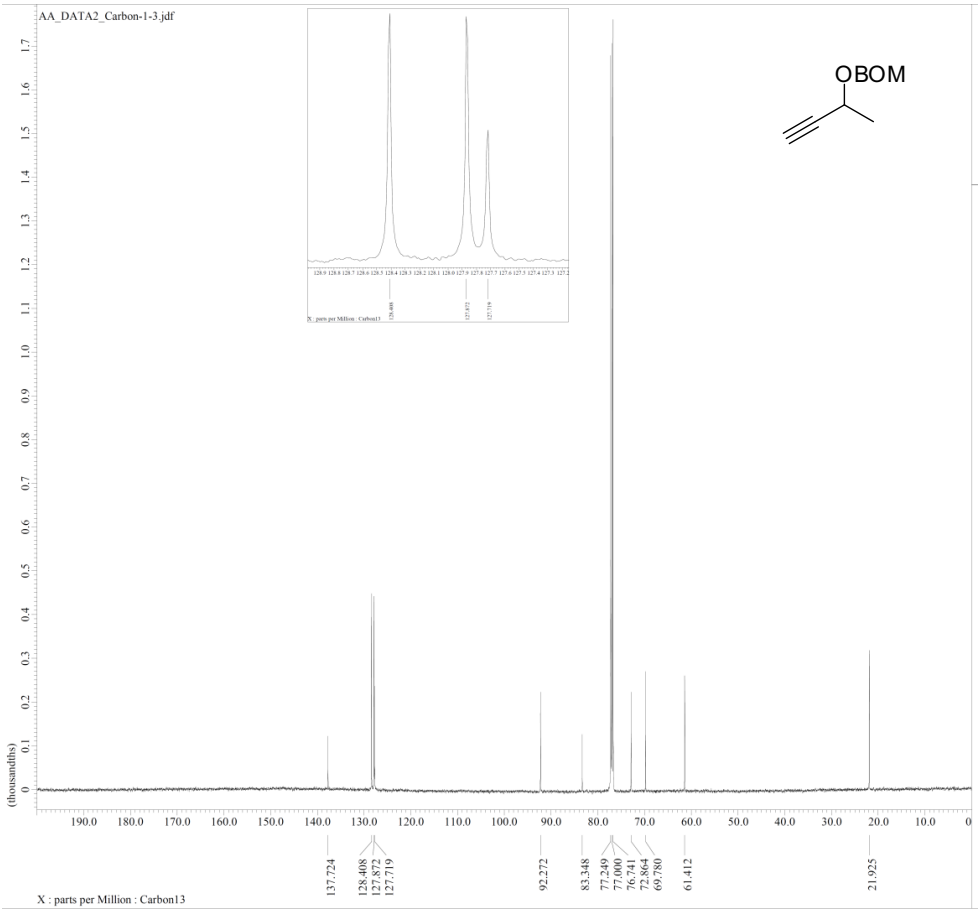


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---- PROCESSING PARAMETERS ----
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fft( 1, TRUE, TRUE )
machinephase
ppm

以下に由来:: AA_DATA2_Carbon-1-1.jdf
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Revision_Time           = 14-MAY-2018 15:01:

Comment                 = single pulse decou
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Dim_Units               = [ppm]
Dimensions              = X
Spectrometer            = JNM-ECZ500R/S1

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X_Domain                = 13C
X_Freq                  = 124.5010059[MHz]
X_Offset                = 100[ppm]
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Irr_Offset              = 5[ppm]
Clipped                 = TRUE
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Total_Scans             = 1024

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X_Angle                 = 30[deg]
X_Atn                   = 11[dB]
X_Pulse                 = 3.75333333[us]
Irr_Atn_Dec             = 21.339[dB]
Irr_Atn_Dec_Calc        = 21.339[dB]
Irr_Atn_Dec_Default_Calc = 21.339[dB]
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Irr_Dec_Freq            = 495.13191398[MHz]
Irr_Dec_Merit_Factor    = 2.2
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Irr_Noe                 = TRUE
Irr_Noise               = WALTZ
Irr_Offset_Default      = 5[ppm]
Irr_Pwidth              = 92[us]
Irr_Pwidth_Default      = 92[us]
Irr_Pwidth_Default_Calc = 92[us]
Irr_Pwidth_Temp1        = 92[us]
Irr_Wurst               = FALSE
Decimation_Rate         = 0
Initial_Wait            = 1[s]
Noe_Time                = 2[s]
Noe_Time_Flag           = FALSE
Relaxation_Delay_Calc   = 0[s]
Relaxation_Delay_Temp   = 2[s]
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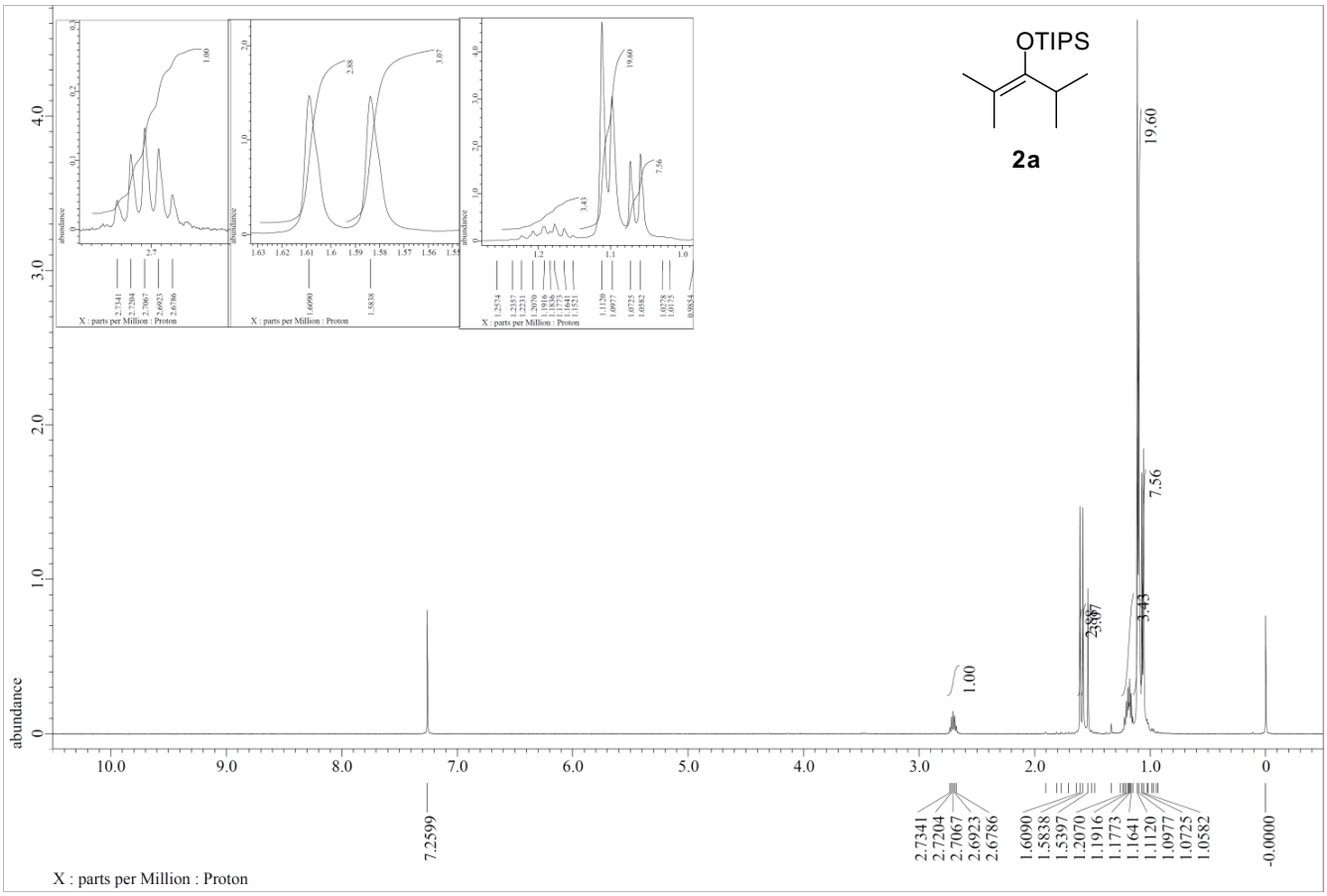
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2a
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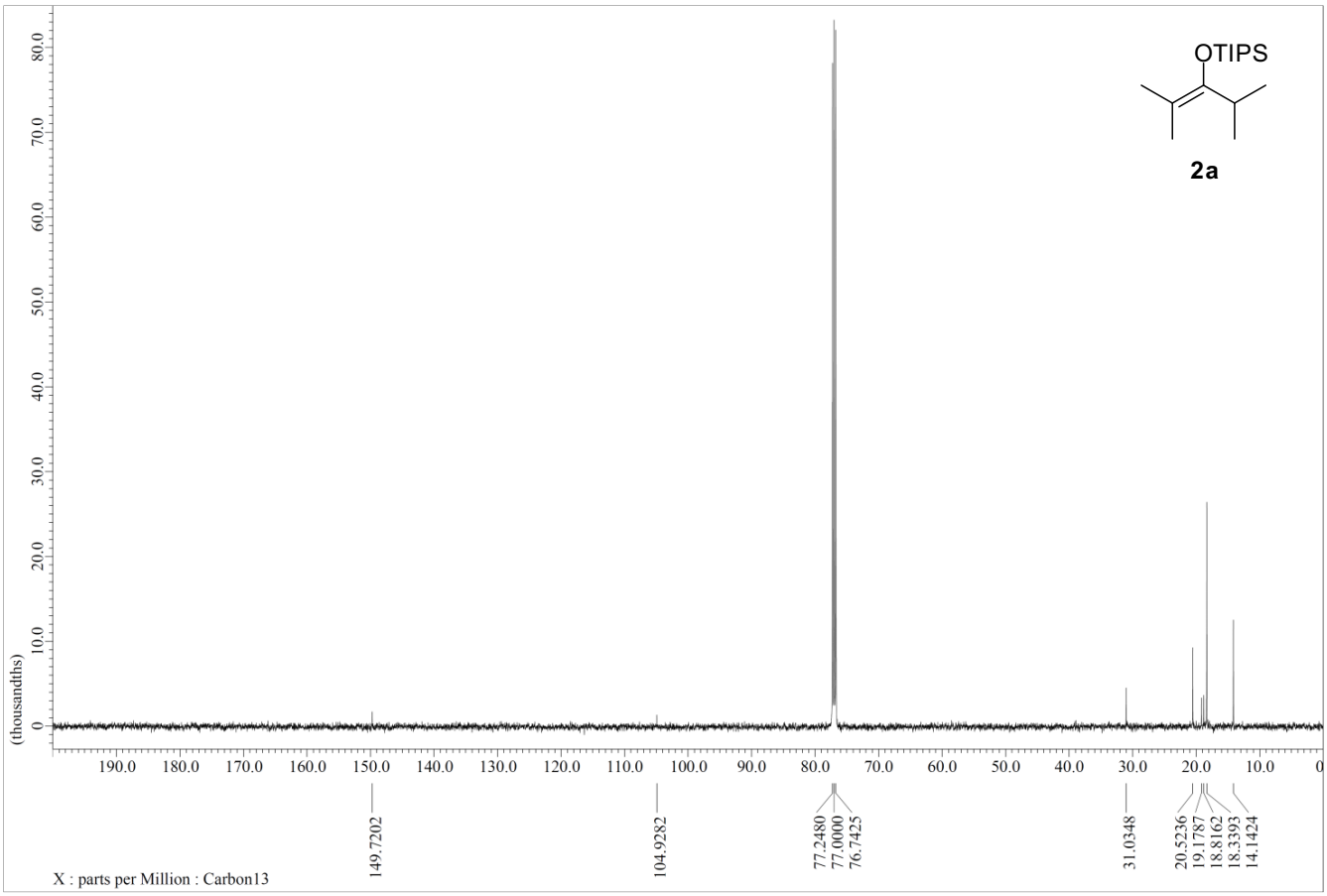
X : parts per Million : Proton
7.2599
2.7341
2.7204
2.7067
2.6923
2.6786
1.6090
1.5838
1.5397
1.2070
1.1916
1.1773
1.1641
1.1120
1.0977
1.0725
1.0582
-0.0000
19.60
7.56
3.43
1.00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(thousandths)
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31.0348
20.5236
19.1787
18.8162
18.3393
14.1424


OTIPS
2c
19.66
3.36
3.17
3.00
0.99
abundance
X : parts per Million : Proton
7.4673
7.2955
7.2600
7.0481
6.2969
6.1263
6.1228
6.1205
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4.7738
3.5450
3.4866
3.4729
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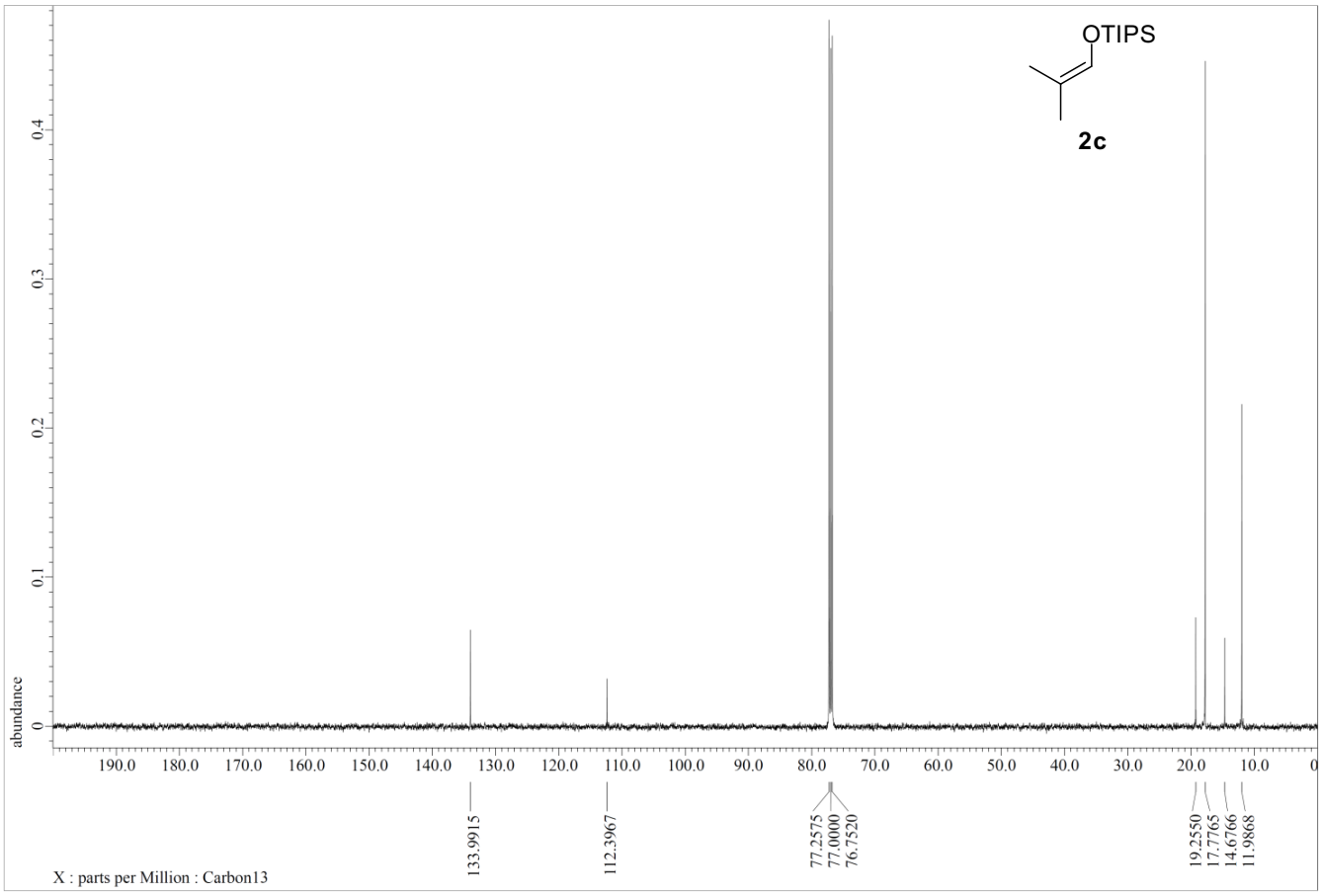
OTIPS
2c
abundance
X : parts per Million : Carbon13
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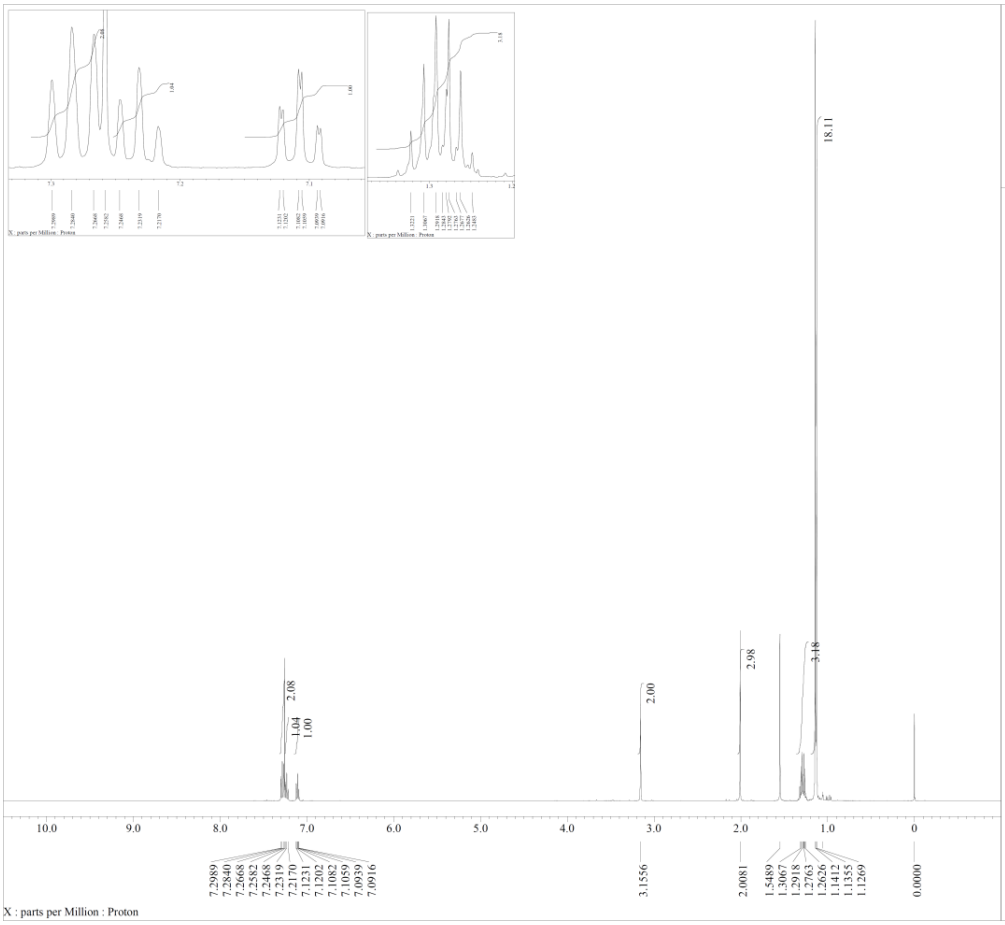
11.9868

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zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm

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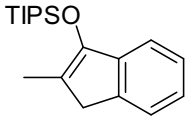
Solvent           = CHLOROFORM-D
Creation_Time     = 17-APR-2016 13:15:16
Revision_Time     = 17-APR-2016 13:20:25
Current_Time      = 17-APR-2016 13:20:59

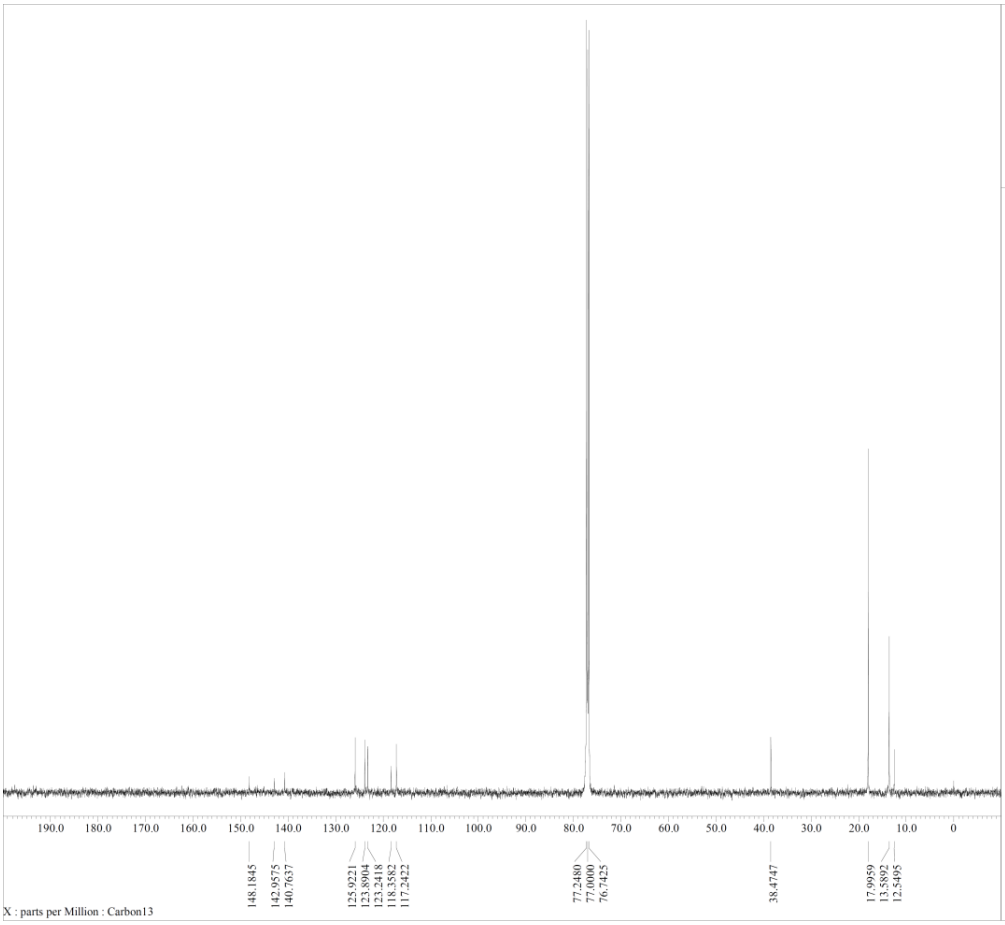
Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = Proton
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.7473579[T] (500[MHz])
X_Acq_Duration    = 3.49175808[s]
X_Domain          = 1H
X_Freq            = 500.15991521[MHz]
X_Offset          = 5.0[ppm]
X_Points          = 32768
X_Prescans        = 1
X_Resolution      = 0.28638868[Hz]
X_Sweep           = 9.38438438[kHz]
X_Sweep_Clipped   = 7.50750751[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Trl_Domain        = Proton
Trl_Freq          = 500.15991521[MHz]
Trl_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay = 5[s]
Recvr_Gain        = 46
Temp_Get          = 23.6[dC]
X_90_Width        = 12.9[us]
X_Acq_Time        = 3.49175808[s]
X_Angle           = 45[deg]
X_Atn             = 4.5[dB]
X_Pulse           = 6.45[us]
Irr_Mode          = Off
Trl_Mode          = Off
DanTe_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 8.49175808[s]
```



2i




```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm

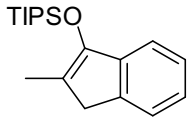
以下に曲来:: HS_2263_product_Carbon-1-1.jdf

Filename          = HS_2263_product_Carbon-1-3
Author            = iwasawa
Experiment        = carbon.jxp
Sample_Id         = HS_2263_product
Solvent           = CHLOROFORM-D
Creation_Time     = 16-APR-2016 16:24:29
Revision_Time     = 16-APR-2016 17:25:13
Current_Time      = 16-APR-2016 17:26:00

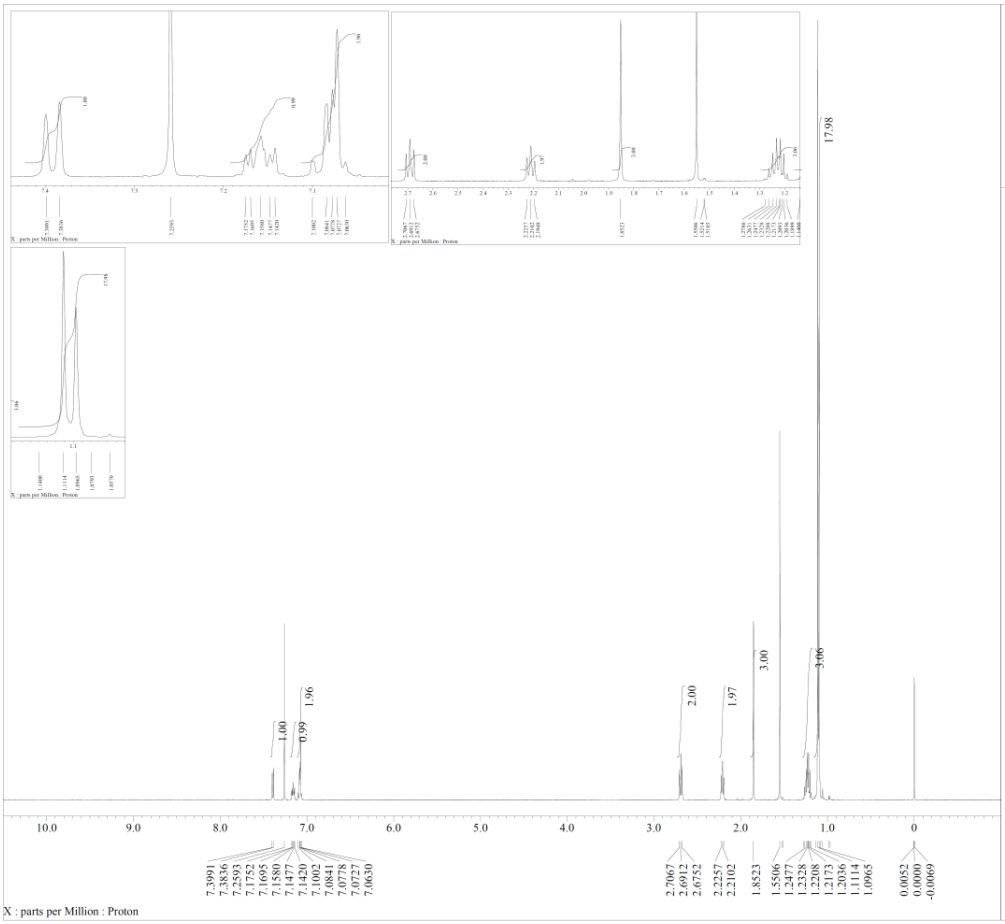
Comment           = single pulse decoupled gat
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.7473579[T] (500[MHz])
X_Acq_Duration    = 0.83361792[s]
X_Domain          = 13C
X_Freq            = 125.76529768[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.19959034[Hz]
X_Sweep           = 39.3081761[kHz]
X_Sweep_Clipped   = 31.44654088[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 1024
Total_Scans       = 1024

Relaxation_Delay = 2[s]
Recvr_Gain        = 46
Temp_Get          = 24.5[dC]
X_90_Width        = 10.4[us]
X_Acq_Time        = 0.83361792[s]
X_Angle           = 30[deg]
X_Atn             = 5.6[dB]
X_Pulse           = 3.46666667[us]
Irr_Atn_Dec       = 21.564[dB]
Irr_Atn_Noe       = 21.564[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 92[us]
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 2.83361792[s]
```



2i




```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm

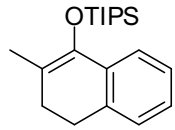
以下に由来:: HS_2264_product_proton-1-1.jdf
```

```
Filename          = HS_2264_product_proton-1-6
Author            = iwasawa
Experiment        = proton.jxp
Sample_Id         = HS_2264_product
Solvent           = CHLOROFORM-D
Creation_Time     = 16-APR-2016 17:26:24
Revision_Time     = 16-APR-2016 17:31:52
Current_Time      = 16-APR-2016 17:33:34

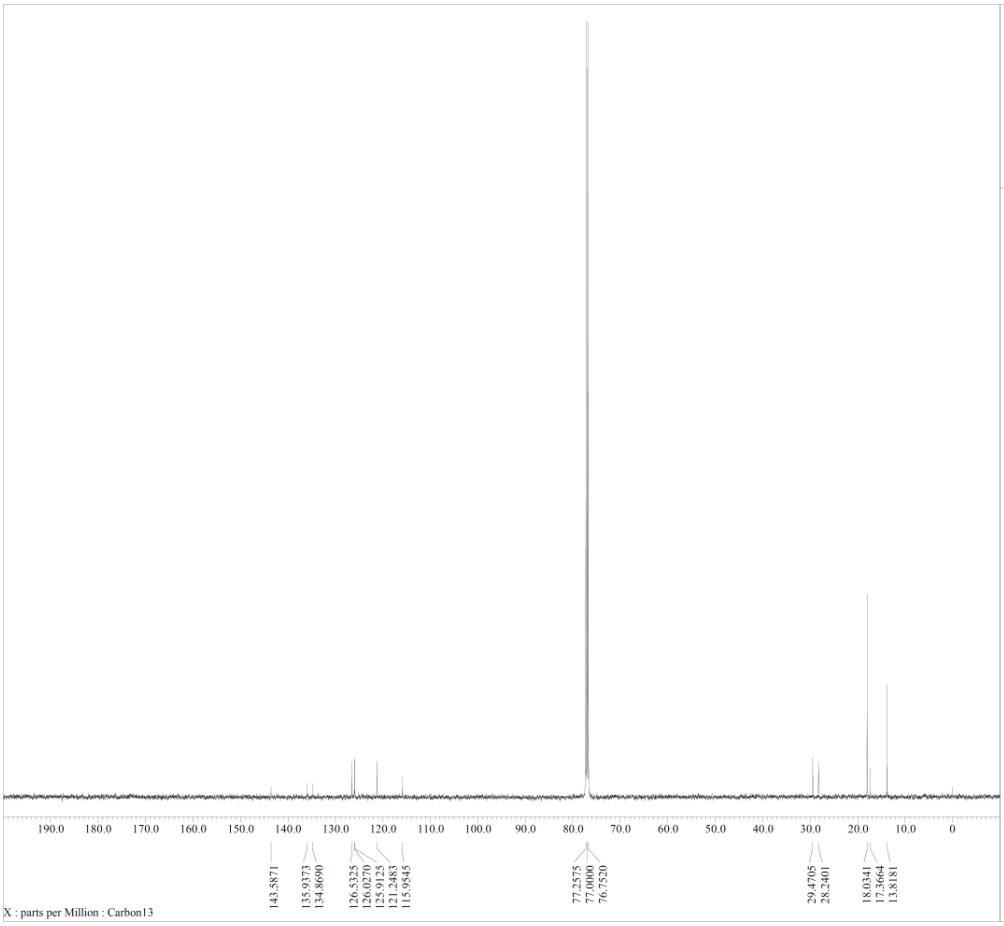
Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = Proton
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.7473579[T] (500[MHz])
X_Acq_Duration    = 3.49175808[s]
X_Domain          = 1H
X_Freq            = 500.15991521[MHz]
X_Offset          = 5.0[ppm]
X_Points          = 32768
X_Prescans        = 1
X_Resolution      = 0.28638868[Hz]
X_Sweep           = 9.38438438[kHz]
X_Sweep_Clipped   = 7.50750751[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Trl_Domain        = Proton
Trl_Freq          = 500.15991521[MHz]
Trl_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay = 5[s]
Recvr_Gain        = 50
Temp_Get          = 24[dC]
X_90_Width        = 12.9[us]
X_Acq_Time        = 3.49175808[s]
X_Angle           = 45[deg]
X_Atn             = 4.5[dB]
X_Pulse           = 6.45[us]
Irr_Mode          = Off
Trl_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 8.49175808[s]
```



2k




```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm

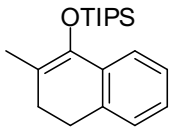
以下に由来:: HS_2264_product_Carbon-2-1.jdf
```

```
Filename          = HS_2264_product_Carbon-2-7
Author            = iwasawa
Experiment        = carbon.jxp
Sample_Id         = HS_2264_product
Solvent           = CHLOROFORM-D
Creation_Time     = 16-APR-2016 17:32:15
Revision_Time     = 17-APR-2016 13:15:35
Current_Time      = 17-APR-2016 13:15:56

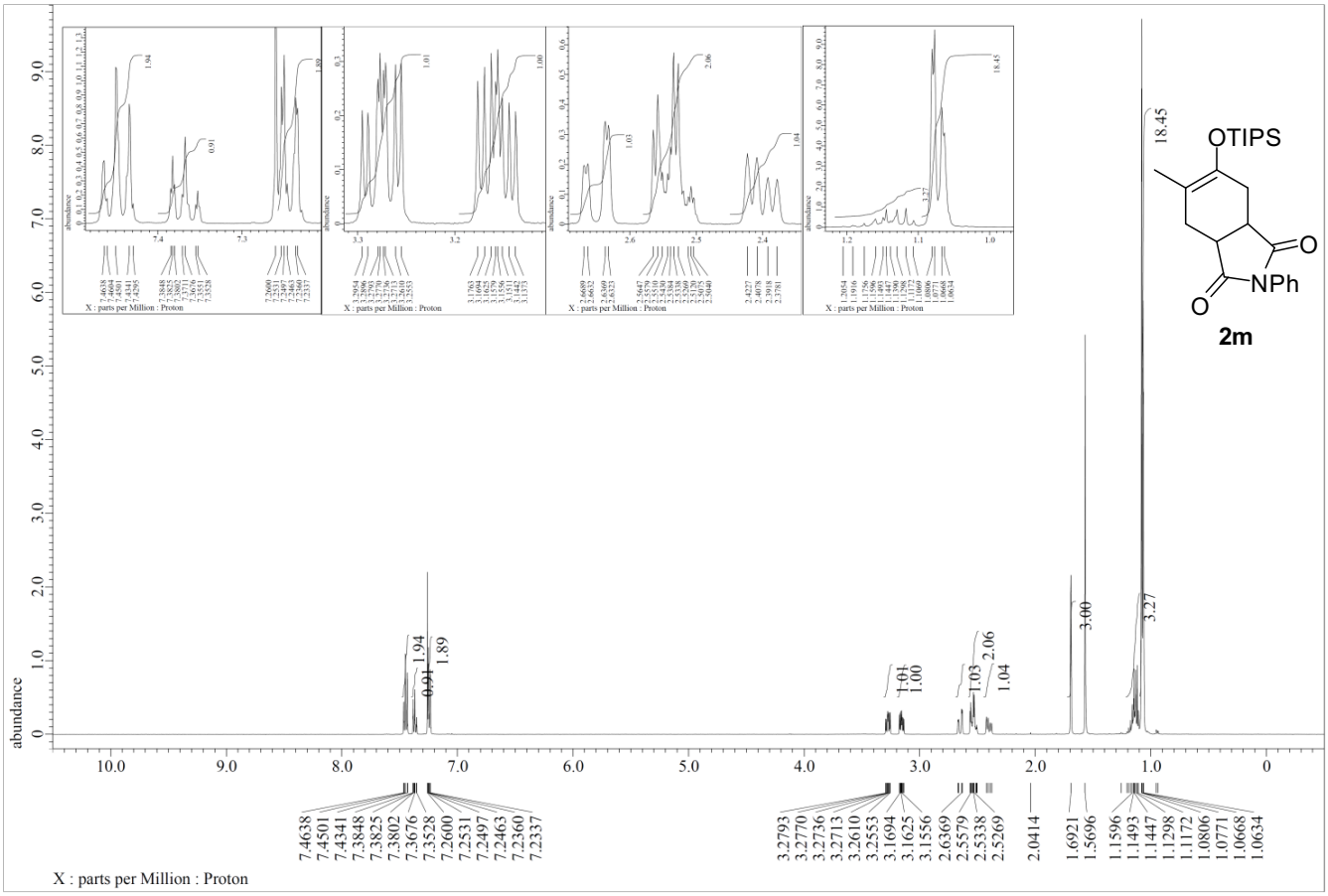
Comment           = single pulse decoupled gat
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

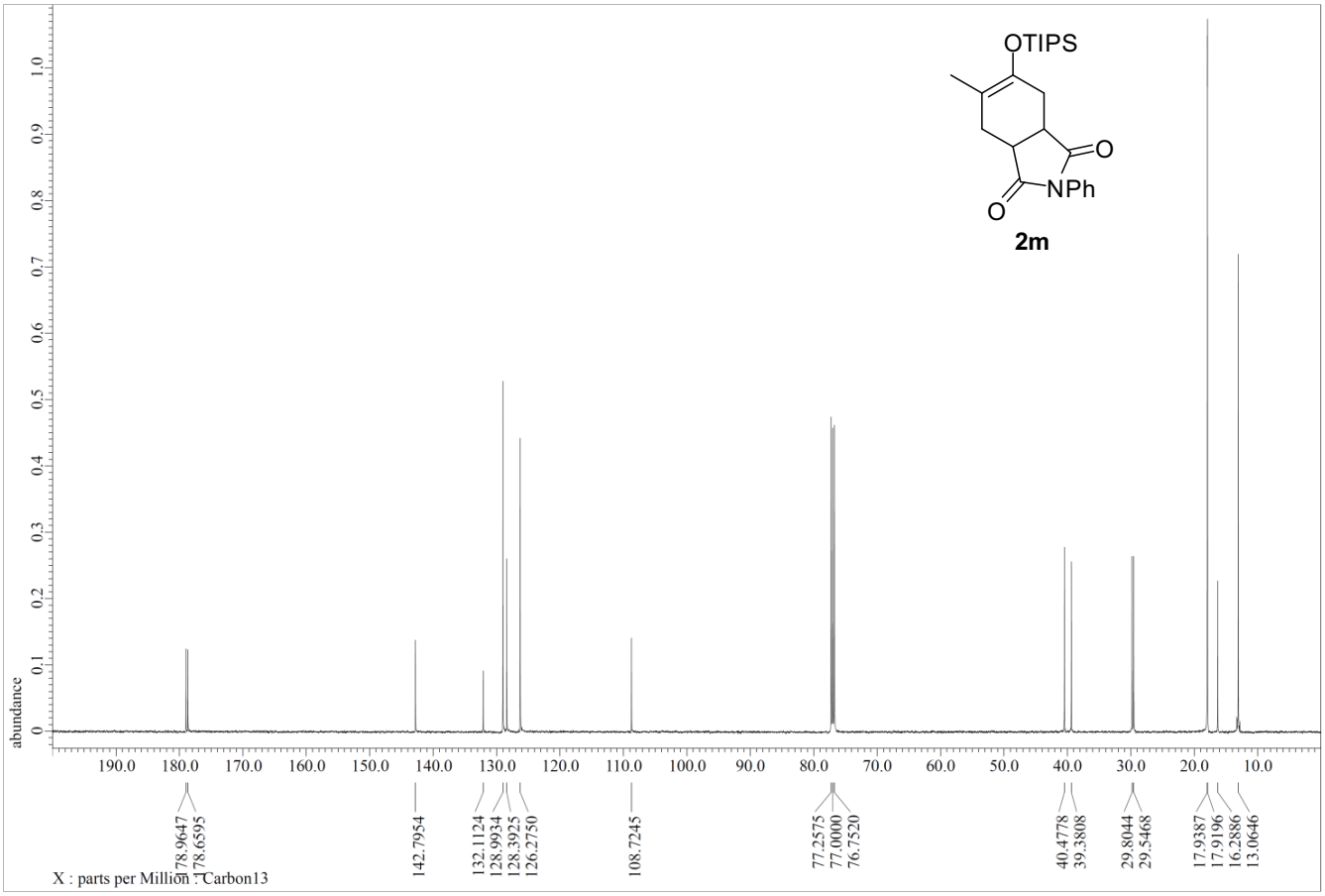
Field_Strength    = 11.7473579[T] (500[MHz])
X_Acq_Duration    = 0.83361792[s]
X_Domain          = 13C
X_Freq            = 125.76529768[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.19959034[Hz]
X_Sweep           = 39.3081761[kHz]
X_Sweep_Clipped   = 31.44654088[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 1024
Total_Scans       = 1024

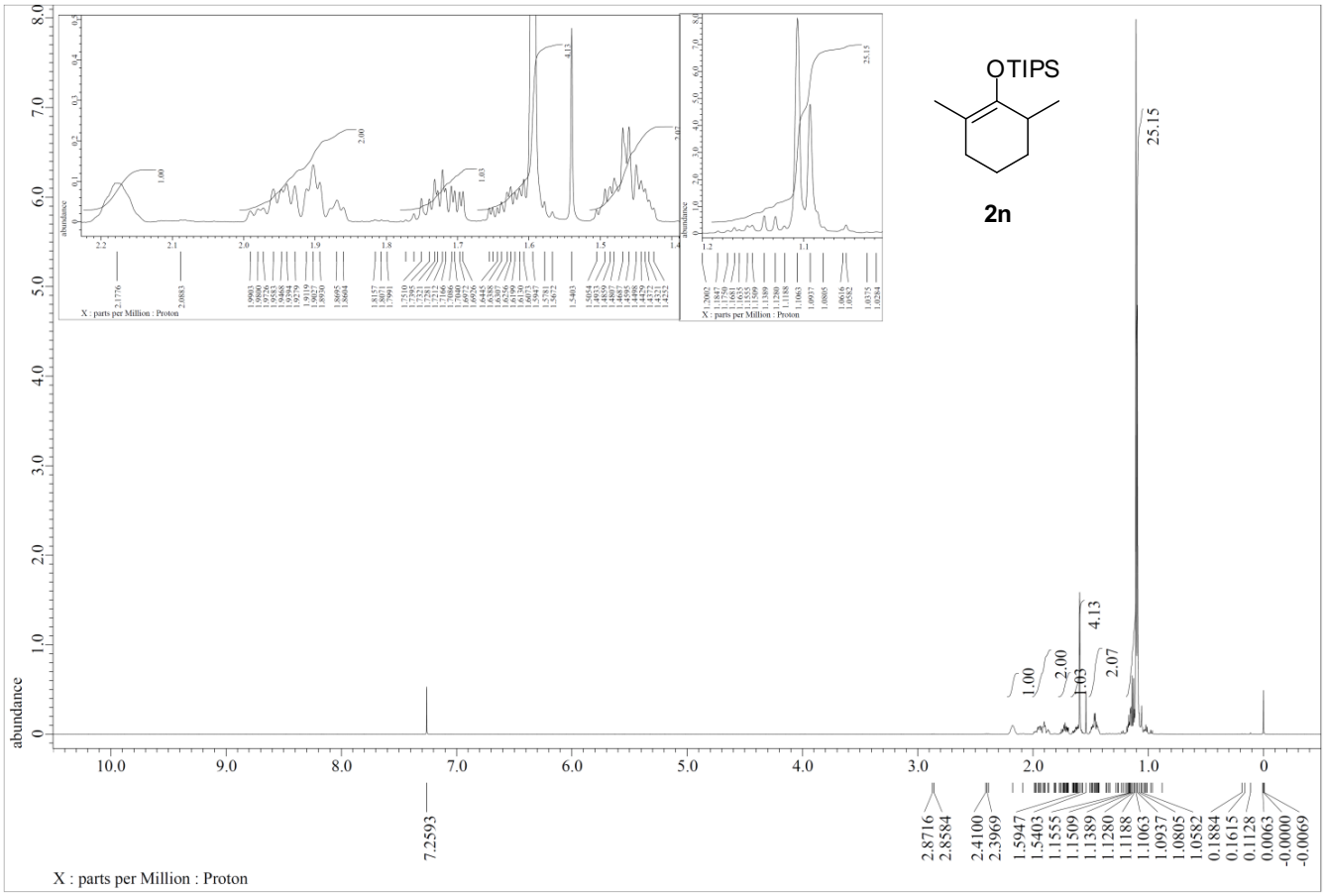
Relaxation_Delay = 2[s]
Recvr_Gain        = 50
Temp_Get          = 24.5[dC]
X_90_Width        = 10.4[us]
X_Acq_Time        = 0.83361792[s]
X_Angle           = 30[deg]
X_Atn             = 5.6[dB]
X_Pulse           = 3.46666667[us]
Irr_Atn_Dec       = 21.564[dB]
Irr_Atn_Noe       = 21.564[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 92[us]
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 2.83361792[s]
```

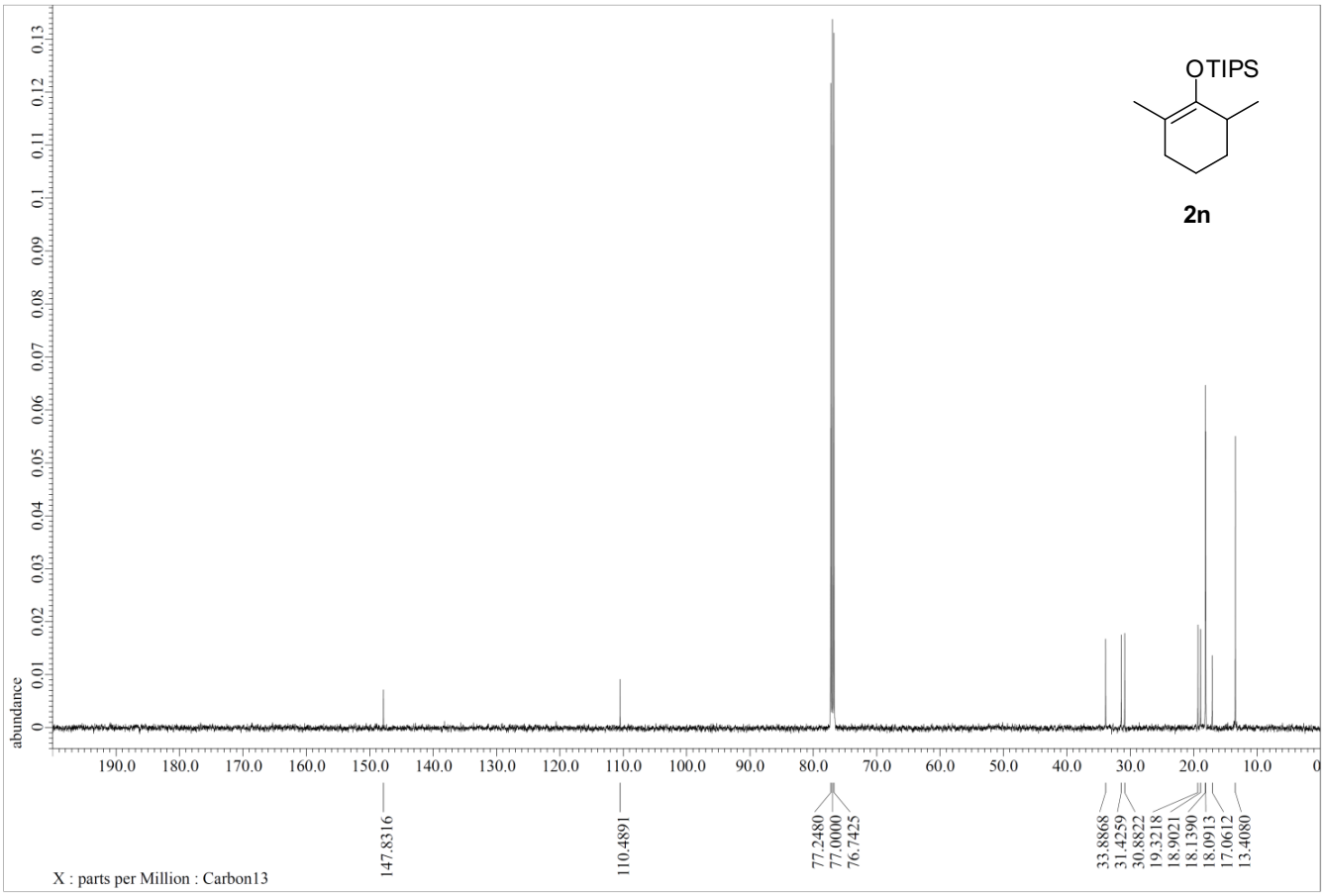


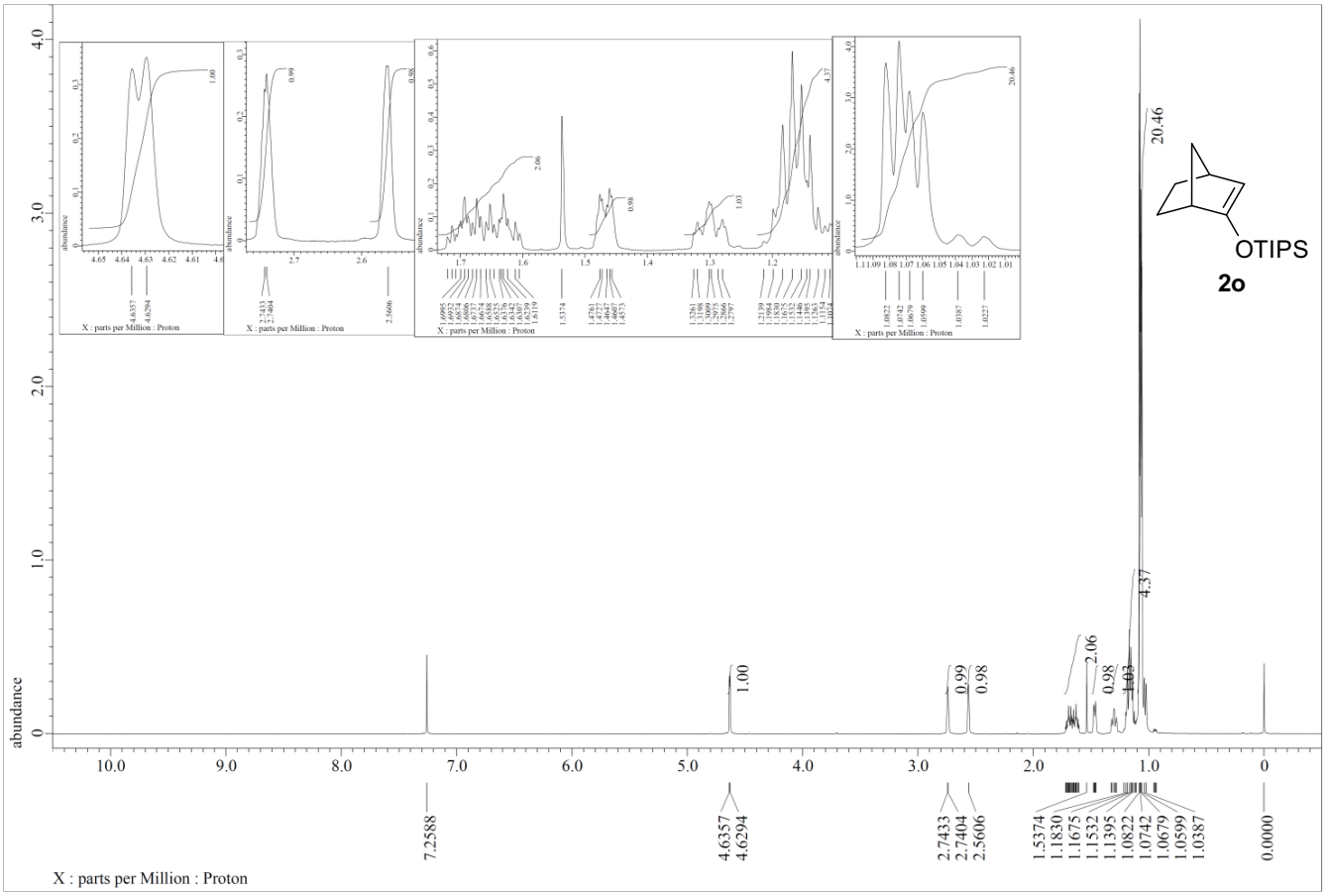
2k

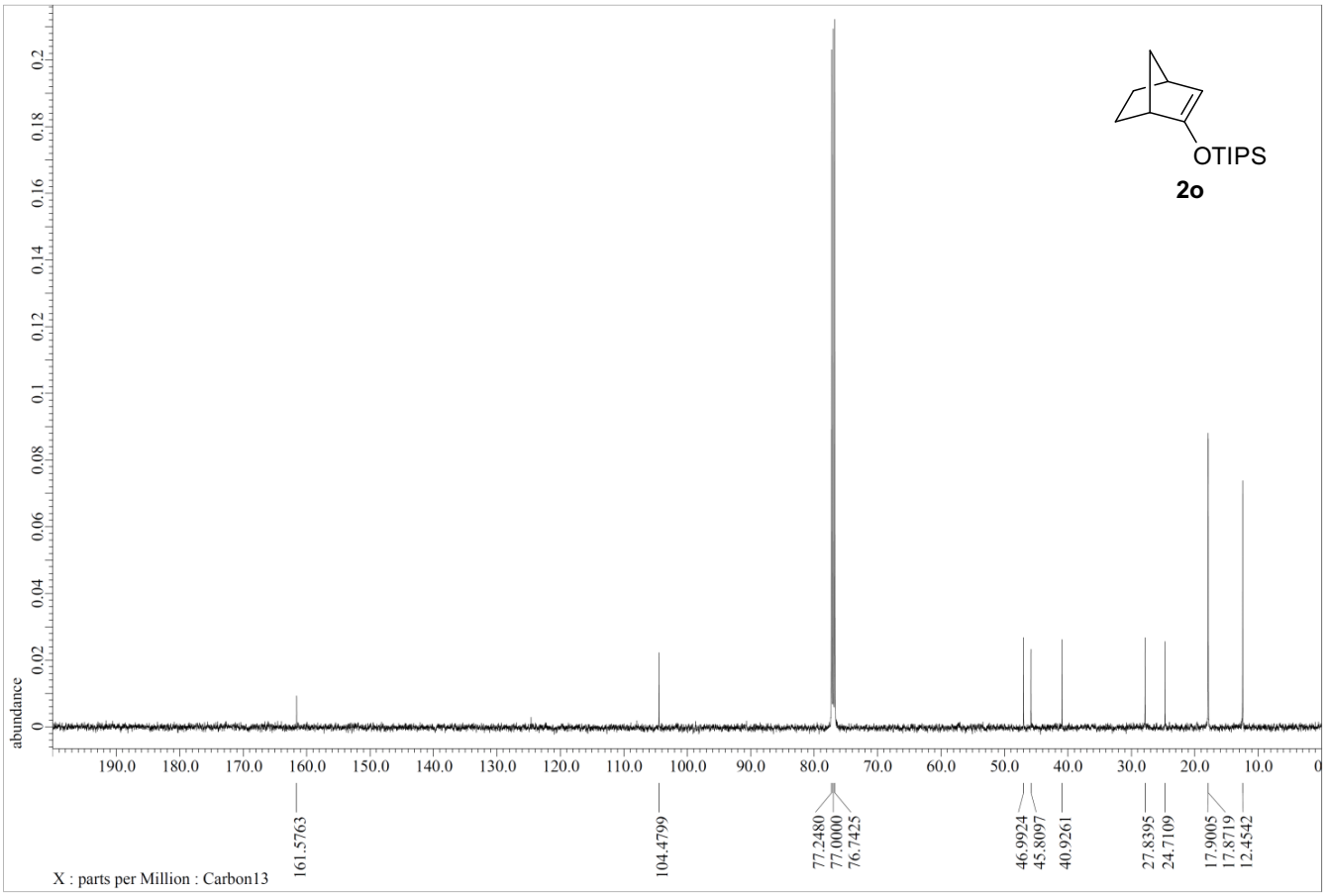

OTIPS
NPh
2m
abundance
X : parts per Million : Proton

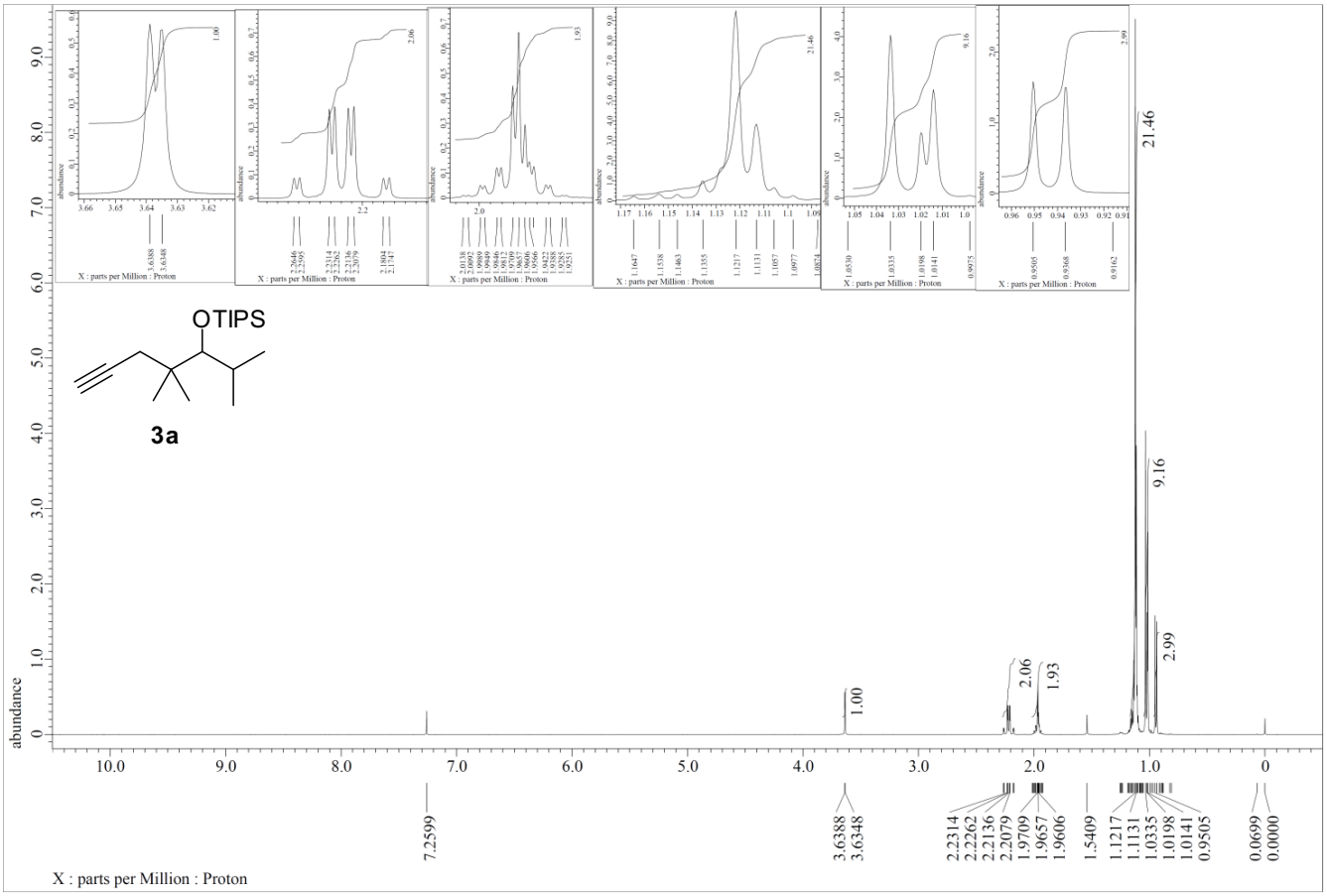

OTIPS
NPh
2m
abundance
X : parts per Million : Carbon13

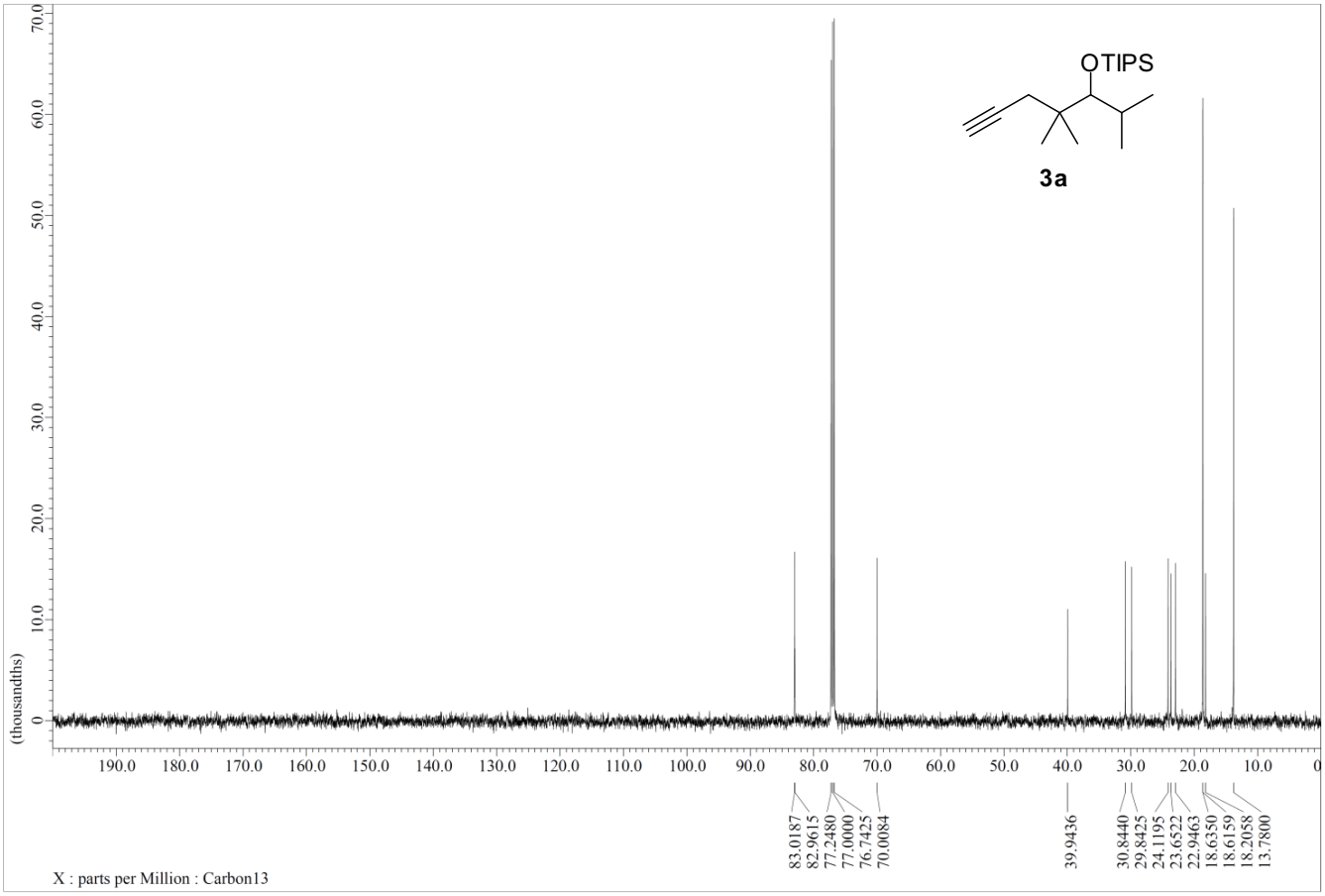

OTIPS
2n
25.15
4.13
2.07
2.00
1.00
1.03
7.2593
2.8716
2.8584
2.4100
2.3969
1.5947
1.5403
1.1555
1.1509
1.1389
1.1280
1.1188
1.1063
1.0937
1.0805
1.0582
0.1884
0.1615
0.1128
0.0063
-0.0000
-0.0069
abundance
X : parts per Million : Proton

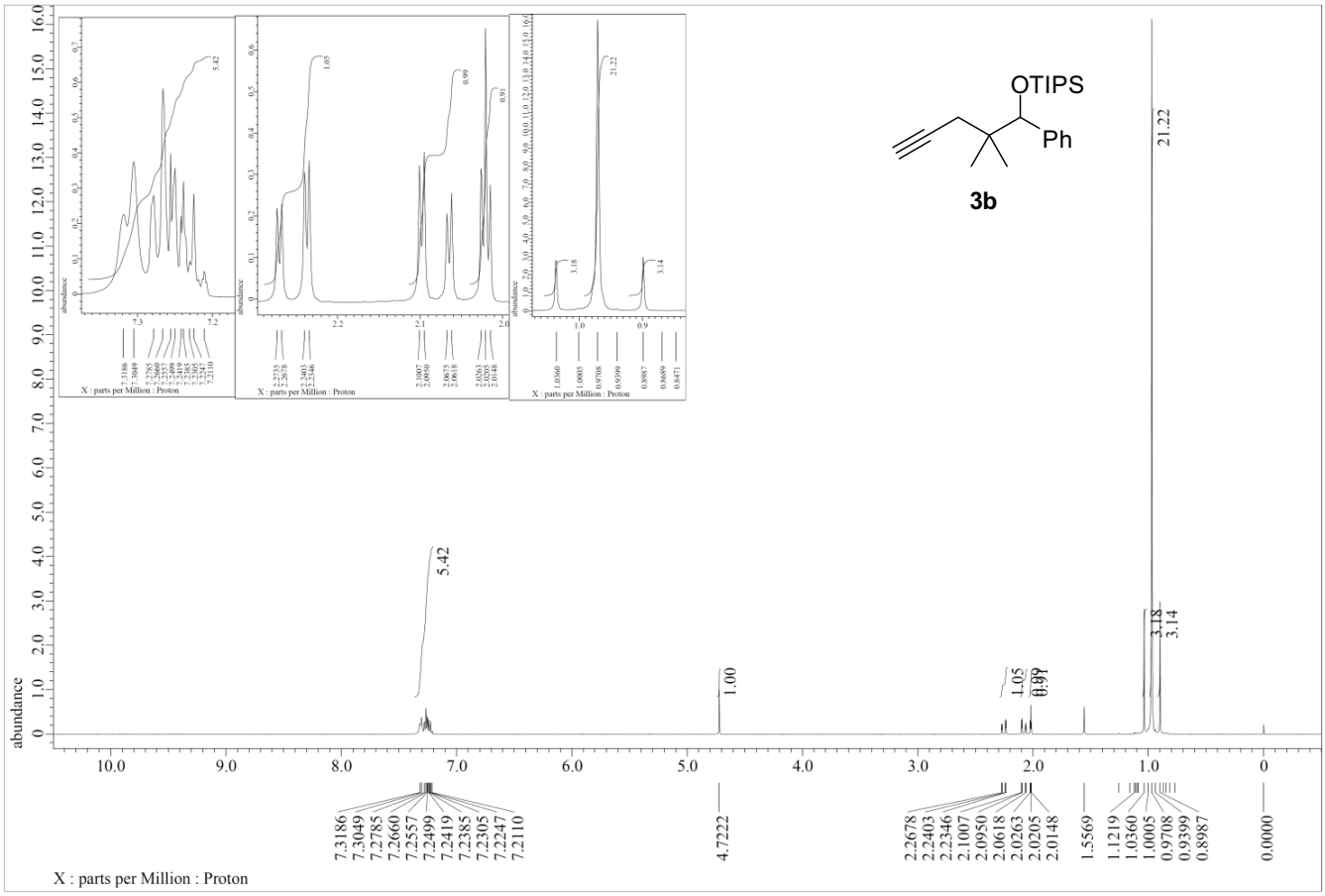

OTIPS
2n
147.8316
110.4891
77.2480
77.0000
76.7425
33.8868
31.4259
30.8822
19.3218
18.9021
18.1390
18.0913
17.0612
13.4080
abundance
X : parts per Million : Carbon13

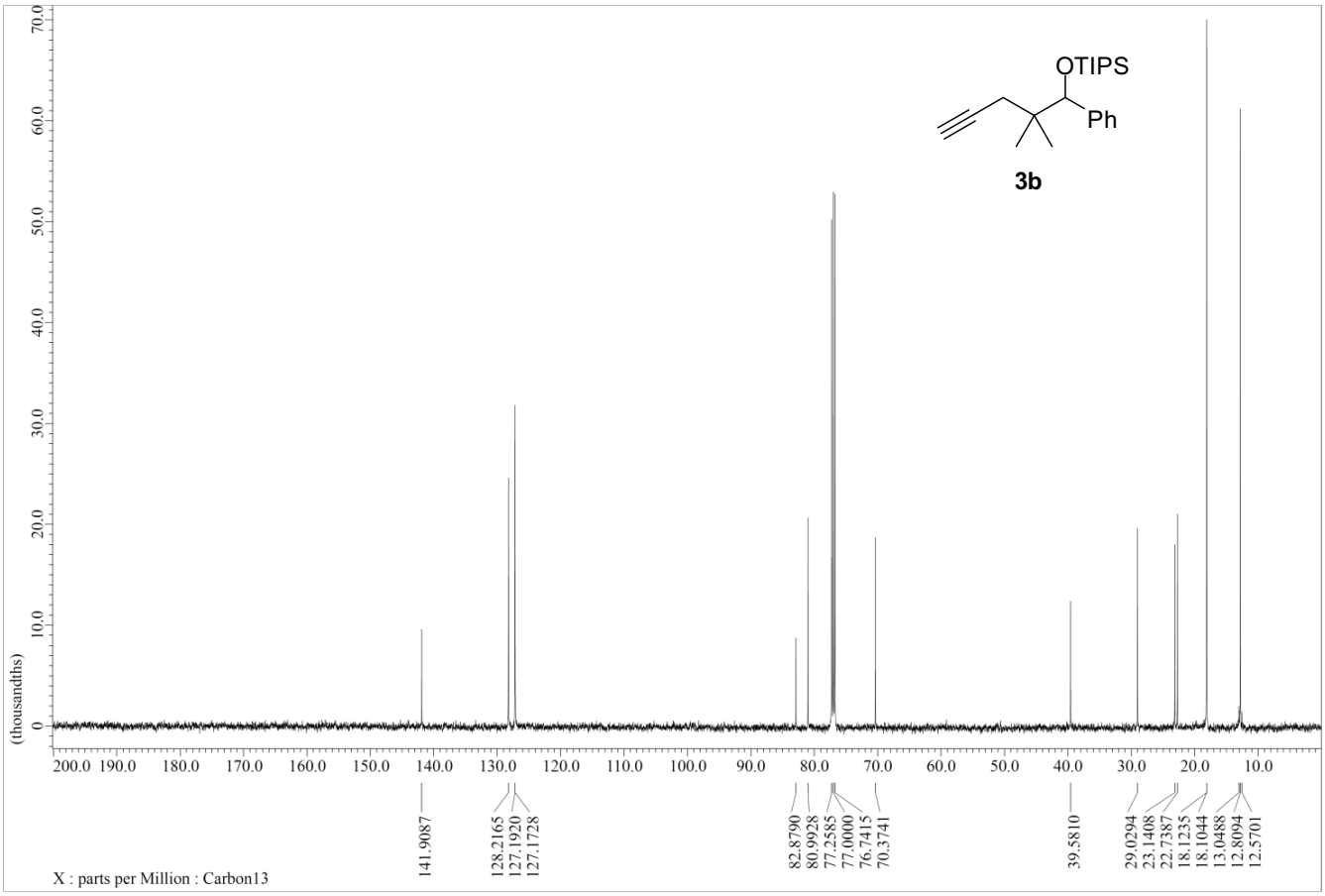

OTIPS
2o
X : parts per Million : Proton

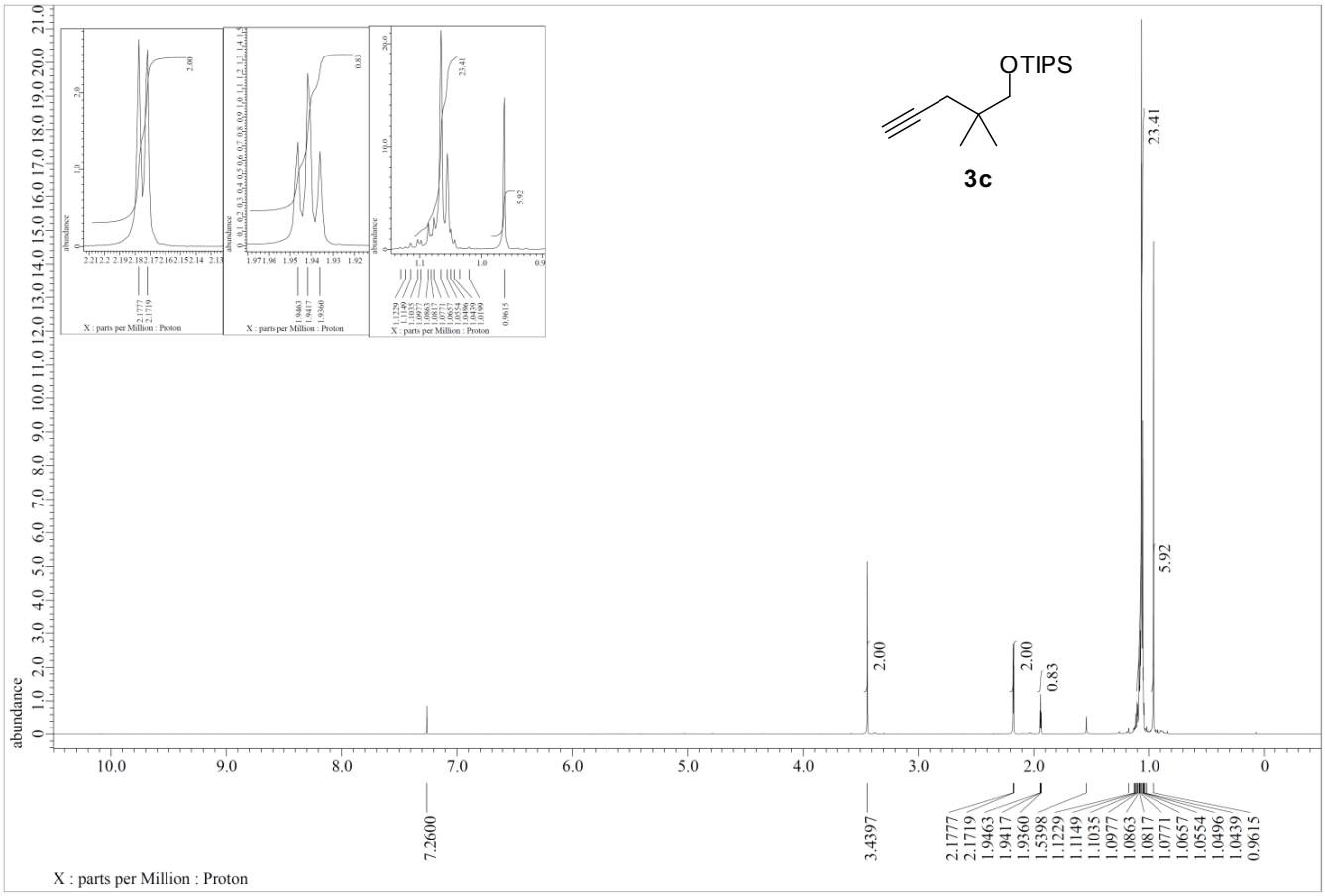

OTIPS
2o
X : parts per Million : Carbon13

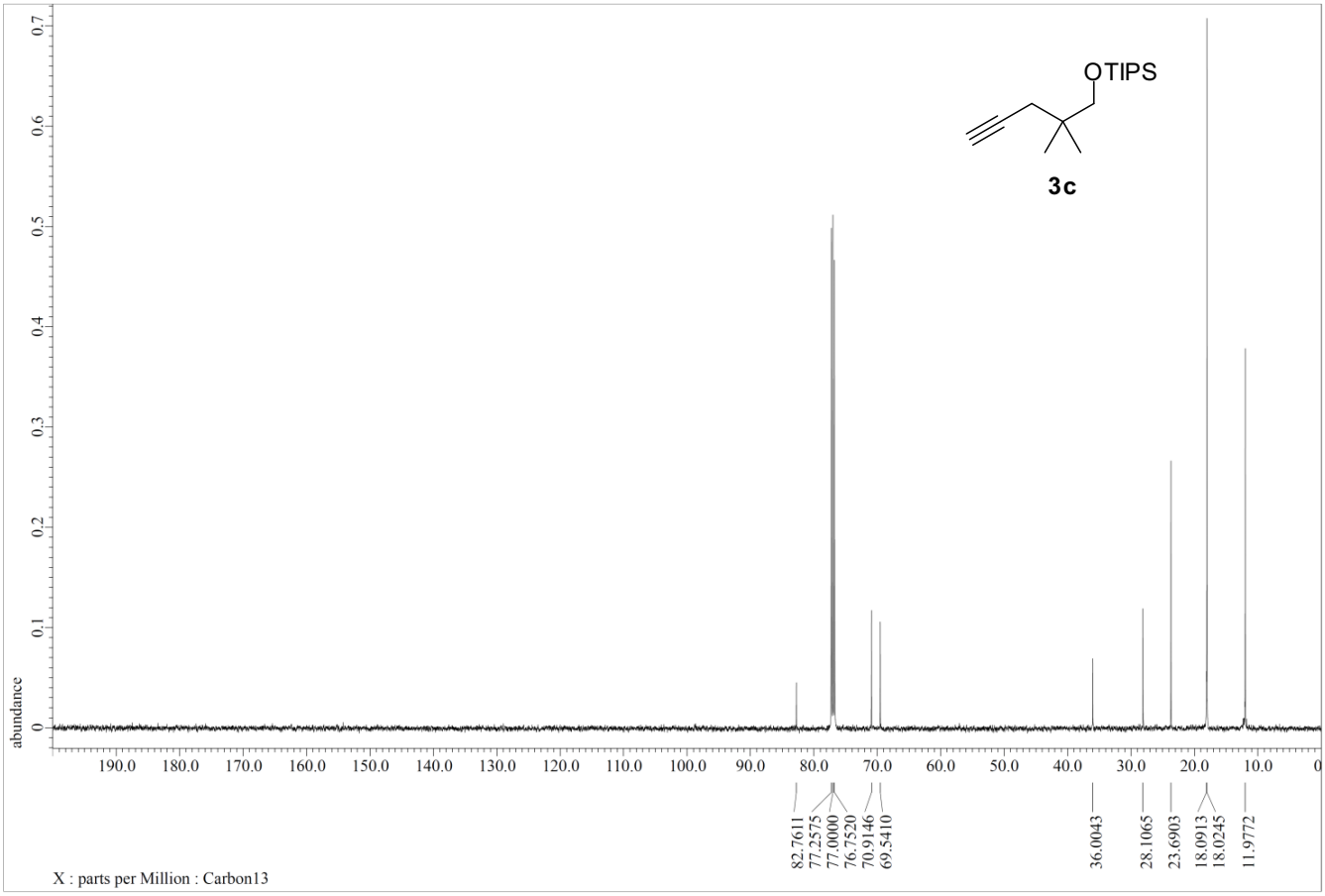

OTIPS
3a
abundance
X : parts per Million : Proton
7.2599
3.6388
3.6348
2.2314
2.2262
2.2136
2.2079
1.9709
1.9657
1.9606
1.5409
1.1217
1.1131
1.0335
1.0198
1.0141
0.9505
0.0699
0.0000
1.00
2.06
1.93
21.46
9.16
2.99

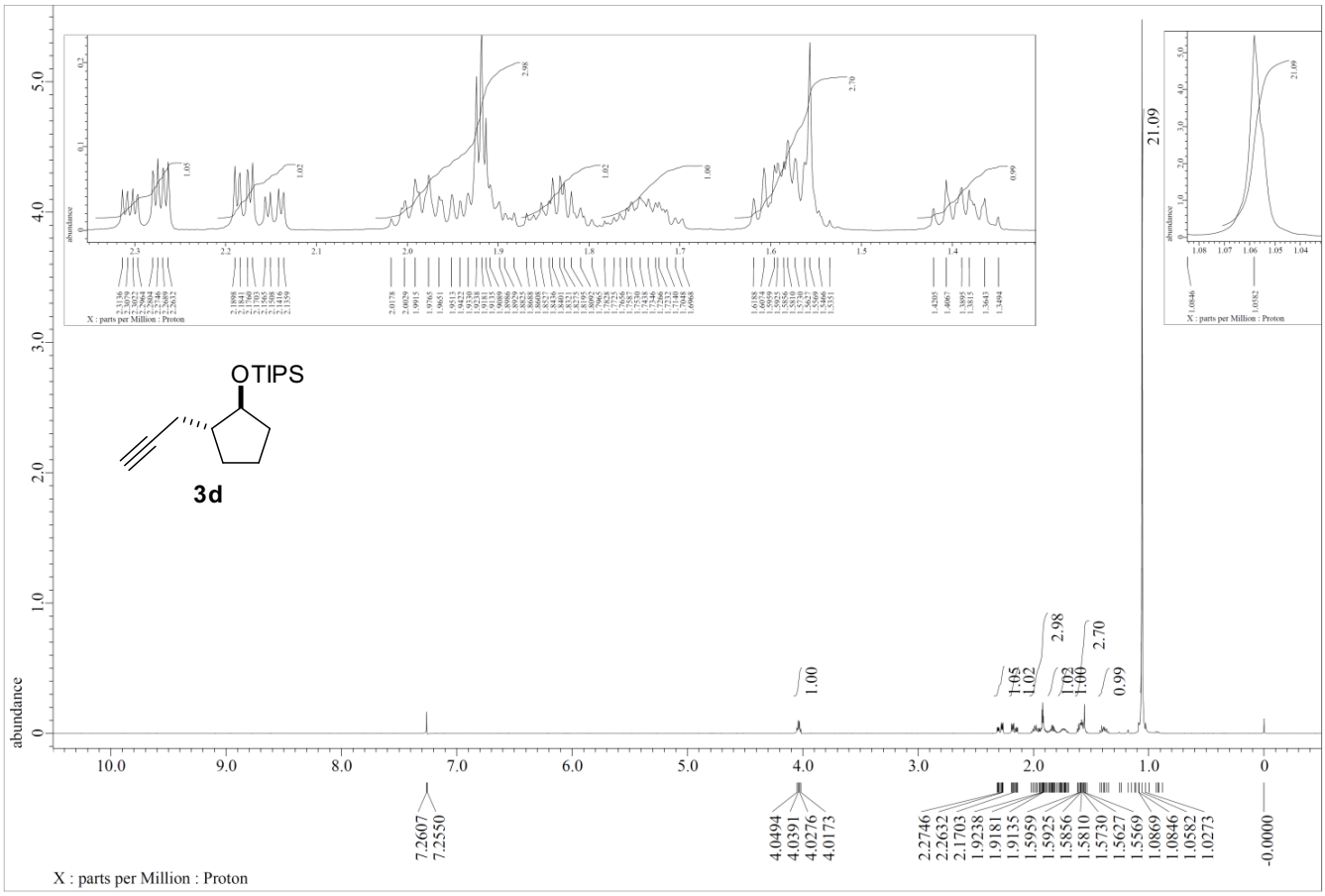

OTIPS
3a
(thousandths)
X : parts per Million : Carbon13
83.0187
82.9615
77.2480
77.0000
76.7425
70.0084
39.9436
30.8440
29.8425
24.1195
23.6522
22.9463
18.6350
18.6159
18.2058
13.7800

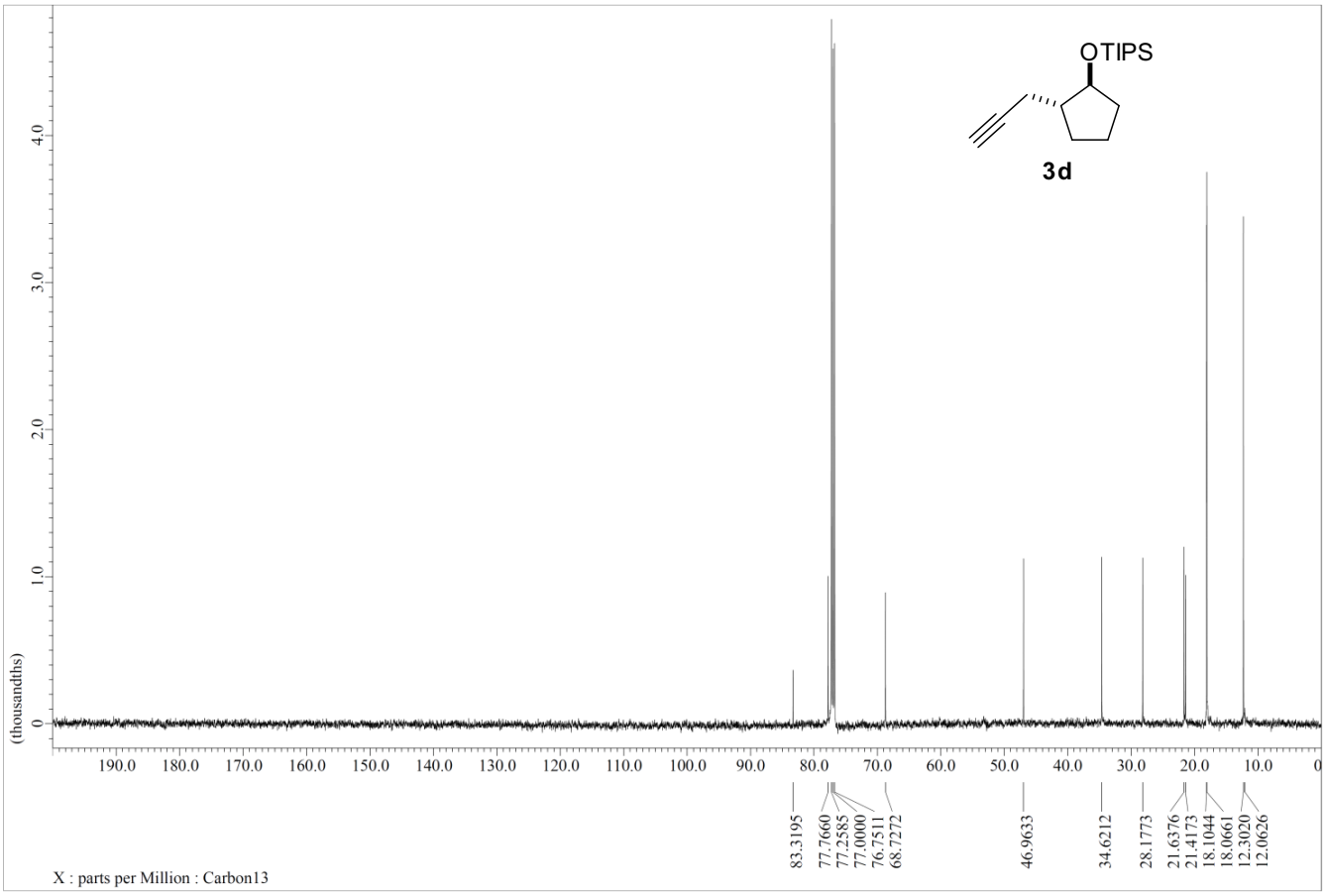

OTIPS
Ph
3b
abundance
X : parts per Million : Proton
5.42
1.00
21.22
3.18
3.14
7.3186
7.3049
7.2785
7.2660
7.2557
7.2499
7.2419
7.2385
7.2305
7.2247
7.2110
4.7222
2.2678
2.2403
2.2346
2.1007
2.0950
2.0618
2.0263
2.0205
2.0148
1.5569
1.1219
1.0360
1.0005
0.9708
0.9399
0.8987
0.0000

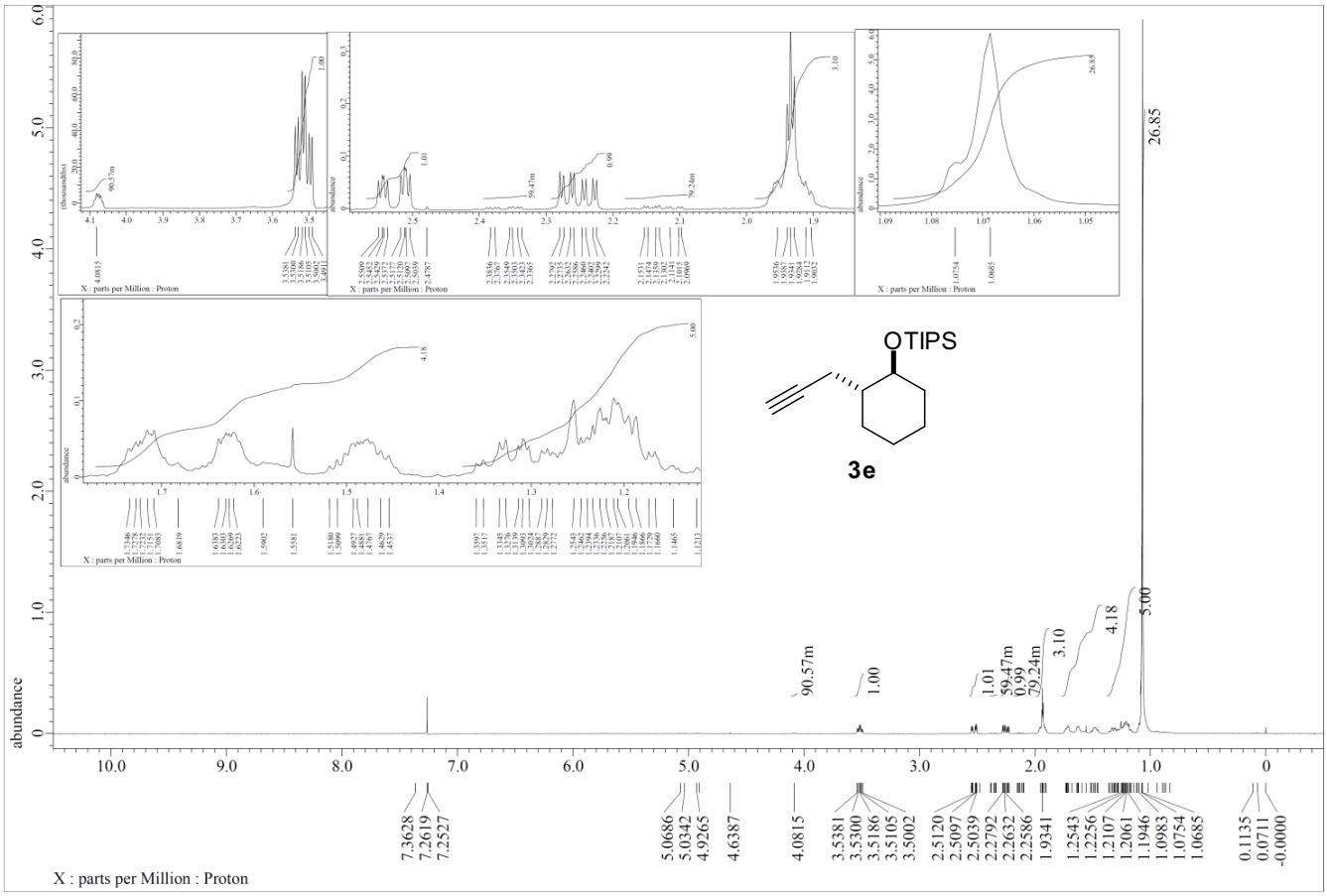

OTIPS
Ph
3b
(thousandths)
X : parts per Million : Carbon13
141.9087
128.2165
127.1920
127.1728
82.8790
80.9928
77.2585
77.0000
76.7415
70.3741
39.5810
29.0294
23.1408
22.7387
18.1235
18.1044
13.0488
12.8094
12.5701

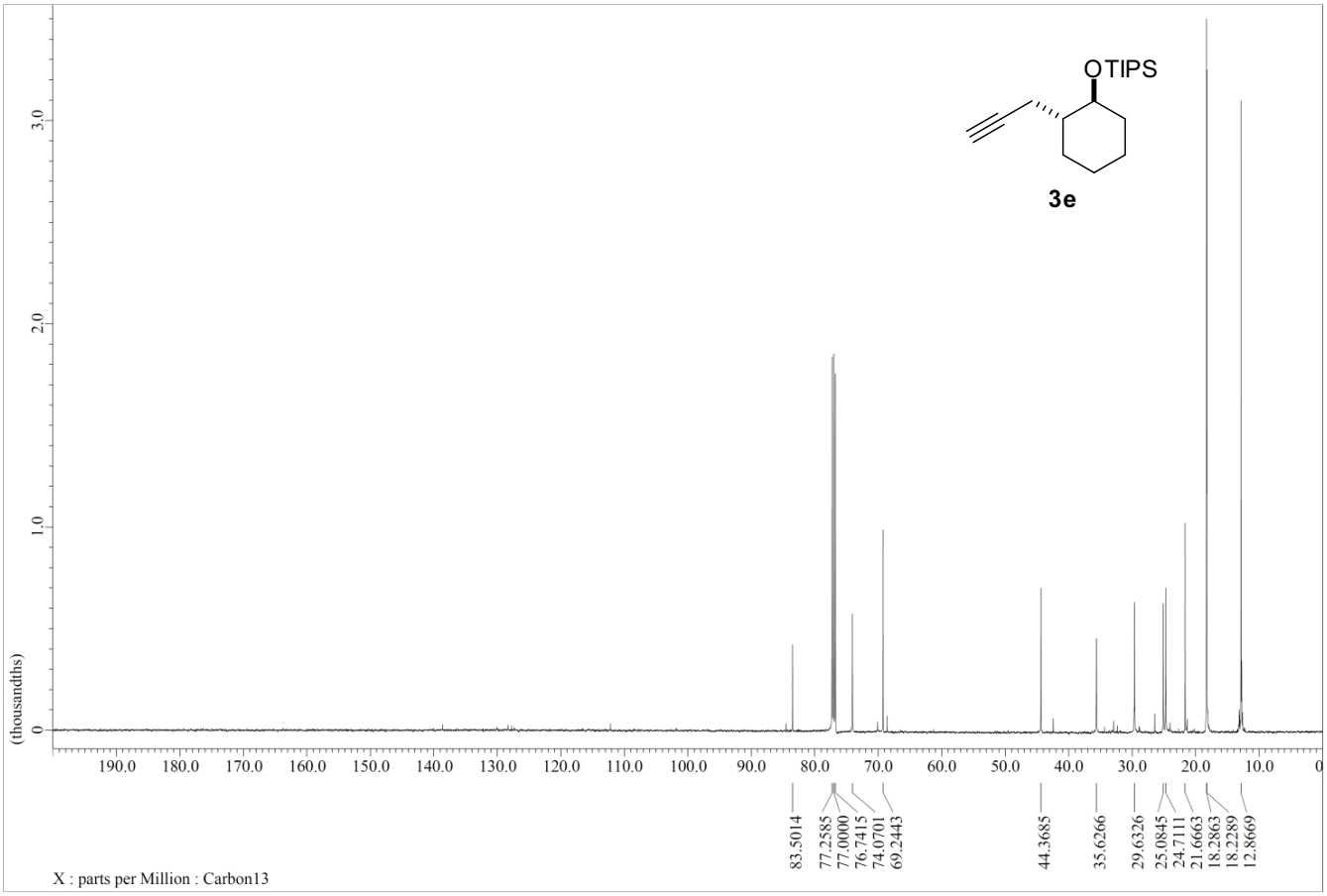

OTIPS
3c
23.41
5.92
2.00
2.00
0.83
abundance
7.2600
3.4397
2.1777
2.1719
1.9463
1.9417
1.9360
1.5398
1.1229
1.1149
1.1035
1.0977
1.0863
1.0817
1.0771
1.0657
1.0554
1.0496
1.0439
0.9615
X : parts per Million : Proton

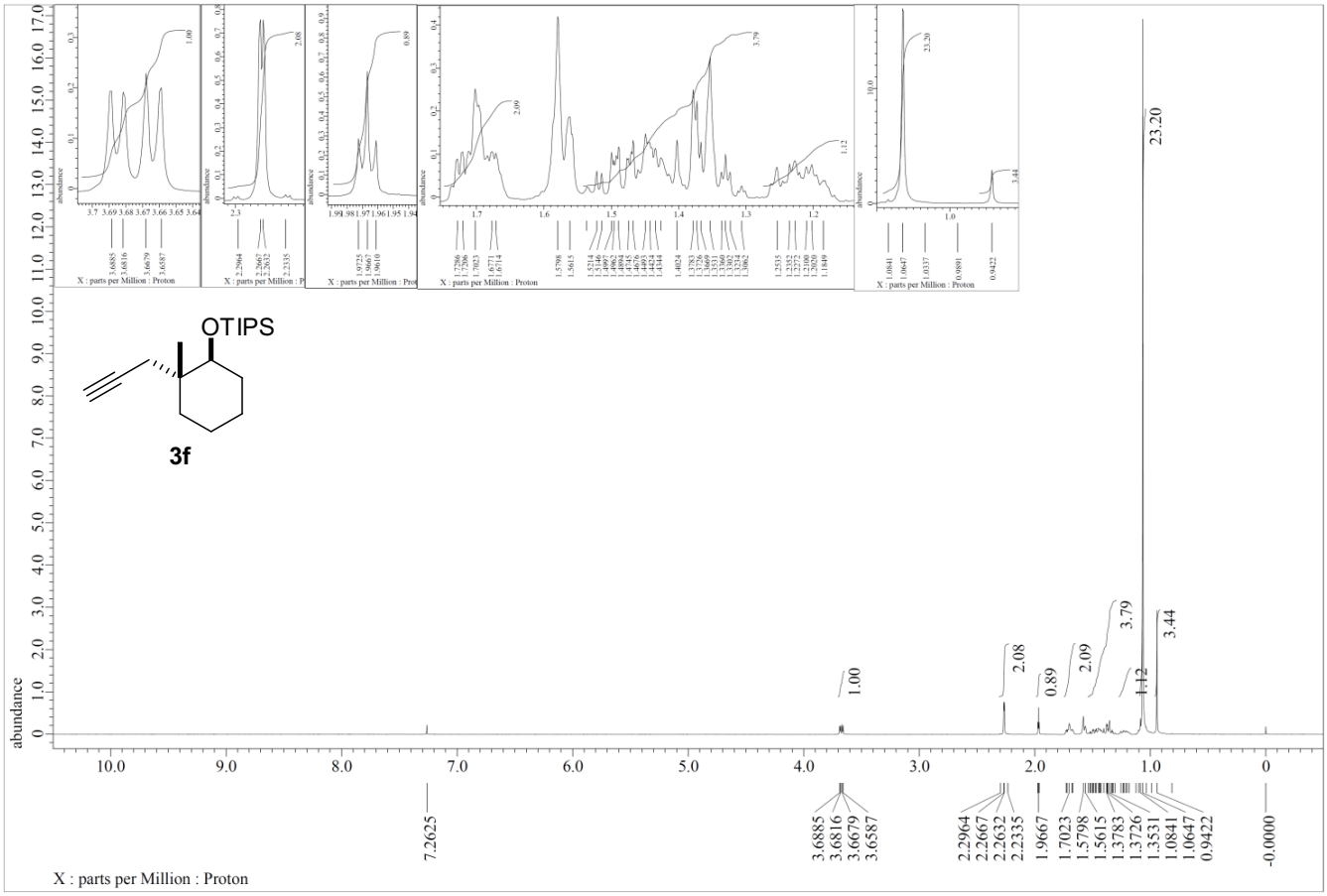

OTIPS
3c
abundance
82.7611
77.2575
77.0000
76.7520
70.9146
69.5410
36.0043
28.1065
23.6903
18.0913
18.0245
11.9772
X : parts per Million : Carbon13

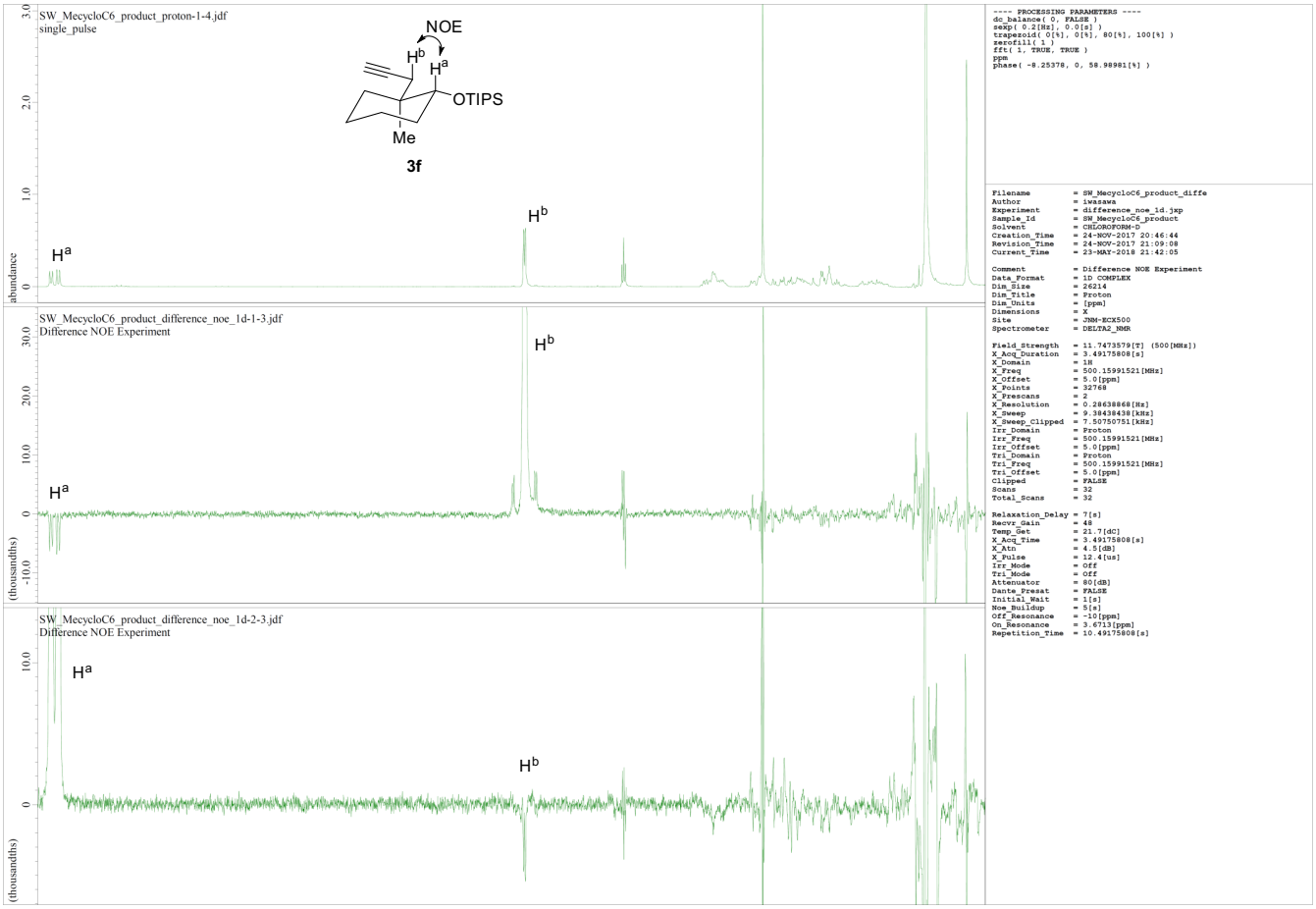

OTIPS
3d
abundance
X : parts per Million : Proton
7.2607
7.2550
4.0494
4.0391
4.0276
4.0173
2.2746
2.2632
2.1703
1.9238
1.9181
1.9135
1.5959
1.5925
1.5856
1.5810
1.5730
1.5627
1.5569
1.0869
1.0846
1.0582
1.0273
-0.0000
21.09

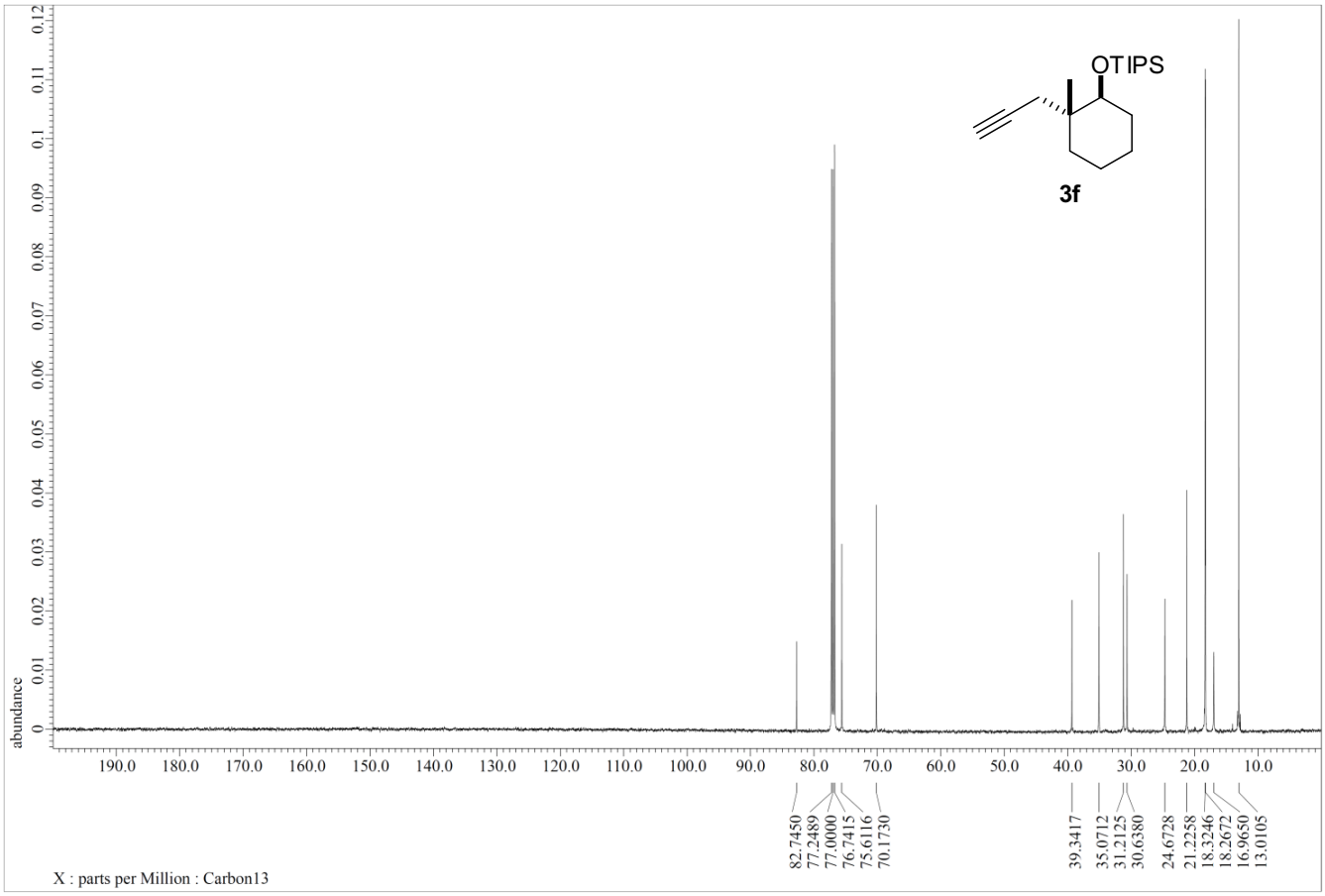

OTIPS
3d
(thousandths)
X : parts per Million : Carbon13
83.3195
77.7660
77.2585
77.0000
76.7511
68.7272
46.9633
34.6212
28.1773
21.6376
21.4173
18.1044
18.0661
12.3020
12.0626

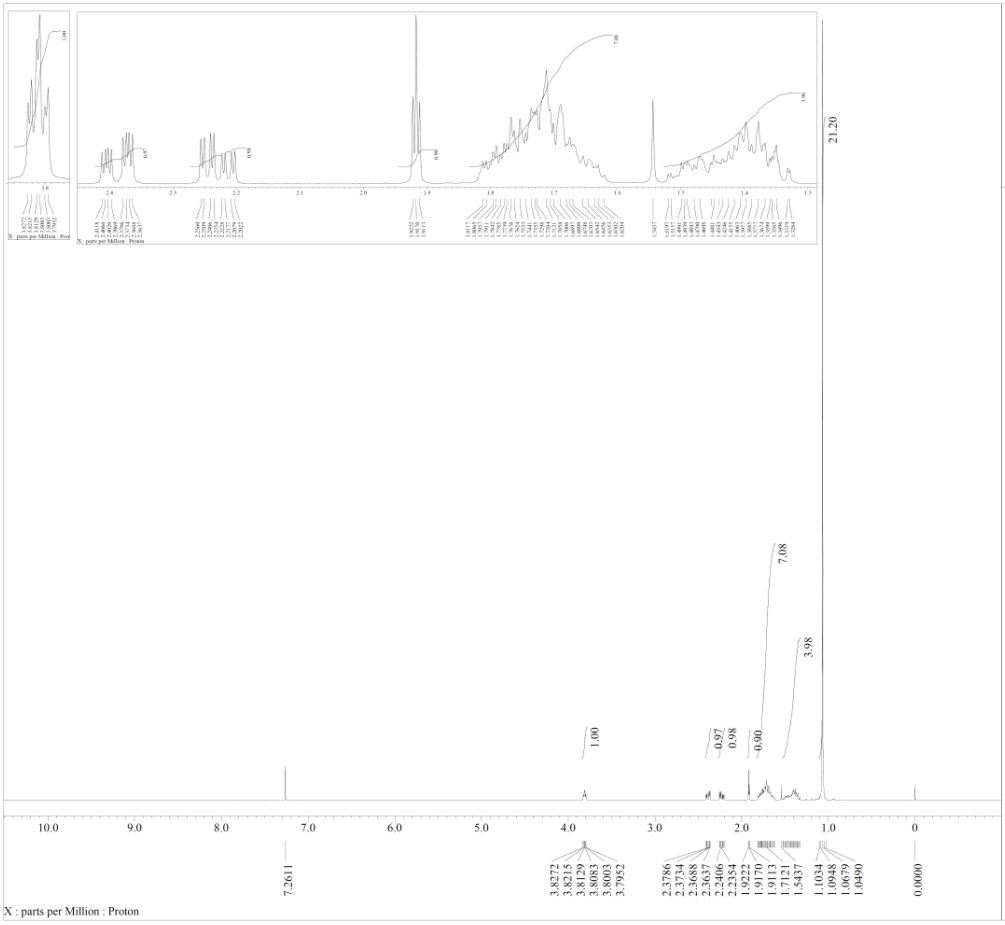

OTIPS
3e
X : parts per Million : Proton
abundance


OTIPS
3e
X : parts per Million : Carbon13
(thousandths)


OTIPS
3f
abundance
X : parts per Million : Proton
7.2625
3.6885
3.6816
3.6679
3.6587
2.2964
2.2667
2.2632
2.2335
1.9667
1.7023
1.5798
1.5615
1.3783
1.3726
1.3531
1.0841
1.0647
0.9422
-0.0000
1.00
2.08
0.89
2.09
3.79
1.12
3.44
23.20


SW_MecycloC6_product_proton-1-4.jdf
single_pulse
NOE
Hb
Ha
OTIPS
Me
3f
Ha
Hb
abundance
SW_MecycloC6_product_difference_noe_1d-1-3.jdf
Difference NOE Experiment
Ha
Hb
(thousandths)
SW_MecycloC6_product_difference_noe_1d-2-3.jdf
Difference NOE Experiment
Ha
Hb
(thousandths)
---- PROCESSING PARAMETERS ----
dc_balance(0, FALSE)
sexp(0.2[Hz], 0.0[s])
trapezoid(0[%], 0[%], 80[%], 100[%])
zerofill(1)
fft(1, TRUE, TRUE)
ppm
phase(-8.25378, 0, 58.98981[%])
Filename = SW_MecycloC6_product_diffe
Author = iwasawa
Experiment = difference_noe_1d.jxp
Sample_Id = SW_MecycloC6_product
Solvent = CHLOROFORM-D
Creation_Time = 24-NOV-2017 20:46:44
Revision_Time = 24-NOV-2017 21:09:08
Current_Time = 23-MAY-2018 21:42:05
Comment = Difference NOE Experiment
Data_Format = 1D COMPLEX
Dim_Size = 26214
Dim_Title = Proton
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECX500
Spectrometer = DELTA2_NMR
Field_Strength = 11.7473579[T] (500[MHz])
X_Acq_Duration = 3.49175808[s]
X_Domain = 1H
X_Freq = 500.15991521[MHz]
X_Offset = 5.0[ppm]
X_Points = 32768
X_Prescans = 2
X_Resolution = 0.28638868[Hz]
X_Sweep = 9.38438438[kHz]
X_Sweep_Clipped = 7.50750751[kHz]
Irr_Domain = Proton
Irr_Freq = 500.15991521[MHz]
Irr_Offset = 5.0[ppm]
Tri_Domain = Proton
Tri_Freq = 500.15991521[MHz]
Tri_Offset = 5.0[ppm]
Clipped = FALSE
Scans = 32
Total_Scans = 32
Relaxation_Delay = 7[s]
Recvr_Gain = 48
Temp_Get = 21.7[dC]
X_Acq_Time = 3.49175808[s]
X_Atn = 4.5[dB]
X_Pulse = 12.4[us]
Irr_Mode = Off
Tri_Mode = Off
Attenuator = 80[dB]
Dante_Presat = FALSE
Initial_Wait = 1[s]
Noe_Buildup = 5[s]
Off_Resonance = -10[ppm]
On_Resonance = 3.6713[ppm]
Repetition_Time = 10.49175808[s]






```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm

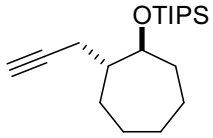
以下に由来:: HS_2236_p-major_proton-1-1.jdf
```

```
Filename          = HS_2236_p-major_proton-1-6
Author            = iwasawa
Experiment        = proton.jxp
Sample_Id         = HS_2236_p-major
Solvent           = CHLOROFORM-D
Creation_Time     = 17-MAR-2016 15:50:57
Revision_Time     = 17-MAR-2016 15:54:59
Current_Time      = 17-MAR-2016 15:56:33

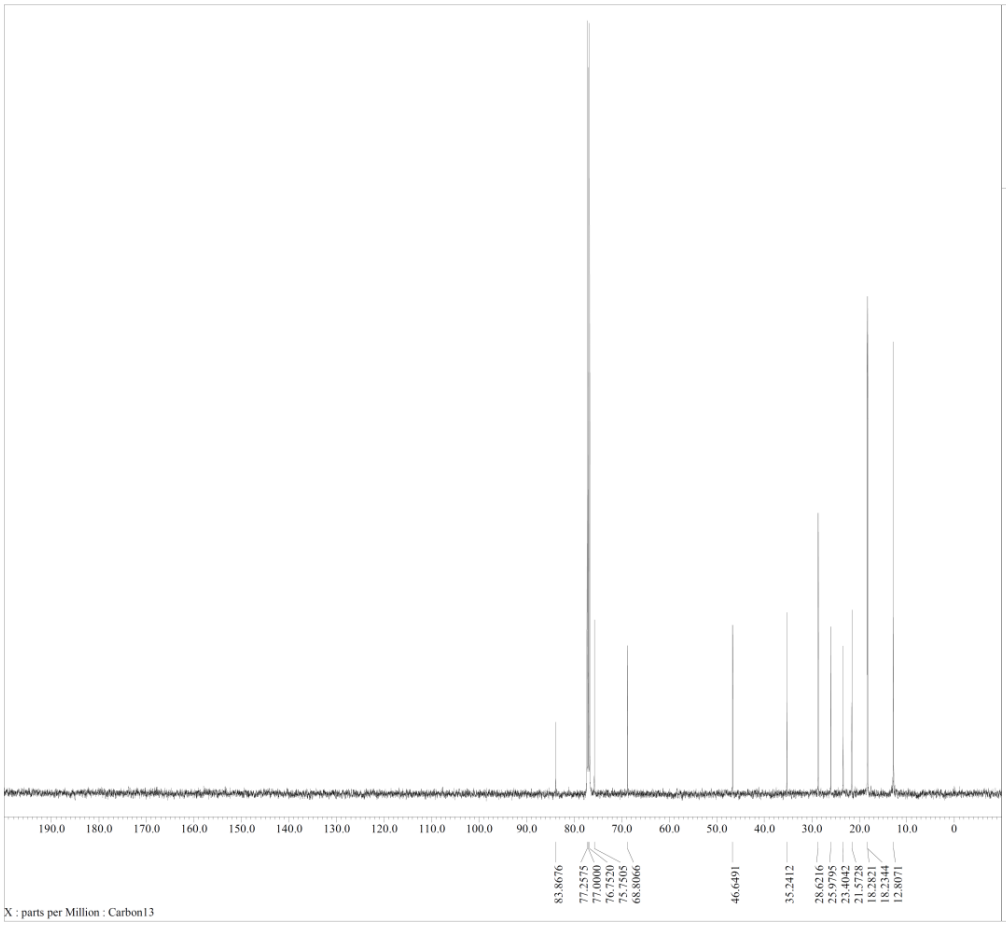
Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = Proton
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.7473579[T] (500[MHz])
X_Acq_Duration    = 3.49175808[s]
X_Domain          = 1H
X_Freq            = 500.15991521[MHz]
X_Offset          = 5.0[ppm]
X_Points          = 32768
X_Prescans        = 1
X_Resolution      = 0.28638868[Hz]
X_Sweep           = 9.38438438[kHz]
X_Sweep_Clipped   = 7.50750751[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Tri_Domain        = Proton
Tri_Freq          = 500.15991521[MHz]
Tri_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay  = 5[s]
Recvr_Gain        = 36
Temp_Get          = 22.5[dC]
X_90_Width        = 12.9[us]
X_Acq_Time        = 3.49175808[s]
X_Angle           = 45[deg]
X_Atn             = 4.5[dB]
X_Pulse           = 6.45[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 8.49175808[s]
```



3g-major




```
---- PROCESSING PARAMETERS ----
do_balance( 0, FALSE )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm

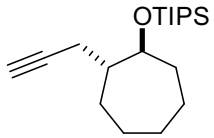
以下に由来:: HS_2236_p-major_Carbon-1-1.jdf
```

```
Filename          = HS_2236_p-major_Carbon-1-5
Author            = iwasawa
Experiment        = carbon.jxp
Sample_Id         = HS_2236_p-major
Solvent           = CHLOROFORM-D
Creation_Time     = 17-MAR-2016 16:12:29
Revision_Time     = 17-MAR-2016 16:39:37
Current_Time      = 17-MAR-2016 16:40:13

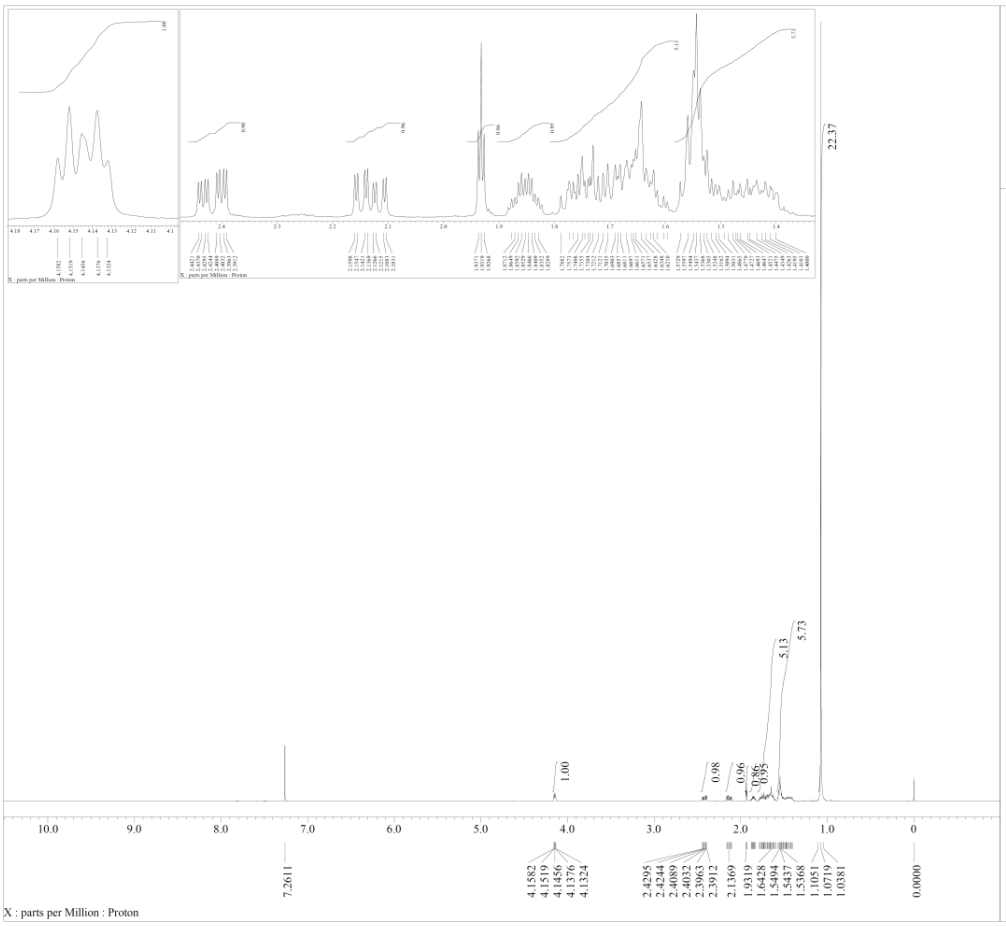
Comment           = single pulse decoupled gat
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.7473579[T] (500[MHz])
X_Acq_Duration    = 0.83361792[s]
X_Domain          = 13C
X_Freq            = 125.76529768[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.19959034[Hz]
X_Sweep           = 39.3081761[kHz]
X_Sweep_Clipped   = 31.44654088[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 488
Total_Scans       = 488

Relaxation_Delay = 2[s]
Recvr_Gain        = 36
Temp_Set          = 22.9[dC]
X_90_Width        = 10.4[us]
X_Acq_Time        = 0.83361792[s]
X_Angle           = 30[deg]
X_Atn             = 5.6[dB]
X_Pulse           = 3.46666667[us]
Irr_Atn_Dec       = 21.56[dB]
Irr_Atn_Noe       = 21.56[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 92[us]
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 2.83361792[s]
```



3g-major




```
---- PROCESSING PARAMETERS ----
do_balance( 0, FALSE )
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm

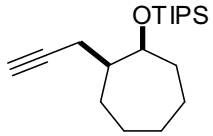
以下に由来:: HS_2236_minor-p_proton-1-1.jdf
```

```
Filename          = HS_2236_minor-p_proton-1-5
Author            = iwasawa
Experiment        = proton.jxp
Sample_Id         = HS_2236_minor-p
Solvent           = CHLOROFORM-D
Creation_Time     = 18-MAR-2016 10:57:48
Revision_Time     = 18-MAR-2016 11:03:47
Current_Time      = 18-MAR-2016 11:04:17

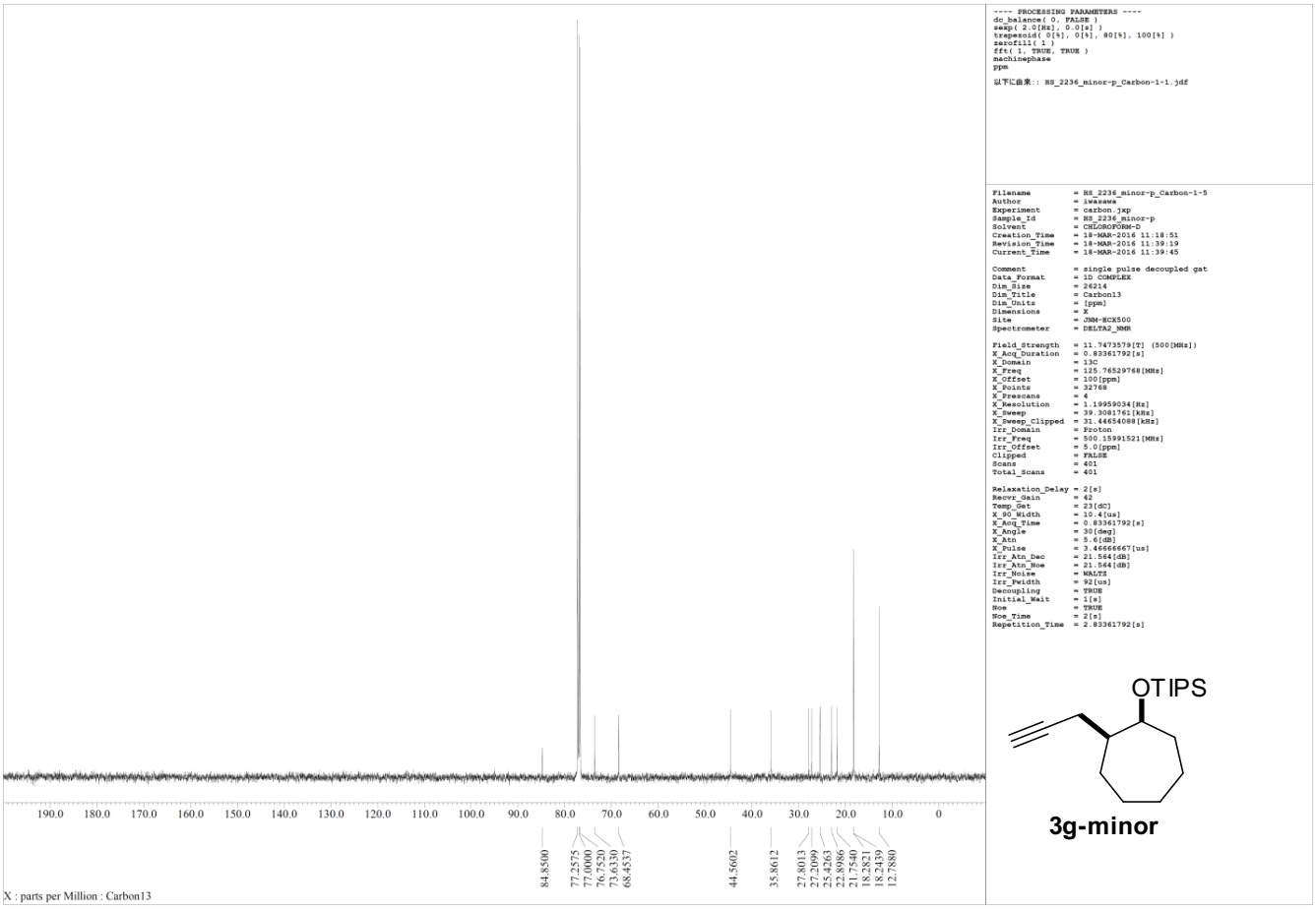
Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = Proton
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

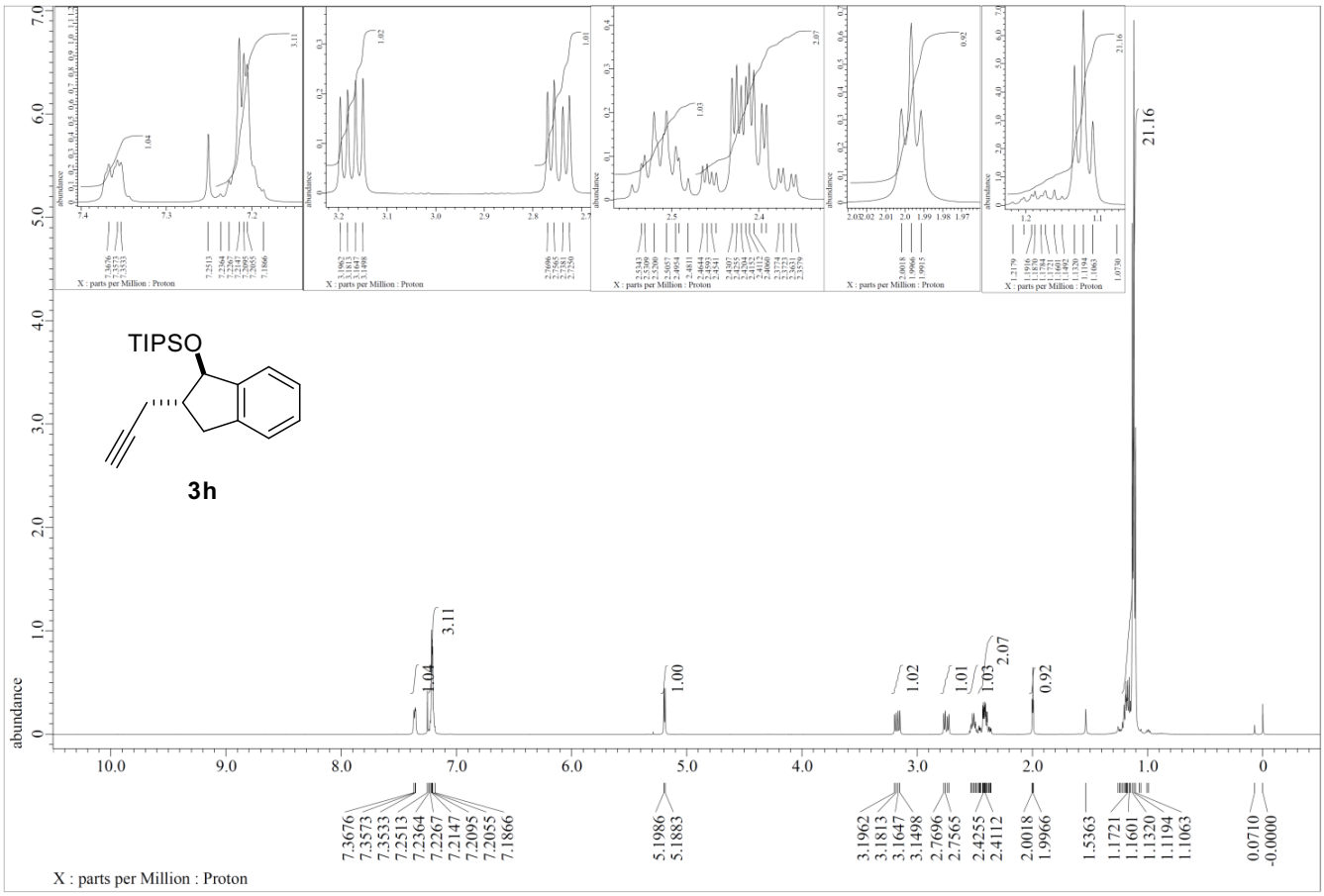
Field_Strength    = 11.7473579[T] (500[MHz])
X_Acq_Duration    = 3.49175808[s]
X_Domain          = 1H
X_Freq            = 500.15991521[MHz]
X_Offset          = 5.0[ppm]
X_Points          = 32768
X_Prescans        = 1
X_Resolution      = 0.28638868[Hz]
X_Sweep           = 9.38438438[kHz]
X_Sweep_Clipped   = 7.50750751[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Tri_Domain        = Proton
Tri_Freq          = 500.15991521[MHz]
Tri_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

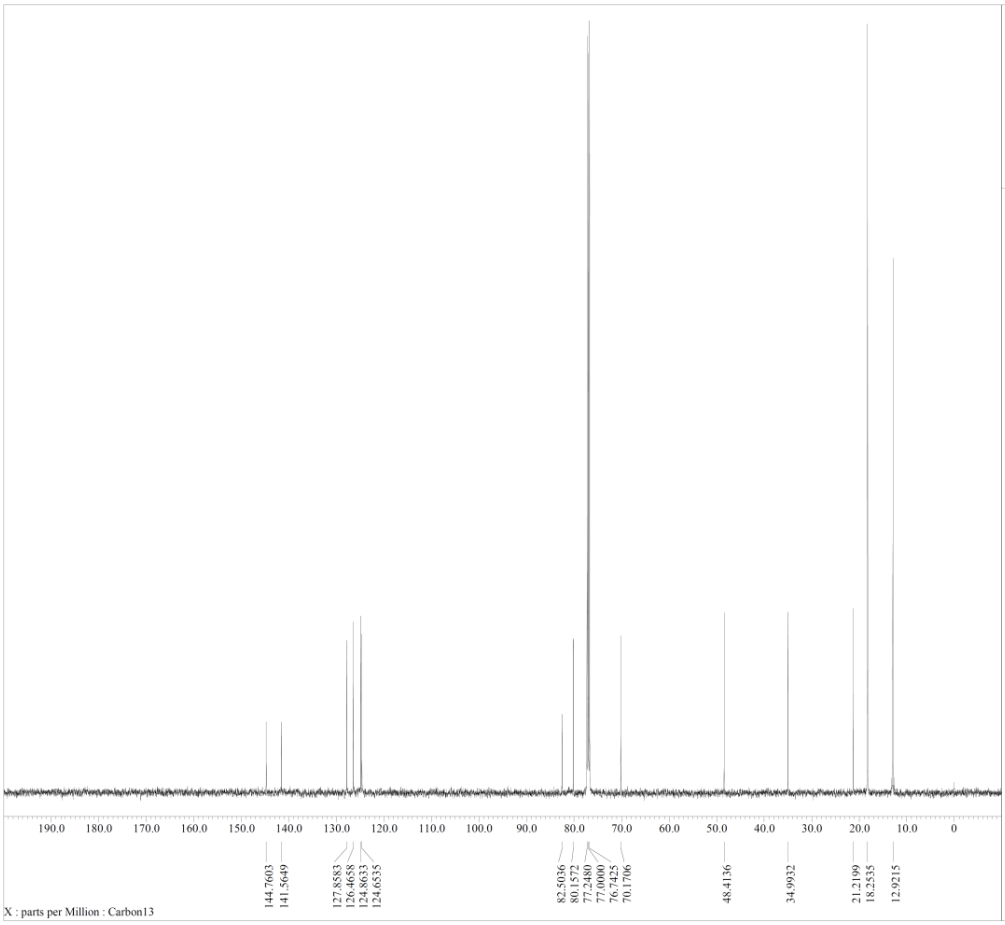
Relaxation_Delay = 5[s]
Recvr_Gain        = 42
Temp_Set          = 22.4[dC]
X_90_Width        = 12.9[us]
X_Acq_Time        = 3.49175808[s]
X_Angle           = 45[deg]
X_Atn             = 4.5[dB]
X_Pulse           = 6.45[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 8.49175808[s]
```



3g-minor


---- PROCESSING PARAMETERS ----
dc_balance(0, FALSE)
sexp(2.0[Hz], 0.0[s])
trapezoid(0[%], 0[%], 80[%], 100[%])
zerofill(1)
fft(1, TRUE, TRUE)
machinephase
ppm
以下に由来:: HS_2236_minor-p_Carbon-1-1.jdf
Filename = HS_2236_minor-p_Carbon-1-5
Author = iwasawa
Experiment = carbon.jxp
Sample_Id = HS_2236_minor-p
Solvent = CHLOROFORM-D
Creation_Time = 18-MAR-2016 11:18:51
Revision_Time = 18-MAR-2016 11:39:19
Current_Time = 18-MAR-2016 11:39:45
Comment = single pulse decoupled gat
Data_Format = 1D COMPLEX
Dim_Size = 26214
Dim_Title = Carbon13
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECX500
Spectrometer = DELTA2_NMR
Field_Strength = 11.7473579[T] (500[MHz])
X_Acq_Duration = 0.83361792[s]
X_Domain = 13C
X_Freq = 125.76529768[MHz]
X_Offset = 100[ppm]
X_Points = 32768
X_Prescans = 4
X_Resolution = 1.19959034[Hz]
X_Sweep = 39.3081761[kHz]
X_Sweep_clipped = 31.44654088[kHz]
Irr_Domain = Proton
Irr_Freq = 500.15991521[MHz]
Irr_Offset = 5.0[ppm]
Clipped = FALSE
Scans = 401
Total_Scans = 401
Relaxation_Delay = 2[s]
Recvr_Gain = 42
Temp_Get = 23[dC]
X_90_Width = 10.4[us]
X_Acq_Time = 0.83361792[s]
X_Angle = 30[deg]
X_Atn = 5.6[dB]
X_Pulse = 3.46666667[us]
Irr_Atn_Dec = 21.564[dB]
Irr_Atn_Noe = 21.564[dB]
Irr_Noise = WALTZ
Irr_Pwidth = 92[us]
Decoupling = TRUE
Initial_Wait = 1[s]
Noe = TRUE
Noe_Time = 2[s]
Repetition_Time = 2.83361792[s]
OTIPS
3g-minor
84.8500
77.2575
77.0000
76.7520
73.6330
68.4537
44.5602
35.8612
27.8013
27.2099
25.4263
22.8986
21.7540
18.2821
18.2439
12.7880
X : parts per Million : Carbon13


TIPSO
3h
21.16
3.11
1.04
1.00
1.02
1.01
1.03
2.07
0.92
abundance
7.3676
7.3573
7.3533
7.2513
7.2364
7.2267
7.2147
7.2095
7.2055
7.1866
5.1986
5.1883
3.1962
3.1813
3.1647
3.1498
2.7696
2.7565
2.4255
2.4112
2.0018
1.9966
1.5363
1.1721
1.1601
1.1320
1.1194
1.1063
0.0710
-0.0000
X : parts per Million : Proton




```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm

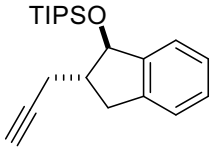
以下に由来:: HS_2239_2-purified-major_Carbon-1-1.j
```

```
Filename          = HS_2239_2-purified-major_C
Author            = iwasawa
Experiment        = carbon.jxp
Sample_Id         = HS_2239_2-purified-major
Solvent           = CHLOROFORM-D
Creation_Time     = 18-MAR-2016 13:23:56
Revision_Time     = 18-MAR-2016 15:06:35
Current_Time      = 18-MAR-2016 15:07:20

Comment           = single pulse decoupled gat
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.7473579[T] (500[MHz])
X_Acq_Duration    = 0.83361792[s]
X_Domain          = 13C
X_Freq            = 125.76529768[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.19959034[Hz]
X_Sweep           = 39.3081761[kHz]
X_Sweep_Clipped   = 31.44654088[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 512
Total_Scans       = 512

Relaxation_Delay = 2[s]
Recvr_Gain        = 36
Temp_Get          = 23.7[dC]
X_90_Width        = 10.4[us]
X_Acq_Time        = 0.83361792[s]
X_Angle           = 30[deg]
X_Atn             = 5.6[dB]
X_Pulse           = 3.46666667[us]
Irr_Atn_Dec       = 21.564[dB]
Irr_Atn_Noe       = 21.564[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 92[us]
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 2.83361792[s]
```



3h


```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm

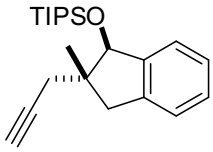
以下に由来:: HS_2285_purified_proton-1-1.jdf
```

```
Filename          = HS_2285_purified_proton-1-
Author            = iwasawa
Experiment        = proton.jxp
Sample_Id         = HS_2285_purified
Solvent           = CHLOROFORM-D
Creation_Time     = 14-MAY-2016 18:21:38
Revision_Time     = 14-MAY-2016 18:26:57
Current_Time      = 14-MAY-2016 18:28:15

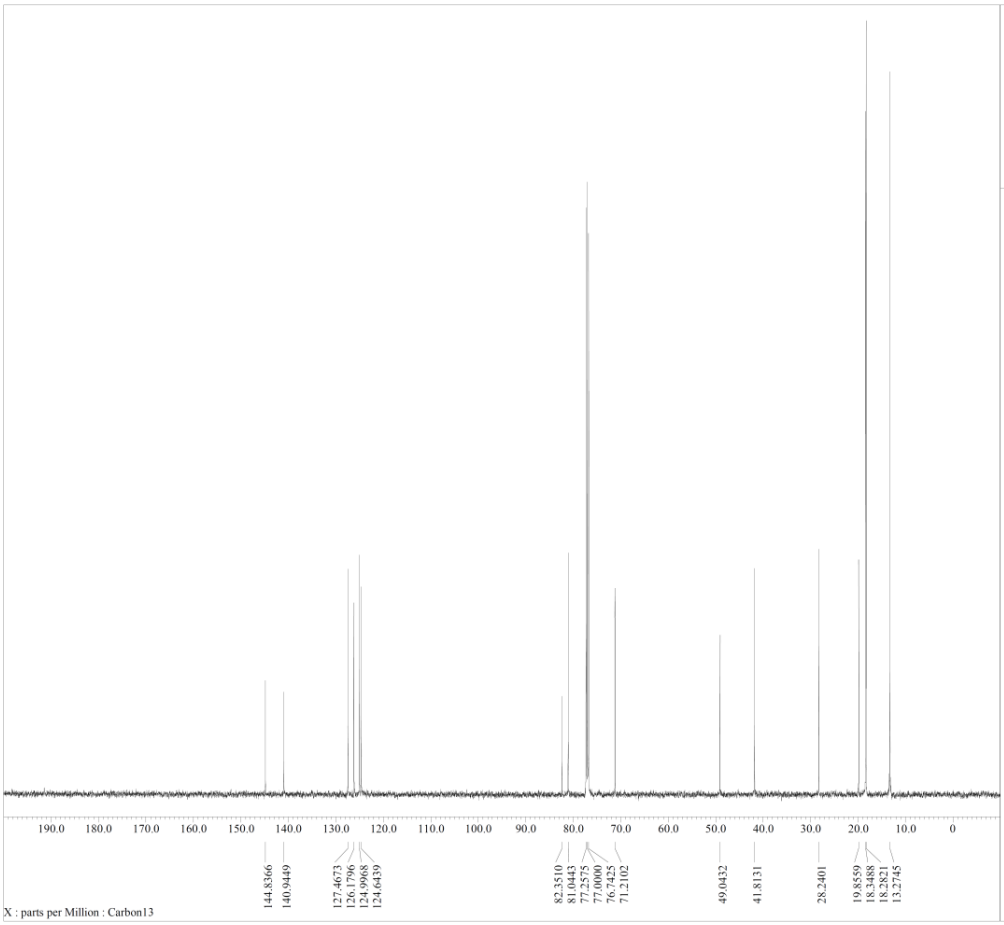
Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = Proton
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.7473579[T] (500[MHz])
X_Acq_Duration    = 3.49175808[s]
X_Domain          = 1H
X_Freq            = 500.15991521[MHz]
X_Offset          = 5.0[ppm]
X_Points          = 32768
X_Prescans        = 1
X_Resolution      = 0.28638868[Hz]
X_Sweep           = 9.38438438[kHz]
X_Sweep_Clipped   = 7.50750751[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Tri_Domain        = Proton
Tri_Freq          = 500.15991521[MHz]
Tri_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay = 5[s]
Recvr_Gain        = 34
Temp_Get          = 25.8[dC]
X_90_Width        = 12.9[us]
X_Acq_Time        = 3.49175808[s]
X_Angle           = 45[deg]
X_Atn             = 4.5[dB]
X_Pulse           = 6.45[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 8.49175808[s]
```



3i




```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm

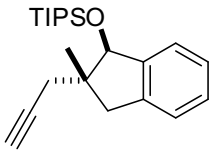
以下に由来:: HS_2285_purified_Carbon-1-1.jdf
```

```
Filename          = HS_2285_purified_Carbon-1-
Author            = iwasawa
Experiment        = carbon.jxp
Sample_Id         = HS_2285_purified
Solvent           = CHLOROFORM-D
Creation_Time     = 14-MAY-2016 18:33:02
Revision_Time     = 14-MAY-2016 20:56:05
Current_Time      = 14-MAY-2016 20:56:22

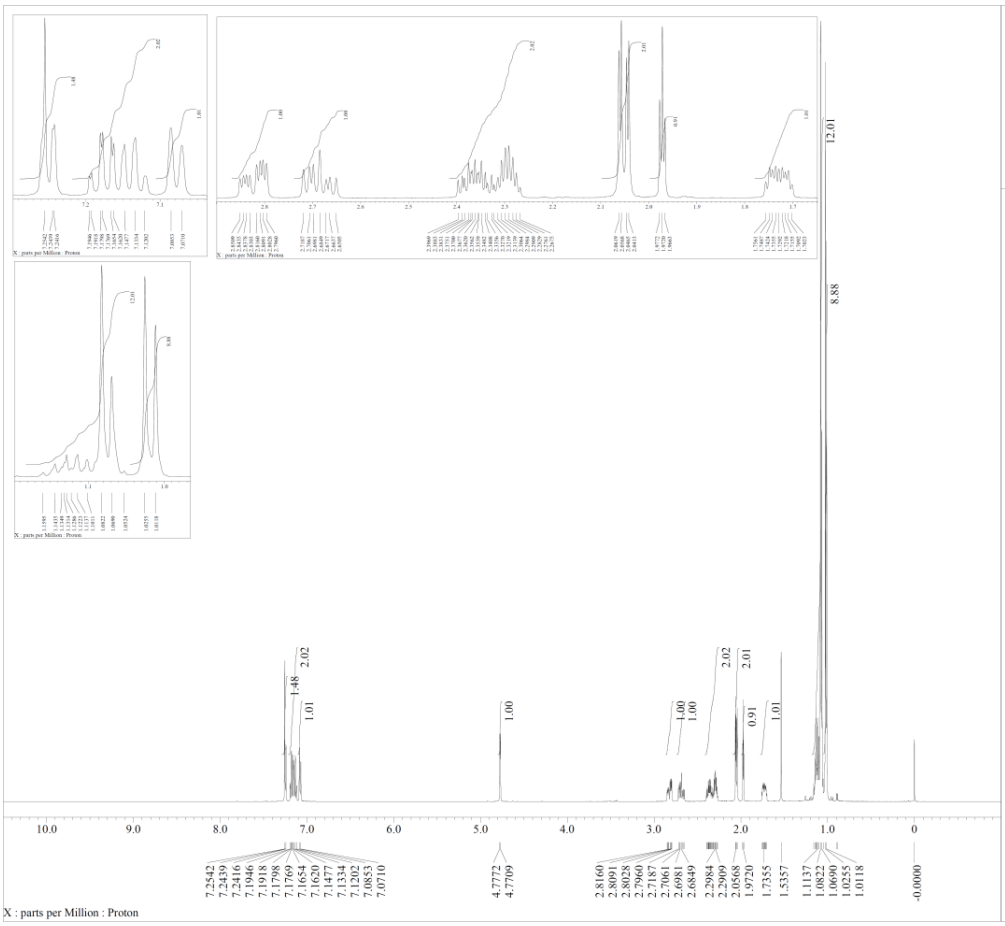
Comment           = single pulse decoupled gat
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.7473579[T] (500[MHz])
X_Acq_Duration    = 0.83361792[s]
X_Domain          = 13C
X_Freq            = 125.76529768[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.19959034[Hz]
X_Sweep           = 39.30981761[kHz]
X_Sweep_Clipped   = 31.44654088[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 512
Total_Scans       = 512

Relaxation_Delay  = 2[s]
Recvr_Gain        = 34
Temp_Set          = 26.3[dC]
X_90_Width        = 10.4[us]
X_Acq_Time        = 0.83361792[s]
X_Angle           = 30[deg]
X_Atn             = 5.6[dB]
X_Pulse           = 3.46666667[us]
Irr_Atn_Dec       = 21.564[dB]
Irr_Atn_Noe       = 21.564[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 92[us]
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 2.83361792[s]
```



3i




```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm

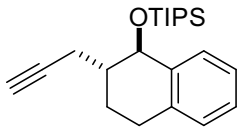
以下に由来:: HS_2218_major_proton-2-1.jdf
```

```
Filename          = HS_2218_major_proton-2-5.j
Author            = iwasawa
Experiment        = proton.jxp
Sample_Id         = HS_2218_major
Solvent           = CHLOROFORM-D
Creation_Time     = 24-MAY-2016 11:53:11
Revision_Time     = 24-MAY-2016 11:59:12
Current_Time      = 24-MAY-2016 12:00:27

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = Proton
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.7473579[T] (500[MHz])
X_Acq_Duration    = 3.49175808[s]
X_Domain          = 1H
X_Freq            = 500.15991521[MHz]
X_Offset          = 5.0[ppm]
X_Points          = 32768
X_Prescans        = 1
X_Resolution      = 0.28638868[Hz]
X_Sweep           = 9.38438438[kHz]
X_Sweep_Clipped   = 7.50750751[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Tri_Domain        = Proton
Tri_Freq          = 500.15991521[MHz]
Tri_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay  = 5[s]
Recvr_Gain        = 38
Temp_Set          = 25.8[dC]
X_90_Width        = 12.9[us]
X_Acq_Time        = 3.49175808[s]
X_Angle           = 45[deg]
X_Atn             = 4.5[dB]
X_Pulse           = 6.45[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 8.49175808[s]
```



3j

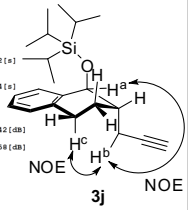

```
---- PROCESSING PARAMETERS ----
sexp( 5.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
ppm
machinephase
[transpose]
sexp( 5.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 2 )
fft( 1, TRUE, TRUE )
ppm
machinephase
[transpose]
```

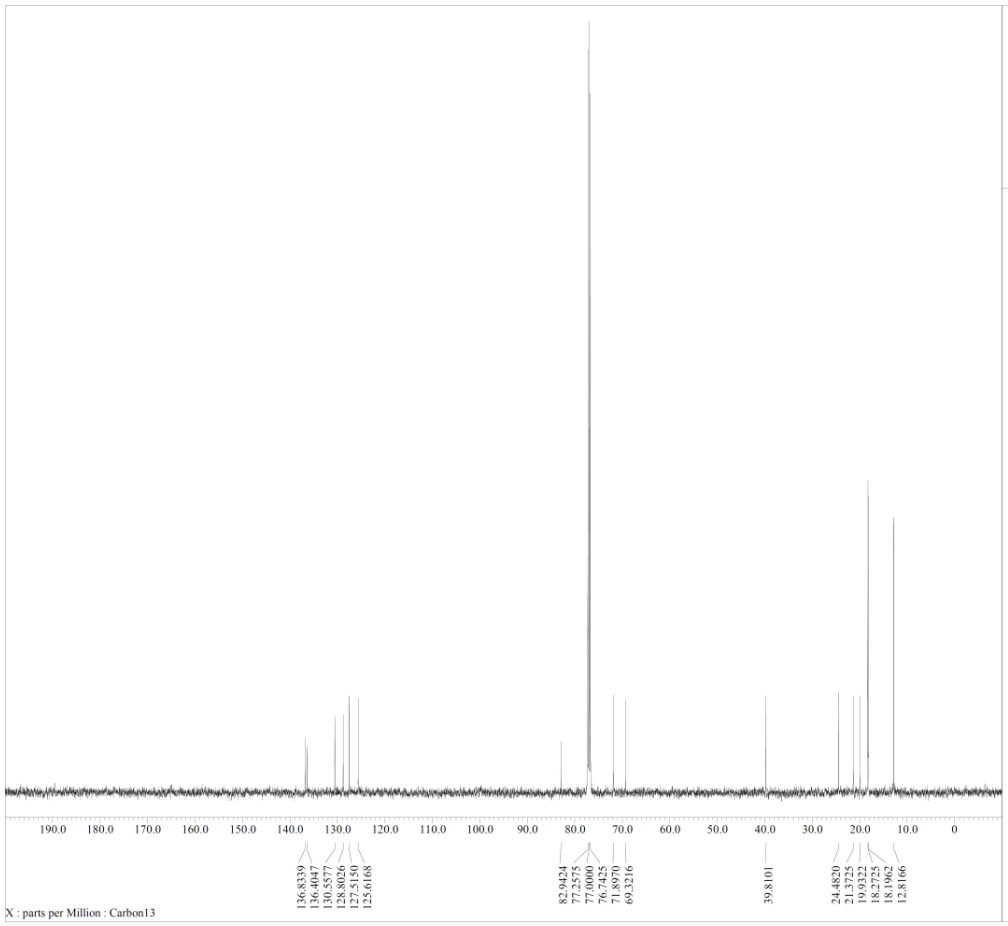
```
Filename          = SW_tetraloneH_pro_NOESY-1-
Author            = iwasawa
Experiment        = noesy.jxp
Sample_Id         = SW_tetraloneH_pro
Solvent           = CHLOROFORM-D
Creation_Time     = 26-NOV-2017 17:01:42
Revision_Time     = 30-NOV-2017 22:45:46
Current_Time      = 23-MAY-2018 19:13:11

Comment           = phase sensitive noesy
Data_Format       = 2D COMPLEX COMPLEX
Dim_Size          = 1638, 1024
Dim_Title         = Proton Proton
Dim_Units         = [ppm] [ppm]
Dimensions        = X Y
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.7473579[T]  (500[MHz])
X_Acq_Duration    = 0.40927232[s]
X_Domain          = 1H
X_Freq            = 500.15991521[MHz]
X_Offset          = 4[ppm]
X_Points          = 2048
X_Prescans        = 4
X_Resolution      = 2.44336094[Hz]
X_Sweep           = 5.00400032[kHz]
X_Sweep_Clipped   = 4.00320256[kHz]
Y_Domain          = 1H
Y_Freq            = 500.15991521[MHz]
Y_Offset          = 4[ppm]
Y_Points          = 512
Y_Prescans        = 0
Y_Resolution      = 7.8150008[Hz]
Y_Sweep           = 4.00128041[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Tri_Domain        = Proton
Tri_Freq          = 500.15991521[MHz]
Tri_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 16
Total_Scans       = 8192

Relaxation_Delay = 2[s]
Recvr_Gain        = 38
Temp_Get          = 21.4[dC]
Mix_Time          = 0.5[s]
X_Acq_Time        = 0.40927232[s]
X_Atn             = 4.5[dB]
X_Pulse           = 12.4[us]
Y_Acq_Time        = 0.12795904[s]
Y_F1_Correction   = 180.0
Irr_Mode          = Off
Tri_Mode          = Off
Adiabatic_Pulse   = 50[ms]
B1_Attn           = 43.80211242[dB]
Band_Width        = 30[kHz]
Chirp_Atn         = 31.19788758[dB]
Chirp_Pulse       = 50[ms]
Chirp_Shape       = CHIRP
Chirp_Smooth      = 10[%]
Dante_Presat      = FALSE
Grad_Spoil        = 1[ms]
Grad_Spoil_Amp    = 6[mT/m]
Grad_Sgf_Amp      = 24[mT/m]
Hard_Square_Atn   = 75[dB]
Initial_Wait      = 1[s]
Mix_Time2         = 0.448998[s]
Phase_1           = {(0, 180, 0, 180, 0, 180,
Q                 = 2
Repetition_Time   = 2.40927232[s]
Scramble          = 1[ms]
T1                = 0.109088[ms]
T1_Cal1           = 0.109088[ms]
T1_Cal2           = 0.234048[ms]
T1_Cal3           = 0.359008[ms]
T1_Cal4           = 0.483968[ms]
T1_Cal5           = 0.608928[ms]
T1_Cal6           = 0.733888[ms]
Zf_Factor         = 3
```






```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm

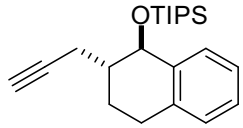
以下に由来:: HS_2218_major_Carbon-1-1.jdf
```

```
Filename          = HS_2218_major_Carbon-1-6.j
Author            = iwasawa
Experiment        = carbon.jxp
Sample_Id         = HS_2218_major
Solvent           = CHLOROFORM-D
Creation_Time     = 24-MAY-2016 12:09:33
Revision_Time     = 24-MAY-2016 14:02:21
Current_Time      = 24-MAY-2016 14:02:42

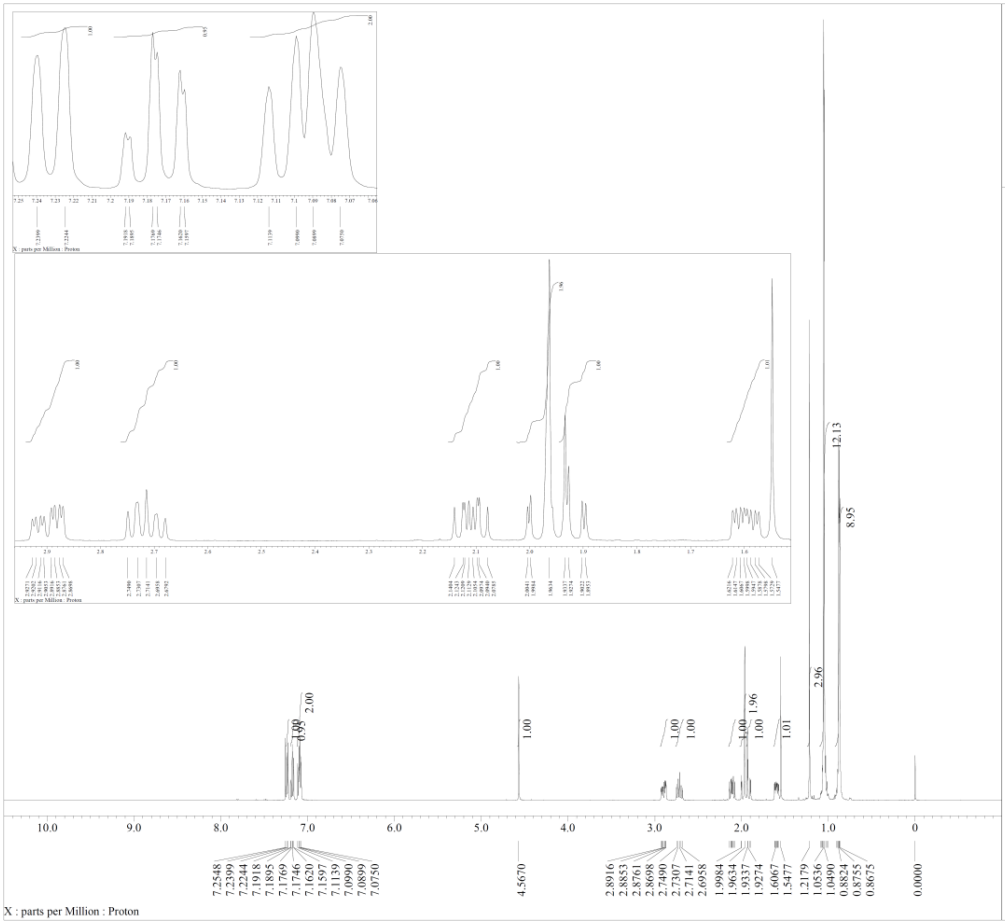
Comment           = single pulse decoupled gat
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.7473579[T]  (500[MHz])
X_Acq_Duration    = 0.83361792[s]
X_Domain          = 13C
X_Freq            = 125.76529768[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.19959034[Hz]
X_Sweep           = 39.3081761[kHz]
X_Sweep_Clipped   = 31.44654088[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 512
Total_Scans       = 512

Relaxation_Delay = 2[s]
Recvr_Gain        = 38
Temp_Get          = 26.3[dC]
X_90_Width        = 10.4[us]
X_Acq_Time        = 0.83361792[s]
X_Angle           = 30[deg]
X_Atn             = 5.6[dB]
X_Pulse           = 3.46666667[us]
Irr_Atn_Dec       = 21.564[dB]
Irr_Atn_Noe       = 21.564[dB]
Irr_Noise         = WALTZ
Irr_Pwidth        = 92[us]
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 2.83361792[s]
```



3j




```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm

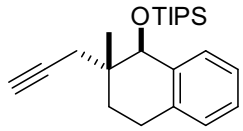
以下に由来:: HS_2284_purified_proton-1-1.jdf
```

```
Filename          = HS_2284_purified_proton-1-
Author            = iwasawa
Experiment        = proton.jxp
Sample_Id         = HS_2284_purified
Solvent           = CHLOROFORM-D
Creation_Time     = 14-MAY-2016 13:53:10
Revision_Time     = 14-MAY-2016 14:06:13
Current_Time      = 14-MAY-2016 14:09:07

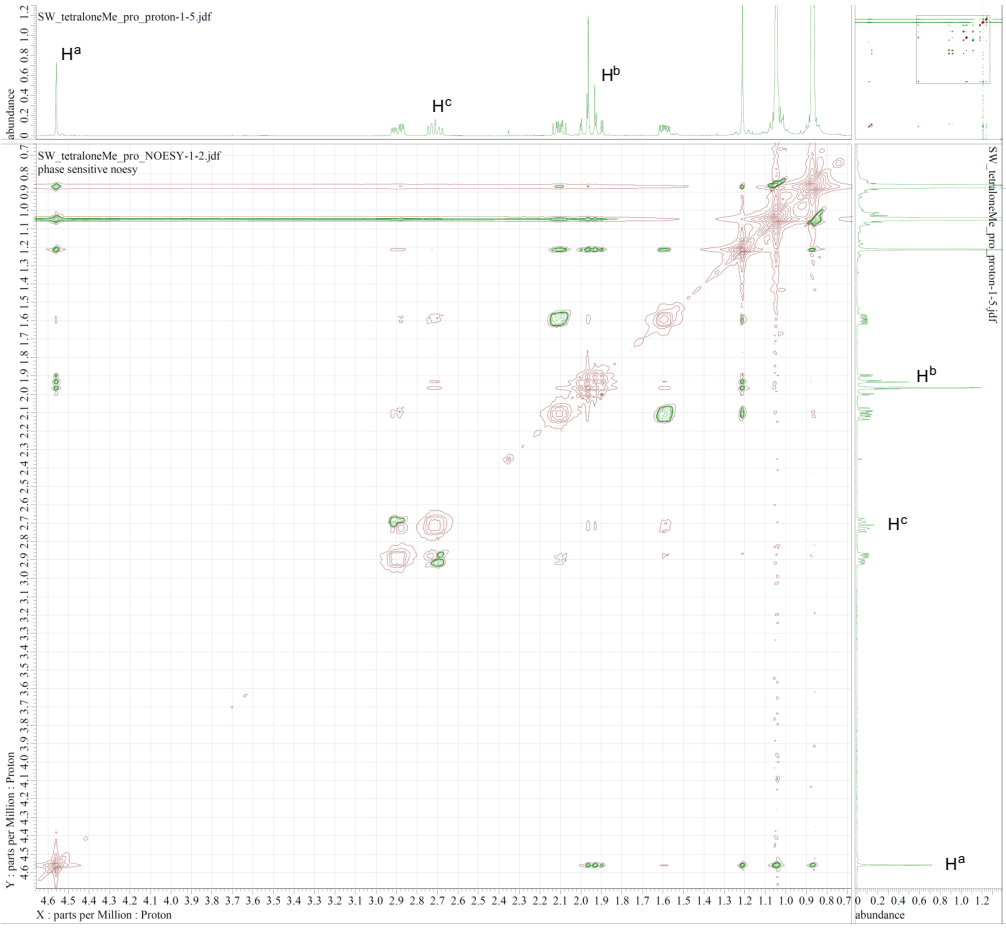
Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = Proton
Dim_Units         = [ppm]
Dimensions        = X
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

Field_Strength    = 11.7473579[T] (500[MHz])
X_Acq_Duration    = 3.49175808[s]
X_Domain          = 1H
X_Freq            = 500.15991521[MHz]
X_Offset          = 5.0[ppm]
X_Points          = 32768
X_Prescans        = 1
X_Resolution      = 0.28638868[Hz]
X_Sweep           = 9.38438438[kHz]
X_Sweep_Clipped   = 7.50750751[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Tri_Domain        = Proton
Tri_Freq          = 500.15991521[MHz]
Tri_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay = 5[s]
Recvr_Gain        = 34
Temp_Get          = 25.8[dC]
X_90_Width        = 12.9[us]
X_Acq_Time        = 3.49175808[s]
X_Angle           = 45[deg]
X_Atn             = 4.5[dB]
X_Pulse           = 6.45[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 8.49175808[s]
```



3k



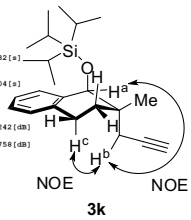

```
---- PROCESSING PARAMETERS ----
sexp( 5.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
ppm
machinephase
[transpose]
sexp( 5.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 2 )
fft( 1, TRUE, TRUE )
ppm
machinephase
[transpose]
```

```
Filename          = SW_tetraloneMe_pro_NOESY-1
Author            = iwasawa
Experiment        = noesy.jxp
Sample_Id         = SW_tetraloneMe_pro
Solvent           = CHLOROFORM-D
Creation_Time     = 25-NOV-2017 18:33:54
Revision_Time     = 23-MAY-2018 19:15:16
Current_Time      = 23-MAY-2018 19:27:40

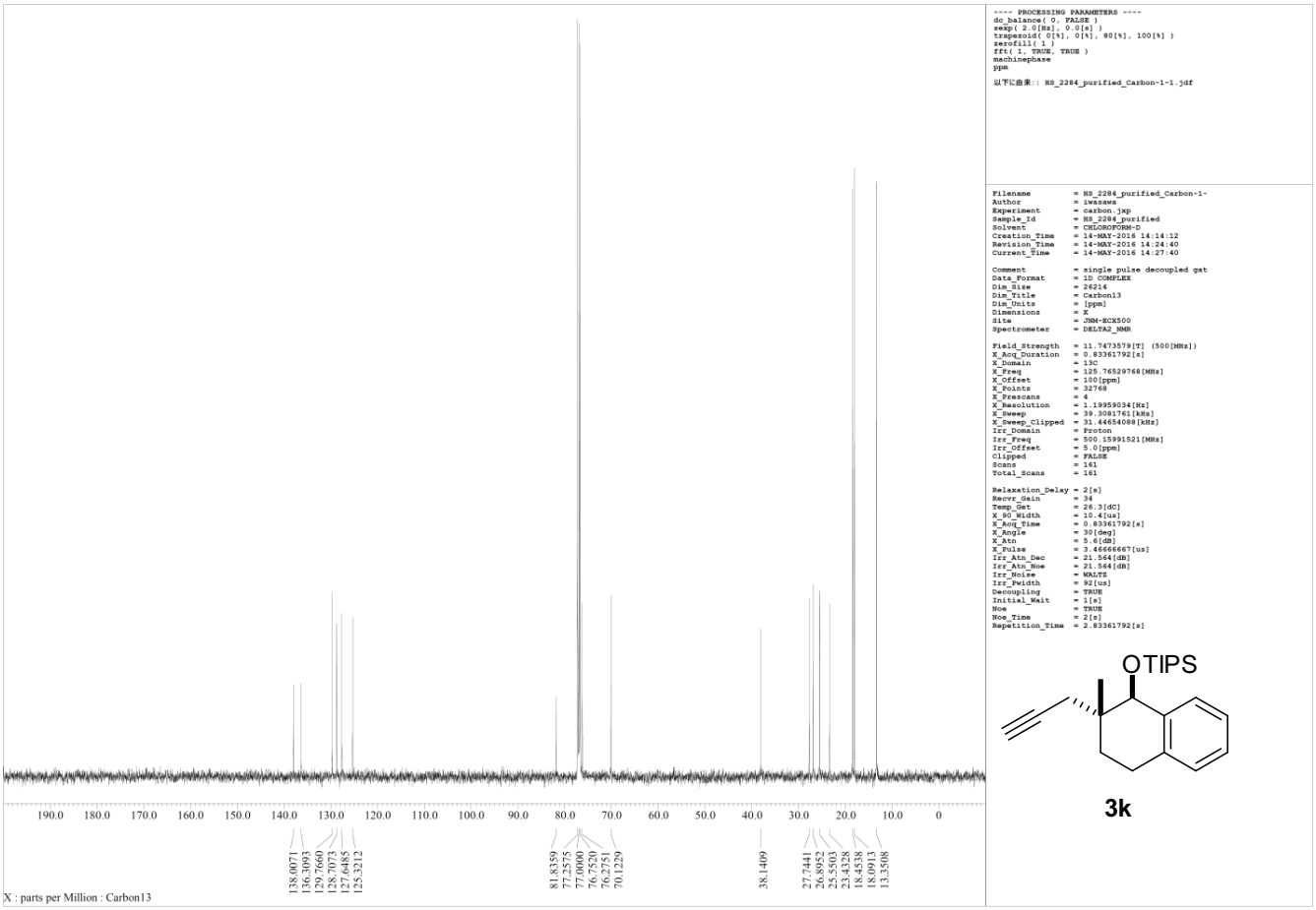
Comment           = phase sensitive noesy
Data_Format       = 2D COMPLEX COMPLEX
Dim_Size          = 1638, 1024
Dim_Title         = Proton Proton
Dim_Units         = [ppm] [ppm]
Dimensions        = X Y
Site              = JNM-ECX500
Spectrometer      = DELTA2_NMR

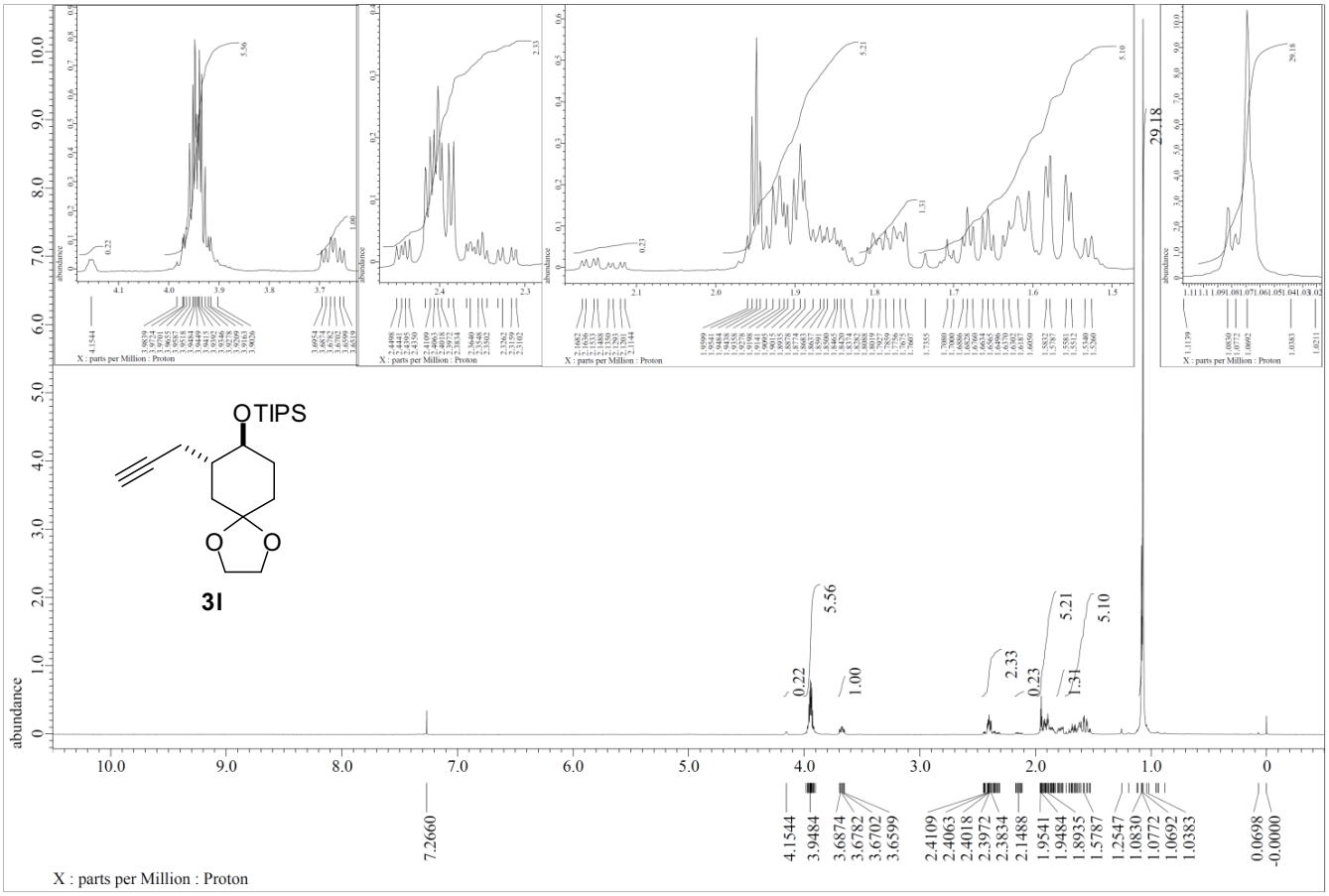
Field_Strength    = 11.7473579[T] (500[MHz])
X_Acq_Duration    = 0.40927232[s]
X_Domain          = 1H
X_Freq            = 500.15991521[MHz]
X_Offset          = 4[ppm]
X_Points          = 2048
X_Prescans        = 4
X_Resolution      = 2.44336094[Hz]
X_Sweep           = 5.0040032[kHz]
X_Sweep_Clipped   = 4.00320256[kHz]
Y_Domain          = 1H
Y_Freq            = 500.15991521[MHz]
Y_Offset          = 4[ppm]
Y_Points          = 512
Y_Prescans        = 0
Y_Resolution      = 7.8150008[Hz]
Y_Sweep           = 4.00128041[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Tri_Domain        = Proton
Tri_Freq          = 500.15991521[MHz]
Tri_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 16
Total_Scans       = 8192

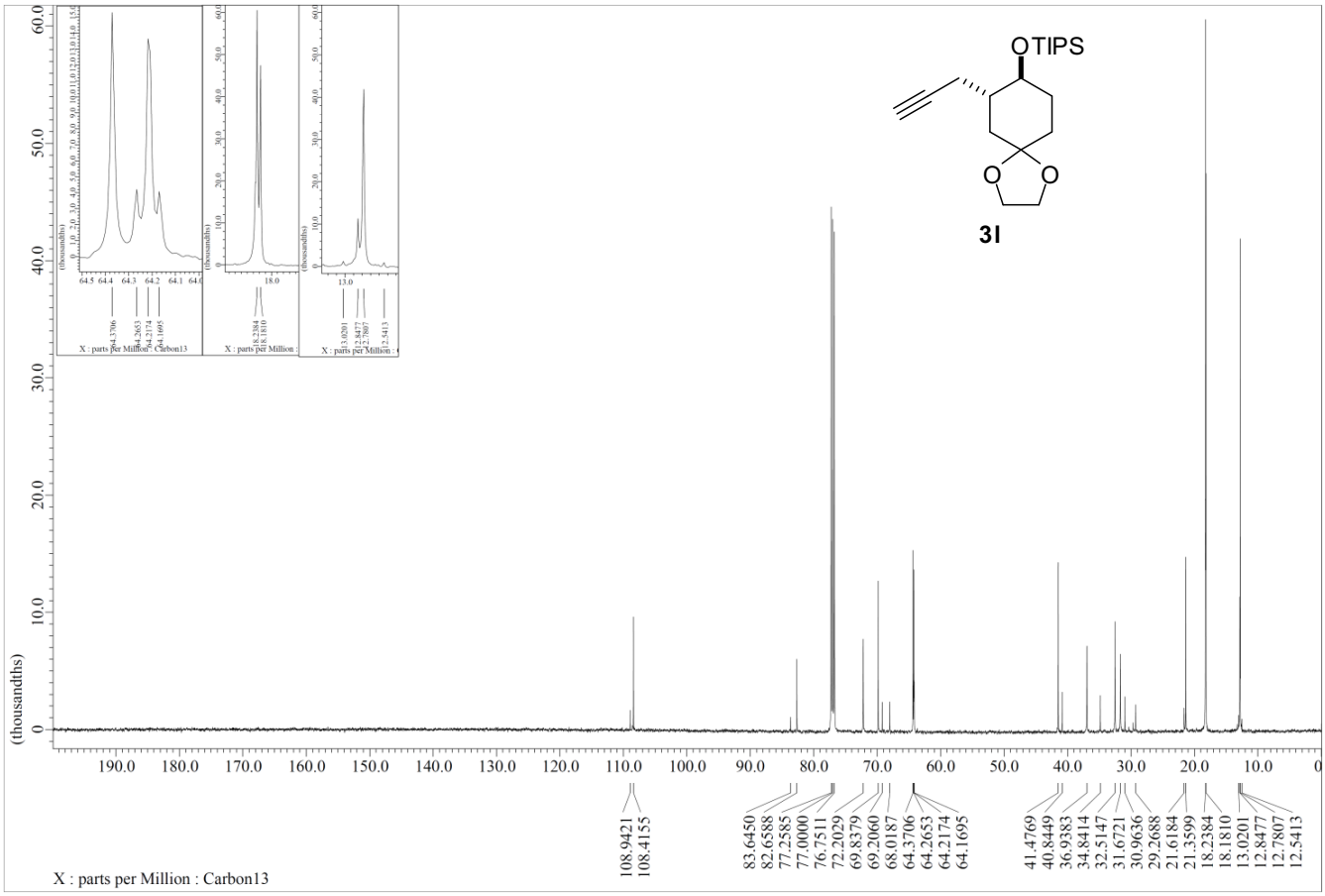
Relaxation_Delay = 2[s]
Recvr_Gain        = 44
Temp_Get          = 21.3[dC]
Mix_Time          = 0.5[s]
X_Acq_Time        = 0.40927232[s]
X_Atn             = 4.5[dB]
X_Pulse           = 12.4[us]
Y_Acq_Time        = 0.12795904[s]
Y_Pi_Correction   = 180.0
Irr_Mode          = Off
Tri_Mode          = Off
Adiabatic_Pulse   = 50[ms]
Bi_Attn           = 43.80211242[dB]
Band_Width        = 30[kHz]
Chirp_Atn         = 31.19788758[dB]
Chirp_Pulse       = 50[ms]
Chirp_Shape       = CHIRP
Chirp_Smooth      = 10[%]
Dante_Presat      = FALSE
Grad_Spoil        = 1[ms]
Grad_Spoil_Amp    = 6[mT/m]
Grad_Zqf_Amp      = 24[mT/m]
Hard_Square_Atn   = 75[dB]
Initial_Wait      = 1[s]
Mix_Time2         = 0.448998[s]
Phase_1           = {(0, 180, 0, 180, 0, 180,
Q                 = 2
Repetition_Time   = 2.40927232[s]
Scramble          = 1[ms]
T1                = 0.109088[ms]
T1_Cal1           = 0.109088[ms]
T1_Cal2           = 0.234048[ms]
T1_Cal3           = 0.359008[ms]
T1_Cal4           = 0.483968[ms]
T1_Cal5           = 0.608928[ms]
T1_Cal6           = 0.733888[ms]
Zf_Factor         = 3
```

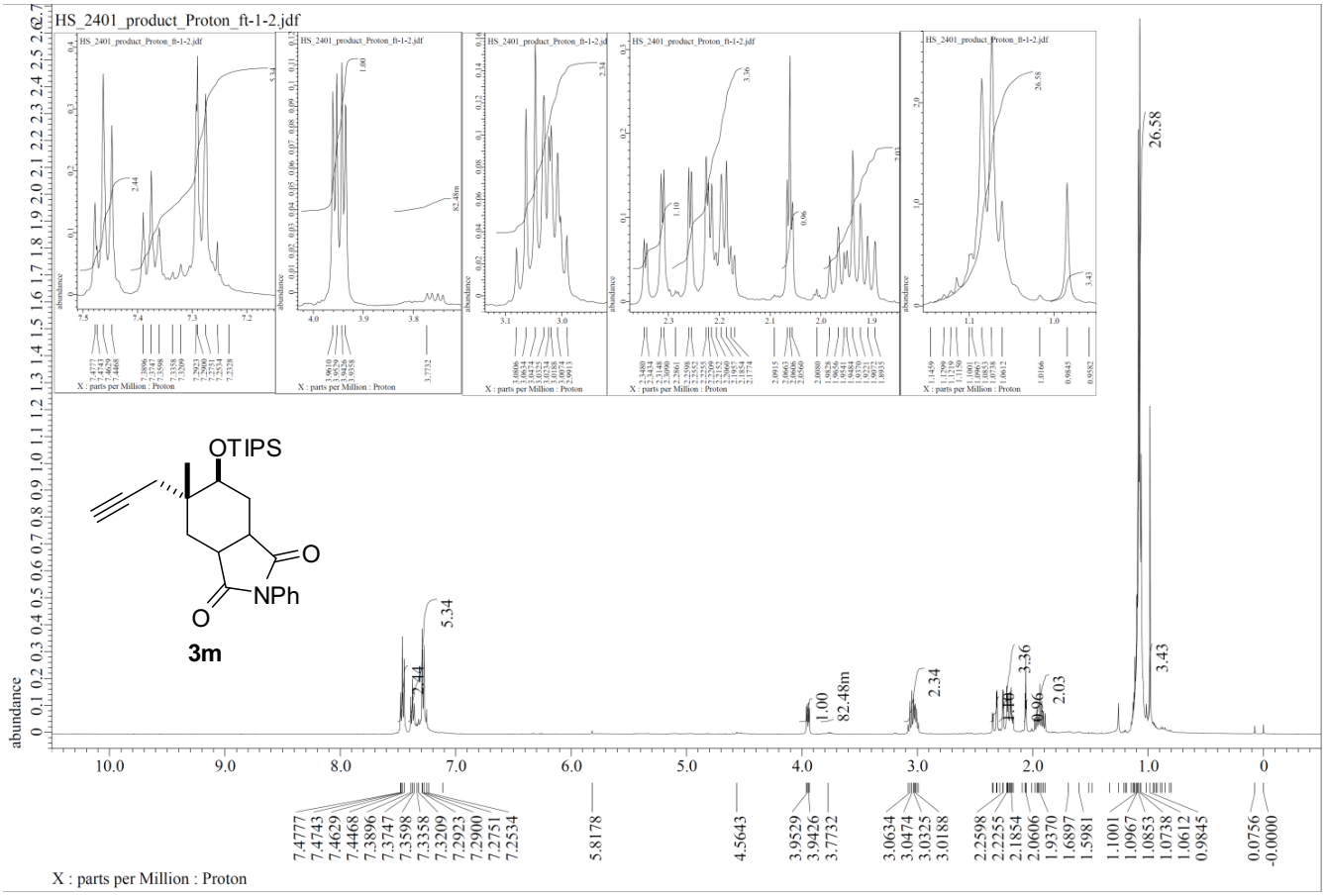


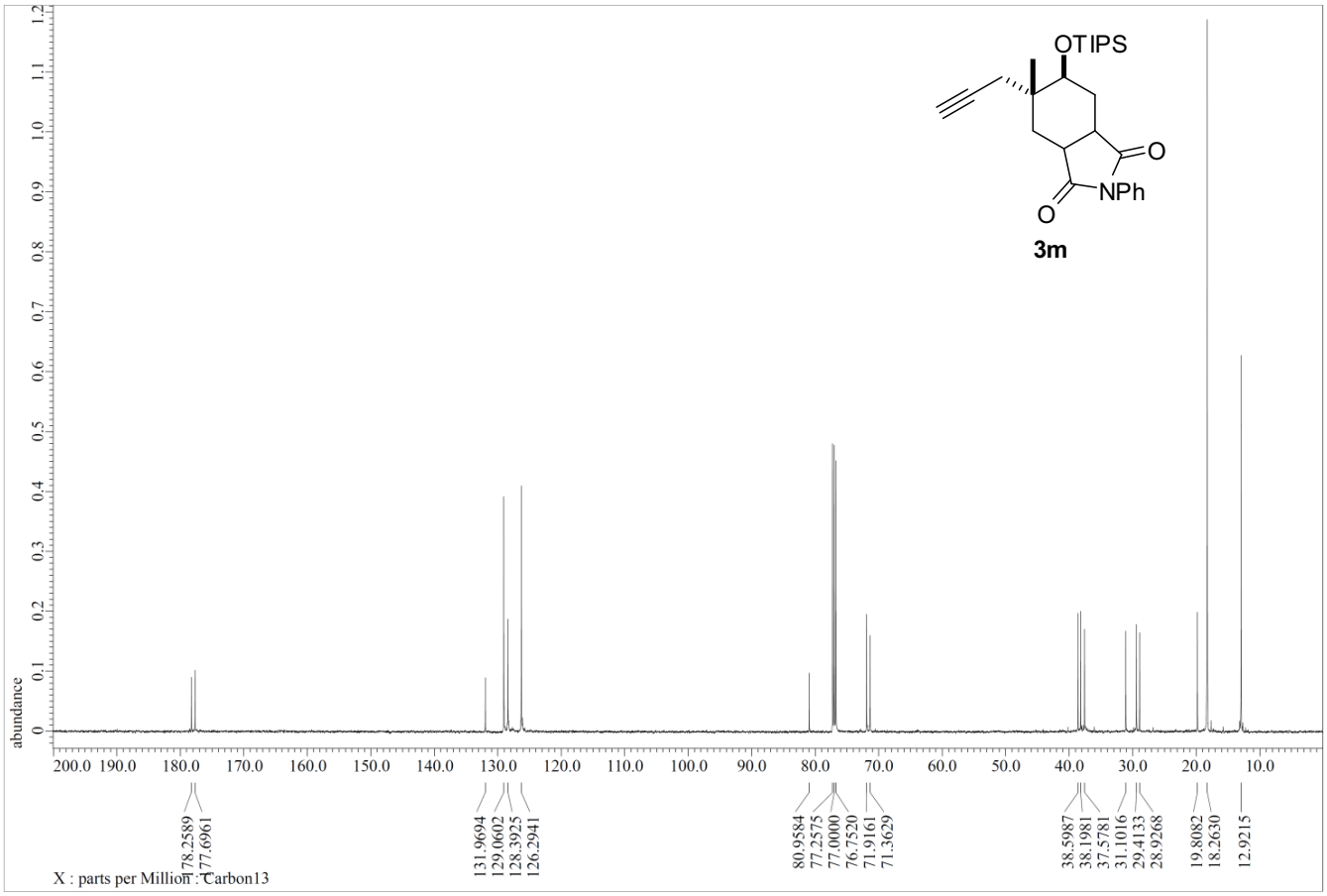
3k

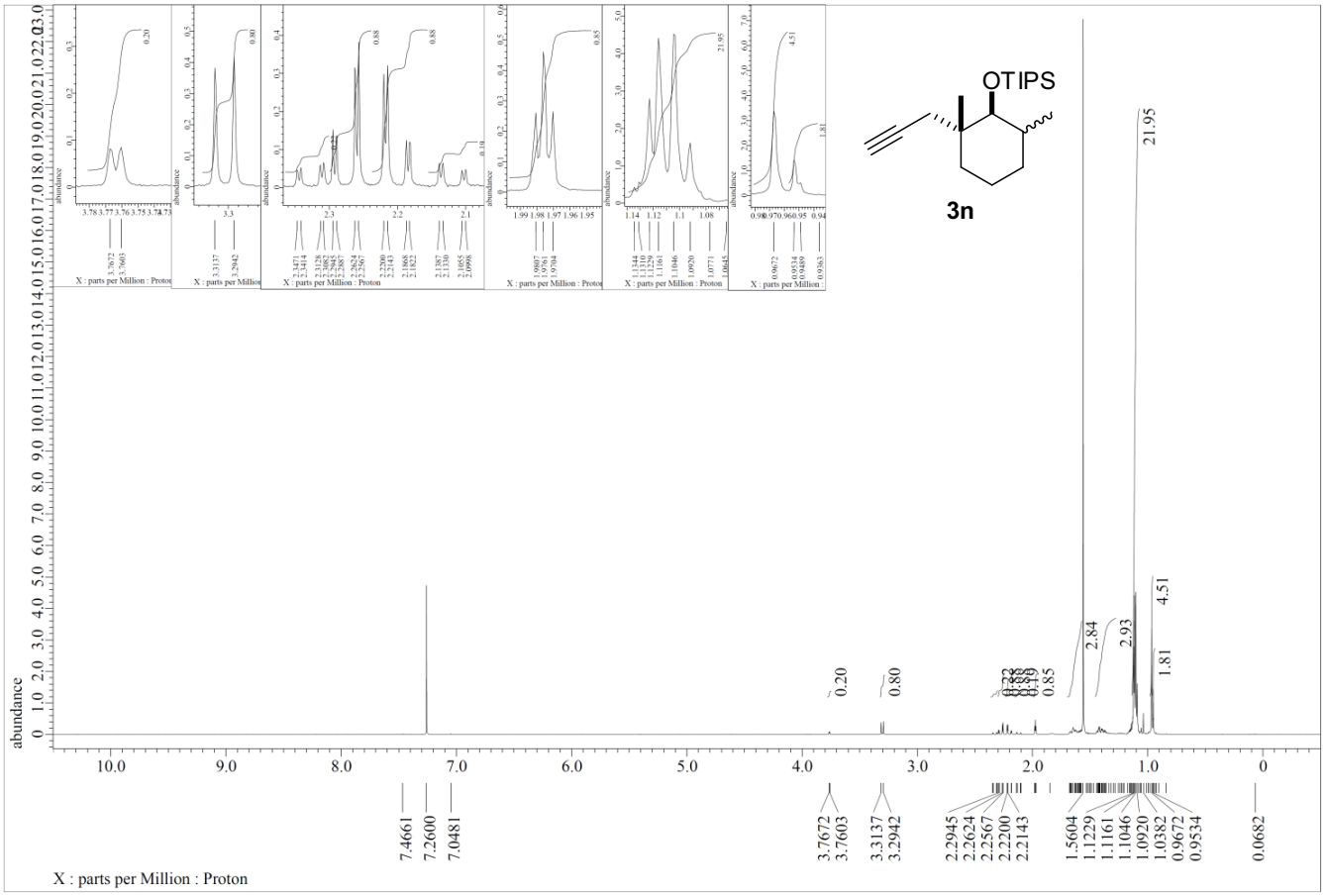

---- PROCESSING PARAMETERS ----
dc_balance(0, FALSE)
expr(2.0[Hz], 0.0[s])
trapezoid(0[%], 0[%], 80[%], 100[%])
zerofill(1)
fft(1, TRUE, TRUE)
machinephase
ppm
以下に曲来:: HS_2284_purified_Carbon-1-1.jdf
Filename = HS_2284_purified_Carbon-1-
Author = iwasawa
Experiment = carbon.jxp
Sample_Id = HS_2284_purified
Solvent = CHLOROFORM-D
Creation_Time = 14-MAY-2016 14:14:12
Revision_Time = 14-MAY-2016 14:24:40
Current_Time = 14-MAY-2016 14:27:40
Comment = single pulse decoupled gat
Data_Format = 1D COMPLEX
Dim_Size = 26214
Dim_Title = Carbon13
Dim_Units = [ppm]
Dimensions = X
Site = JNM-ECX500
Spectrometer = DELTA2_NMR
Field_Strength = 11.7473579[T] (500[MHz])
X_Acq_Duration = 0.83361792[s]
X_Domain = 13C
X_Freq = 125.76529768[MHz]
X_Offset = 100[ppm]
X_Points = 32768
X_Prescans = 4
X_Resolution = 1.19959034[Hz]
X_Sweep = 39.3081761[kHz]
X_Sweep_clipped = 31.44654088[kHz]
Irr_Domain = Proton
Irr_Freq = 500.15991521[MHz]
Irr_Offset = 5.0[ppm]
Clipped = FALSE
Scans = 161
Total_Scans = 161
Relaxation_Delay = 2[s]
Recvr_Gain = 34
Temp_Get = 26.3[dC]
X_90_Width = 10.4[us]
X_Acq_Time = 0.83361792[s]
X_Angle = 30[deg]
X_Atn = 5.6[dB]
X_Pulse = 3.46666667[us]
Irr_Atn_Dec = 21.564[dB]
Irr_Atn_Noe = 21.564[dB]
Irr_Noise = WALTZ
Irr_Pwidth = 92[us]
Decoupling = TRUE
Initial_Wait = 1[s]
Noe = TRUE
Noe_Time = 2[s]
Repetition_Time = 2.83361792[s]
OTIPS
3k
X : parts per Million : Carbon13

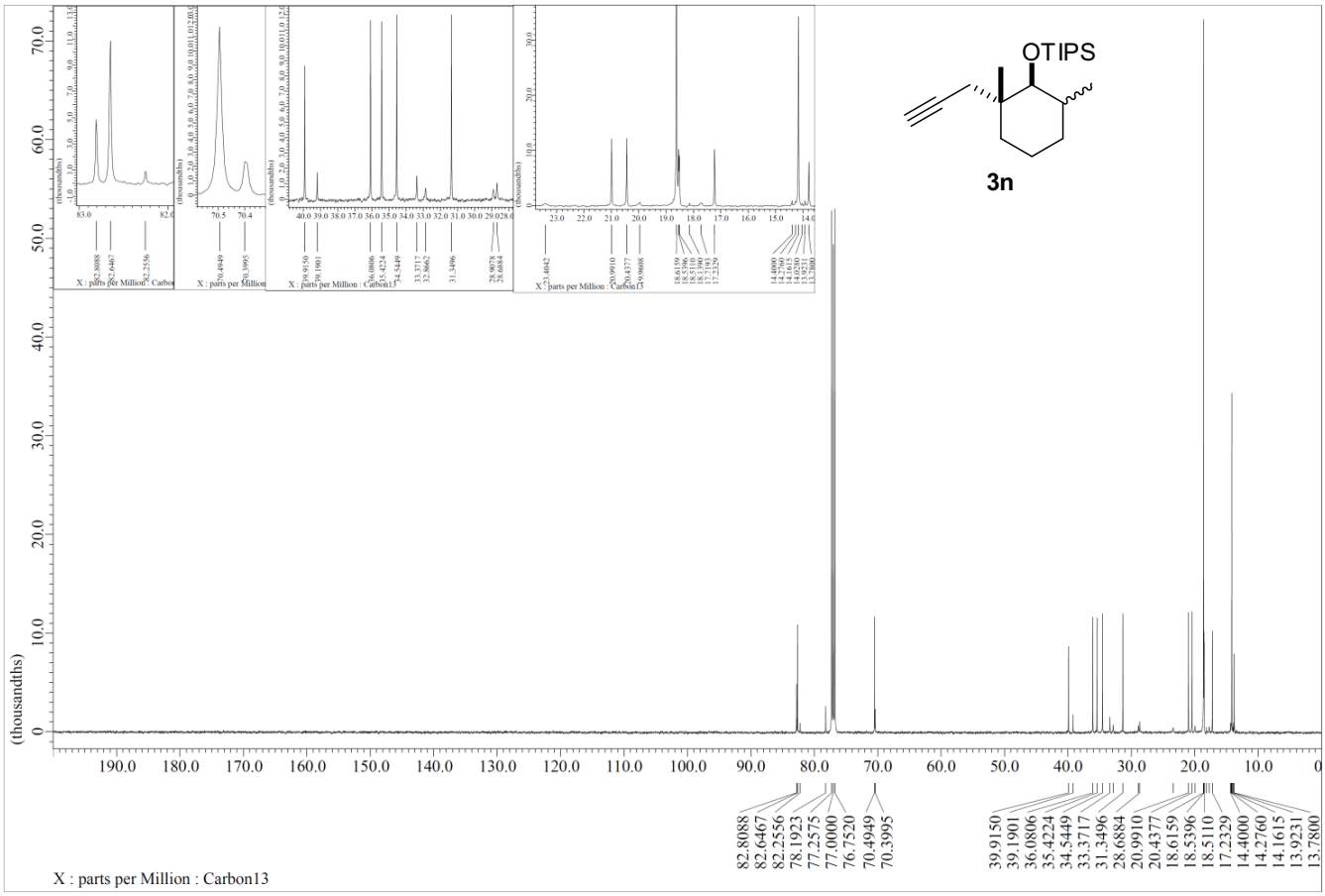

OTIPS
3l
X : parts per Million : Proton

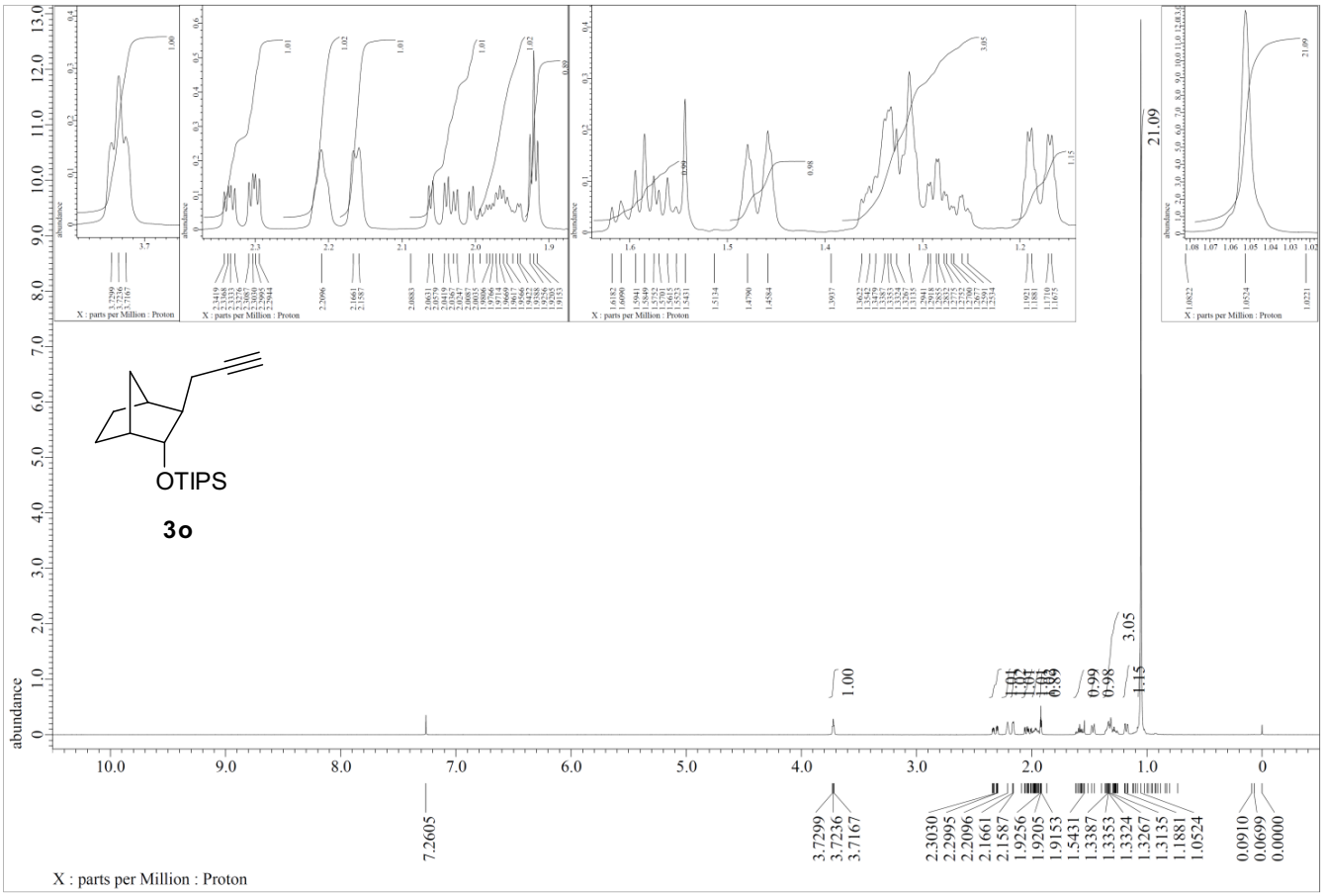

OTIPS
O
O
3l
(thousandths)
X : parts per Million : Carbon13

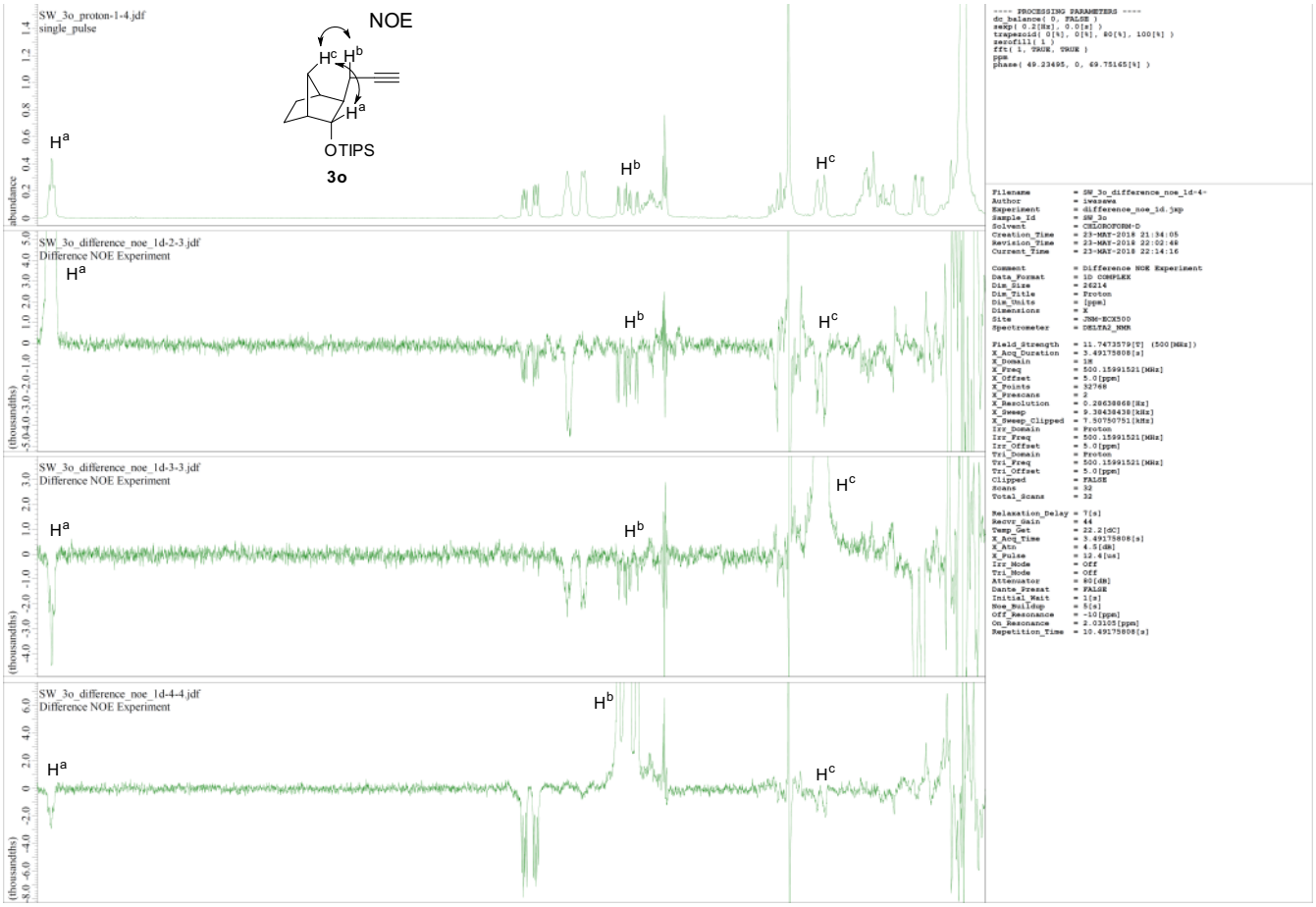

HS_2401_product_Proton_ft-1-2.jdf
OTIPS
O
NPh
O
3m
abundance
X : parts per Million : Proton

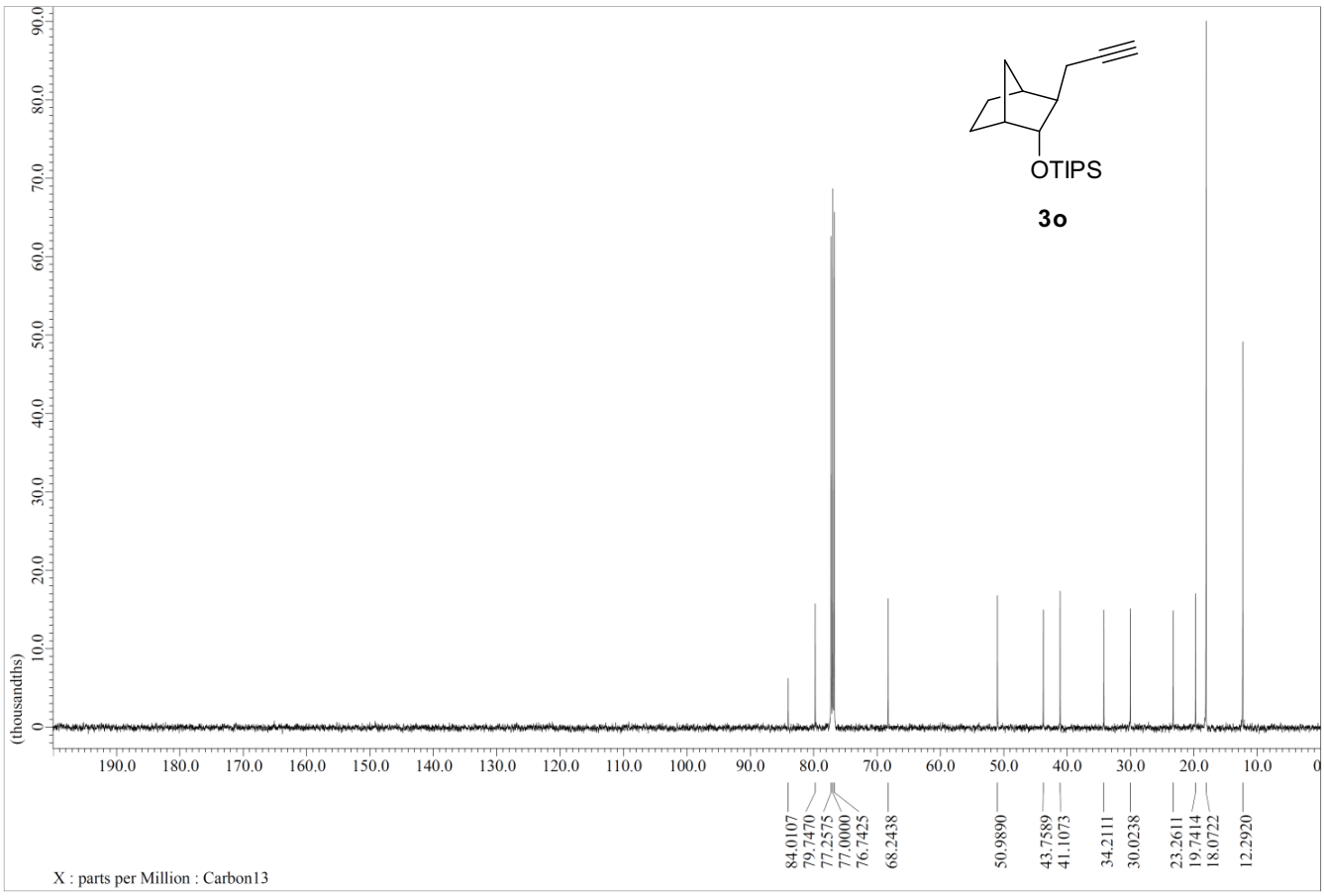

OTIPS
O
NPh
O
3m
abundance
78.2589
77.6961
131.9694
129.0602
128.3925
126.2941
80.9584
77.2575
77.0000
76.7520
71.9161
71.3629
38.5987
38.1981
37.5781
31.1016
29.4133
28.9268
19.8082
18.2630
12.9215
X : parts per Million : Carbon13

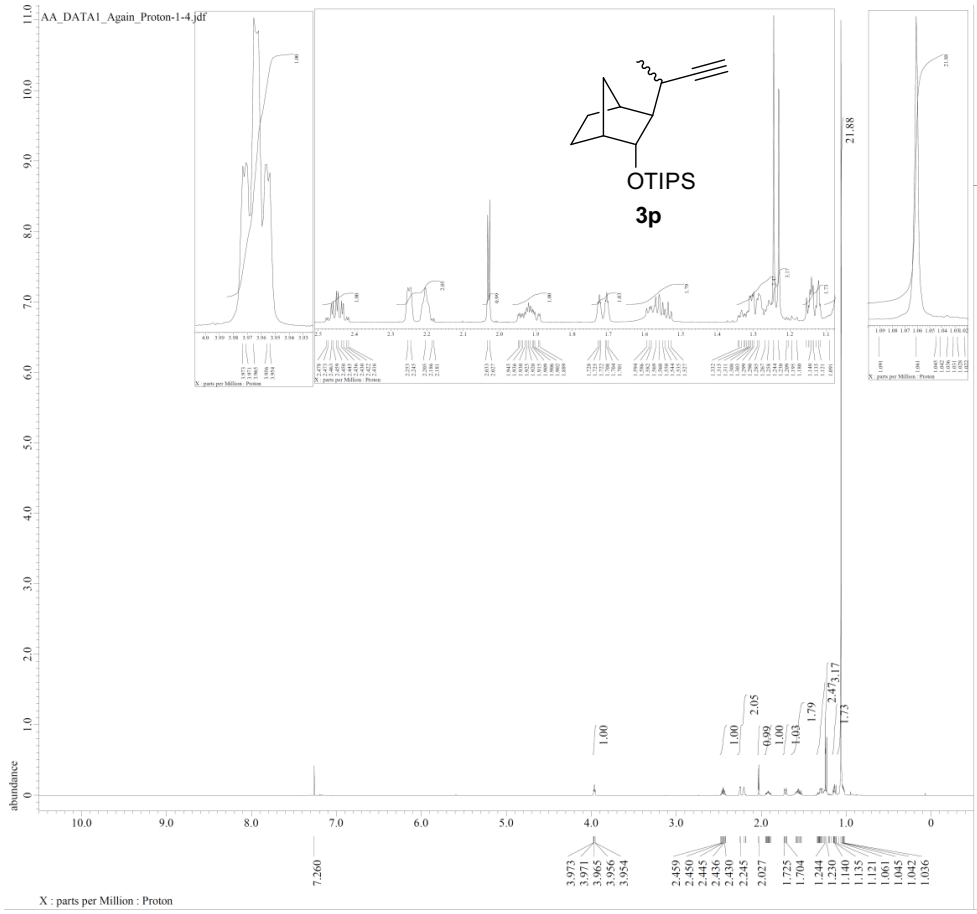

OTIPS
3n
abundance
7.4661
7.2600
7.0481
3.7672
3.7603
3.3137
3.2942
2.2945
2.2624
2.2567
2.2200
2.2143
1.5604
1.1229
1.1161
1.1046
1.0920
1.0382
0.9672
0.9534
0.0682
0.20
0.80
0.85
2.84
2.93
21.95
4.51
1.81
X : parts per Million : Proton


OTIPS
3n
(thousandths)
X : parts per Million : Carbon13


OTIPS
3o
abundance
X : parts per Million : Proton


SW_3o_proton-1-4.jdf
single_pulse
NOE
OTIPS
3o
SW_3o_difference_noe_1d-2-3.jdf
Difference NOE Experiment
SW_3o_difference_noe_1d-3-3.jdf
Difference NOE Experiment
SW_3o_difference_noe_1d-4-4.jdf
Difference NOE Experiment


OTIPS
3o
(thousandths)
84.0107
79.7470
77.2575
77.0000
76.7425
68.2438
50.9890
43.7589
41.1073
34.2111
30.0238
23.2611
19.7414
18.0722
12.2920
X : parts per Million : Carbon13




```
---- PROCESSING PARAMETERS ----
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm

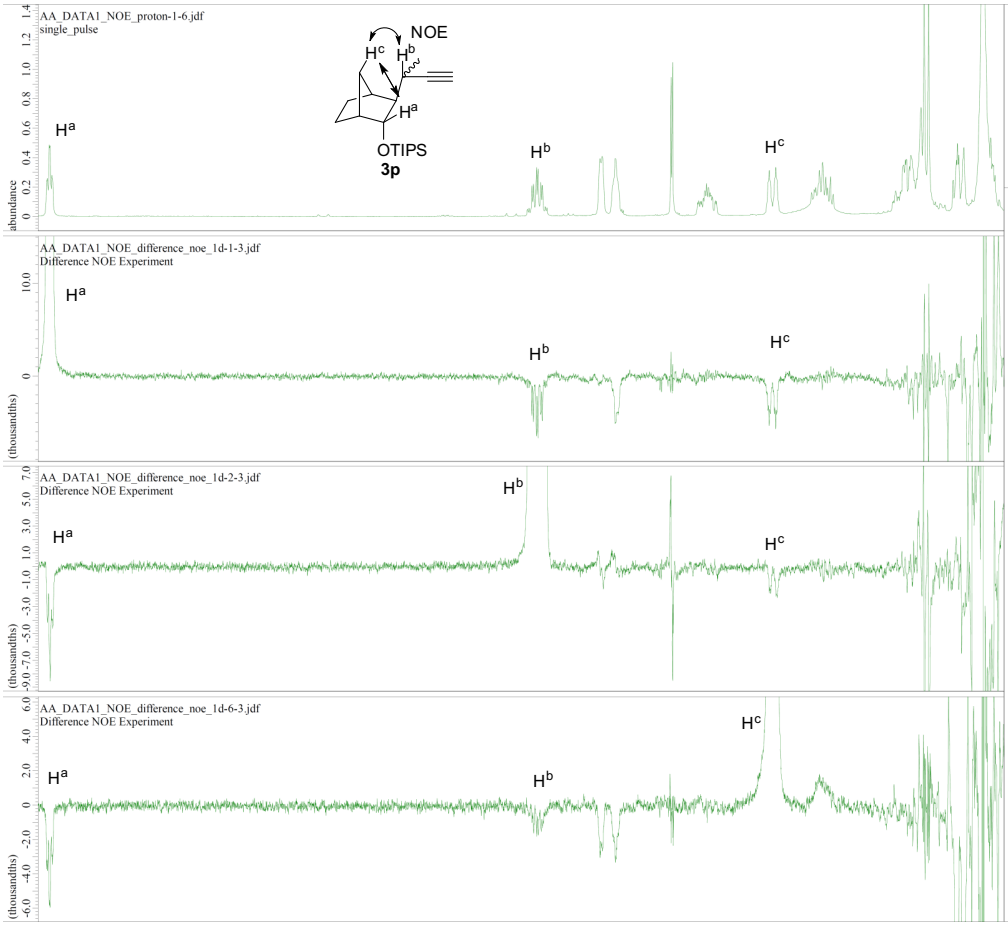
以下に由来:: AA_DATA1_Again_Proton-1-1.jdf
```

```
Filename              = AA_DATA1_Again_Proton
Author                = delta
Experiment            = proton.jxp
Sample_Id             = AA_DATA1_Again
Solvent               = CHLOROFORM-D
Actual_Start_Time     = 12-MAY-2018 21:07:03
Revision_Time         = 14-MAY-2018 15:32:25

Comment               = single_pulse
Data_Format           = 1D COMPLEX
Dim_Size              = 13107
Dim_Title             = Proton
Dim_Units             = [ppm]
Dimensions            = X
Spectrometer          = JNM-ECZ500R/S1

Field_Strength        = 11.62926421[T] (500[M
X_Acq_Duration        = 1.76422912[s]
X_Domain              = 1H
X_Freq                = 495.13191398[MHz]
X_Offset              = 5[ppm]
X_Points              = 16384
X_Prescans            = 1
X_Resolution          = 0.5668198[Hz]
X_Sweep               = 9.28677563[kHz]
X_Sweep_Clipped       = 7.42942051[kHz]
Irr_Domain            = Proton
Irr_Freq              = 495.13191398[MHz]
Irr_Offset            = 5[ppm]
Tri_Domain            = Proton
Tri_Freq              = 495.13191398[MHz]
Tri_Offset            = 5[ppm]
Clipped               = FALSE
Scans                 = 16
Total_Scans           = 16

Relaxation_Delay      = 5[s]
Recvr_Gain            = 56
Temp_Get              = 21.6[dC]
X_90_Width            = 11.53[us]
X_Acq_Time            = 1.76422912[s]
X_Angle               = 45[deg]
X_Atn                 = 3.3[dB]
X_Pulse               = 5.765[us]
Irr_Mode              = Off
Tri_Mode              = Off
Dante_Loop            = 500
Dante_Presat          = FALSE
Decimation_Rate       = 0
Initial_Wait          = 1[s]
Phase                 = {0, 90, 270, 180, 180
Presat_Time           = 5[s]
Presat_Time_Flag      = FALSE
Relaxation_Delay_Calc = 0[s]
Relaxation_Delay_Temp = 5[s]
Repetition_Time       = 6.76422912[s]
```



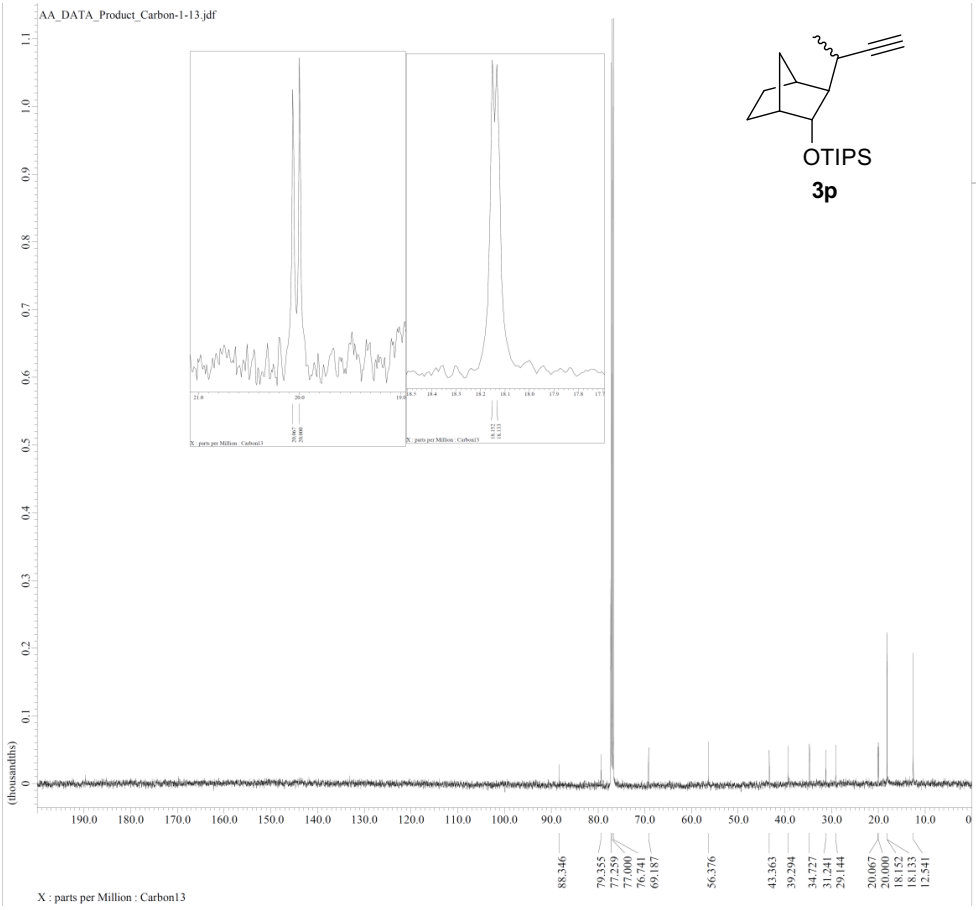

```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
ppm
phase( 58.13168, 0, 71.82314[%] )
```

```
Filename              = AA_DATA1_NOE_difference_no
Author                = iwasawa
Experiment            = difference_noe_1d.jxp
Sample_Id             = AA_DATA1_NOE
Solvent               = CHLOROFORM-D
Creation_Time         = 24-MAY-2018 23:07:13
Revision_Time         = 25-MAY-2018 16:52:12
Current_Time          = 25-MAY-2018 16:54:28

Comment               = Difference NOE Experiment
Data_Format           = 1D COMPLEX
Dim_Size              = 26214
Dim_Title             = Proton
Dim_Units             = [ppm]
Dimensions            = X
Site                  = JNM-ECX500
Spectrometer          = DELTA2_NMR

Field_Strength        = 11.7473579[T] (500[MHz])
X_Acq_Duration        = 3.49175808[s]
X_Domain              = 1H
X_Freq                = 500.15991521[MHz]
X_Offset              = 5.0[ppm]
X_Points              = 32768
X_Prescans            = 2
X_Resolution          = 0.28638868[Hz]
X_Sweep               = 9.38438438[kHz]
X_Sweep_Clipped       = 7.50750751[kHz]
Irr_Domain            = Proton
Irr_Freq              = 500.15991521[MHz]
Irr_Offset            = 5.0[ppm]
Tri_Domain            = Proton
Tri_Freq              = 500.15991521[MHz]
Tri_Offset            = 5.0[ppm]
Clipped               = FALSE
Scans                 = 32
Total_Scans           = 32

Relaxation_Delay      = 7[s]
Recvr_Gain            = 44
Temp_Get              = 22[dC]
X_Acq_Time            = 3.49175808[s]
X_Atn                 = 4.5[dB]
X_Pulse               = 12.4[us]
Irr_Mode              = Off
Tri_Mode              = Off
Attenuator            = 80[dB]
Dante_Presat          = FALSE
Initial_Wait          = 1[s]
Noe_Buildup           = 5[s]
Off_Resonance         = -10[ppm]
On_Resonance          = 1.7104[ppm]
Repetition_Time       = 10.49175808[s]
```



3p

```
---- PROCESSING PARAMETERS ----
sexp( 2.0[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm
reference( 77.09668[ppm], 77[ppm] )
phase( -2, 0, 59.12715[%] )

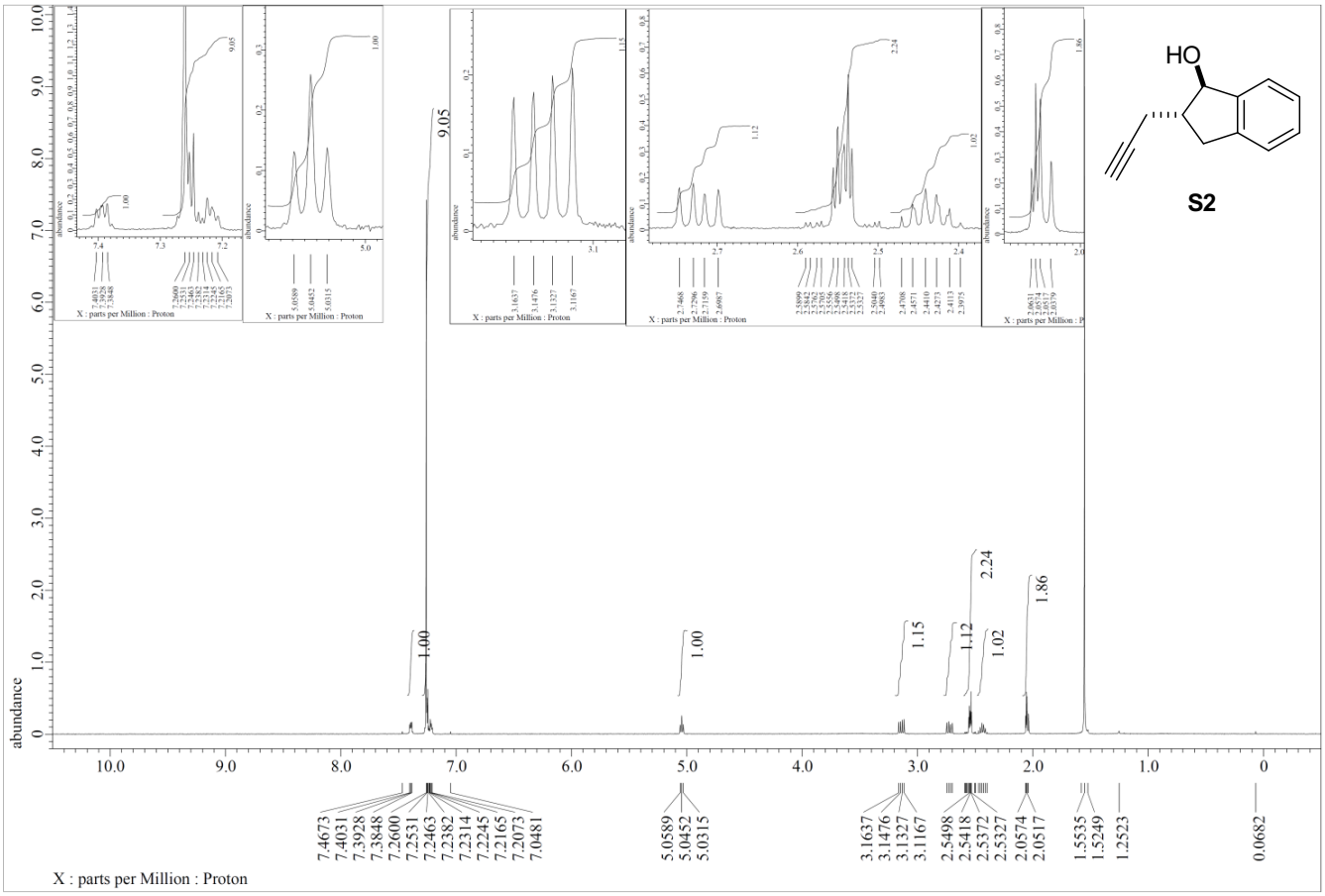
以下に由来:: AA_DATA_Product_Carbon-1-1.jdf
```

```
Filename                  = AA_DATA_Product_Ca
Author                    = delta
Experiment                = carbon.jxp
Sample_Id                 = AA_DATA_Product
Solvent                   = CHLOROFORM-D
Actual_Start_Time         = 12-MAY-2018 14:22:
Revision_Time             = 12-MAY-2018 16:37:

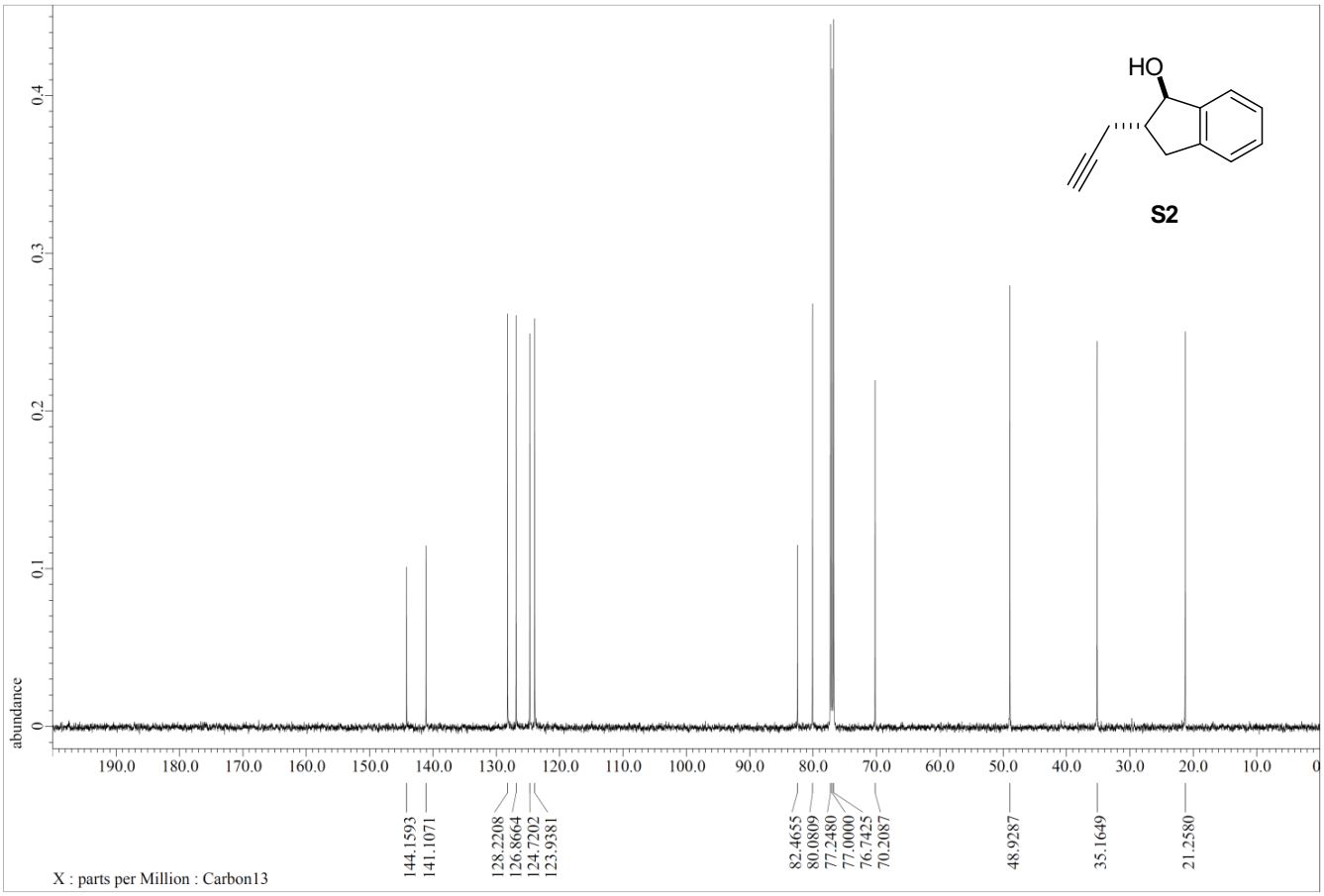
Comment                   = single pulse decou
Data_Format               = 1D COMPLEX
Dim_Size                  = 26214
Dim_Title                 = Carbon13
Dim_Units                 = [ppm]
Dimensions                = X
Spectrometer              = JNM-ECZ500R/S1

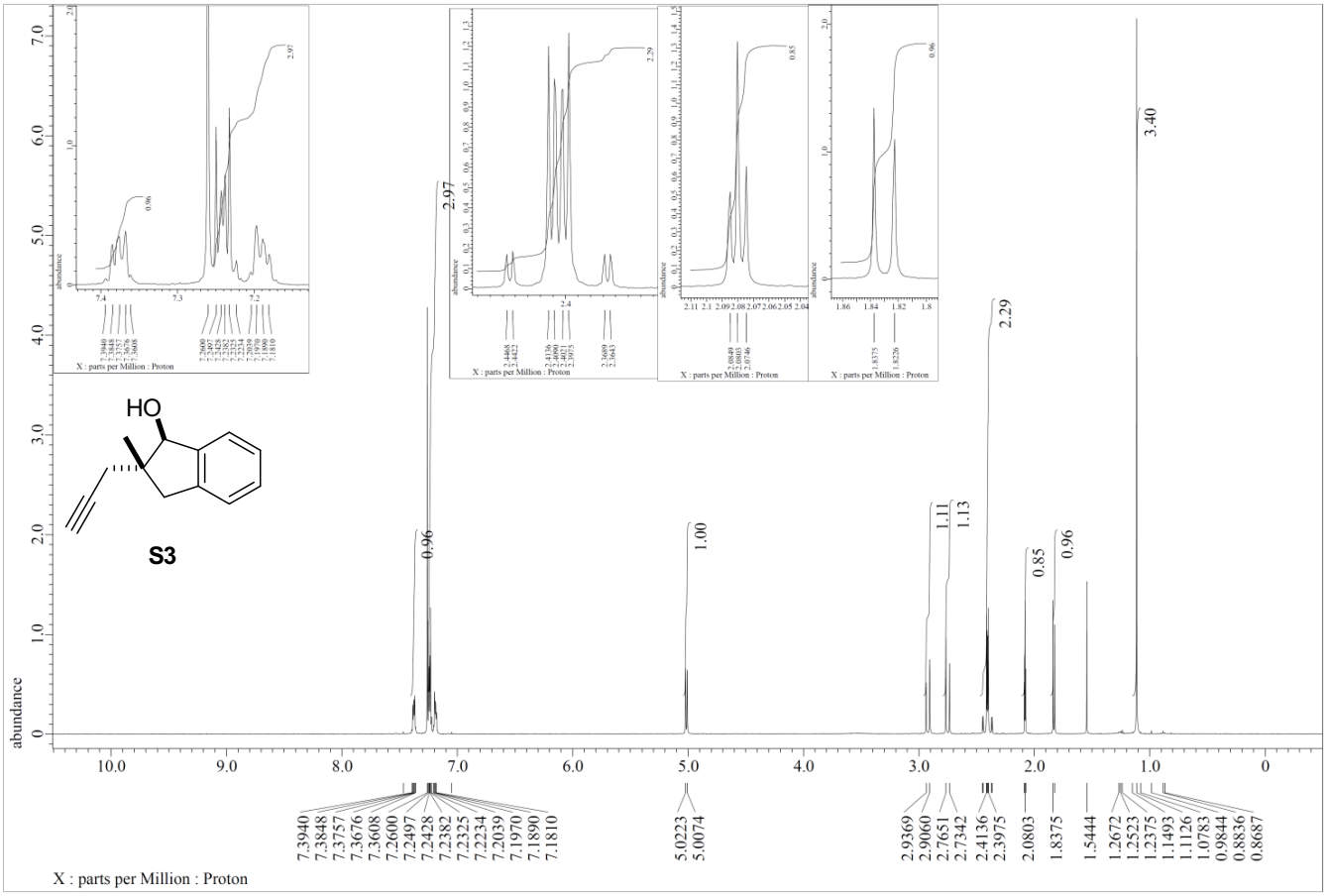
Field_Strength            = 11.62926421[T] (50
X_Acq_Duration            = 0.8388608[s]
X_Domain                  = 13C
X_Freq                    = 124.5010059[MHz]
X_Offset                  = 100[ppm]
X_Points                  = 32768
X_Prescans                = 4
X_Resolution              = 1.1920929[Hz]
X_Sweep                   = 39.0625[kHz]
X_Sweep_Clipped           = 31.25[kHz]
Irr_Domain                = Proton
Irr_Freq                  = 495.13191398[MHz]
Irr_Offset                = 5[ppm]
Clipped                   = TRUE
Scans                     = 1150
Total_Scans               = 1150

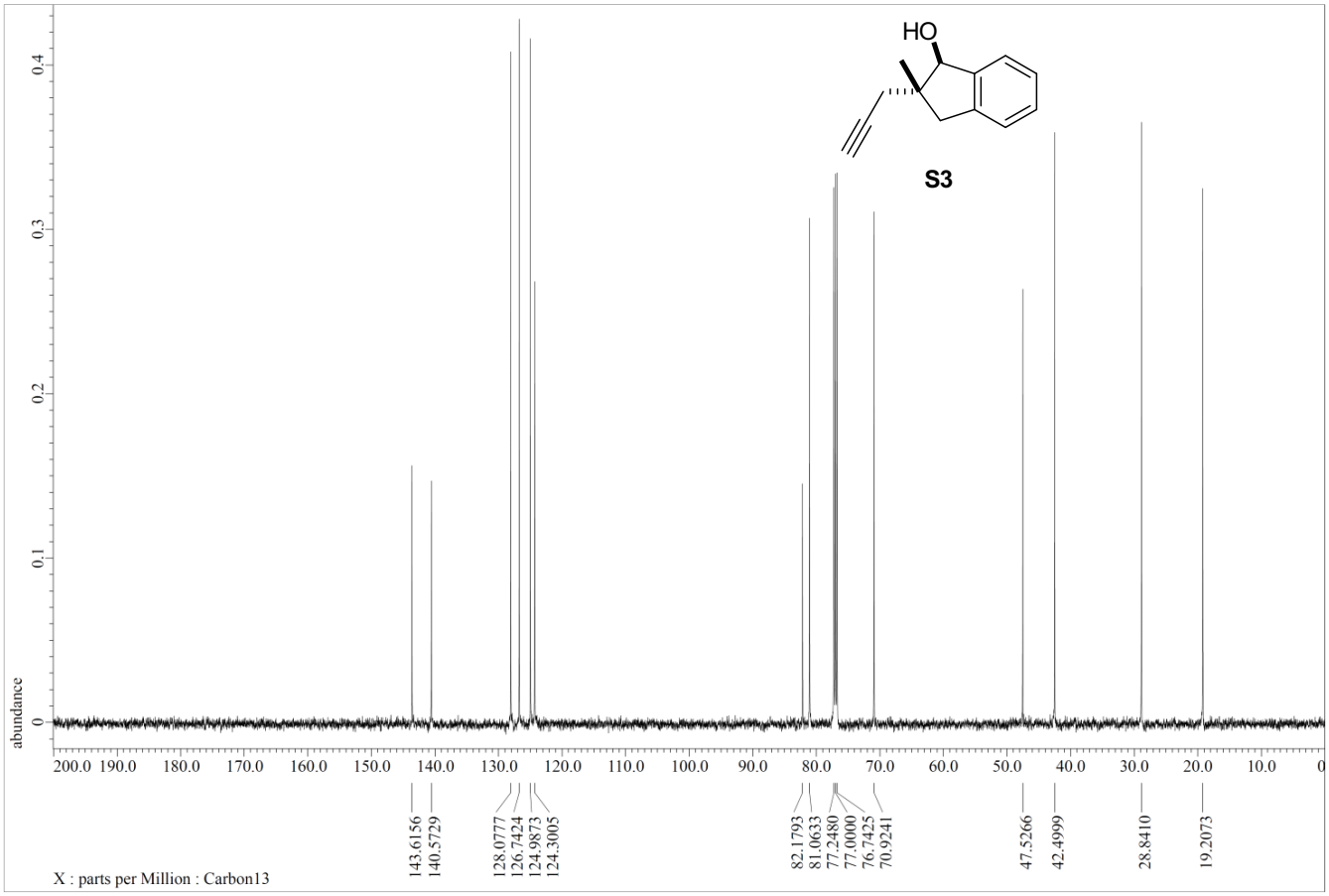
Relaxation_Delay          = 2[s]
Recvr_Gain                = 36
Temp_Get                  = 21.9[dC]
X_90_Width                = 11.26[us]
X_Acq_Time                = 0.8388608[s]
X_Angle                   = 30[deg]
X_Atn                     = 11[dB]
X_Pulse                   = 3.75333333[us]
Irr_Atn_Dec               = 21.339[dB]
Irr_Atn_Dec_Calc          = 21.339[dB]
Irr_Atn_Dec_Default_Calc  = 21.339[dB]
Irr_Atn_Noe               = 21.339[dB]
Irr_Dec_Bandwidth_Hz      = 5.97826087[kHz]
Irr_Dec_Bandwidth_Ppm     = 12.07407703[ppm]
Irr_Dec_Freq              = 495.13191398[MHz]
Irr_Dec_Merit_Factor      = 2.2
Irr_Decoupling            = TRUE
Irr_Noe                   = TRUE
Irr_Noise                 = WALTZ
Irr_Offset_Default        = 5[ppm]
Irr_Pwidth                = 92[us]
Irr_Pwidth_Default        = 92[us]
Irr_Pwidth_Default_Calc   = 92[us]
Irr_Pwidth_Temp1          = 92[us]
Irr_Wurst                 = FALSE
Decimation_Rate           = 0
Initial_Wait              = 1[s]
Noe_Time                  = 2[s]
Noe_Time_Flag             = FALSE
Relaxation_Delay_Calc     = 0[s]
Relaxation_Delay_Temp     = 2[s]
Repetition_Time           = 2.8388608[s]
```

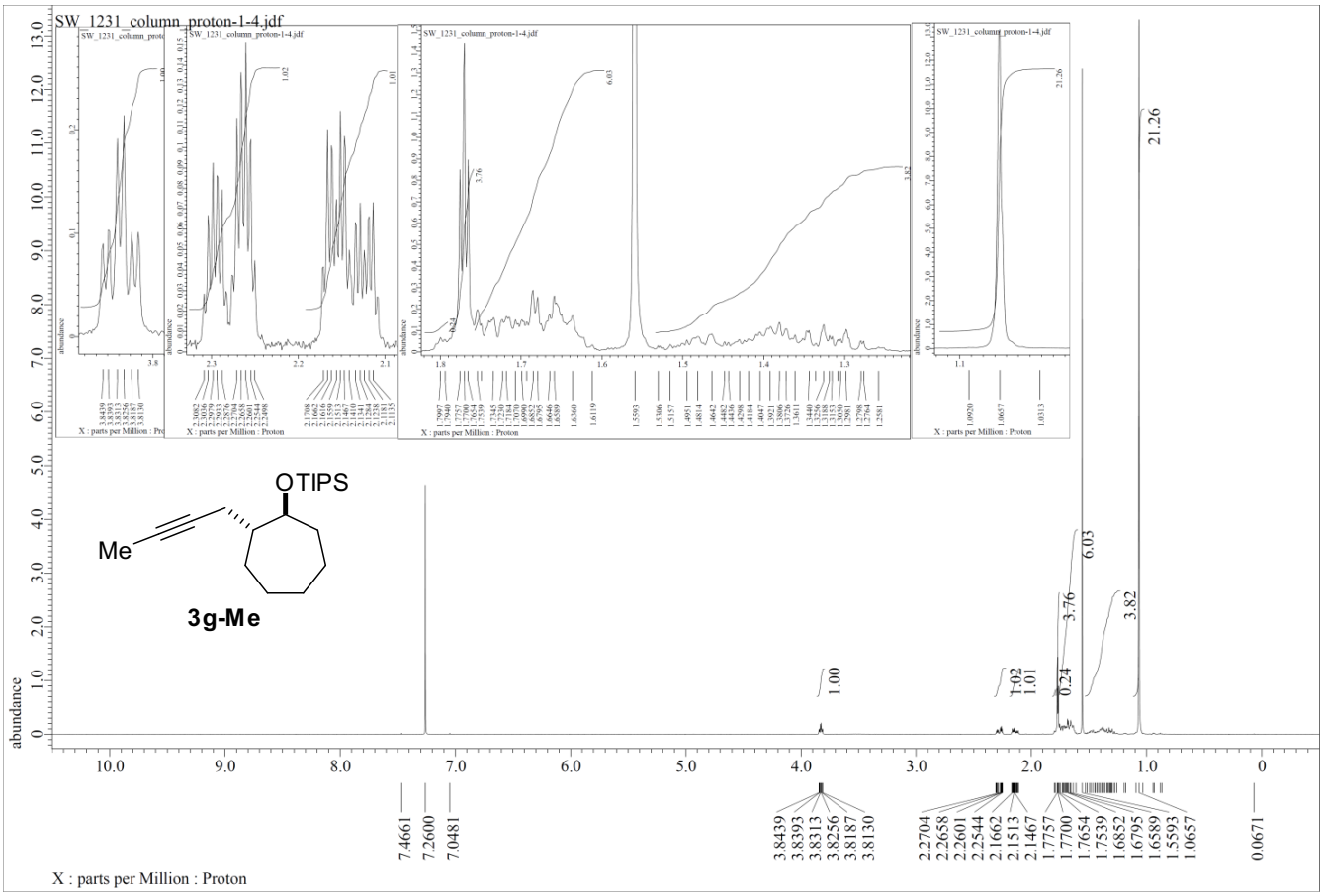


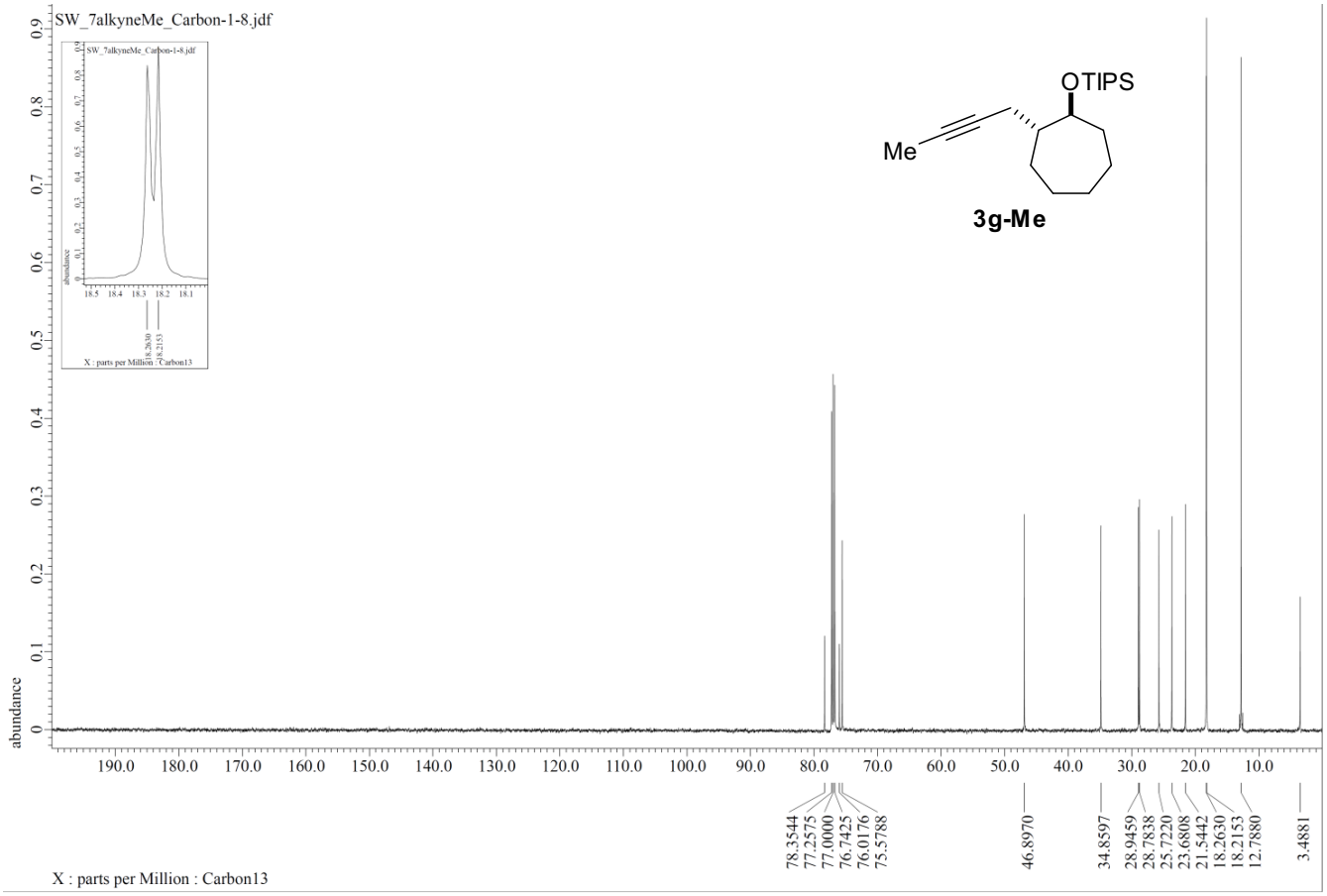
S2

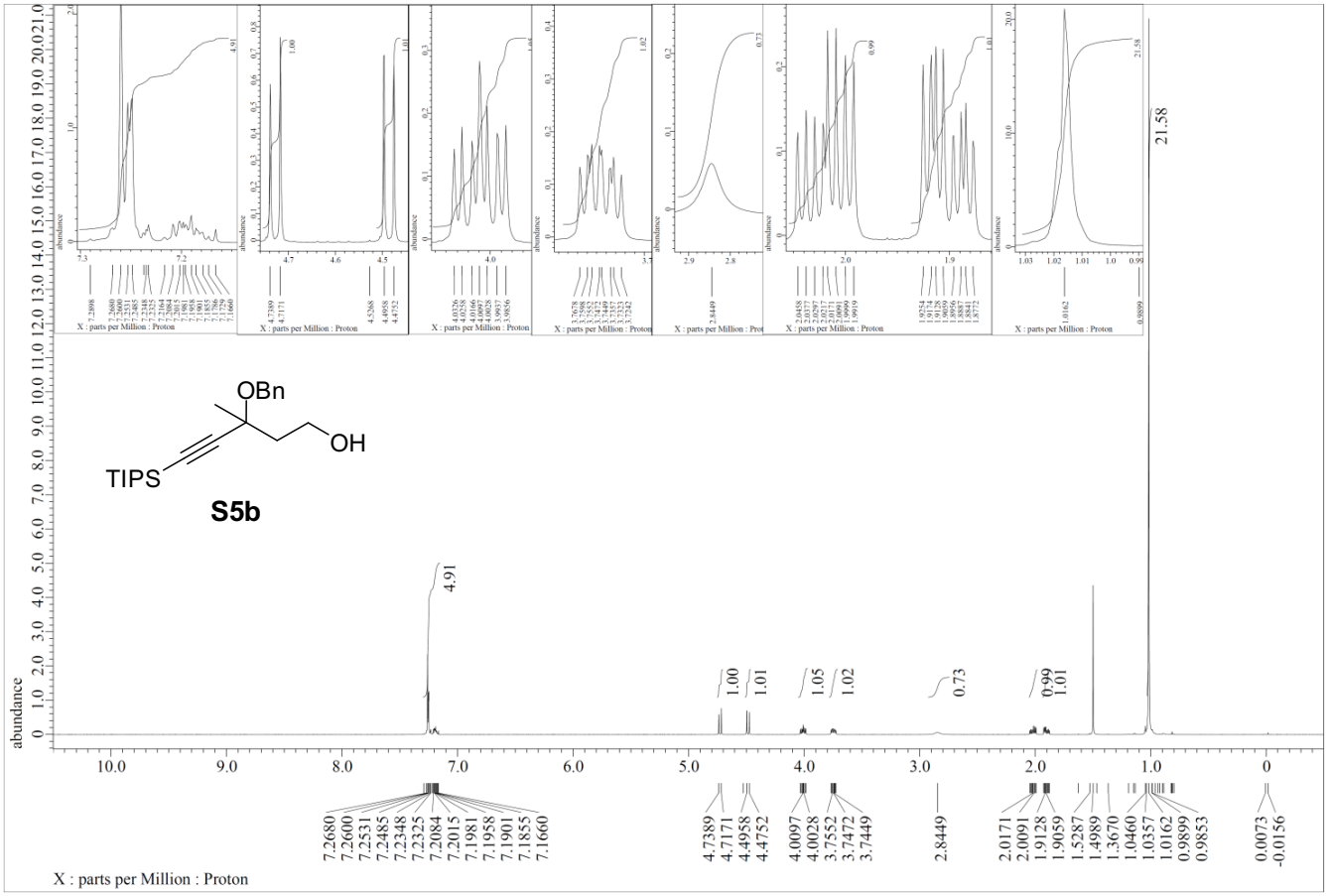

HO
S2
abundance
144.1593
141.1071
128.2208
126.8664
124.7202
123.9381
82.4655
80.0809
77.2480
77.0000
76.7425
70.2087
48.9287
35.1649
21.2580
X : parts per Million : Carbon13

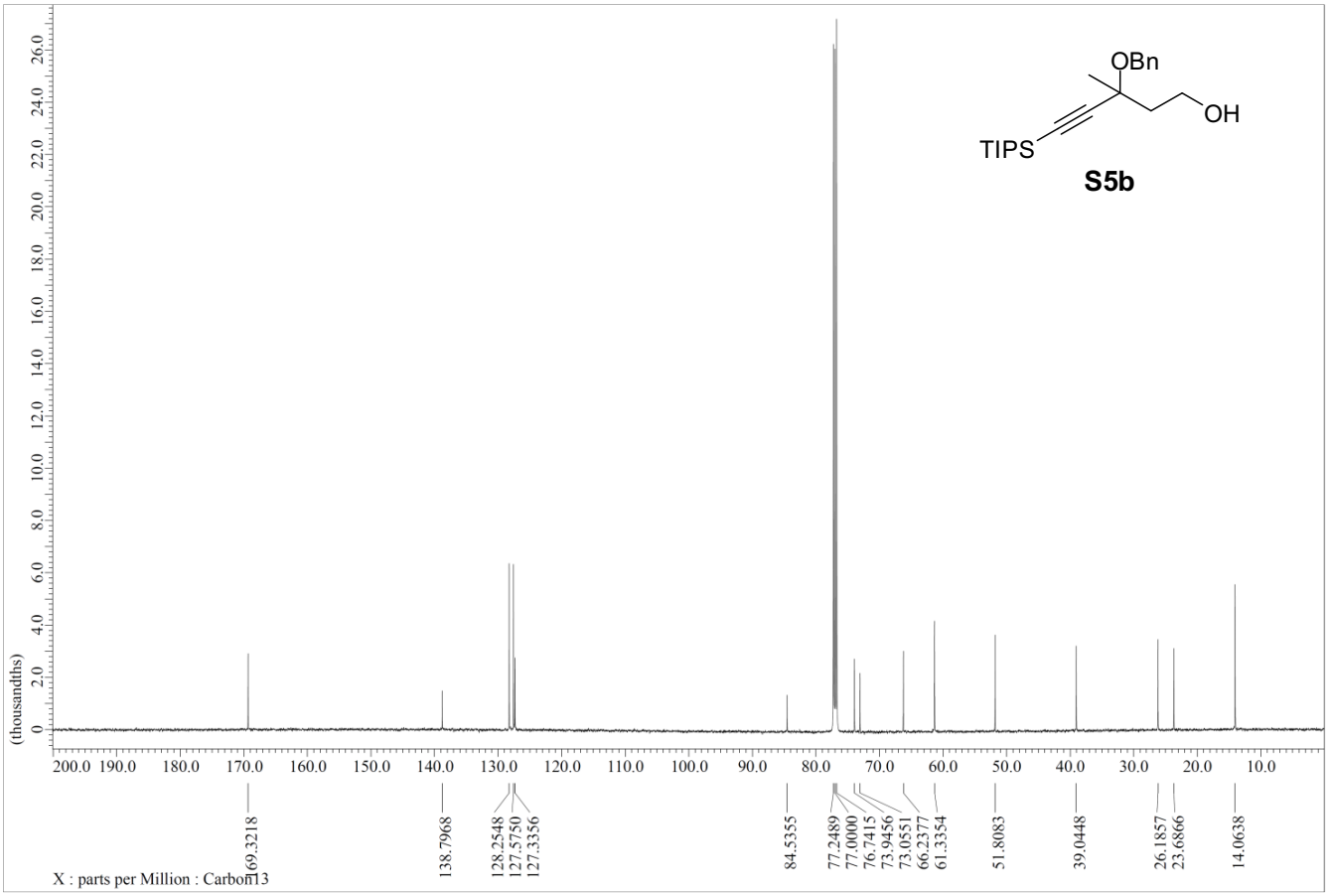

HO
S3
abundance
7.3940
7.3848
7.3757
7.3676
7.3608
7.2600
7.2497
7.2428
7.2382
7.2325
7.2234
7.2039
7.1970
7.1890
7.1810
5.0223
5.0074
2.9369
2.9060
2.7651
2.7342
2.4136
2.3975
2.0803
1.8375
1.5444
1.2672
1.2523
1.2375
1.1493
1.1126
1.0783
0.9844
0.8836
0.8687
X : parts per Million : Proton

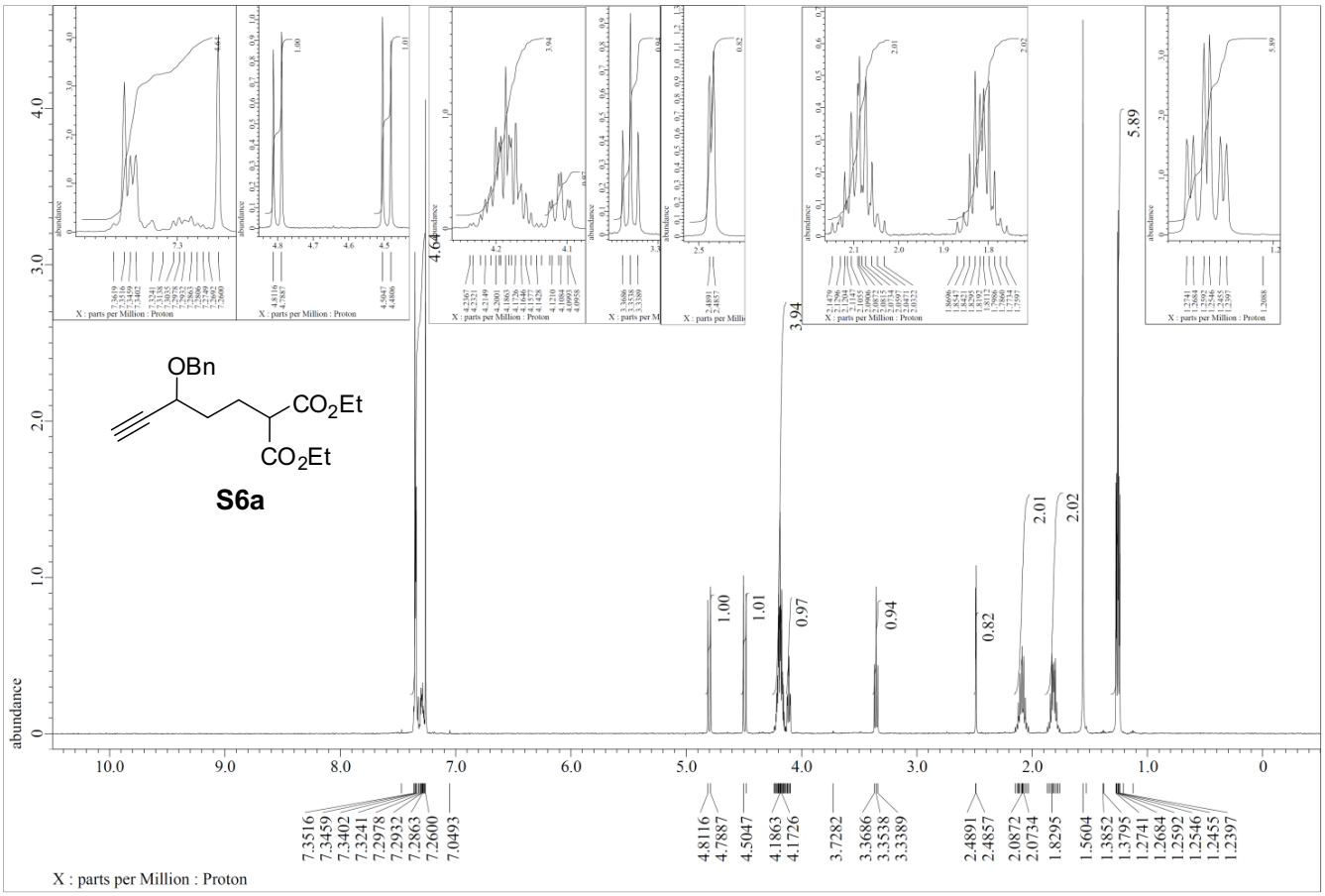

HO
S3
abundance
143.6156
140.5729
128.0777
126.7424
124.9873
124.3005
82.1793
81.0633
77.2480
77.0000
76.7425
70.9241
47.5266
42.4999
28.8410
19.2073
X : parts per Million : Carbon13

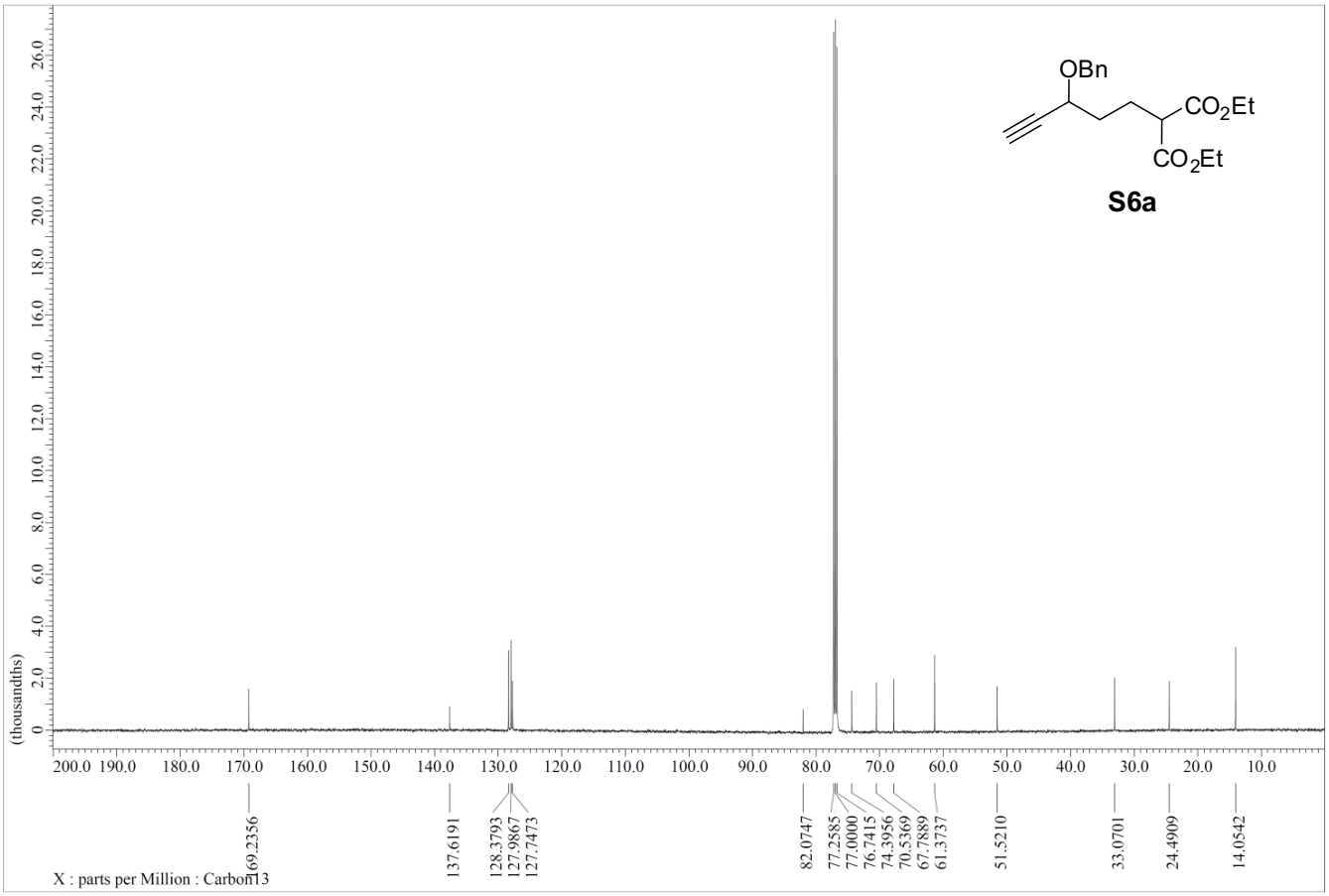

SW_1231_column_proton-1-4.jdf
OTIPS
Me
3g-Me
abundance
21.26
6.03
3.76
3.82
1.00
1.02
1.01
0.24
7.4661
7.2600
7.0481
3.8439
3.8393
3.8313
3.8256
3.8187
3.8130
2.2704
2.2658
2.2601
2.2544
2.1662
2.1513
2.1467
1.7757
1.7700
1.7654
1.7539
1.6852
1.6795
1.6589
1.5593
1.0657
0.0671
X : parts per Million : Proton

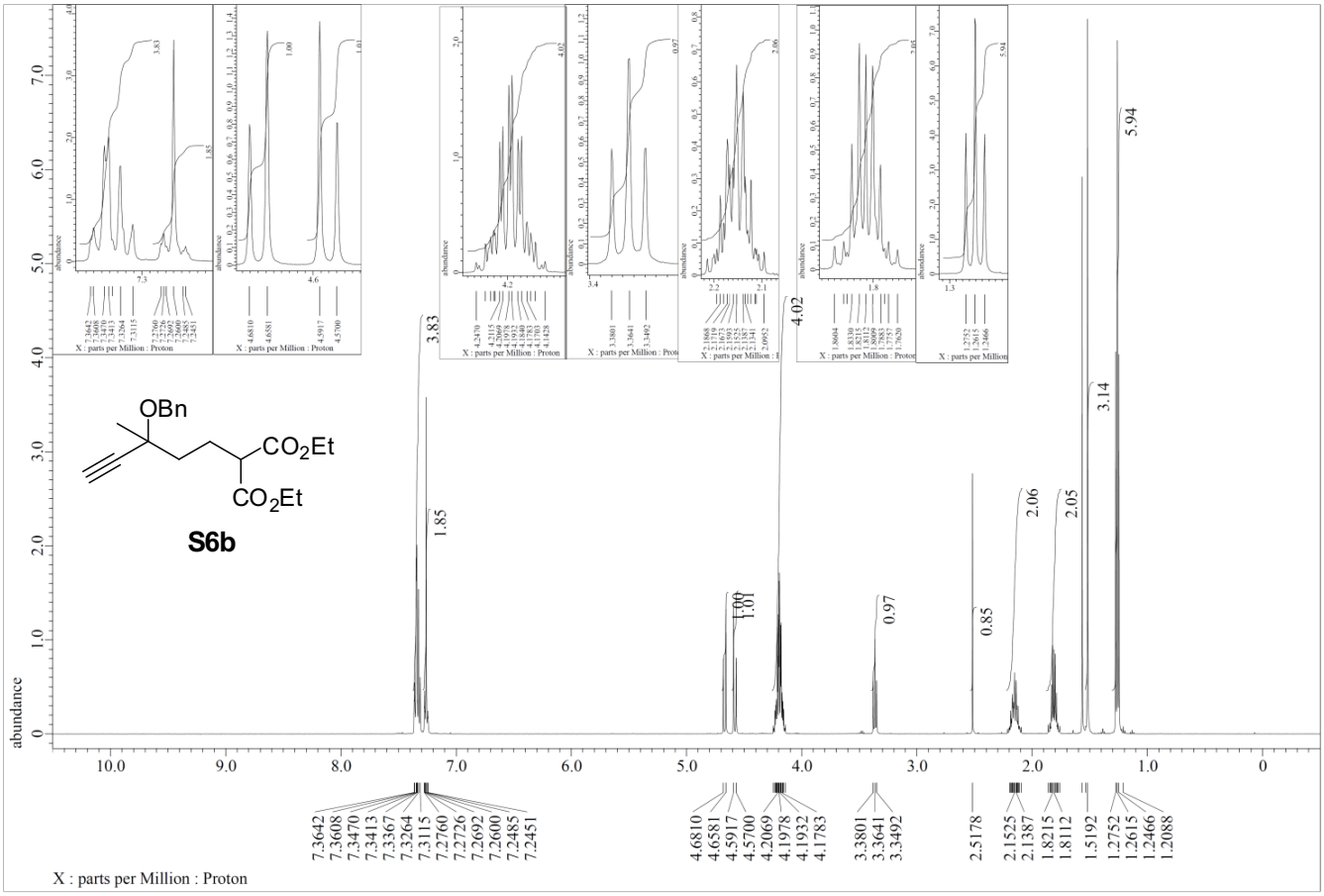

SW_7alkyneMe_Carbon-1-8.jdf
OTIPS
Me
3g-Me
abundance
78.3544
77.2575
77.0000
76.7425
76.0176
75.5788
46.8970
34.8597
28.9459
28.7838
25.7220
23.6808
21.5442
18.2630
18.2153
12.7880
3.4881
X : parts per Million : Carbon13

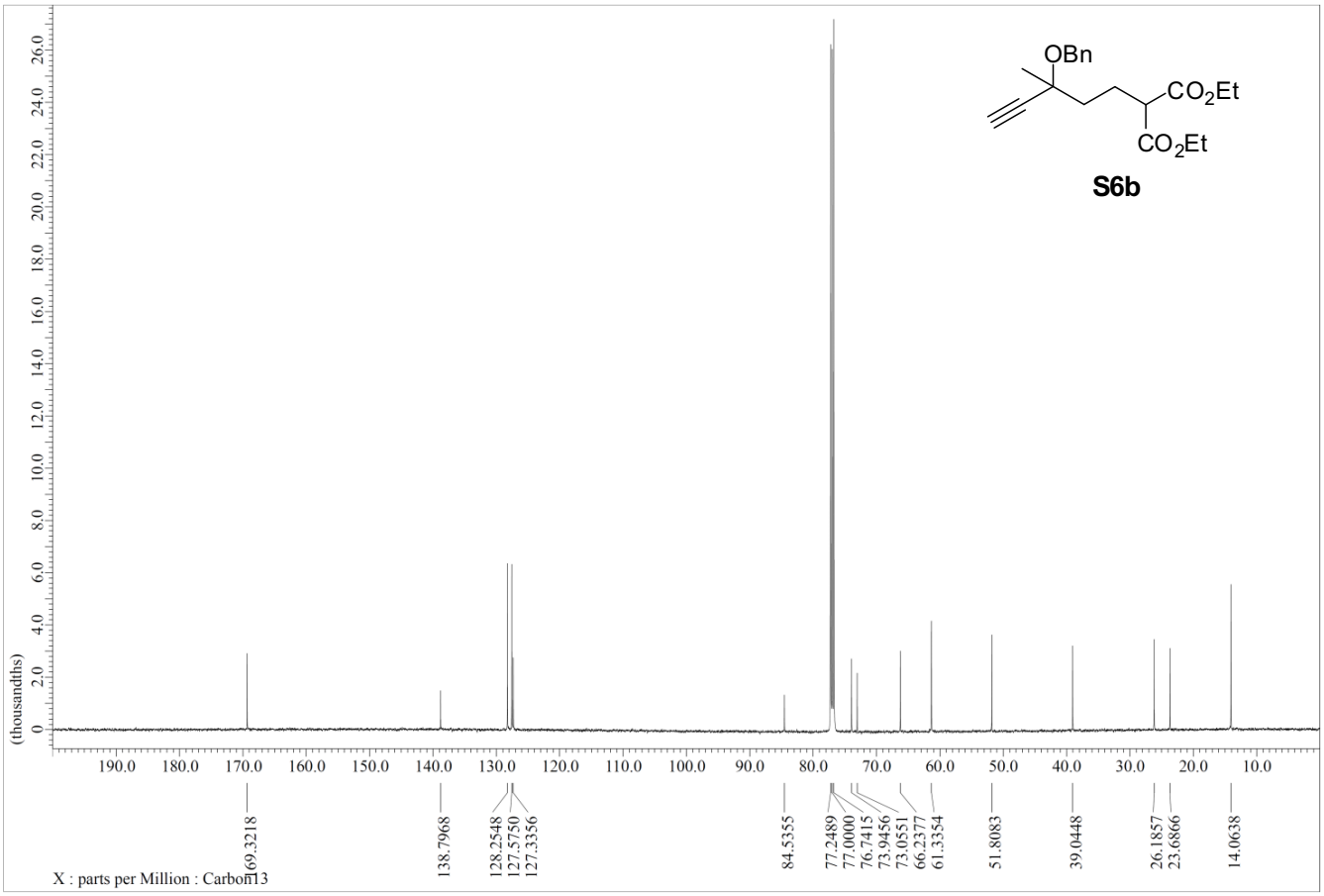

OBn
OH
TIPS
S5b
4.91
1.00
1.01
1.05
1.02
0.73
0.99
1.01
21.58
abundance
7.2680
7.2600
7.2531
7.2485
7.2348
7.2325
7.2084
7.2015
7.1981
7.1958
7.1901
7.1855
7.1660
4.7389
4.7171
4.4958
4.4752
4.0097
4.0028
3.7552
3.7472
3.7449
2.8449
2.0171
2.0091
1.9128
1.9059
1.5287
1.4989
1.3670
1.0460
1.0357
1.0162
0.9899
0.9853
0.0073
-0.0156
X : parts per Million : Proton

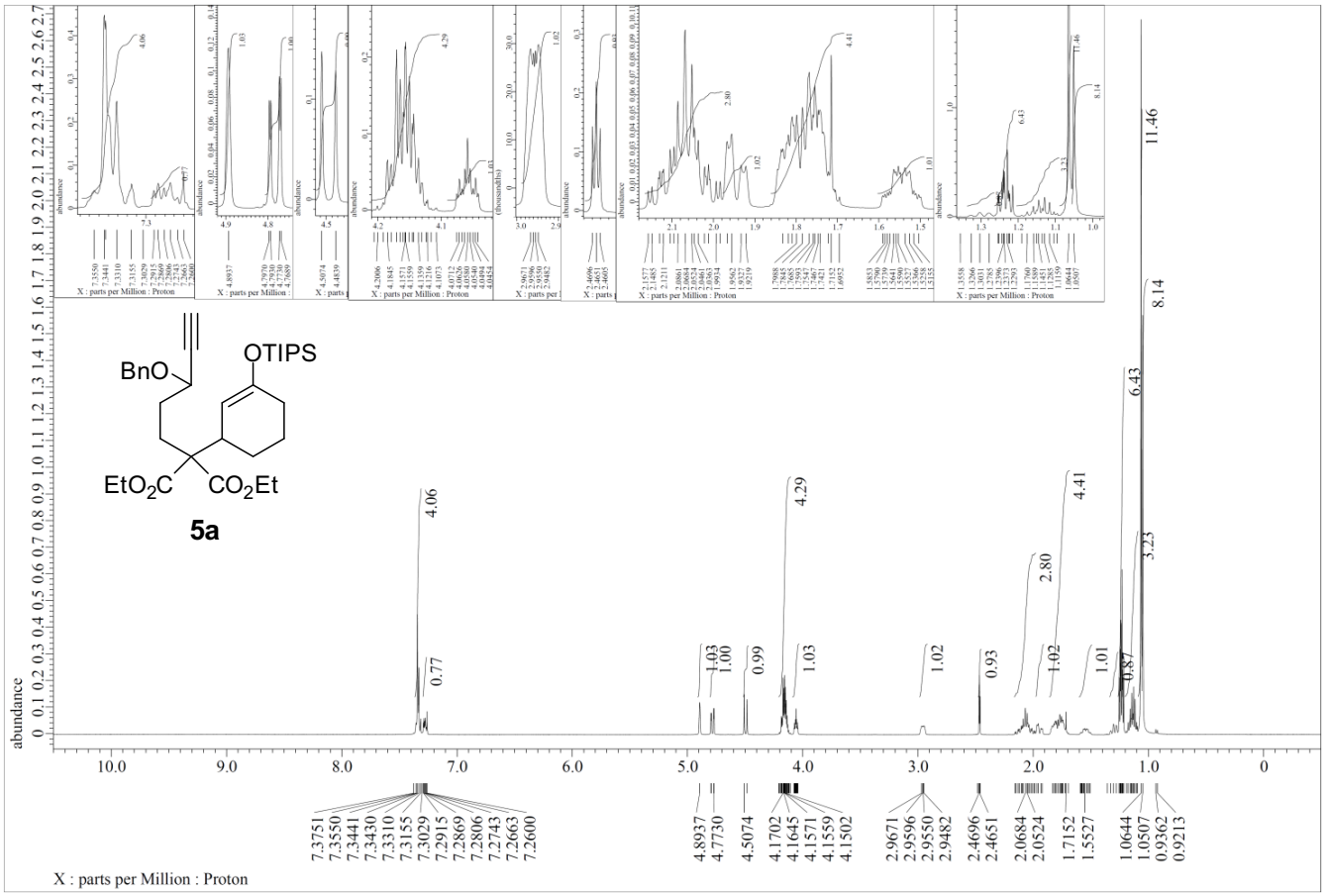

OBn
OH
TIPS
S5b
(thousandths)
169.3218
138.7968
128.2548
127.5750
127.3356
84.5355
77.2489
77.0000
76.7415
73.9456
73.0551
66.2377
61.3354
51.8083
39.0448
26.1857
23.6866
14.0638
X : parts per Million : Carbon13

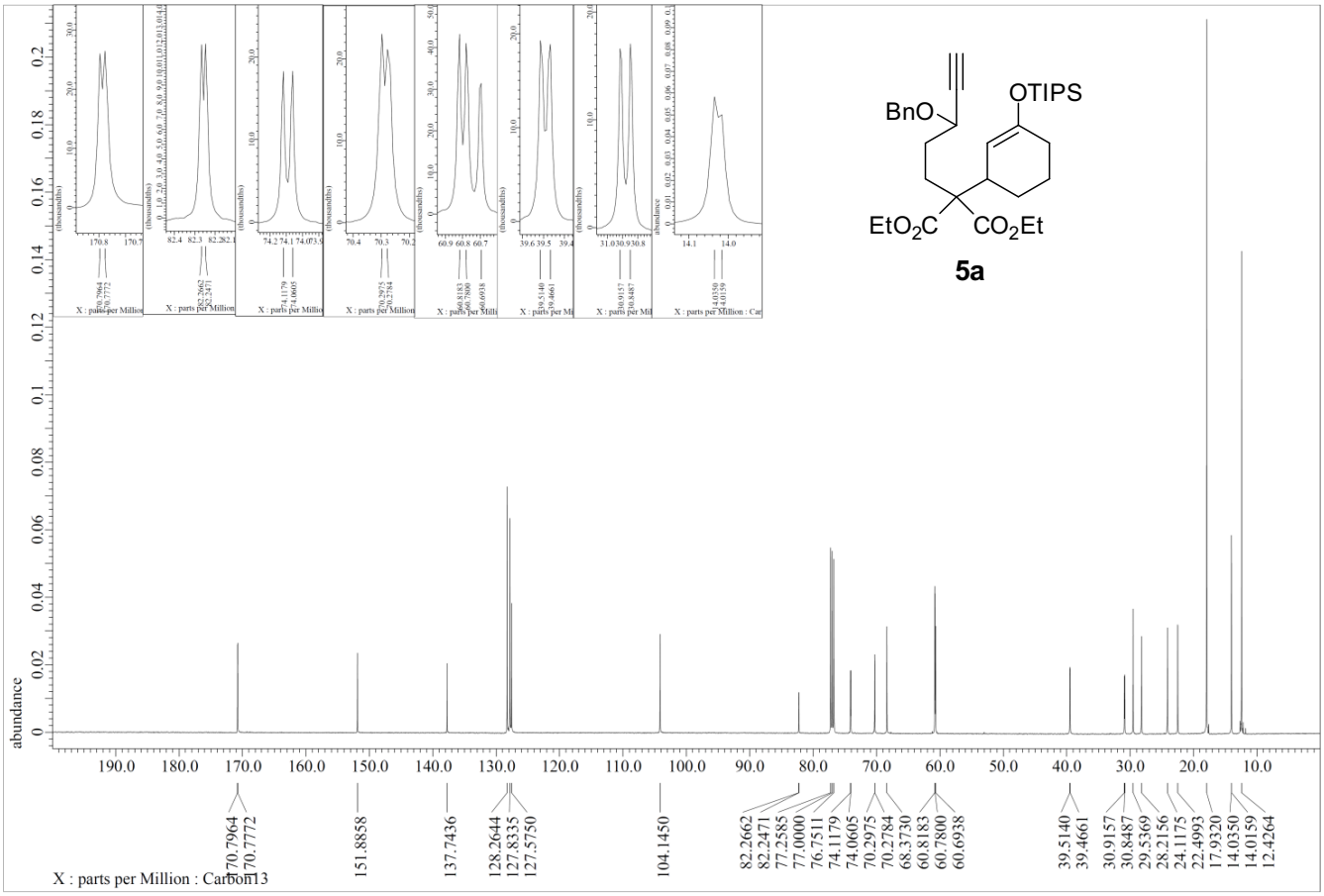

OBn
CO2Et
CO2Et
S6a
4.64
3.94
5.89
2.01
2.02
1.00
1.01
0.97
0.94
0.82
abundance
7.3516
7.3459
7.3402
7.3241
7.2978
7.2932
7.2863
7.2600
7.0493
4.8116
4.7887
4.5047
4.1863
4.1726
3.7282
3.3686
3.3538
3.3389
2.4891
2.4857
2.0872
2.0734
1.8295
1.5604
1.3852
1.3795
1.2741
1.2684
1.2592
1.2546
1.2455
1.2397
X : parts per Million : Proton

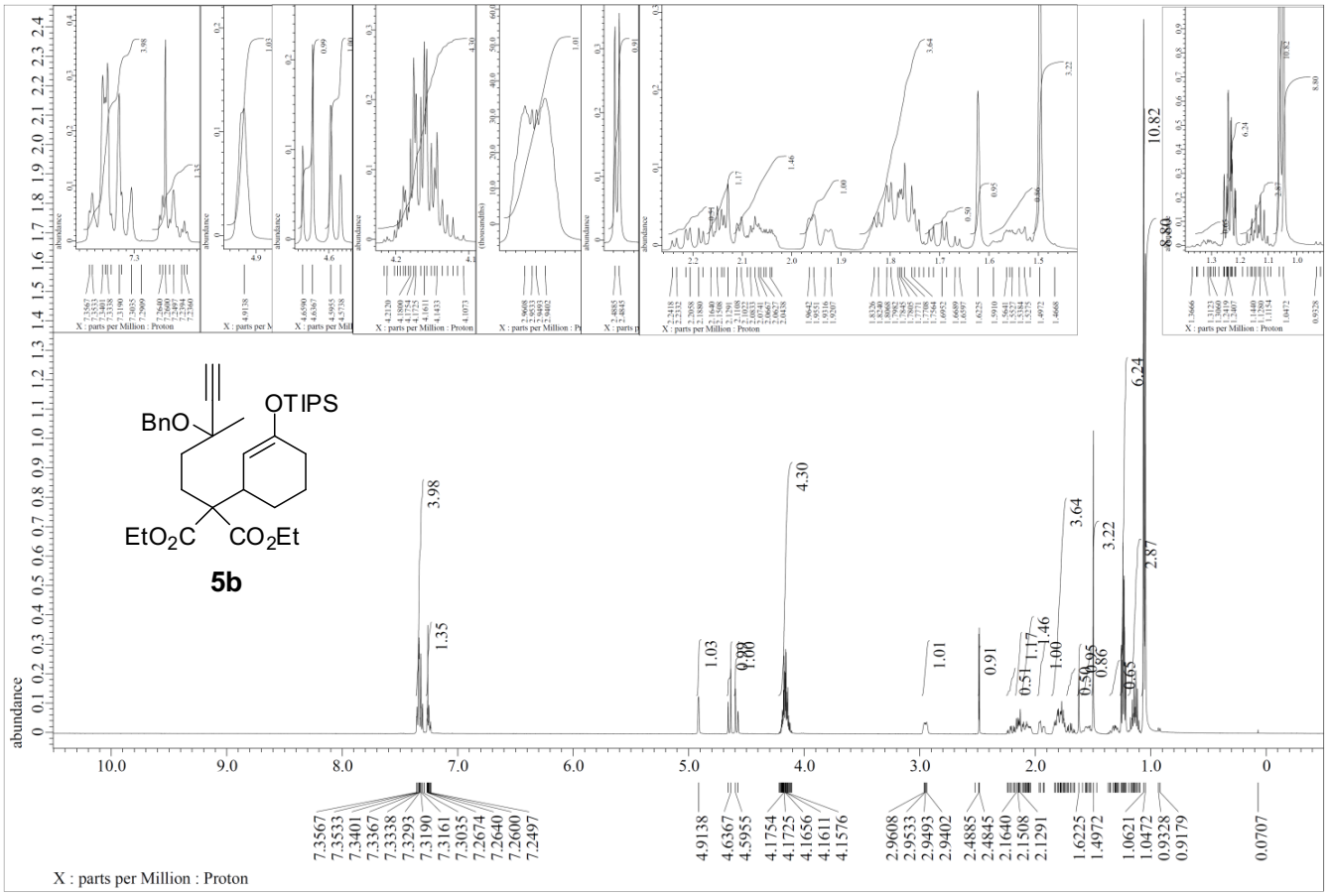

OBn
CO2Et
CO2Et
S6a
(thousandths)
169.2356
137.6191
128.3793
127.9867
127.7473
82.0747
77.2585
77.0000
76.7415
74.3956
70.5369
67.7889
61.3737
51.5210
33.0701
24.4909
14.0542
X : parts per Million : Carbon13

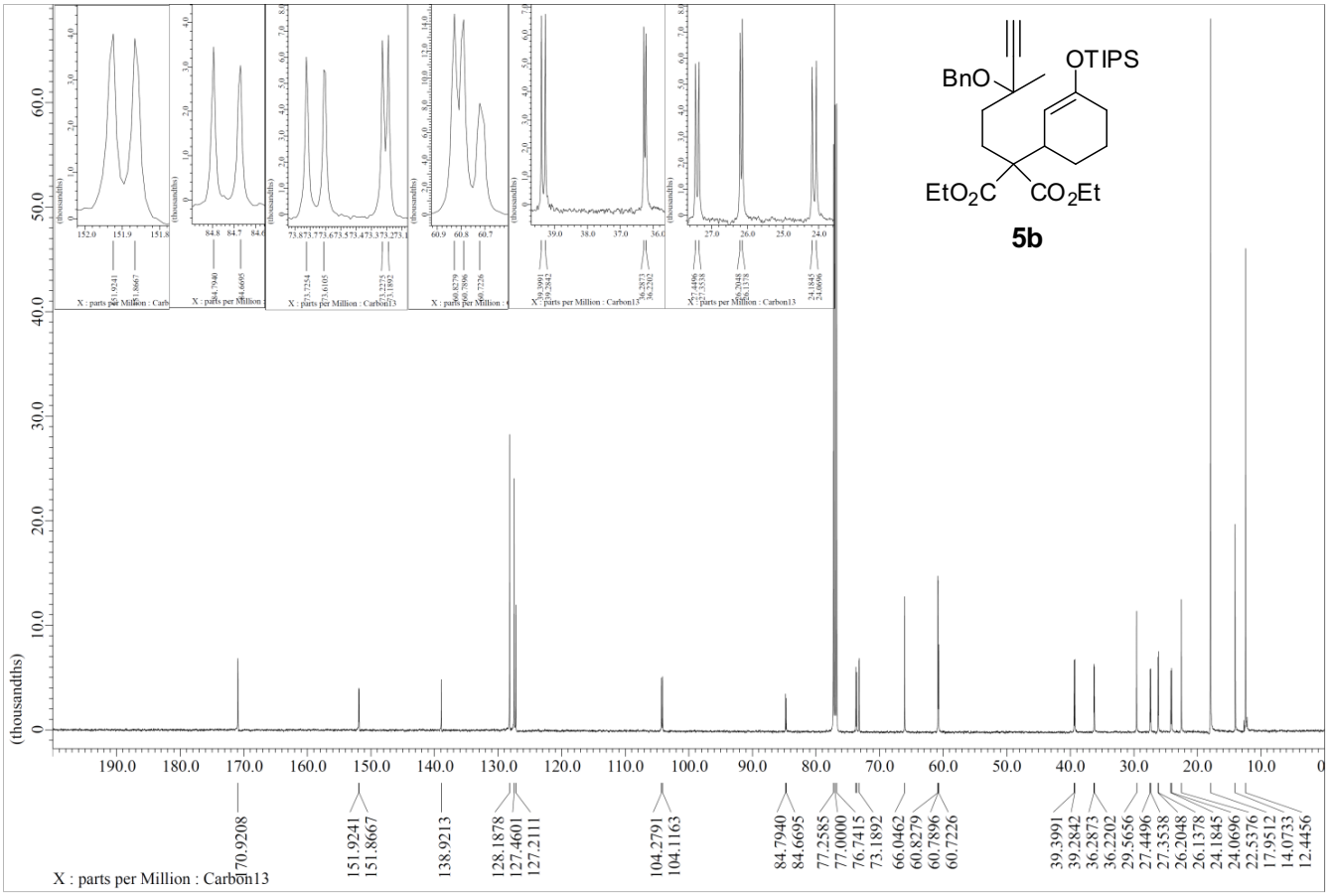

OBn
CO2Et
CO2Et
S6b
abundance
3.83
1.85
1.00
1.01
4.02
0.97
0.85
2.06
2.05
3.14
5.94
7.3642
7.3608
7.3470
7.3413
7.3367
7.3264
7.3115
7.2760
7.2726
7.2692
7.2600
7.2485
7.2451
4.6810
4.6581
4.5917
4.5700
4.2069
4.1978
4.1932
4.1783
3.3801
3.3641
3.3492
2.5178
2.1525
2.1387
1.8215
1.8112
1.5192
1.2752
1.2615
1.2466
1.2088
X : parts per Million : Proton

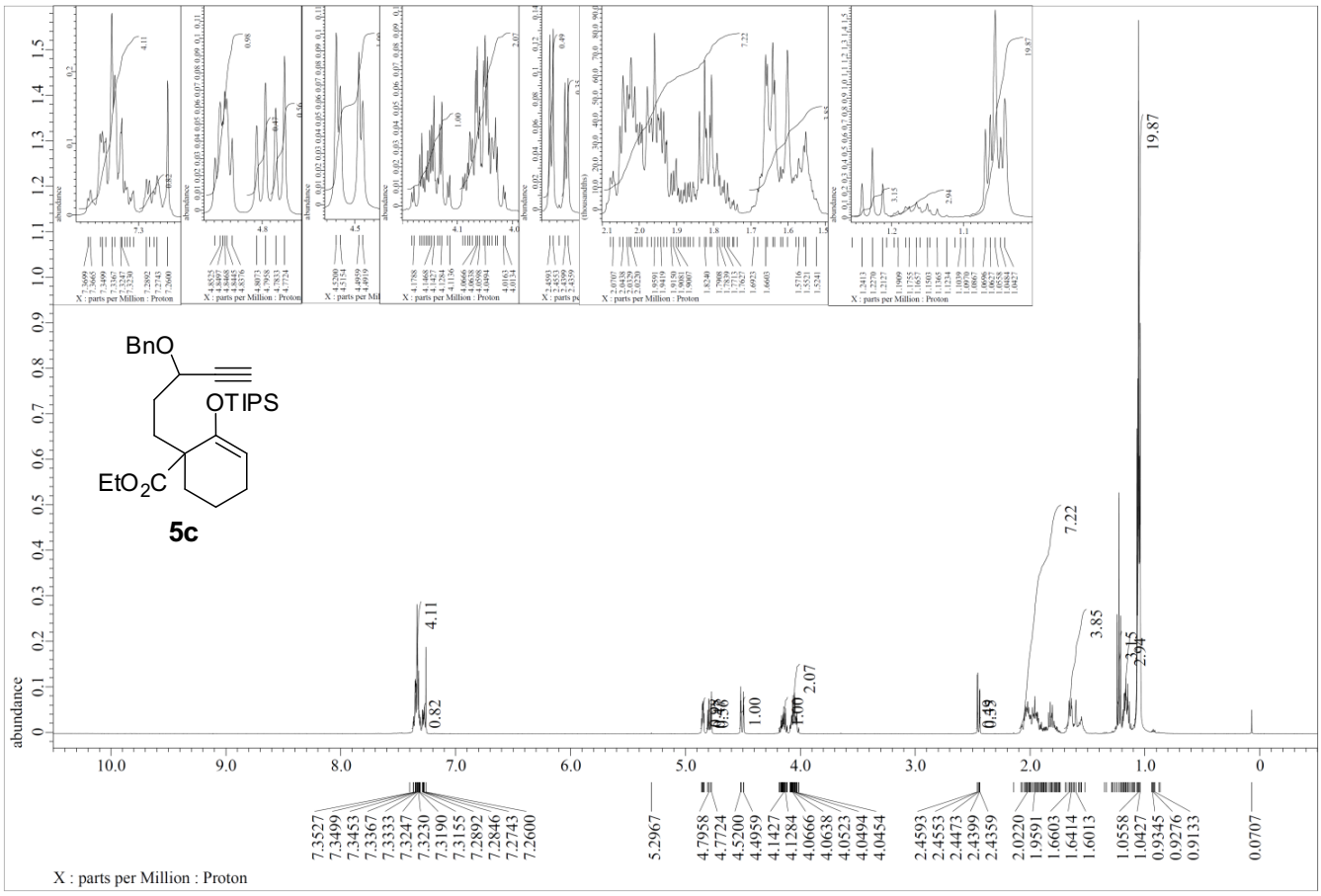

OBn
CO2Et
CO2Et
S6b
(thousandths)
169.3218
138.7968
128.2548
127.5750
127.3356
84.5355
77.2489
77.0000
76.7415
73.9456
73.0551
66.2377
61.3354
51.8083
39.0448
26.1857
23.6866
14.0638
X : parts per Million : Carbon13

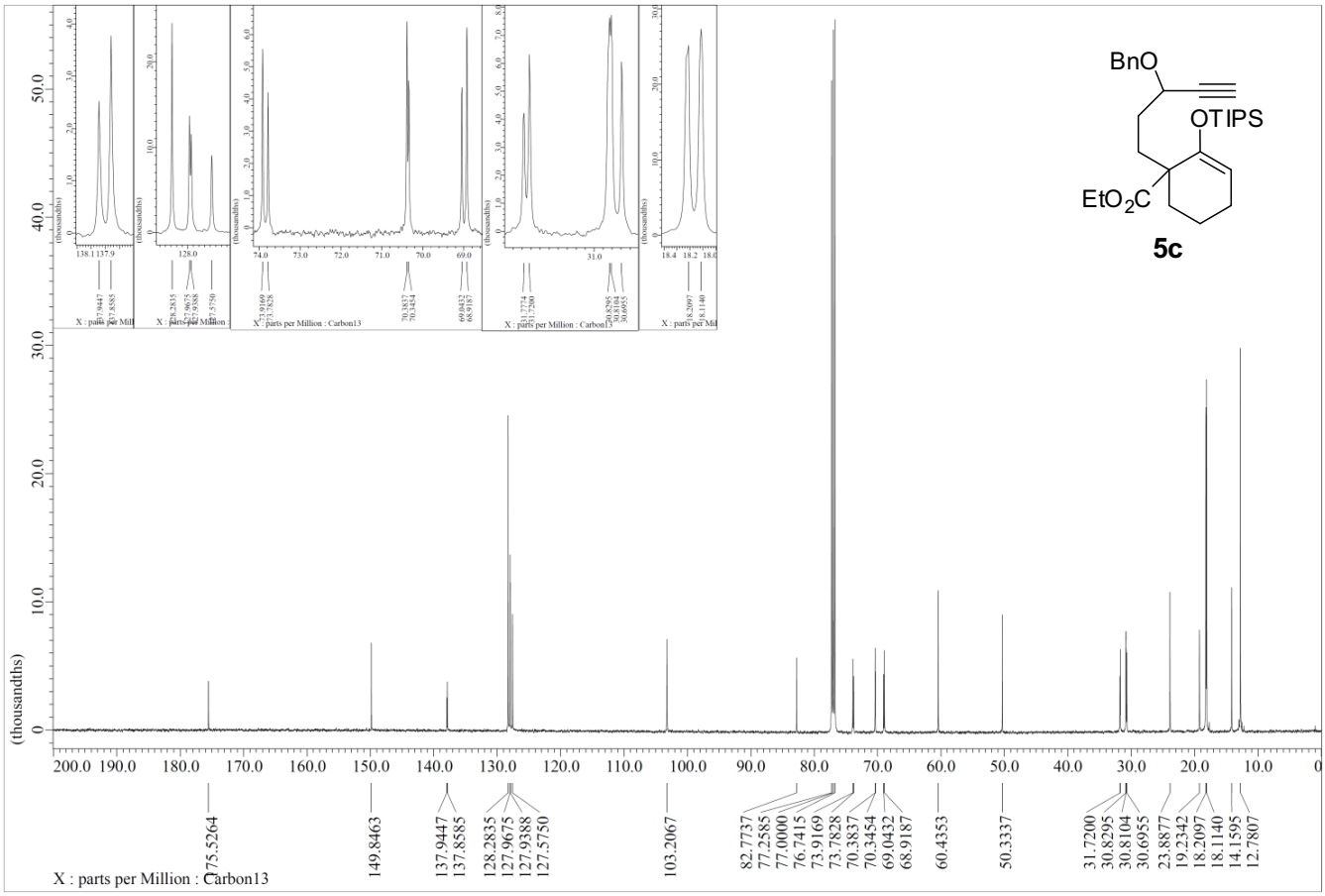

BnO
OTIPS
EtO2C
CO2Et
5a
abundance
4.06
0.77
1.03
1.00
0.99
4.29
1.03
1.02
0.93
2.80
1.02
4.41
1.01
0.87
3.23
6.43
8.14
11.46
7.3751
7.3550
7.3441
7.3430
7.3310
7.3155
7.3029
7.2915
7.2869
7.2806
7.2743
7.2663
7.2600
4.8937
4.7730
4.5074
4.1702
4.1645
4.1571
4.1559
4.1502
2.9671
2.9596
2.9550
2.9482
2.4696
2.4651
2.0684
2.0524
1.7152
1.5527
1.0644
1.0507
0.9362
0.9213
X : parts per Million : Proton

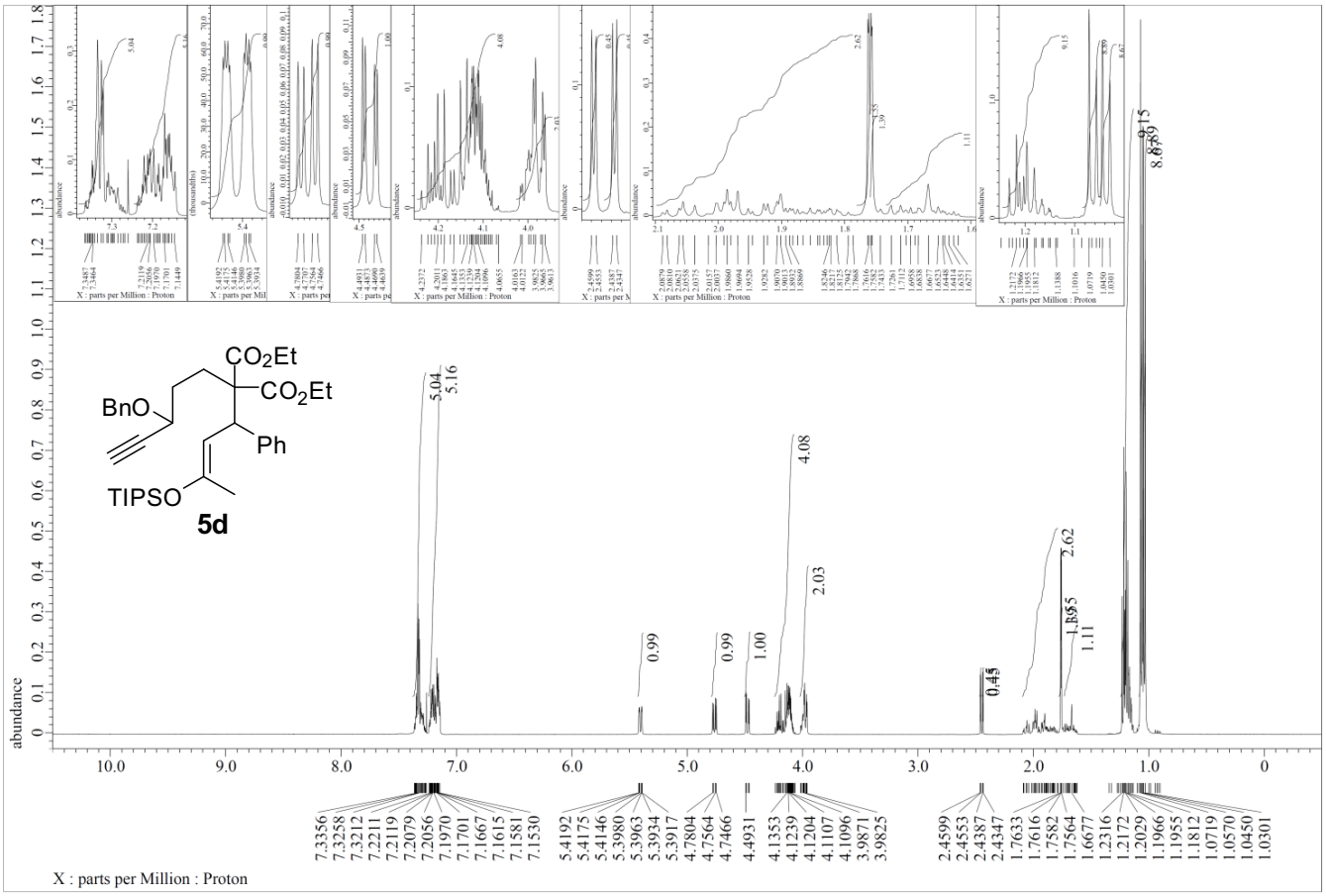

BnO
OTIPS
EtO2C
CO2Et
5a
abundance
X : parts per Million : Carbon13
70.7964
70.7772
151.8858
137.7436
128.2644
127.8335
127.5750
104.1450
82.2662
82.2471
77.2585
77.0000
76.7511
74.1179
74.0605
70.2975
70.2784
68.3730
60.8183
60.7800
60.6938
39.5140
39.4661
30.9157
30.8487
29.5369
28.2156
24.1175
22.4993
17.9320
14.0350
14.0159
12.4264

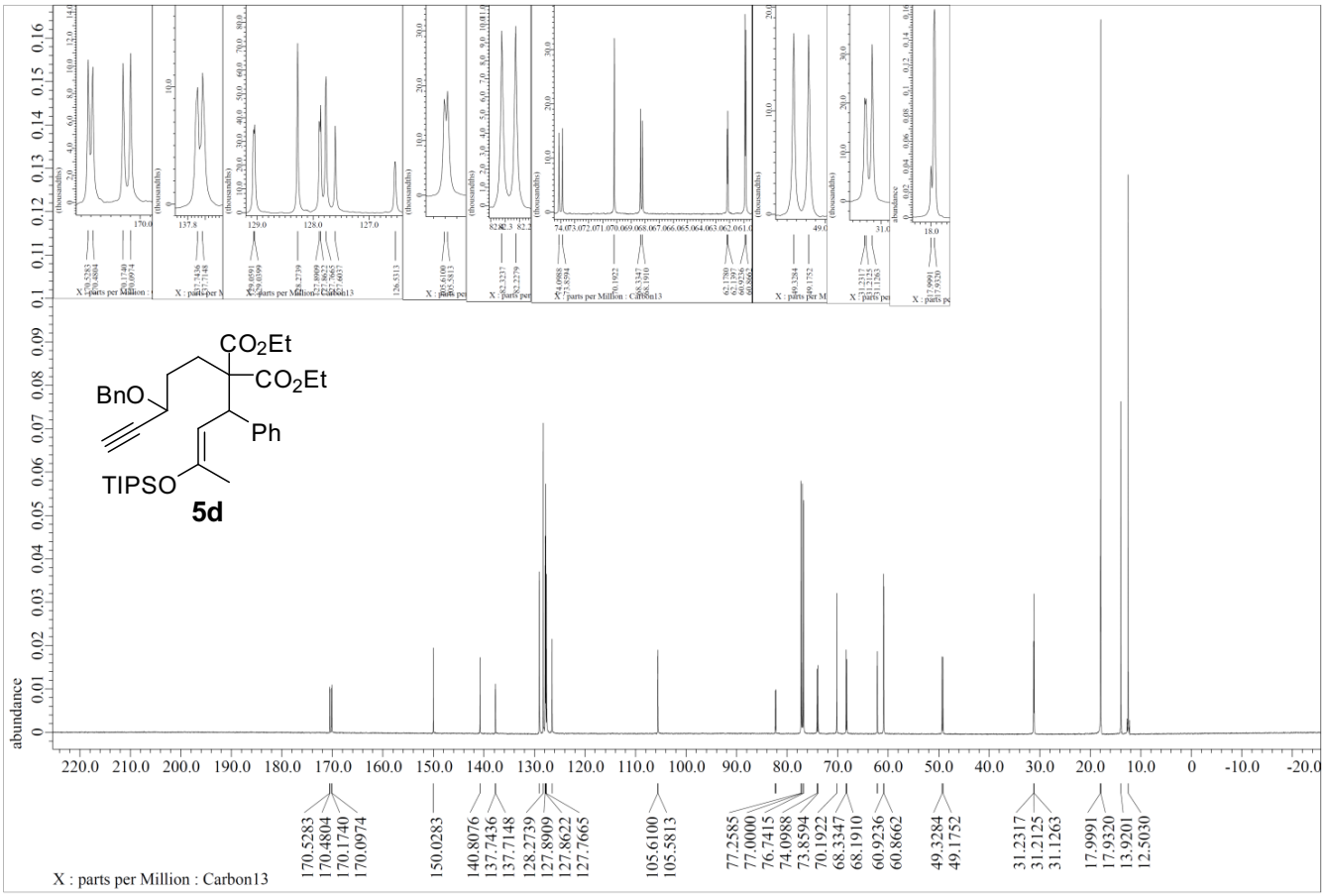

BnO
OTIPS
EtO2C
CO2Et
5b
abundance
X : parts per Million : Proton
3.98
1.35
1.03
4.30
1.01
0.91
3.64
3.22
2.87
6.24
10.82
8.80
7.3567
7.3533
7.3401
7.3367
7.3338
7.3293
7.3190
7.3161
7.3035
7.2674
7.2640
7.2600
7.2497
4.9138
4.6367
4.5955
4.1754
4.1725
4.1656
4.1611
4.1576
2.9608
2.9533
2.9493
2.9402
2.4885
2.4845
2.1640
2.1508
2.1291
1.6225
1.4972
1.0621
1.0472
0.9328
0.9179
0.0707

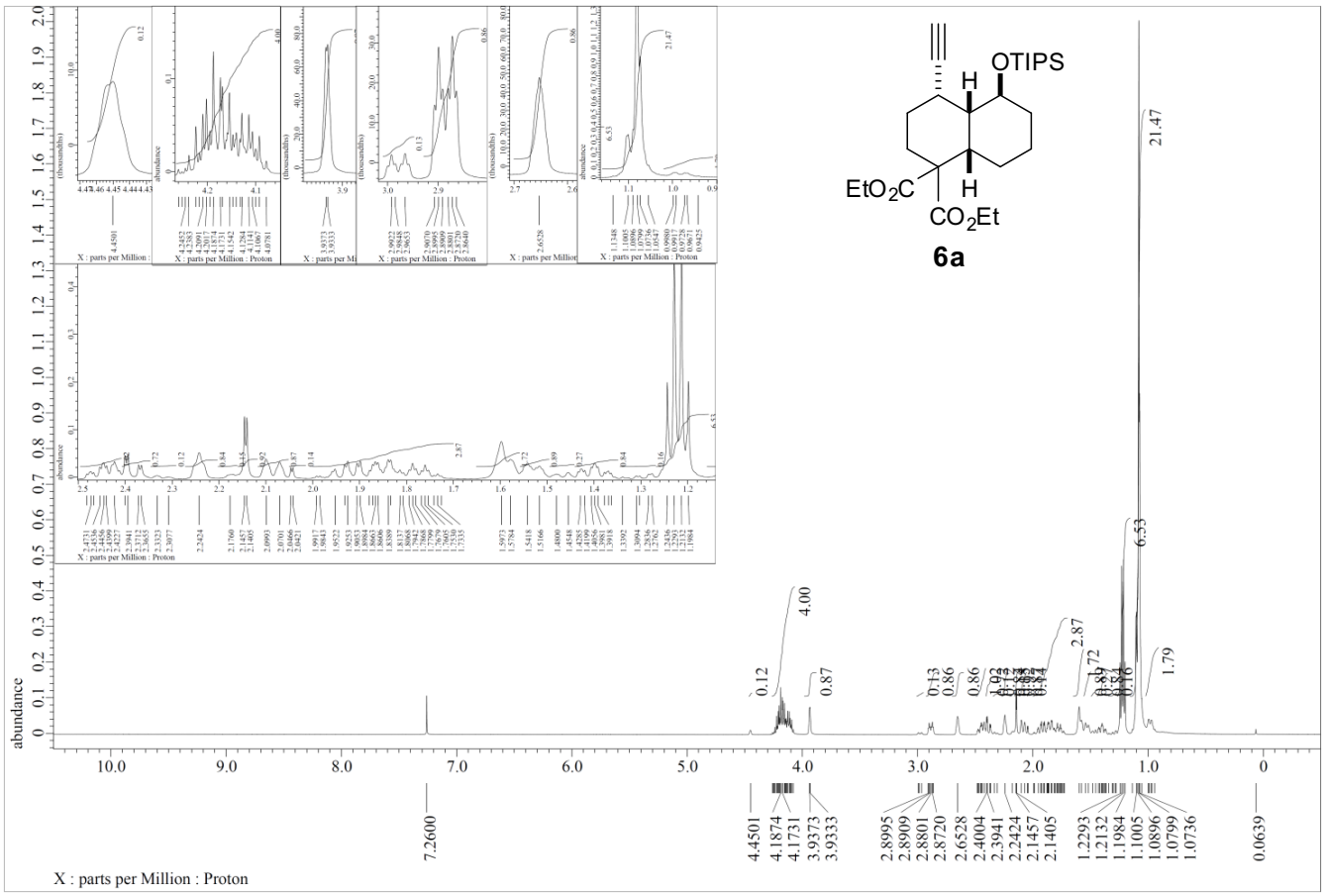

BnO
OTIPS
EtO2C
CO2Et
5b
(thousandths)
X : parts per Million : Carbon13
70.9208
151.9241
151.8667
138.9213
128.1878
127.4601
127.2111
104.2791
104.1163
84.7940
84.6695
77.2585
77.0000
76.7415
73.1892
66.0462
60.8279
60.7896
60.7226
39.3991
39.2842
36.2873
36.2202
29.5656
27.4496
27.3538
26.2048
26.1378
24.1845
24.0696
22.5376
17.9512
14.0733
12.4456

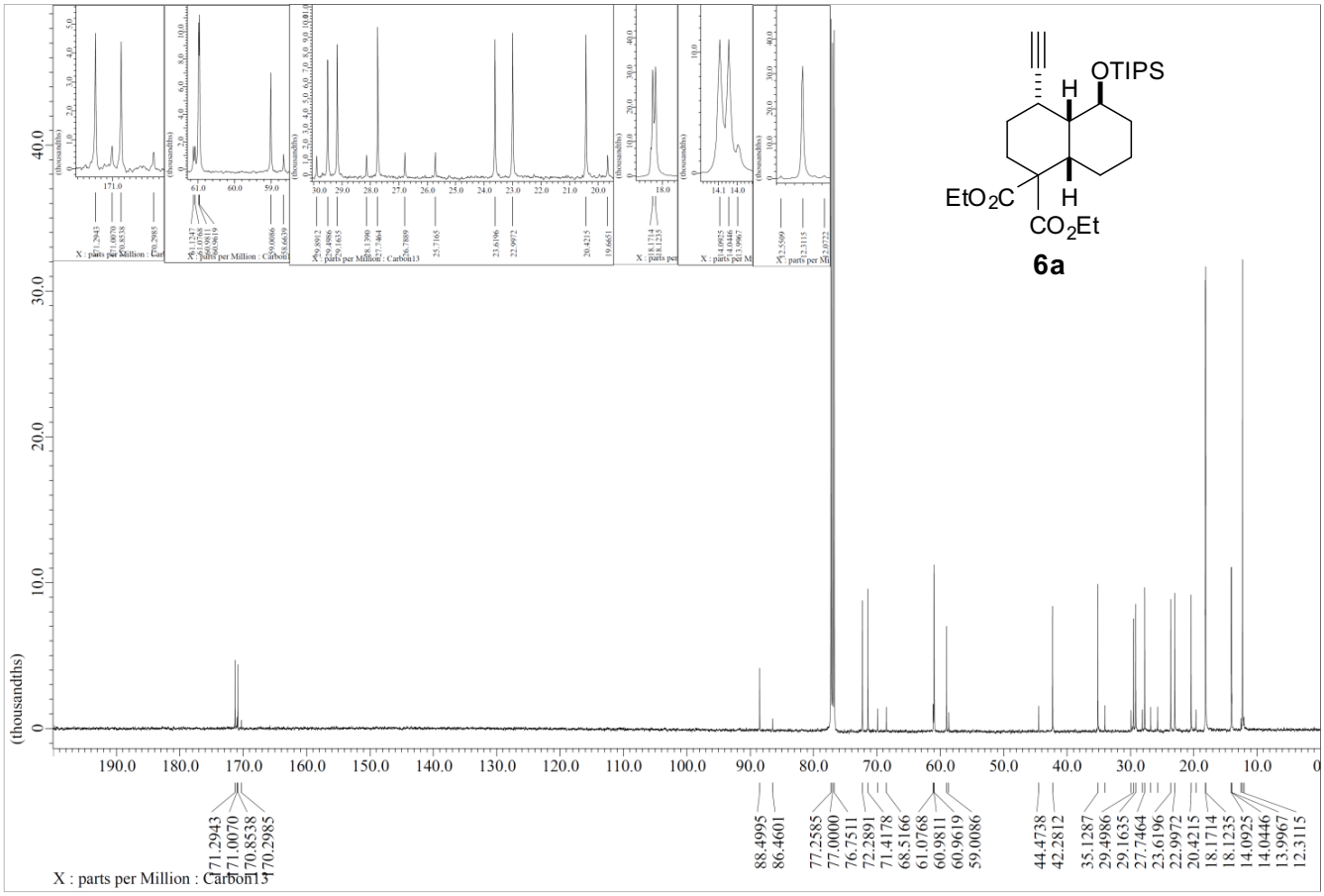

BnO
OTIPS
EtO2C
5c
abundance
X : parts per Million : Proton
19.87
7.22
4.11
3.85
2.15
2.94
2.07
1.00
0.82
0.49
7.3527
7.3499
7.3453
7.3367
7.3333
7.3247
7.3230
7.3190
7.3155
7.2892
7.2846
7.2743
7.2600
5.2967
4.7958
4.7724
4.5200
4.4959
4.1427
4.1284
4.0666
4.0638
4.0523
4.0494
4.0454
2.4593
2.4553
2.4473
2.4399
2.4359
2.0220
1.9591
1.6603
1.6414
1.6013
1.0558
1.0427
0.9345
0.9276
0.9133
0.0707

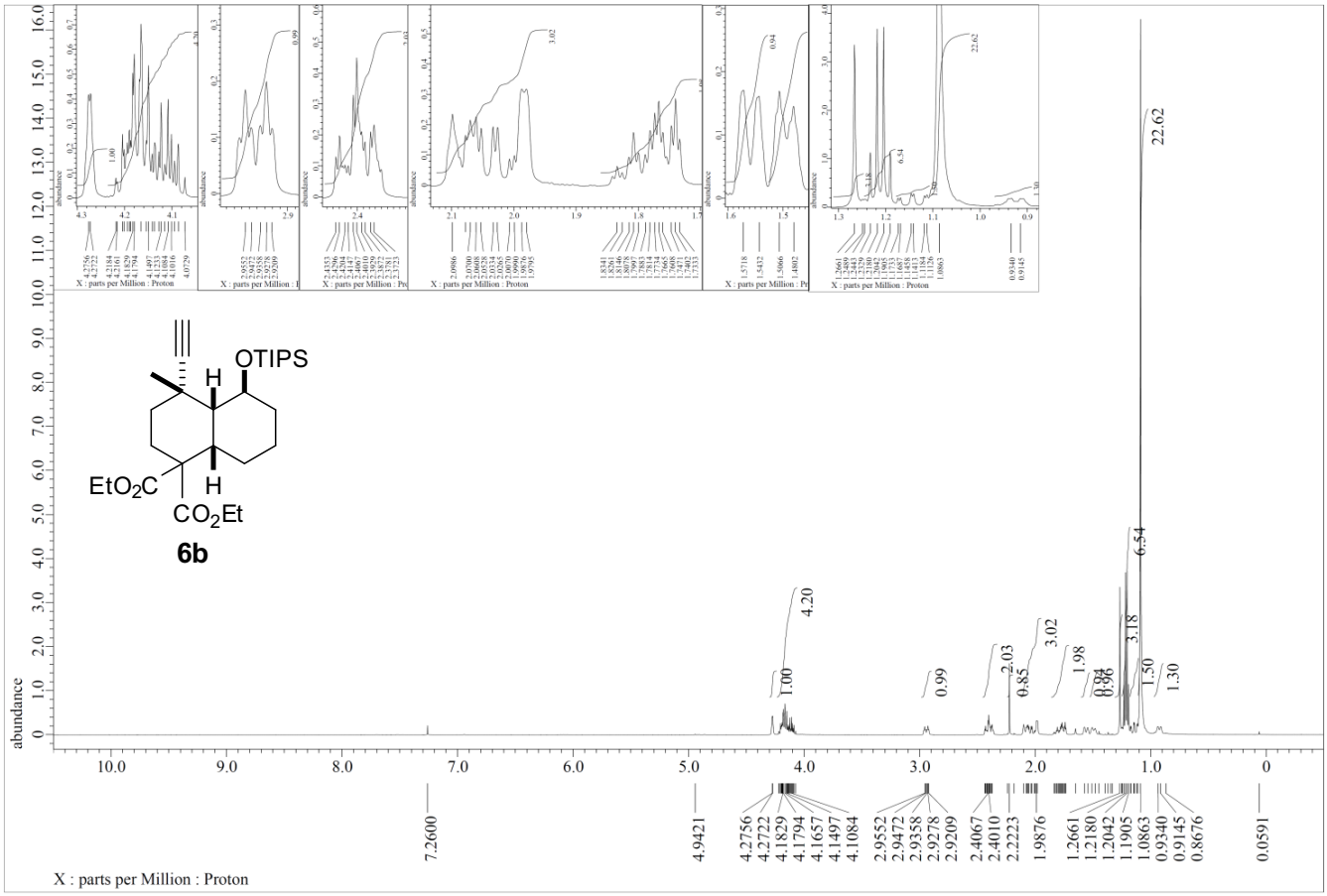

BnO
OTIPS
EtO2C
5c
(thousandths)
X : parts per Million : Carbon13
175.5264
149.8463
137.9447
137.8585
128.2835
127.9675
127.9388
127.5750
103.2067
82.7737
77.2585
77.0000
76.7415
73.9169
73.7828
70.3837
70.3454
69.0432
68.9187
60.4353
50.3337
31.7200
30.8295
30.8104
30.6955
23.8877
19.2342
18.2097
18.1140
14.1595
12.7807

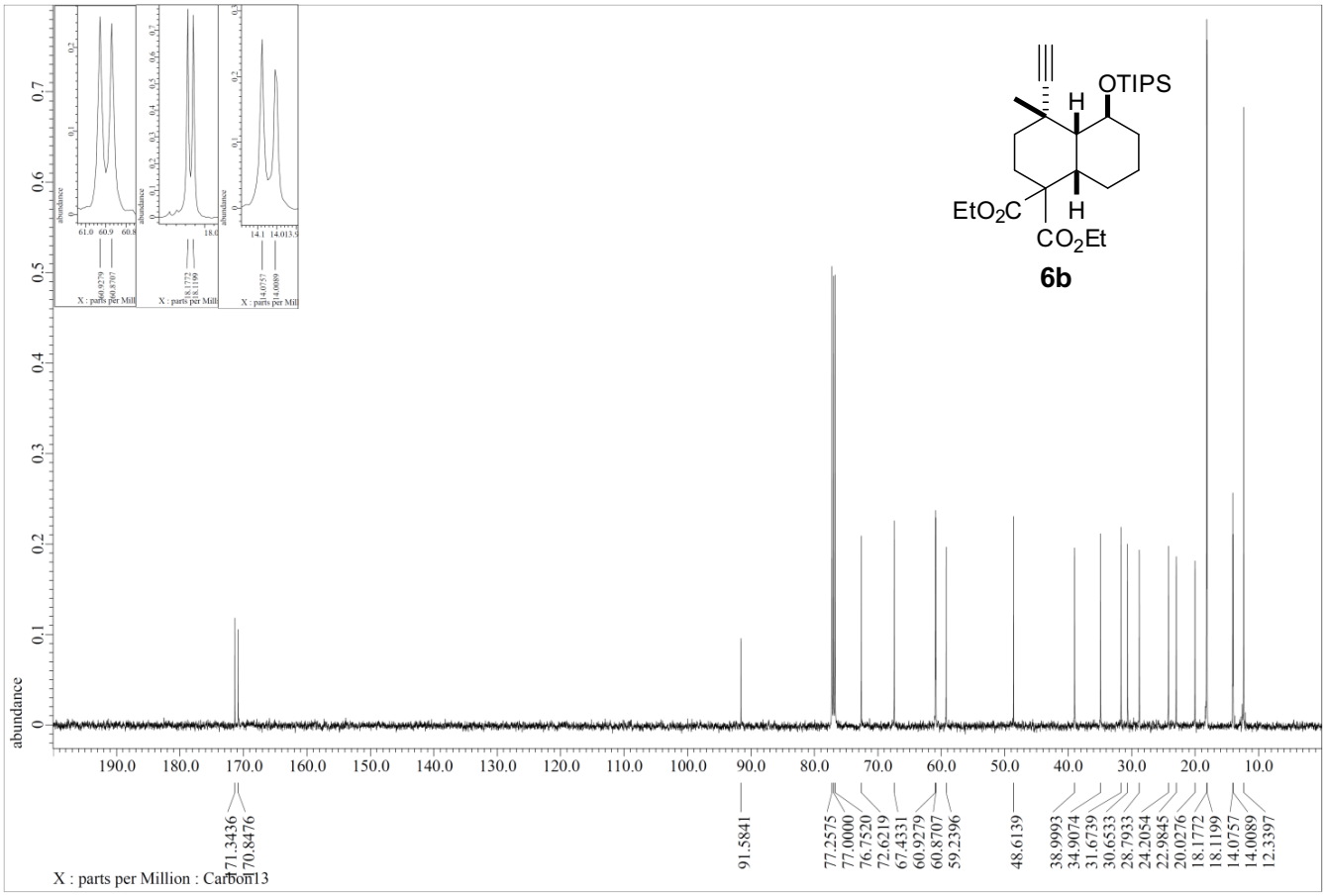

CO2Et
CO2Et
BnO
Ph
TIPSO
5d
abundance
X : parts per Million : Proton
7.3356
7.3258
7.3212
7.2211
7.2119
7.2079
7.2056
7.1970
7.1701
7.1667
7.1615
7.1581
7.1530
5.4192
5.4175
5.4146
5.3980
5.3963
5.3934
5.3917
4.7804
4.7564
4.7466
4.4931
4.1353
4.1239
4.1204
4.1107
4.1096
3.9871
3.9825
2.4599
2.4553
2.4387
2.4347
1.7633
1.7616
1.7582
1.7564
1.6677
1.2316
1.2172
1.2029
1.1966
1.1955
1.1812
1.0719
1.0570
1.0450
1.0301

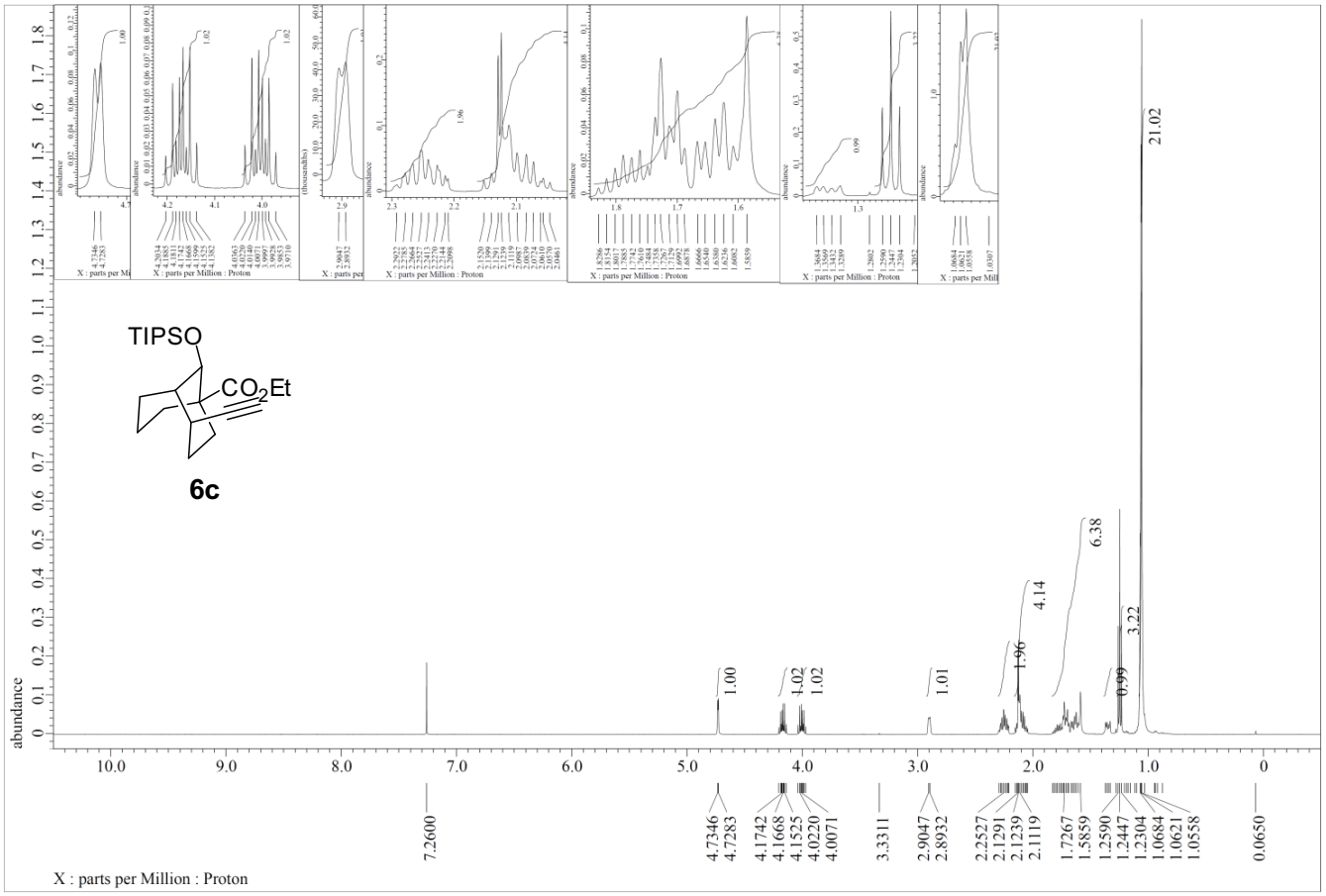

CO2Et
CO2Et
BnO
Ph
TIPSO
5d
abundance
X : parts per Million : Carbon13

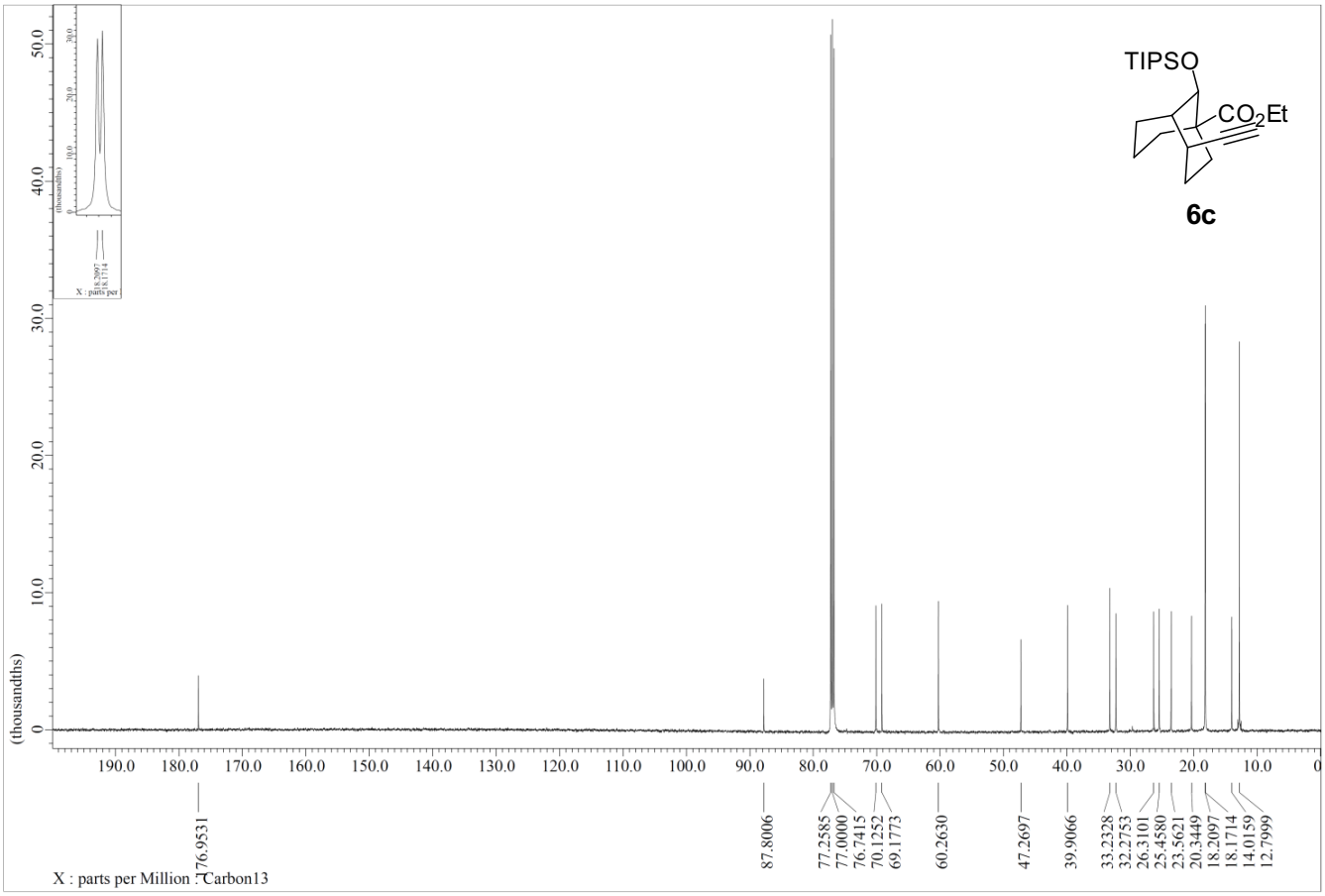

OTIPS
H
EtO2C
H
CO2Et
6a
abundance
X : parts per Million : Proton

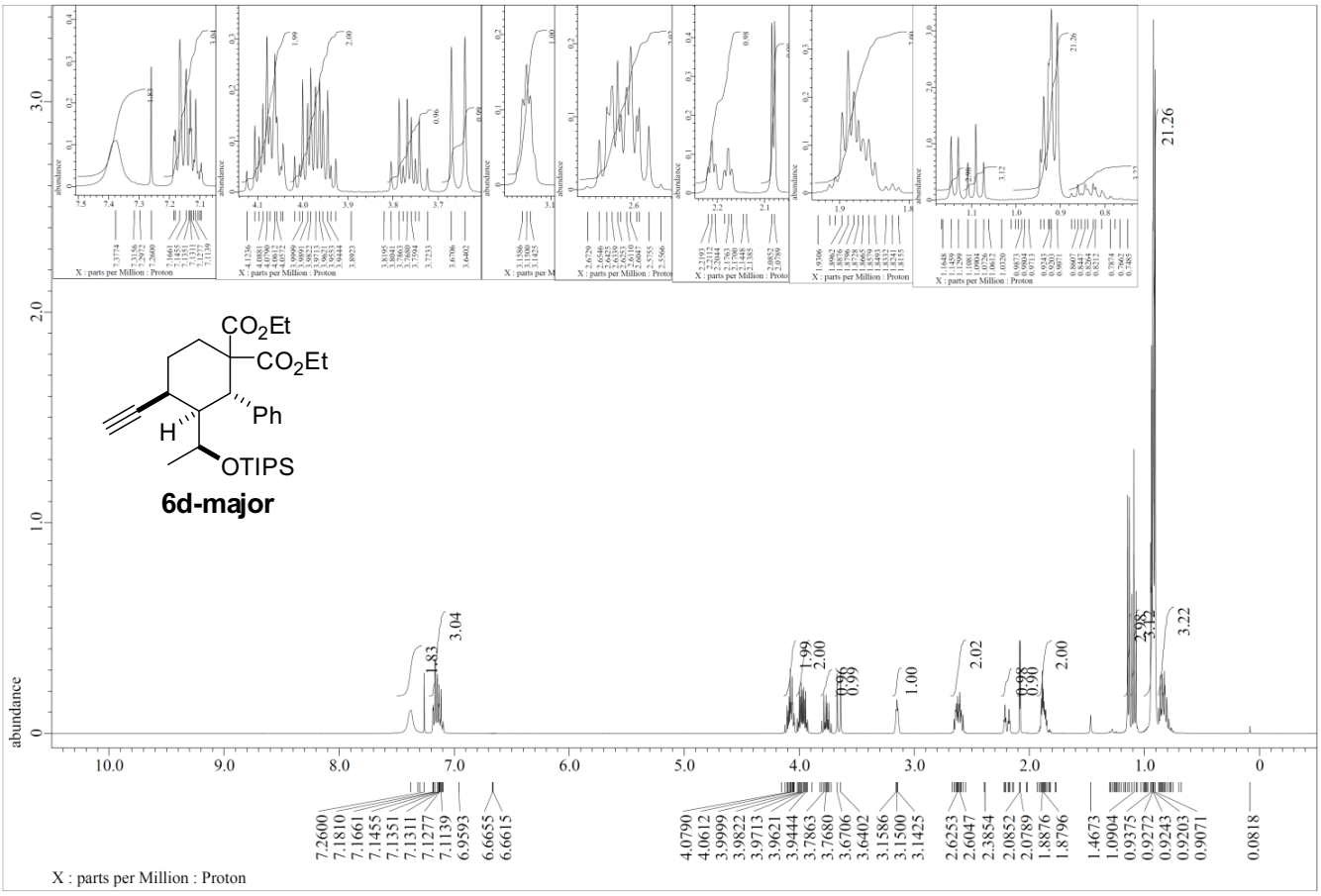

OTIPS
H
EtO2C
H
CO2Et
6a
(thousandths)
X : parts per Million : Carbon13

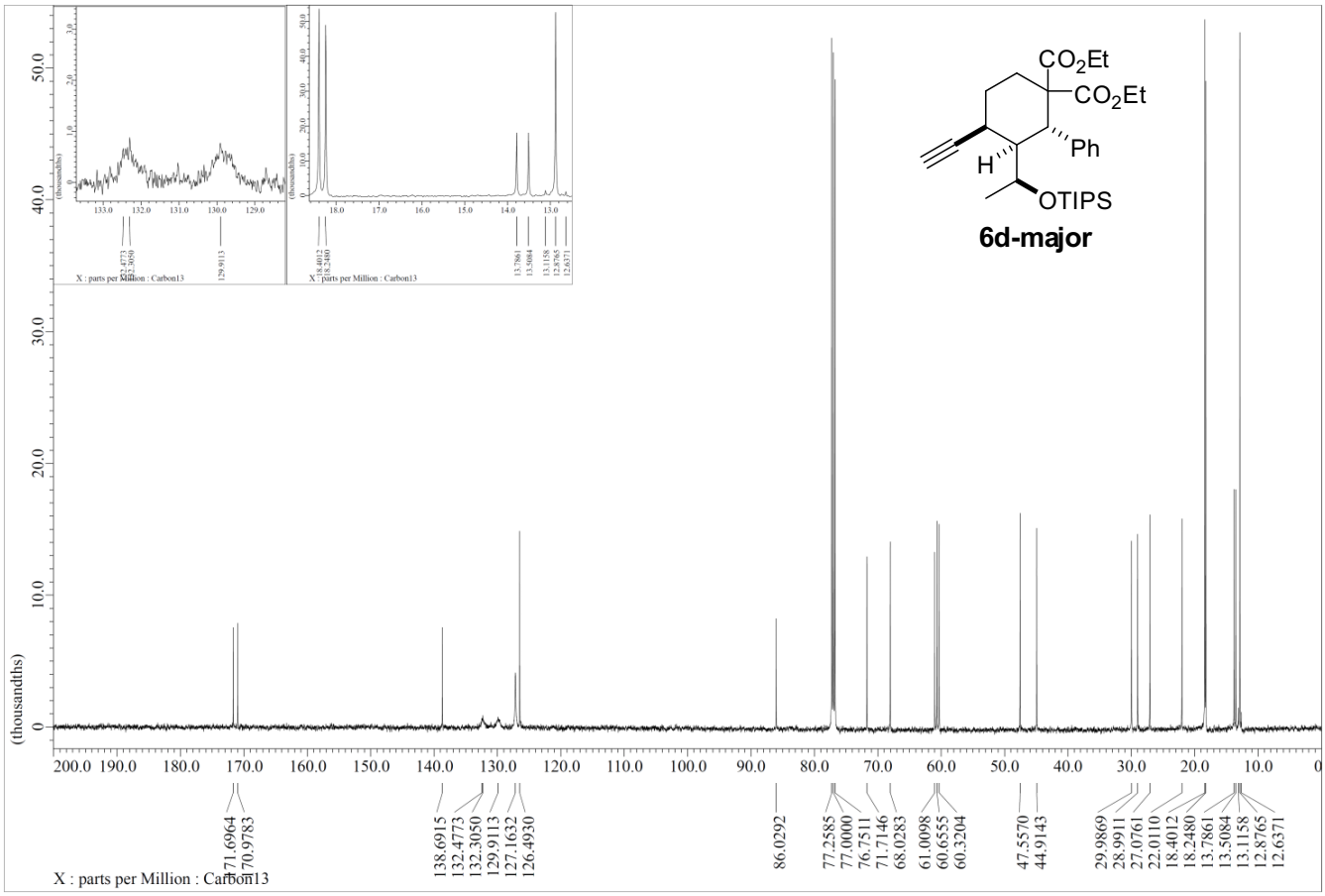

OTIPS
H
EtO2C
H
CO2Et
6b
abundance
X : parts per Million : Proton

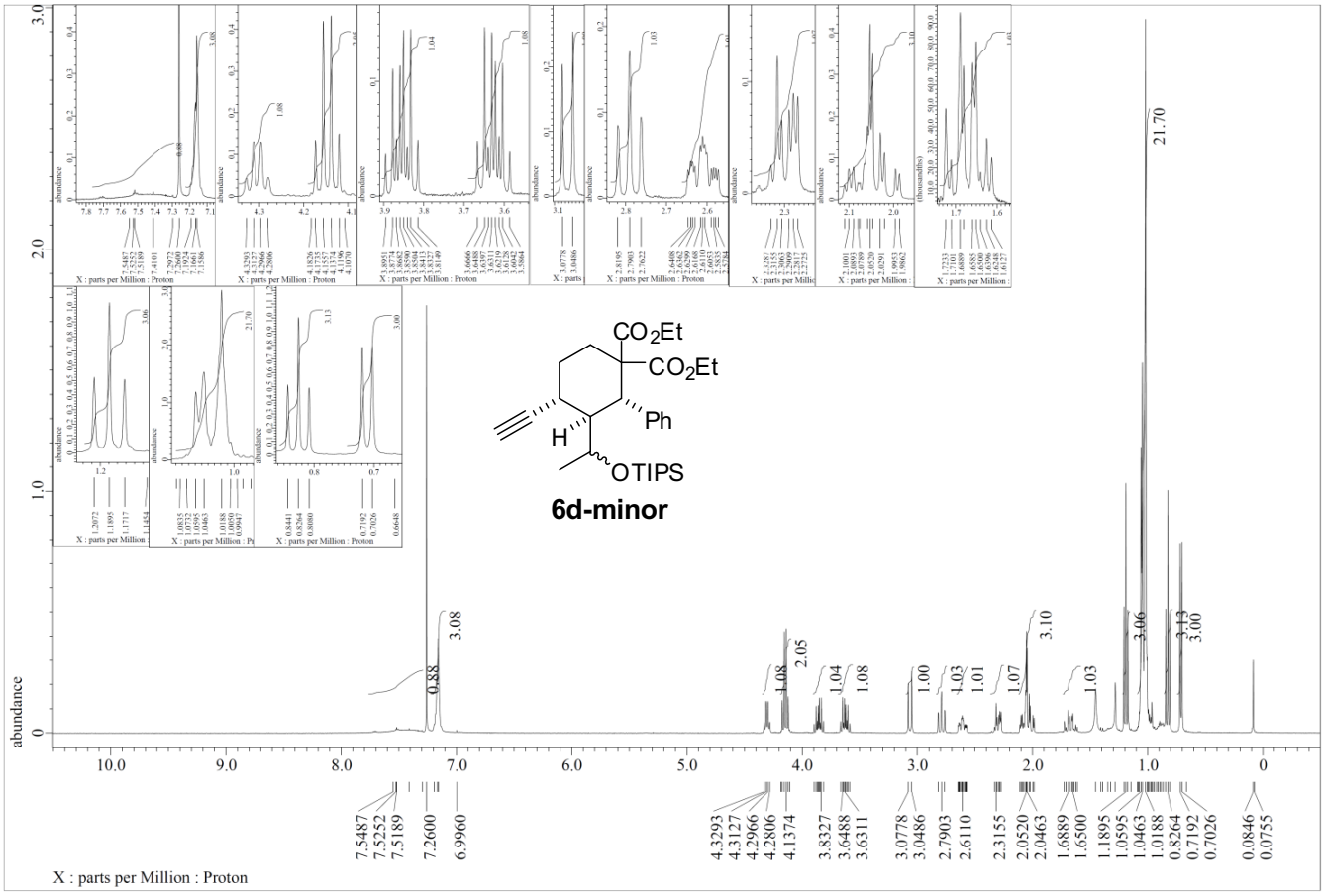

OTIPS
H
EtO2C
H
CO2Et
6b
abundance
X : parts per Million : Carbon13
171.3436
170.8476
91.5841
77.2575
77.0000
76.7520
72.6219
67.4331
60.9279
60.8707
59.2396
48.6139
38.9993
34.9074
31.6739
30.6533
28.7933
24.2054
22.9845
20.0276
18.1772
18.1199
14.0757
14.0089
12.3397

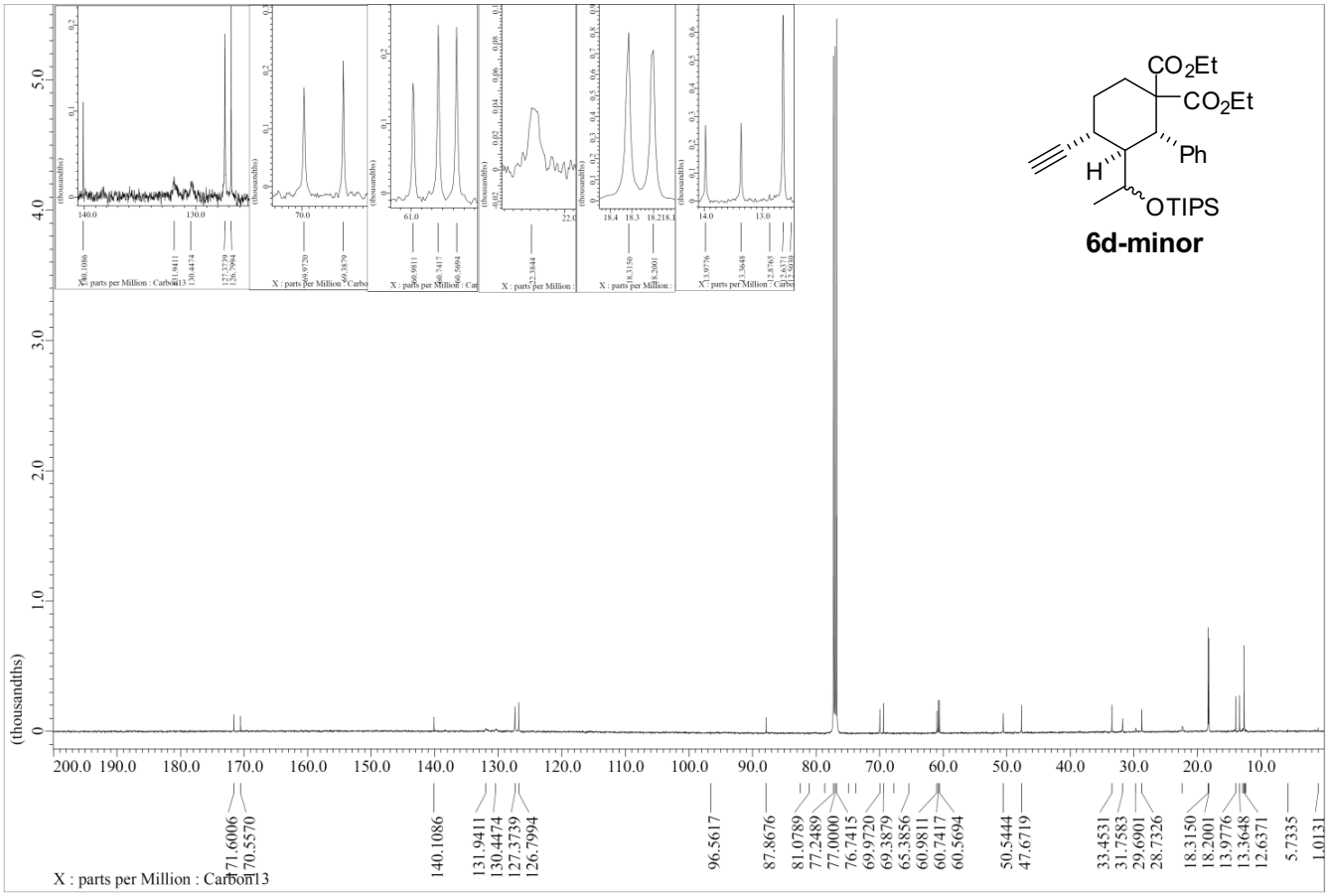

TIPSO
CO2Et
6c
abundance
X : parts per Million : Proton
21.02
6.38
4.14
3.22
1.96
1.00
1.02
1.02
1.01
0.99
7.2600
4.7346
4.7283
4.1742
4.1668
4.1525
4.0220
4.0071
3.3311
2.9047
2.8932
2.2527
2.1291
2.1239
2.1119
1.7267
1.5859
1.2590
1.2447
1.2304
1.0684
1.0621
1.0558
0.0650

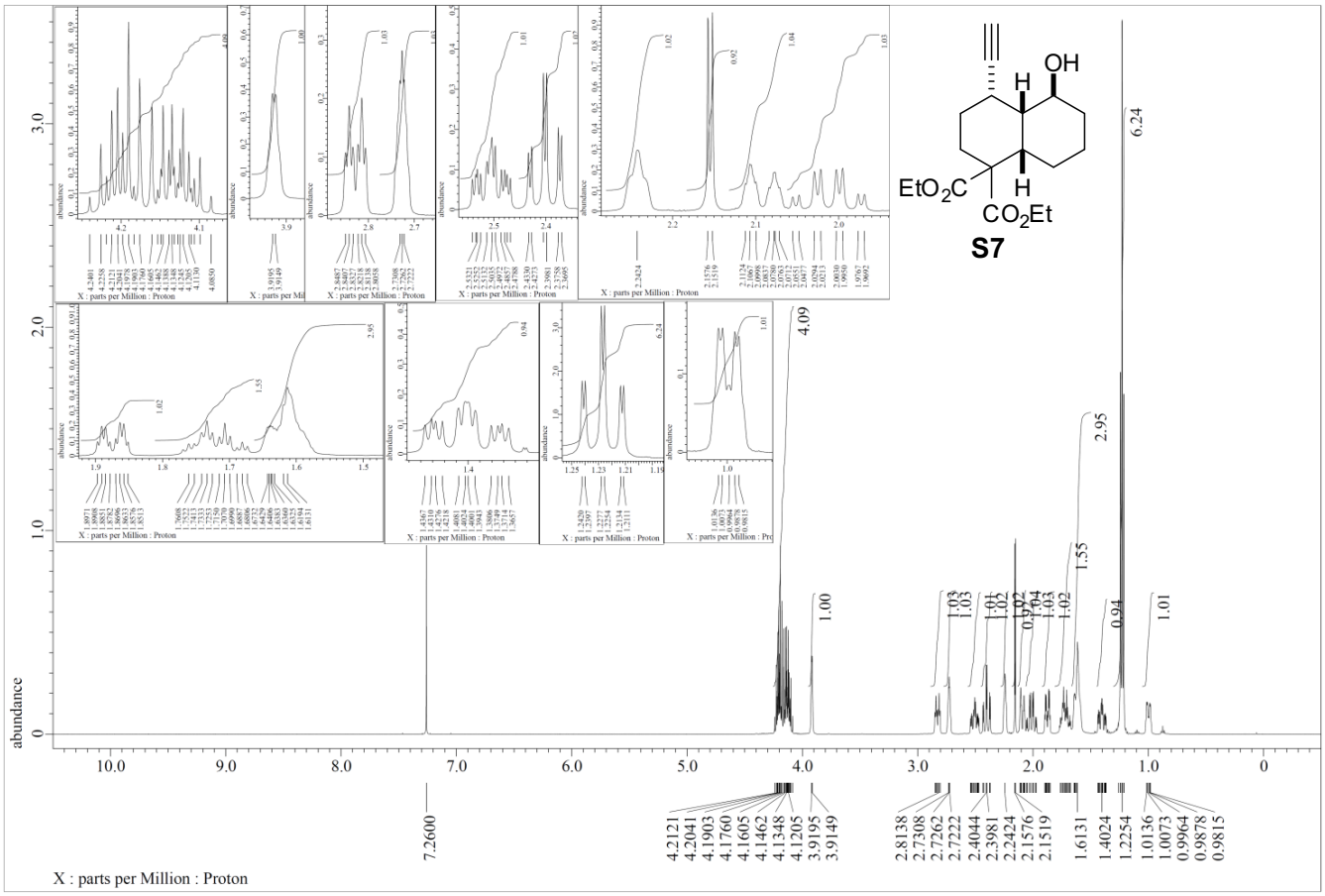

TIPSO
CO2Et
6c
(thousandths)
X : parts per Million : Carbon13
176.9531
87.8006
77.2585
77.0000
76.7415
70.1252
69.1773
60.2630
47.2697
39.9066
33.2328
32.2753
26.3101
25.4580
23.5621
20.3449
18.2097
18.1714
14.0159
12.7999

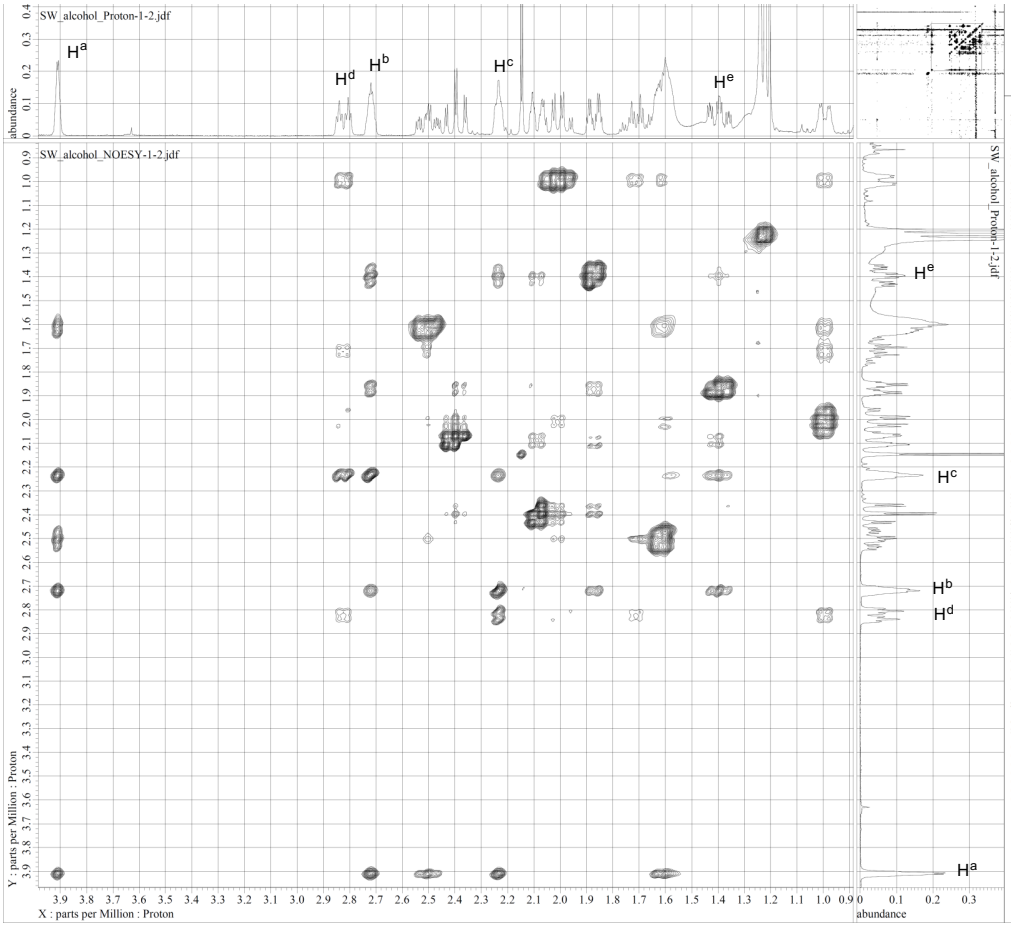

CO2Et
CO2Et
Ph
H
OTIPS
6d-major
abundance
X : parts per Million : Proton
7.2600
7.1810
7.1661
7.1455
7.1351
7.1311
7.1277
7.1139
6.9593
6.6655
6.6615
4.0790
4.0612
3.9999
3.9822
3.9713
3.9621
3.9444
3.7863
3.7680
3.6706
3.6402
3.1586
3.1500
3.1425
2.6253
2.6047
2.3854
2.0852
2.0789
1.8876
1.8796
1.4673
1.0904
0.9375
0.9272
0.9243
0.9203
0.9071
0.0818


CO2Et
CO2Et
Ph
H
OTIPS
6d-major
(thousandths)
X : parts per Million : Carbon13


CO2Et
CO2Et
Ph
H
OTIPS
6d-minor
abundance
X : parts per Million : Proton


CO2Et
CO2Et
Ph
H
OTIPS
6d-minor
(thousandths)
X : parts per Million : Carbon13


OH
H
EtO2C
H
CO2Et
S7
abundance
X : parts per Million : Proton



JEOL RESONANCE

```
Filename          = SW_alcohol_NOESY-1-2.jdf
Author            = iwasawa
Experiment        = noesy.jxp
Sample_Id         = SW_alcohol
Solvent           = CHLOROFORM-D
Creation_Time     = 19-FEB-2016 22:41:16
Revision_Time     = 23-MAY-2018 21:51:01
Current_Time      = 23-MAY-2018 21:55:48

Comment           = phase sensitive noesy
Data_Format       = 2D COMPLEX COMPLEX
Dim_Size          = 1638, 1024
Dim_Title         = Proton Proton
Dim_Units         = [ppm] [ppm]
Dimensions        = X Y
Site              = JNM-ECS400
Spectrometer      = DELTA2_NMR

Field_Strength    = 9.389766[T] (400[MHz])
X_Acq_Duration    = 0.45514752[s]
X_Domain          = 1H
X_Freq            = 399.78219838[MHz]
X_Offset          = 4[ppm]
X_Points          = 2048
X_Prescans        = 4
X_Resolution      = 2.19708986[Hz]
X_Sweep           = 4.49964003[kHz]
X_Sweep_Clipped   = 3.59971202[kHz]
Y_Domain          = 1H
Y_Freq            = 399.78219838[MHz]
Y_Offset          = 4[ppm]
Y_Points          = 512
Y_Prescans        = 0
Y_Resolution      = 7.02765184[Hz]
Y_Sweep           = 3.59815774[kHz]
Irr_Domain        = Proton
Irr_Freq          = 399.78219838[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = Proton
Tri_Freq          = 399.78219838[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 4096

Relaxation_Delay  = 1.5[s]
Recvr_Gain        = 42
Temp_Get          = 24[dC]
Mix_Time          = 0.5[s]
X_Acq_Time        = 0.45514752[s]
X_Atn             = 1[dB]
X_Pulse           = 6.19[us]
Y_Acq_Time        = 0.14229504[s]
Y_Pl_Correction   = 180
Irr_Mode          = Off
Tri_Mode          = Off
Adiabatic_Pulse   = 50[ms]
Bl_Attn           = 43.80211242[dB]
Band_Width        = 30[kHz]
Chirp_Atn         = 31.19788758[dB]
Chirp_Pulse       = 50[ms]
Chirp_Shape       = CHIRP
Chirp_Smooth      = 10[%]
Dante_Presat      = FALSE
Grad_Spoil        = 1[ms]
Grad_Spoil_Amp    = 6[mT/m]
Grad_Zqf_Amp      = 24[mT/m]
Hard_Square_Atn   = 75[dB]
Initial_Wait      = 1[s]
Mix_Time2         = 0.448998[s]
Phase_1           = {0, 180, 0, 180, 0, 180,
Q                 = 2
Repetition_Time   = 1.95514752[s]
Scramble          = 1[ms]
T1                = 0.1310368[ms]
T1_Cal1           = 0.1310368[ms]
T1_Cal2           = 0.2699968[ms]
T1_Cal3           = 0.4089568[ms]
T1_Cal4           = 0.5479168[ms]
T1_Cal5           = 0.6868768[ms]
T1_Cal6           = 0.8258368[ms]
Zf_Factor         = 3
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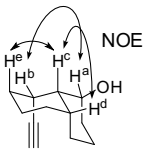
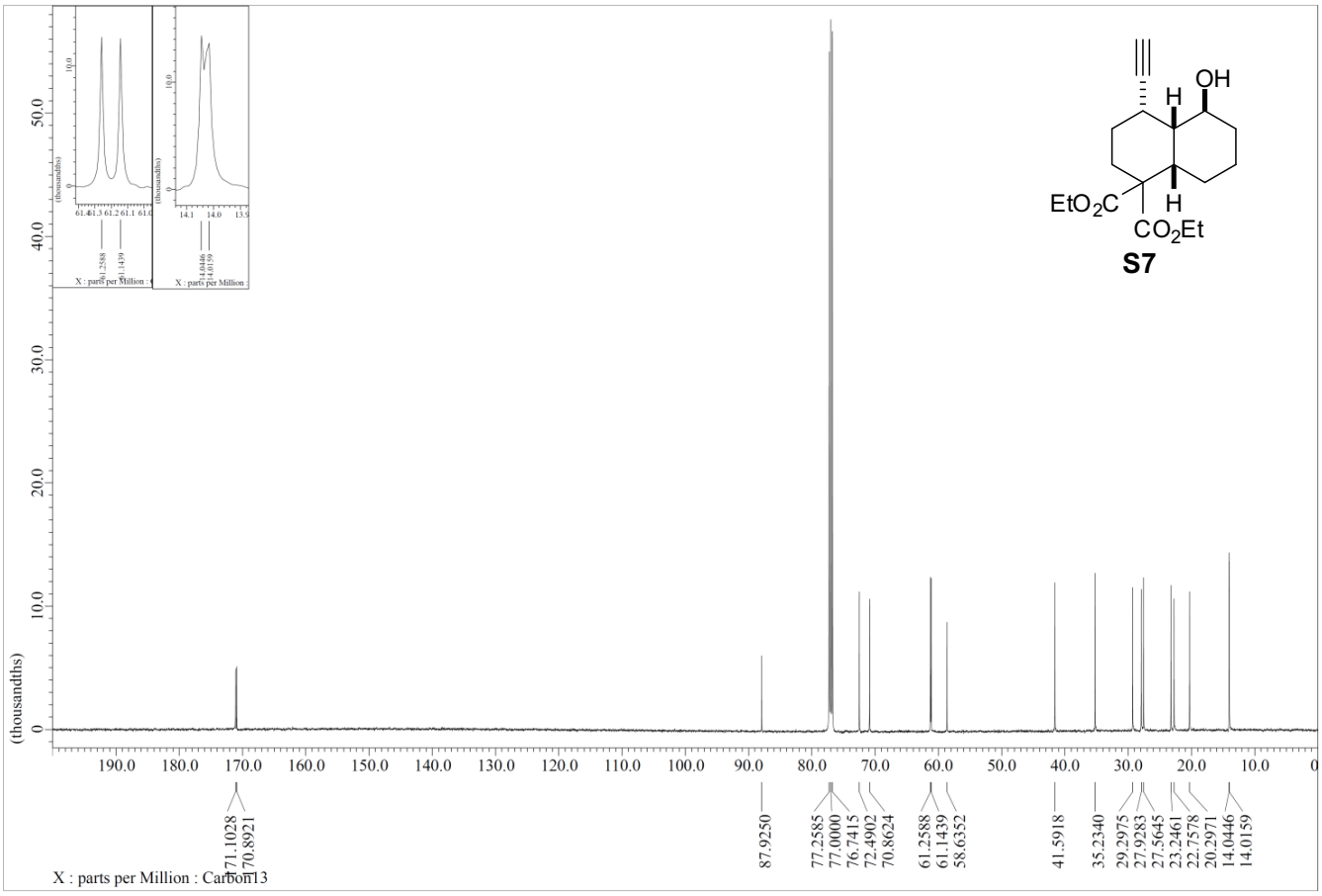


S7



S7