Inhibitory Effect of Ethylene in Ene-Yne Metathesis: the Case for Ruthenacyclobutane Resting States

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SUPPORTING INFORMATION

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General Information

Unless otherwise stated, reactions were conducted with oven-dried glassware under an atmosphere of argon. Solvents were dried by passage through alumina (diethyl ether, THF, dichloromethane) or alumina and Q5 (toluene, benzene) and stored under nitrogen. Ethylene (polymer grade) was obtained from Matheson and used without further purification. Grubbs' ruthenium carbene complexes were purchased from Aldrich or obtained from Materia Inc. (Pasadena, CA) and used as received (unless otherwise noted). The polar isocyanide KO_2CCH_2NC, **3**, was prepared and used for quenching metathesis reactions as reported.[1] Flash and medium-pressure column chromatography were carried out on untreated silica gel 60 (230 - 400 mesh) under air pressure. Thin layer chromatography was performed on glass-backed silica plates (F254, 250 micron thickness), visualized with UV light or stained with iodine, ceric ammonium molybdate or $KMnO_4$ stains. ^1H NMR spectra were recorded at 300 or 400 MHz and ^{13}C NMR spectra were recorded at 75 MHz. NMR chemical shifts are ppm downfield from TMS. All pressure measurements were ±0.1 psig using a 15 psi Marshalltown test gauge.

Ethylene-Alkyne metathesis

Ethylene/argon mixtures were prepared in steel sample vessels by purging with ethylene 3 times, then pressurizing to 80 psig. The vessel was then pressurized with argon to a pressure that produced the desired ethylene mole fraction. The exact ethylene mole fraction of each mixture was determined in a 10 cm infrared cell equipped with CsF windows. The cell was evacuated and filled three times to oil bubbler pressure with the ethylene/argon mixture, then ethylene absorbances at 2070, 2026, 1912 and 1864 cm^{-1} (above a common baseline) were compared to the same absorbances of 100% ethylene recorded in the same way.

Ethylene concentration in CH_2Cl_2 was estimated by ^1H NMR. A 100 mM solution of mesitylene in CD_2Cl_2 was made in a J Young NMR tube. The tube was pressurized and purged 3 times to between 1 and 15 psig with 100% ethylene. The pressurized tube was closed and shaken periodically over 10 min. ^1H NMR spectra were recorded at 400 MHz, 25 °C, using 16

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[1] Galan, B. R.; Kalbarczyk, K. P.; Szczepankiewicz, S.; Keister, J. B.; Diver, S. T., *Org. Lett.* **2007**, *9*, 1203-1206.

scans with a pulse angle of 30° and 10 sec relaxation delay. Further purging to the same pressure produced no change in the observed ethylene peak (5.4 ppm, s, 4H) relative to that of mesitylene (6.8 ppm, s, 3H). The ethylene concentration found was correlated with the partial pressure of ethylene assuming 14.7 psi ambient pressure, and a CD_2Cl_2 partial pressure of 8.7 psi at 25 °C. Ethylene concentrations in CH_2Cl_2 for ethylene and mixtures of ethylene and argon were estimated from a linear regression of concentration vs. ethylene partial pressure (see Fig S1A), assuming solubility in the non-deuterated solvent is not different from that in the deuterated solvent. The data for solubility of ethylene in CH_2Cl_2 at 25 ºC are consistent with published solubility of ethylene in 1,2-dichloroethane at 20 °C,[2] albeit the pressure ranges of these datasets do not overlap.

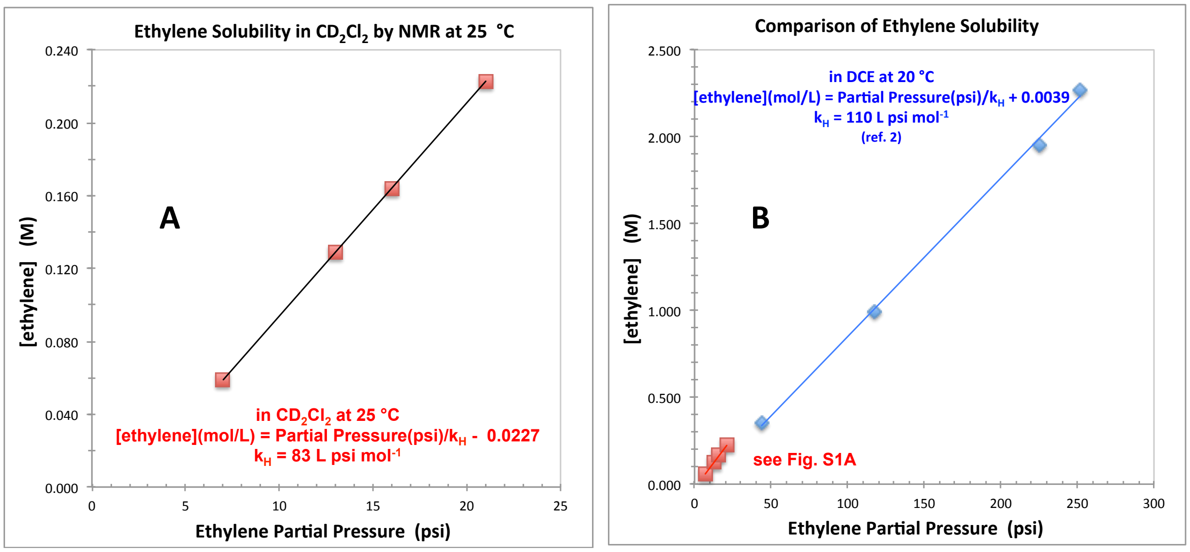

Figure S1. [ethylene] vs. ethylene partial pressure: **A**, solubility in CD_2Cl_2 at 25 °C as determined by NMR. **B**, solubility in 1,2-dichloroethane at 20 °C from ref. 2.

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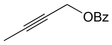
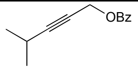
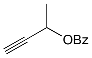
[2] *Solubility Data Series, IUPAC*. Pergamon: Oxford, 1994; Vol. 57, p 259.

Kinetics Measurements

Kinetics were performed using a ReactIR 45m equipped with a K6 conduit, 16mm Comp^{TM} ATR probe and SiComp^{TM} sensor. Reactions were run in a 25 mL flask equipped with a magnetic stirbar, a rubber septum and a size 18 Chem-Thread port sealed with a fluorocarbon o-ring to accommodate the probe. The vessel was dried at 110 °C, then cooled under a flow of dry N_2. The alkynes were dissolved in dry CH_2Cl_2, previously degassed with a stream of argon. The alkyne solution was equilibrated in the vessel immersed in a 25 °C water bath for several minutes under static bubbler pressure of dry N_2. The vessel was then pressurized with ethylene or ethylene/argon mixture to 15 psig then vented and repressurized twice more (CAUTION: *glass vessels under pressure must be adequately shielded to prevent injury in the event of failure*). After 5-10 min at 15 psig, absorbance at 960 cm^{-1} due to ethylene reached a steady level. Catalyst dissolved in CH_2Cl_2 was added by syringe to bring the final volume to 2.9 mL. Reaction kinetics were studied by monitoring the disappearance of specific alkyne substrate absorbances or the increase in specific diene product absorbances. For each reaction, several characteristic IR absorbances were found by examining overlaid spectra from before and after reaction completion. An inclusive list of frequencies is given in Table S1. Not all listed bands were used for all analyses of any given substrate, as some reactions showed drift in some regions, presumably due to changes in water or CO_2 vapor levels in the IR path. Kinetics are characterized by averaging as many monitored trends as is consistent for each run. Complete consumption of the substrate was confirmed for representative kinetics runs by ^{1}H NMR. No kinetic parameters were taken from reactions that failed to go to completion.

Table S1. IR Bands monitored during ethylene-alkyne metathesis reactions

Alkyne Substrate:	 **1a**	 **1b**	 **1c**	 **1d**	 **1e**	 **1f**
IR bands (cm^{-1})	1026 1155 1218 1735* 1755	1096 1160 1735	1340 1597*	1110 1375 1715* 1730	1060 1080* 1137 1168*	1032 1096 1105 1710* 1730 3310

*bands associated with diene products assumed to form at a rate equal to disappearance of alkyne

Calculation of Reaction Rate

Data sets consisting of absorbance vs. time were exported from the ReactIR instrument. Trends in alkyne absorbance were normalized to zero absorbance at a time corresponding to complete alkyne consumption. The data were converted to concentration by dividing absorbances by an effective extinction coefficient found by dividing the absorbance at time = 0 by the initial alkyne concentration. Trends in increasing diene absorption were multiplied by -1, then treated parallel to alkyne trends. The resulting trends gave a set of parallel [alkyne] vs. time curves for each run. In some cases data sets that exhibited excessive noise or anomalous drifts were discarded. Parallel curves for each run were then averaged at each time point. In all cases, [substrate] vs., time data exhibited curved plots suggestive of a first-order dependence on [alkyne]. Initial reaction rates could be estimated by finding the steepest slope (see Fig. S2 A). For **Ru1**, Piers' catalyst, the steepest slope was found within the first 1-2 minutes, and could be quantified over 4-8 data points. For other catalysts, a noticeable induction period was observed before maximum rate was achieved, and an estimate of initial rate was made from the steepest part of the curve. Plots of ln[alkyne] vs. time were linear over the first 50-90% of the course of reactions, and the slopes of these plots did not vary with [alkyne] (see Fig. S2 B). Determination of initial rates at different [alkyne] confirmed a first-order dependence of rate on all alkyne substrates studied (e.g. Fig S3).

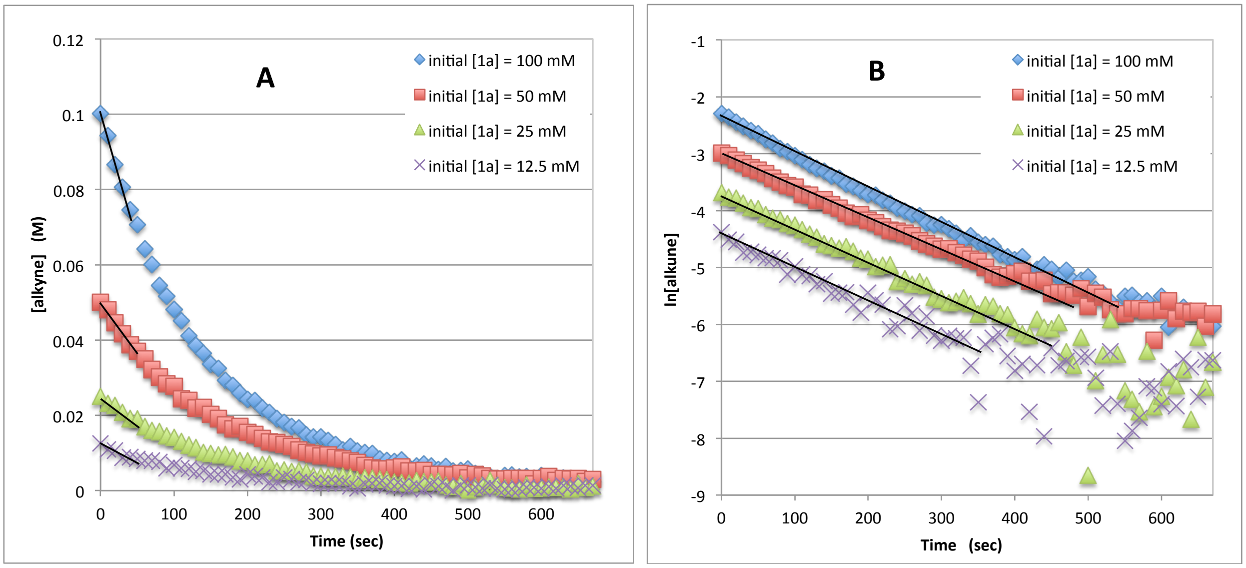


Figure S2. Ethylene-alkyne metathesis of **1a**, [ethylene] = 0.22 M, [**Ru1**] = 0.001 M. **A**: [alkyne] vs. time from IR bands for **1a** at different initial concentrations. Each curve is an average of at least 2 parallel absorption bands. Black lines illustrate the approximate regions (generally <10% reaction) where linear regression yields initial rates (M sec^{-1}). **B**: ln[alkyne] vs. time, at different initial concentrations of **1a**, showing linearity that extends to at least 50% reaction.

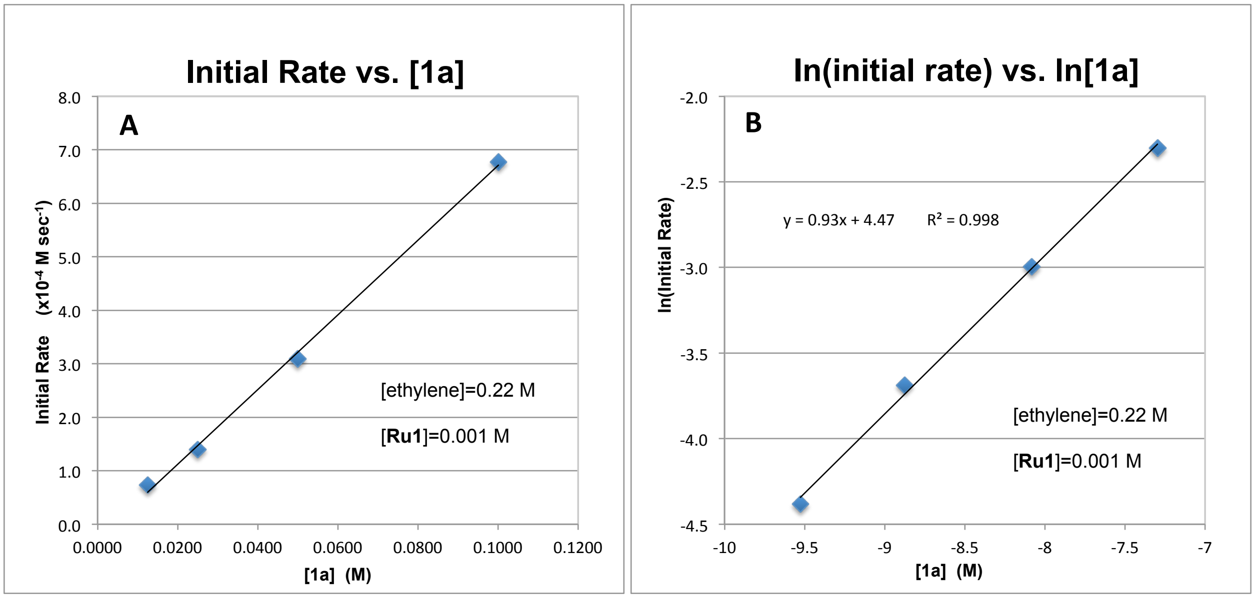


Figure S3. Ethylene-alkyne metathesis of **1a**, [ethylene] = 0.22 M, [**Ru1**] = 0.001 M. **A**: linear increase in initial rate with increasing [alkyne]; **B**: First order dependence on [alkyne] determined from slope of ln(initial rate) vs. ln[alkyne] plot.

Rate Law Determination

Dependencies of ethylene-alkyne reaction rates on catalyst **Ru1** and ethylene concentrations were determined for **1a-f** at constant initial [alkyne]. A k_{obs} was determined from the slope of the ln[alkyne] vs. time plot. Plots of ln($k_{obs)}$ vs. ln[catalyst] exhibited slopes of 1, while ln(k_{obs}) vs. ln[ethylene] had slopes of -1 (see Figure 2). The first order rate constant, k, was found from the rate law: *rate* = k[alkyne]^1[**Ru1**]^1[ethylene]$^{-1}$, where k = k_{obs} [ethylene]^1 [**Ru1**]$^{-1}$. Values of k for **1a-f** are given in Table S2.

Table S2. First Order Rate Constants, k, for Alkyne Substrates 1a-f

entry	**[1a]** **M**	**[Ru1 Piers]** **M**	**[ethylene]** **M**	**k_{obs}** **sec^{-1}**	**initial rate** -δ[alkyne]/δt **M sec^{-1}**	**k** **sec^{-1}**
1	0.050	0.0025	0.220	1.46E-02	6.23E-04	1.29
2	0.050	0.0012	0.220	7.91E-03	3.50E-04	1.45
3	0.050	0.0006	0.220	3.43E-03	1.47E-04	1.26
4	0.050	0.0003	0.220	1.60E-03	8.93E-05	1.17
5	0.0251	0.0010	0.220	5.67E-03	1.47E-04	1.25
6	0.0251	0.0010	0.101	1.02E-02	2.94E-04	1.04
7	0.0251	0.0010	0.071	1.76E-02	3.53E-04	1.24
8	0.0251	0.0010	0.101	1.11E-02	2.34E-04	1.13
9	0.0251	0.0010	0.071	1.57E-02	3.00E-04	1.10
10	0.1001	0.0010	0.220	7.28E-03	6.78E-04	1.60
11	0.0500	0.0010	0.220	6.08E-03	3.09E-04	1.34
12	0.0250	0.0010	0.220	5.79E-03	1.40E-04	1.27
13	0.0125	0.0010	0.220	6.03E-03	7.29E-05	1.33
					Average	1.27
					Std. Dev.	0.14

entry	**[1b]** **M**	**[Ru1 Piers]** **M**	**[ethylene]** **M**	**k_{obs}** **sec^{-1}**	**initial rate** -δ[alkyne]/δt **M sec^{-1}**	**k** **sec^{-1}**
1	0.1001	0.0010	0.220	6.52E-03	5.40E-04	1.43
2	0.0500	0.0010	0.220	6.06E-03	2.53E-04	1.33
3	0.0250	0.0010	0.220	4.15E-03	1.29E-04	0.91
4	0.2000	0.0010	0.220	7.77E-03	1.12E-03	1.71
5	0.0501	0.0005	0.101	6.03E-03	2.86E-04	1.22
6	0.0501	0.0005	0.063	1.16E-02	4.19E-04	1.47
7	0.0501	0.0005	0.063	9.72E-03	3.93E-04	1.23
8	0.0501	0.0005	0.220	2.70E-03	1.26E-04	1.19
9	0.0501	0.0005	0.220	2.65E-03	1.21E-04	1.17
10	0.0501	0.0005	0.101	6.20E-03	2.79E-04	1.26
11	0.0501	0.0020	0.220	9.13E-03	3.86E-04	1.00
12	0.0501	0.0010	0.220	5.27E-03	2.38E-04	1.16
13	0.0501	0.0005	0.220	2.41E-03	1.09E-04	1.06
						1.20
						0.16

entry	[1c] M	[Ru1 Piers] M	[ethylene] M	k_{obs} sec^{-1}	initial rate -δ[alkyne]/δt M sec^{-1}	k sec^{-1}
1	0.100	0.0010	0.220	2.58E-03	2.15E-04	0.57
2	0.050	0.0010	0.220	2.57E-03	1.05E-04	0.57
3	0.200	0.0010	0.220	2.58E-03	4.54E-04	0.57
4	0.101	0.0039	0.220	8.81E-03	9.34E-04	0.50
5	0.101	0.0019	0.220	4.68E-03	4.44E-04	0.54
6	0.101	0.0010	0.220	1.96E-03	2.47E-04	0.44
7	0.025	0.0010	0.220	2.67E-03	7.94E-05	0.59
8	0.025	0.0010	0.111	5.20E-03	1.48E-04	0.58
9	0.025	0.0010	0.144	3.23E-03	9.53E-05	0.46
						0.53
						0.05

entry	[1d] M	[Ru1 Piers] M	[ethylene] M	k_{obs} sec^{-1}	initial rate -δ[alkyne]/δt M sec^{-1}	k sec^{-1}
1	0.100	0.0010	0.220	2.93E-03	2.62E-04	0.64
2	0.050	0.0010	0.220	3.02E-03	1.23E-04	0.66
3	0.025	0.0010	0.220	3.04E-03	6.63E-05	0.67
4	0.050	0.0020	0.220	6.79E-03	2.77E-04	0.75
5	0.050	0.0005	0.220	1.85E-03	6.83E-05	0.81
6	0.050	0.0010	0.220	3.87E-03	1.68E-04	0.85
7	0.026	0.0010	0.220	2.86E-03	1.03E-04	0.63
8	0.026	0.0010	0.111	5.51E-03	1.36E-04	0.61
9	0.026	0.0010	0.144	4.28E-03	9.87E-05	0.62
						0.69
						0.08

entry	**[1e]** **M**	**[Ru1 Piers]** **M**	**[ethylene]** **M**	**k_{obs}** **sec^{-1}**	**initial rate** -δ[alkyne]/δt **M sec^{-1}**	**k** **sec^{-1}**
1	0.100	0.0010	0.220	1.46E-03	1.65E-04	0.32
2	0.050	0.0010	0.220	1.90E-03	9.11E-05	0.42
3	0.025	0.0010	0.220	2.07E-03	4.42E-05	0.46
4	0.025	0.0040	0.220	8.59E-03	2.00E-04	0.47
5	0.025	0.0020	0.220	4.15E-03	1.02E-04	0.46
6	0.025	0.0010	0.220	1.60E-03	4.72E-05	0.35
7	0.021	0.0020	0.220	4.06E-03	7.81E-05	0.45
8	0.021	0.0020	0.111	6.66E-03	1.50E-04	0.37
9	0.021	0.0020	0.144	6.01E-03	1.32E-04	0.43
						0.42
						0.05

entry	**[1f]** **M**	**[Ru1 Piers]** **M**	**[ethylene]** **M**	**k_{obs}** **sec^{-1}**	**initial rate** -δ[alkyne]/δt **M sec^{-1}**	**k** **sec^{-1}**
1	0.050	0.0020	0.220	1.69E-02	5.59E-04	1.86
2	0.050	0.0005	0.220	3.46E-03	1.50E-04	1.52
3	0.050	0.0010	0.220	7.27E-03	3.12E-04	1.60
4	0.100	0.0005	0.220	3.03E-03	2.99E-04	1.34
5	0.050	0.0005	0.220	3.58E-03	1.42E-04	1.58
6	0.025	0.0005	0.220	4.53E-03	7.19E-05	2.00
7	0.025	0.0005	0.116	7.24E-03	1.32E-04	1.64
8	0.025	0.0005	0.144	6.33E-03	1.22E-04	1.79
9	0.025	0.0005	0.220	3.98E-03	9.71E-05	1.72
						1.66
						0.19

Direct Observation of Ruthenacyclobutane Under Ene-Yne Metathesis

In a nitrogen-filled drybox, a 5 mm NMR tube equipped with a Teflon screw cap was charged with 3.3 mg Piers catalyst **Ru1** (3.8 μmole), which was dissolved in 0.6 mL CD_2Cl_2. The tube was removed from the drybox and cooled under a balloon of ethylene gas and agitated for 10 min, then allowed to stand at –78 ˚C for a further 20 min. Neat MTBE (0.5 μL, 3.8 μmole) was added to the NMR tube to serve as internal standard. The hole puncture was sealed with a dab of grease. The sample was lowered into the NMR probe pre-equilibrated at –55 ˚C and a ^1H NMR spectrum was recorded, which showed a ruthenacyclobutane (δ –2.64 and δ 6.64 ppm in a 2H to 4H ratio), as observed by Piers and Romero.[3] Next, a solution of alkyne (3.2 mg, 19 μmol) in 0.15 mL CD_2Cl_2 was added. After 0.5 h at –55 ˚C, the 1,3-diene product was not detected. After 6 min at –40 ˚C, no reaction was detected. At –20 ˚C, after 20 min, 17% conversion to ethylene metathesis product was detected by integration of the downfield resonance of product at δ 4.65 ppm (=CH-C*H₂*OBz) relative to δ 4.59 ppm (C-C*H₂*OBz) for the alkyne reactant. Upon re-cooling to –40 ˚C, the resonances of the ruthenacyclobutane at δ -2.64 and δ 6.64 were seen. At this time, the NMR sample was ejected from the probe and allowed to warm to ambient room temperature (~25 ˚C) for 10 min, then reinserted into the probe precooled at –40 ˚C. The ^1H NMR spectrum showed complete conversion of the alkyne to the resonance at δ 4.65 ppm (=CH-C*H₂*OBz) and the ruthenacyclobutane was evident due to resonances at δ –2.64 and δ 6.64 ppm. After a total time of 104 min, the [ruthenacyclobutane] had diminished by about 11% based on integration of the upfield resonance at δ –2.64 ppm vs. internal standard.

Catalyst Comparison

Initial rates for precatalysts **Ru1-Ru5** were determined as described above using 0.025 M [**1a**], and 0.22 M ethylene. Precatalysts **Ru1**, **Ru3** and **Ru4** were used at 0.001 M, while **Ru2** was used at 0.005 M and **Ru5** was used at 0.002 M. The [alkyne] vs. time plots are shown plotted to reaction completion in Figure S4. Precatalyst **Ru5** showed very rapid initiation, but NMR analysis indicated only ~65% consumption of alkyne substrate before complete catalyst decomposition. Precatalysts **Ru2** and **Ru3** displayed induction periods on the order of 5 minutes before maximal reaction rates were observed. Precatalyst **Ru4** displayed only a few second's delay before reaching maximal initial rate.

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[3] Romero, P. E.; Piers, W. E. *J. Am. Chem. Soc.* **2005**, *127*, 5032-5033.

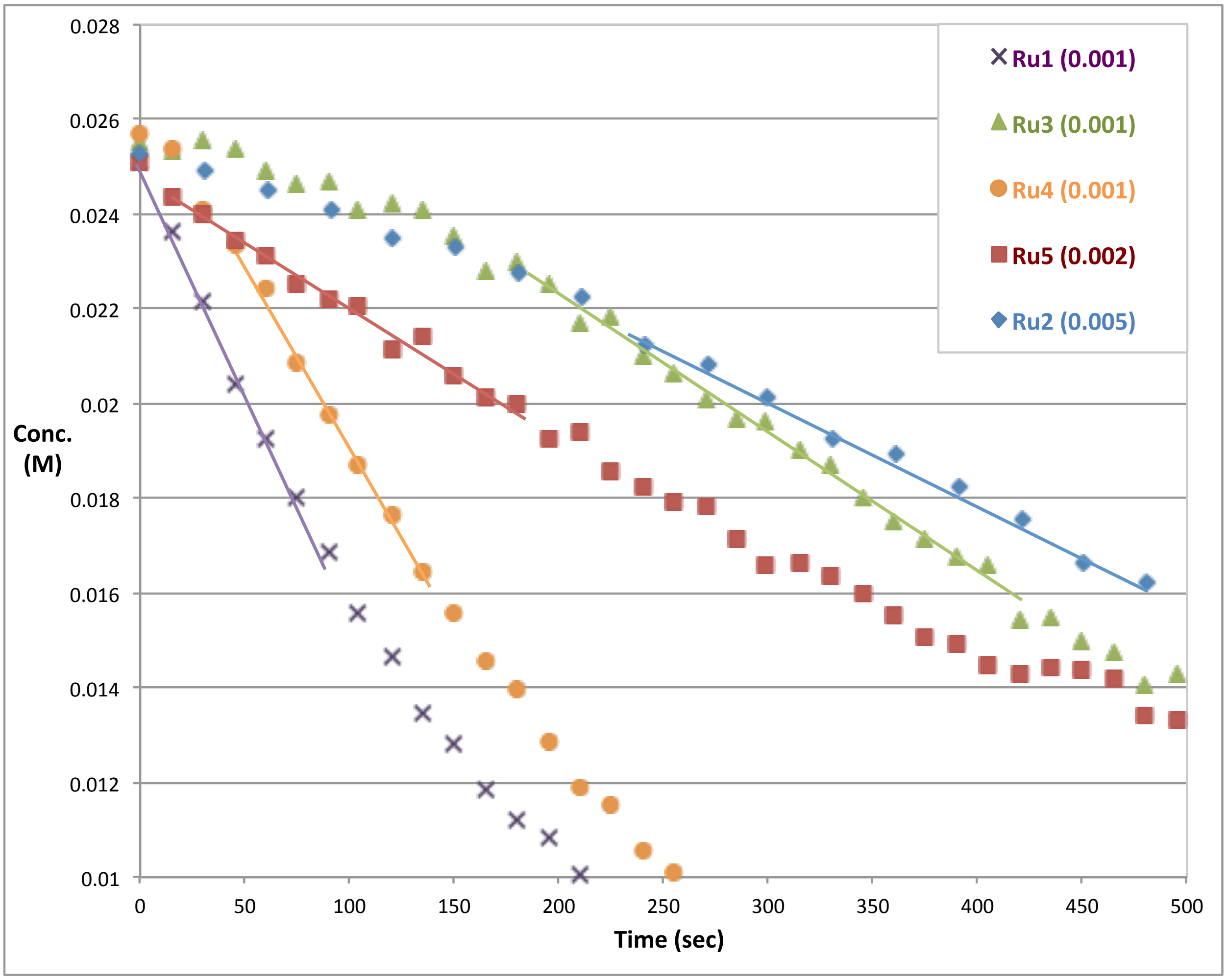


Figure S4. Initial time course for ethylene-**1a** metathesis with different catalysts. The lines represent linear portions of the exponential decay curves with the steepest descent and were used to obtain the initial rates.

Table S3 shows initial rates for ethylene-**1a** metathesis using the catalysts **Ru1-Ru5**. Rates for **Ru2** and **Ru5** were corrected for the higher catalyst concentrations, and initial rates are shown relative to the slowest rate.

Table S3. Relative initial rates for different catalysts

RuX	[1a] M	[RuX] M	[ethylene] M	initial rate M sec-1	corrected M sec-1	rel. rate
1 mM Ru1	0.0250	0.001	0.220	1.40E-04	1.40E-04	30
1 mM Ru3	0.0255	0.001	0.220	2.96E-05	2.96E-05	6
1 mM Ru4	0.0257	0.001	0.220	1.16E-04	1.16E-04	24
2 mM Ru5	0.0253	0.002	0.220	3.68E-05	1.84E-05	4
5 mM Ru2	0.0253	0.005	0.220	2.37E-05	4.74E-06	1

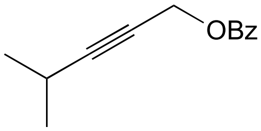
Synthesis

Alkynes **1a, b** and **1d-h** were prepared by acylation of the corresponding alcohols. **1a** and **1d-h** exhibited spectral properties matching previous reports.[4] **1d** is characterized below. **1e** was prepared using Wender's procedure.[5] **1c** was purchased from Alfa Aesar and used without purification. Dienes **2a**, **2c** and **2f** were characterized by ^{1}H and ^{13}C NMR, and were found to be in agreement with literature reports.

*General procedure for ethylene-alkyne metathesis for preparation of dienes **2a-f***

A solution of the alkyne (0.5 mmol) was made in 4.5 mL dry CH_2Cl_2 and the reaction vessel was sealed with a rubber septum, which was secured with wire. The flask was stirred vigorously while ethylene gas was introduced through a 22 ga. needle to 10.0 psig. The flask was vented and repressurized 3 times. After stirring at rt under ethylene for 20 min, 22 mg of **RuX** (0.025 mmol, 5 mol%) in 0.5 mL CH_2Cl_2 was added via syringe. After stirring under ethylene for 1 h, the reaction was quenched by addition of 15 mg of isocyanide **3** (0.125 mmol, 25 mol%) as a solution in 1 mL MeOH. The reaction was vented and stirred for 10 min in air. Volatiles were removed at reduced pressure and the residue was purified by chromatography on silica gel to give the diene product.

Compound Characterization



(1d) Colorless oil; R_f 0.46 (10% Et_2O/hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 (dd, J = 8.2, 1.2 Hz, 2H), 7.55 (tt, J = 7.1, 1.2 Hz, 1H), 7.43 (tt, J = 7.6, 1.6 Hz, 2H), 4.91 (d, J = 2.3 Hz, 2H), 2.61 (septet, J = 7.1 Hz, 1H), 1.18 (d, J = 7.1 Hz, 6H); ^{13}C NMR (75.5 MHz, $CDCl_3$,) δ 166.0, 133.0, 129.9, 129.8, 128.3, 93.0, 73.3, 53.3, 22.7, 20.6; IR (film, cm^{-1}) 3064, 2972,

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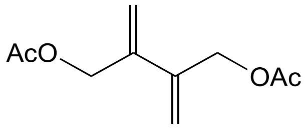
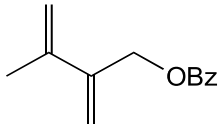
[4] (a) Wuest, F. R.; Berndt, M., *J. Labelled Compd. Radiopharm.* **2006**, *49*, 91-100. (b) Aoyagi, S.; Wang, T. C.; Kibayashi, C., *J. Am. Chem. Soc.* **1993**, *115*, 11393-11409. (c) Hennion, G. F.; Kupiecki, F. P., *J. Org. Chem.* **1953**, *18*, 1601-1609. (d) Peng, Y.; Cui, L.; Zhang, G.; Zhang, L., *J. Am. Chem. Soc.* **2009**, *131*, 5062-5063.

[5] Wender, P. A.; Deschamps, N. M.; Williams, T. J., *Angew. Chem. Int. Ed.* **2004**, *43*, 3076-3079.

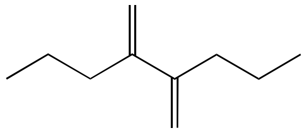
1725(s), 1371, 1268(s), 1177, 1108, 709; HRMS (EI+) *m/z* calcd for $[C_{13}H_{14}O_2]^+$ 202.0988, found 202.09933.



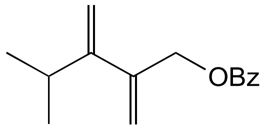
(2a) colorless, low melting solid; R_f 0.45 (50% Et_2O/hexane); ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.34 (s, 2H), 5.32 (s, 2H), 4.78 (s, 4H), 2.10 (s, 6H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 170.6, 139.3, 115.8, 64.9, 20.9 IR (film, cm^{-1}) 2946, 1747(s), 1379, 1220(s), 1156, 1028.



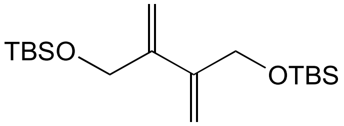
(2b) Colorless oil; R_f 0.46 (10% Et_2O/hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.8 Hz, 2H), 7.55 (t, *J* = 7.0 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 5.37 (s, 1H), 5.34 (s, 1H), 5.16 (s, 1H), 5.08 (s, 1H), 5.05 (s, 2H), 1.97 (s, 3H) ; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 166.2, 142.0, 140.4, 132.9, 130.2, 129.6, 128.3, 115.0, 113.5, 65.3, 20.9; IR (film, cm^{-1}) 3093, 2948, 1720(s), 1602, 1272(s), 1110, 897, 710 cm^{-1}; HRMS (EI+) *m/z* calcd for $[C_{13}H_{14}O_2]^+$ 202.0988, found 202.09877.



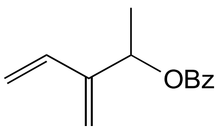
(2c) colorless oil; R_f 0.63 (hexane); ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.05 (d, *J* = 1.2 Hz, 2H), 4.90 (s, 2H) 2.21 (t, *J* = 7.6 Hz, 4H), 1.47 (sextet, *J* = 7.67 Hz, 4H), 0.91 (t, *J* = 7.6 Hz, 6H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 147.7, 111.4, 36.4, 21.7, 13.9.



(2d) colorless oil; R$_f$ 0.50 (10% Et_2O/hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06 (dd, *J* = 8.8, 1.5 Hz, 2H), 7.55 (tt, *J* = 7.6, 1.5 Hz, 1H), 7.43 (tt, *J* = 7.6, 1.7 Hz, 2H), 5.32 (s, 2H), 5.13 (s, 1H), 5.03 (s, 1H), 4.99 (s, 2H), 2.65 (septet, *J* = 6.2 Hz, 1H), 1.10 (d, *J* = 6.2 Hz, 6H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 166.2, 152.2, 142, 8, 132.9, 130.2, 129.6, 128.3, 113.9, 109.8, 66.2, 30.2, 22.1; IR(film, cm^{-1}): 3092, 2934, 1722 (s), 1601, 1269(s), 1112, 900, 710 cm^{-1}; HRMS (EI+) *m/z* calcd for $[C_{15}H_{18}O_2]^+$: 230.1307, found 230.13063.



(2e) colorless oil; R$_f$ 0.54 (5% Et_2O/hexane); ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.29 (s, 2H), 5.10 (s, 2H), 4.33 (s, 4H), 0.93 (s, 18H), 0.08 (s, 12H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 144.1, 110.0, 63.8, 25.9, 18.4; IR(film, cm^{-1}) 2930, 2857, 1601, 1255, 1080, 837 cm^{-1}; HRMS (ESI+) *m/z* calcd for $[C_{18}H_{39}O_2Si_2]^+$; 343.2483 (M+H$^+$); found 343.24850.



(2f) colorless oil; R$_f$ 0.44 (10% Et_2O/hexane); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.07 (dd, *J* = 7.6, 1.7 Hz, 2H), 7.55 (tt, *J* = 7.6, 1.7 Hz, 1H), 7.43 (tt, *J* = 7.6, 1.7 Hz), 6.37 (dd, *J* = 18.0, 11.1 Hz, 1H), 5.85 (q, *J* = 6.4 Hz, 1H), 5.40 (d, *J* = 18.0 Hz, 1H), 5.33 (d, *J* = 1.1 Hz, 1H), 5.19 (s, 1H) , 5.16 (d, *J* = 11.1 Hz, 1H), 1.54 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 165.6, 146.5, 135.7, 132.9, 130.5, 129.5, 128.3, 114.8, 114.7, 70.0, 20.3.

Failed Ethylene-Alkyne Metathesis (Table 1, entries 7 and 8)

Reaction of alkyne **1g** under the standard conditions gave no reaction by TLC (10% Et_2O/hexane). ^{1}H NMR of the crude reaction mixture showed no consumption (± 5%) of **1g** in the presence of an internal standard.

Reaction of alkyne **1h** under the standard conditions exhibited several new spots by TLC (20% Et_2O/hexane). ^{1}H NMR of the crude reaction mixture showed 30% consumption (± 5%) of

1h relative to an internal standard. The crude spectrum showed peaks matching the expected 1,3-diene[6] in approximately 10% yield. Other products could not be identified, though alkyne oligomerization[7] may explain the disagreement between percent conversion and the percent yield of the 1,3-diene.

---

[6] Nájera, C.; Sansano, J. M., *Tetrahedron* **1994**, *50*, 5829-5844.

[7] Diver, S. T.; Kulkarni, A. A.; Clark, D. A.; Peppers, B. P. *J. Am. Chem. Soc.* **2007**, *129*, 5832-5833.

Sample Name:
tmg178c
Data Collected on:
roesy.chem.buffalo.edu-mercury300
Archive directory:

Sample directory:

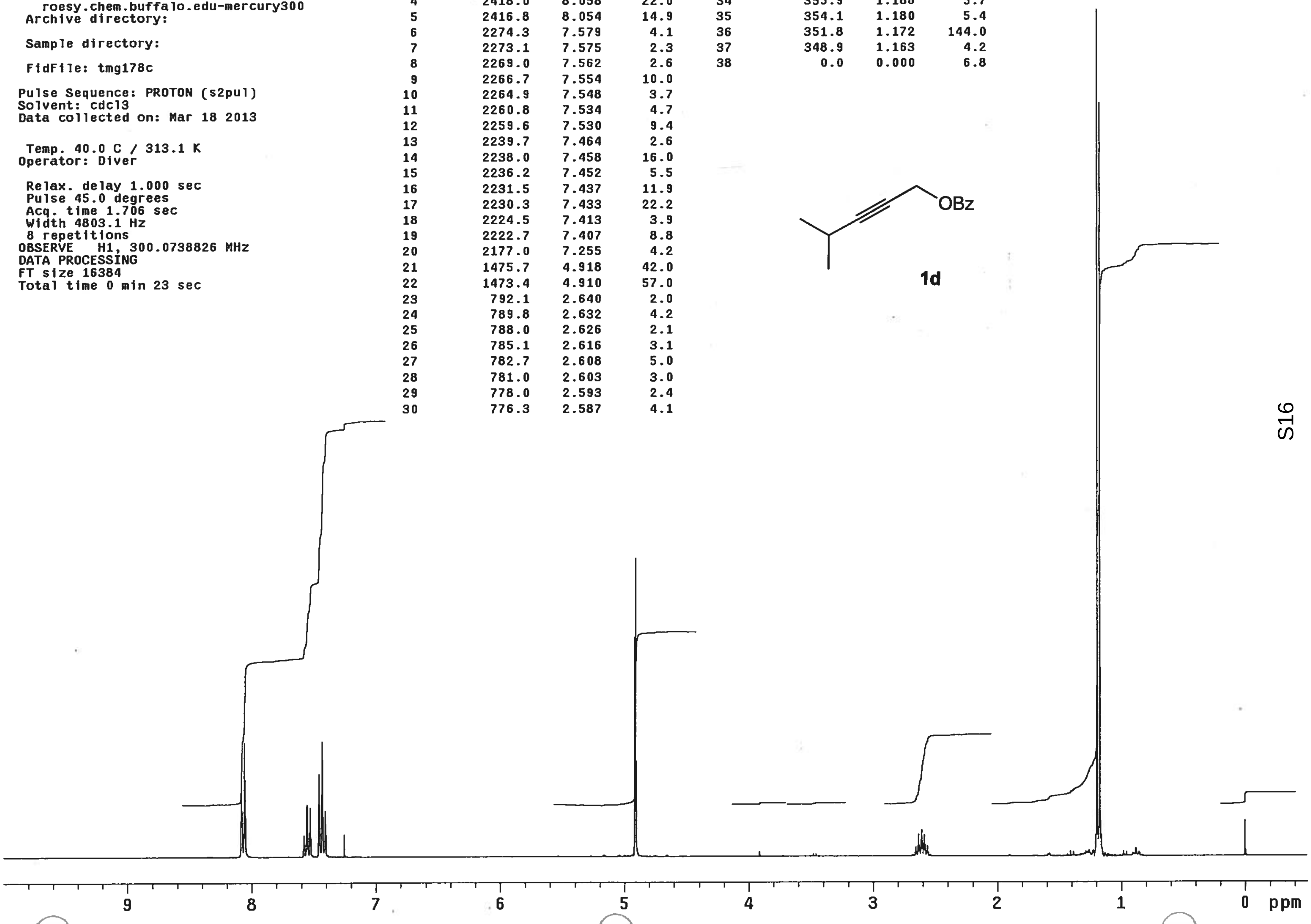
FidFile: tmg178c

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Mar 18 2013

Temp. 40.0 C / 313.1 K
Operator: Diver

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.706 sec
Width 4803.1 Hz
8 repetitions
OBSERVE H1, 300.0738826 MHz
DATA PROCESSING
FT size 16384
Total time 0 min 23 sec

INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	2426.2	8.085	12.3	31	773.9	2.579	2.2
2	2425.0	8.081	16.6	32	769.2	2.564	2.0
3	2420.3	8.066	4.5	33	358.8	1.196	162.0
4	2418.0	8.058	22.0	34	355.9	1.186	5.7
5	2416.8	8.054	14.9	35	354.1	1.180	5.4
6	2274.3	7.579	4.1	36	351.8	1.172	144.0
7	2273.1	7.575	2.3	37	348.9	1.163	4.2
8	2269.0	7.562	2.6	38	0.0	0.000	6.8
9	2266.7	7.554	10.0				
10	2264.9	7.548	3.7				
11	2260.8	7.534	4.7				
12	2259.6	7.530	9.4				
13	2239.7	7.464	2.6				
14	2238.0	7.458	16.0				
15	2236.2	7.452	5.5				
16	2231.5	7.437	11.9				
17	2230.3	7.433	22.2				
18	2224.5	7.413	3.9				
19	2222.7	7.407	8.8				
20	2177.0	7.255	4.2				
21	1475.7	4.918	42.0				
22	1473.4	4.910	57.0				
23	792.1	2.640	2.0				
24	789.8	2.632	4.2				
25	788.0	2.626	2.1				
26	785.1	2.616	3.1				
27	782.7	2.608	5.0				
28	781.0	2.603	3.0				
29	778.0	2.593	2.4				
30	776.3	2.587	4.1				



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STANDARD CARBON PARAMETERS

 Sample Name:
   tmg178c
 Data Collected on:
   roesy.chem.buffalo.edu-mercury300
 Archive directory:

 Sample directory:

 FidFile: CARBON

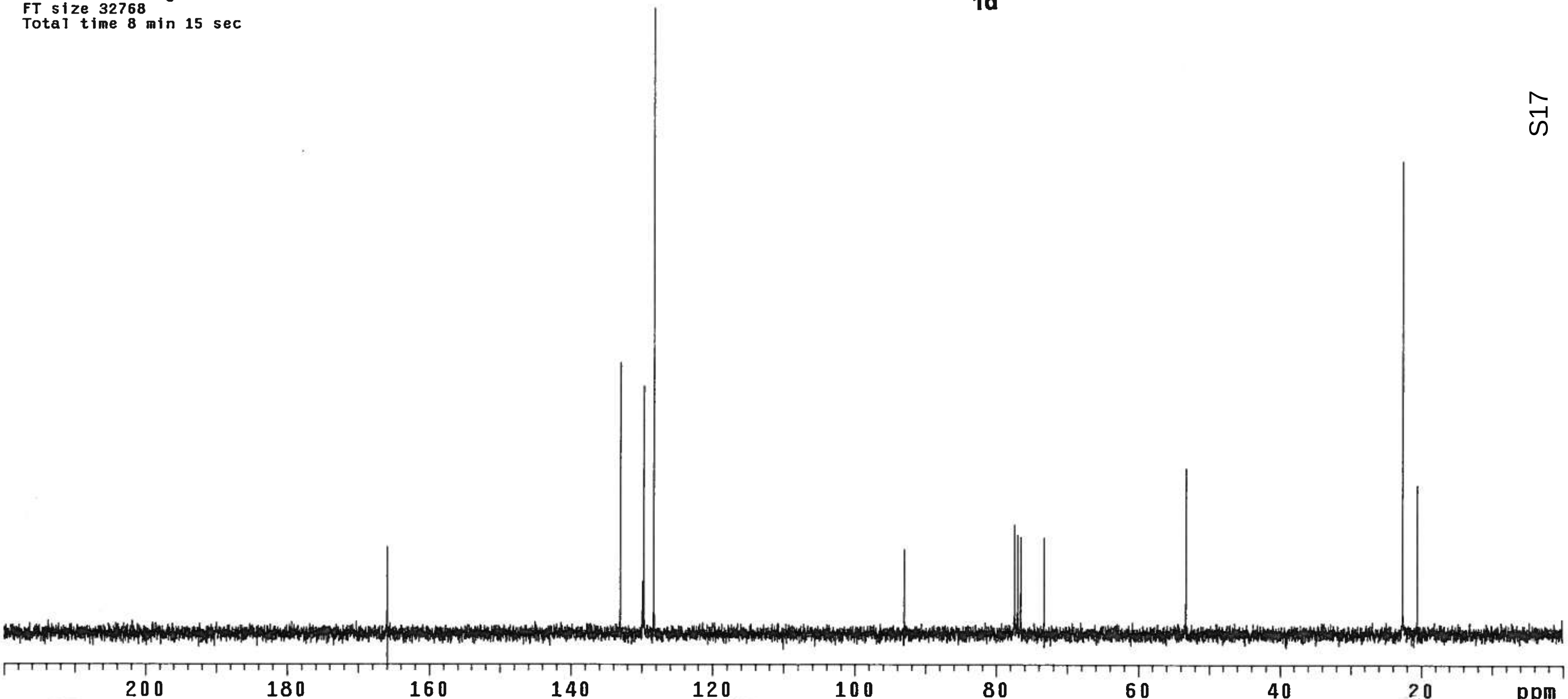
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Mar 18 2013

 Temp. 40.0 C / 313.1 K
Operator: Diver

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 0.868 sec
 Width 18867.9 Hz
 128 repetitions
OBSERVE  C13,  75.4536354 MHz
DECOUPLE  H1, 300.0754430 MHz
 Power 38 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 0.5 Hz
FT size 32768
Total time 8 min 15 sec
```

```
INDEX    FREQUENCY  PPM      HEIGHT
  1       12522.6  165.965     13.9
  2       10038.6  133.044     43.4
  3        9803.7  129.930      8.4
  4        9791.0  129.762     39.7
  5        9682.8  128.328    100.0
  6        7019.1   93.026     13.5
  7        5842.2   77.427     17.5
  8        5809.9   77.000     15.9
  9        5778.8   76.588     15.5
 10        5530.1   73.291     15.4
 11        4020.3   53.282     26.5
 12        1712.5   22.696     75.4
 13        1552.4   20.575     23.8
```

1d



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STANDARD PROTON PARAMETERS

 Sample Name:
   tmg1106b
 Data Collected on:
   roesy.chem.buffalo.edu-mercury300
 Archive directory:

 Sample directory:

 FidFile: PROTON

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: May  2 2013

 Temp. 25.0 C / 298.1 K
Operator: Diver

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 1.706 sec
 Width 4803.1 Hz
 8 repetitions
OBSERVE   H1, 300.0738750 MHz
DATA PROCESSING
FT size 16384
Total time 0 min 23 sec
```

```
INDEX    FREQUENCY   PPM      HEIGHT
  1        2184.6   7.280       2.8
  2        1601.8   5.338      24.3
  3        1594.8   5.315      37.4
  4        1434.1   4.779      56.9
  5         629.7   2.098     151.2
  6         627.9   2.093       2.4
  7         626.2   2.087       2.4
  8           0.0   0.000       4.1
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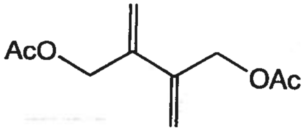
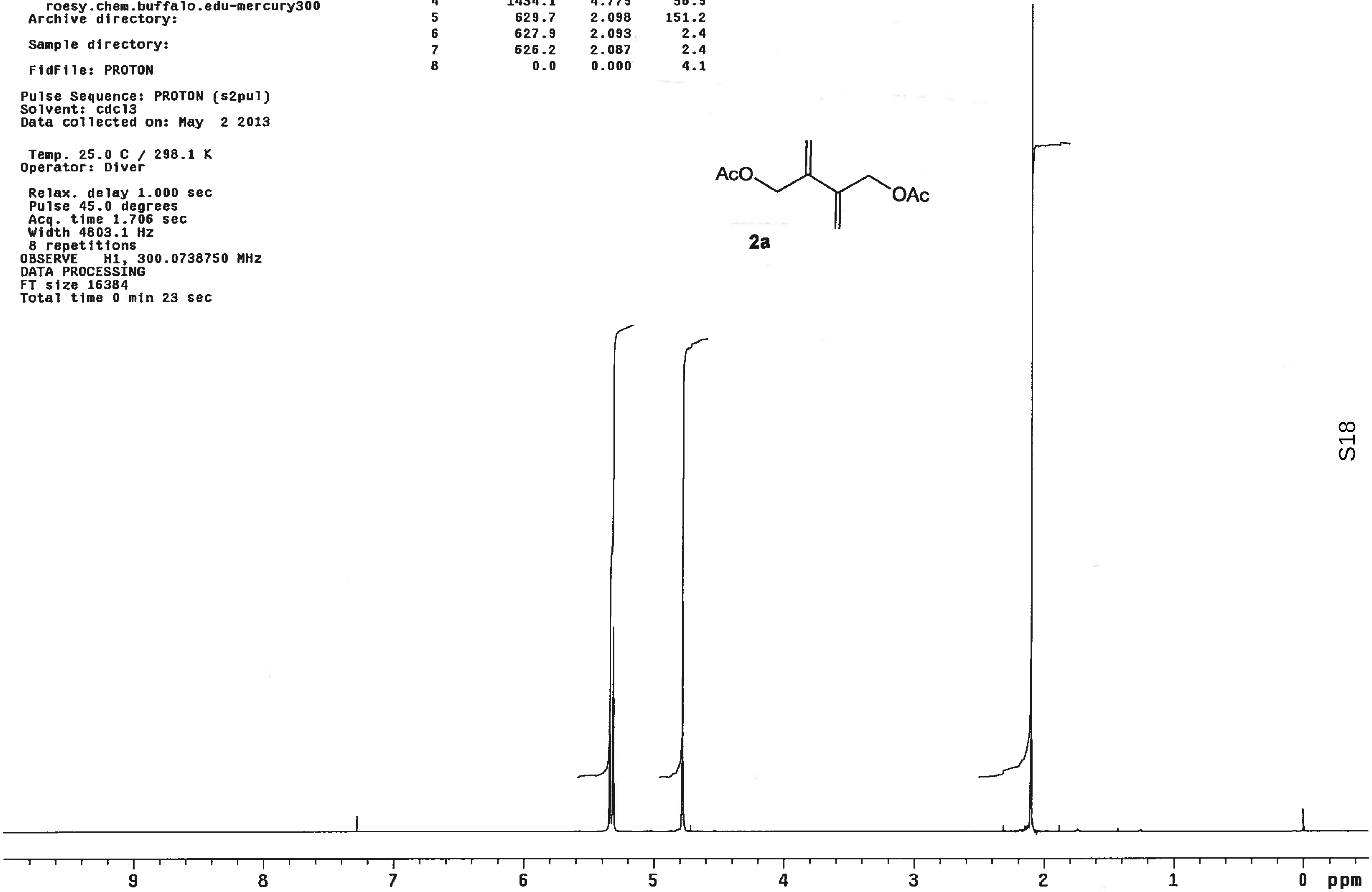


2a



```
STANDARD CARBON PARAMETERS

 Sample Name:
   tmg1106b
 Data Collected on:
   roesy.chem.buffalo.edu-mercury300
 Archive directory:

 Sample directory:

 FidFile: CARBON

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: May  2 2013

 Temp. 25.0 C / 298.1 K
Operator: Diver

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 0.868 sec
 Width 18867.9 Hz
 48 repetitions
OBSERVE  C13,  75.4536400 MHz
DECOUPLE  H1, 300.0754430 MHz
 Power 38 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 0.5 Hz
FT size 32768
Total time 8 min 41 sec
```

```
INDEX    FREQUENCY  PPM     HEIGHT
  1        12869.3  170.559    4.4
  2        10507.3  139.255   16.8
  3         8738.5  115.812   24.1
  4         5842.2   77.427   11.0
  5         5809.9   77.000   11.6
  6         5777.7   76.573   12.2
  7         4895.6   64.882   25.0
  8         1575.5   20.880   15.4
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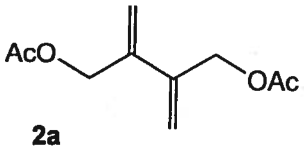
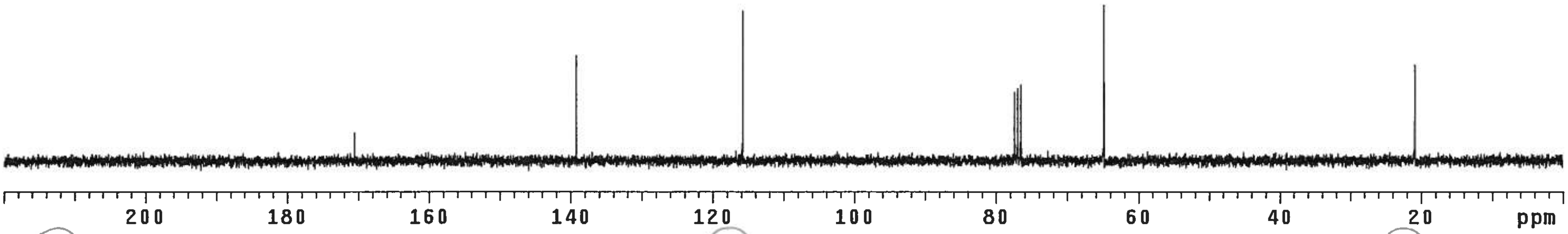


2a



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STANDARD PROTON PARAMETERS

 Sample Name:
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 Data Collected on:
   roesy.chem.buffalo.edu-mercury300
 Archive directory:

 Sample directory:

 FidFile: PROTON

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Apr 30 2013

 Temp. 25.0 C / 298.1 K
Operator: Diver

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 1.706 sec
 Width 4803.1 Hz
 8 repetitions
OBSERVE   H1, 300.0738838 MHz
DATA PROCESSING
FT size 16384
Total time 0 min 23 sec
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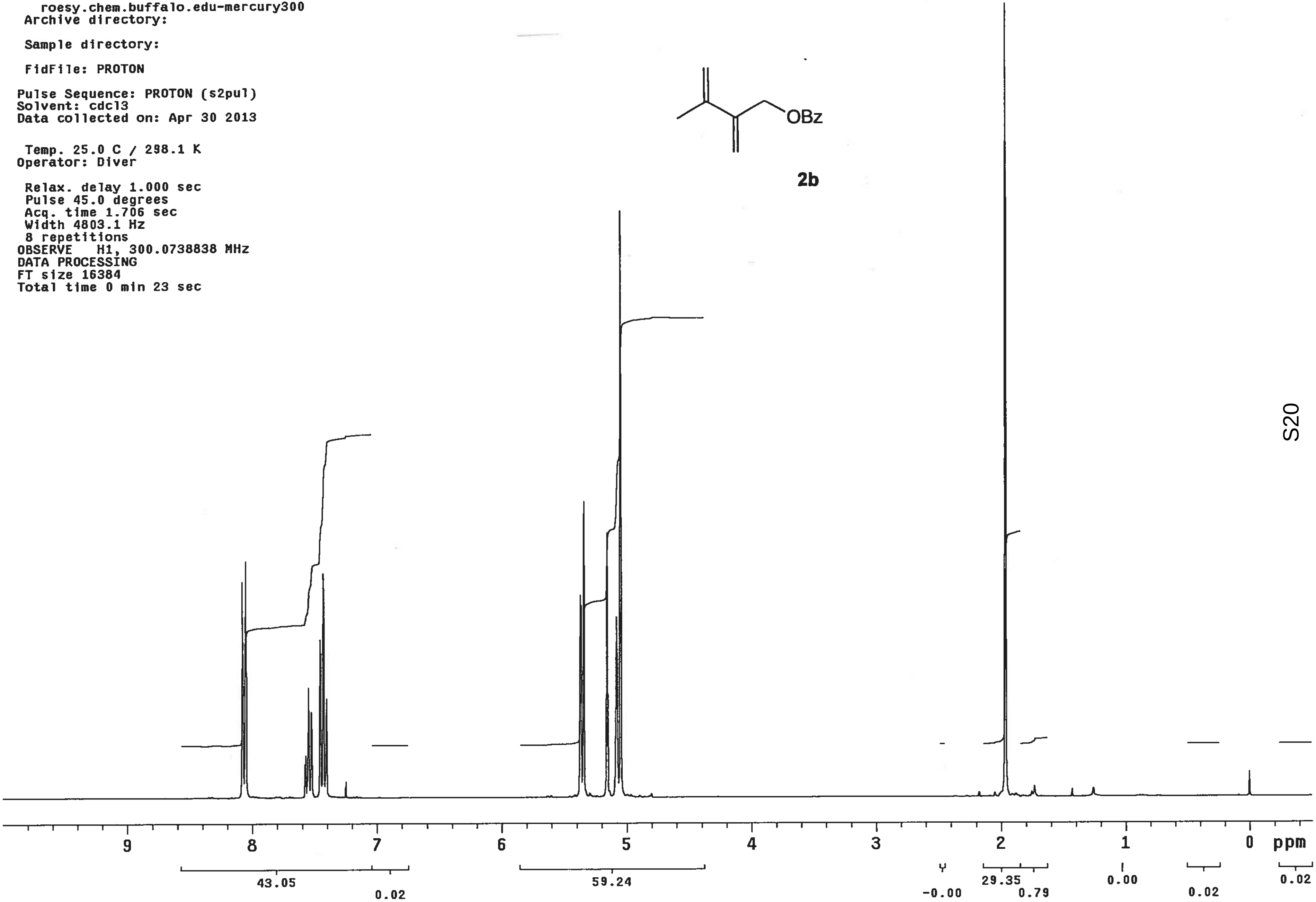
2b

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STANDARD CARBON PARAMETERS

 Sample Name:
   tmg1103b
 Data Collected on:
   roesy.chem.buffalo.edu-mercury300
 Archive directory:

 Sample directory:

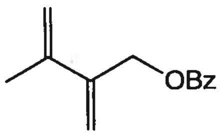
 FidFile: CARBON

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Apr 30 2013

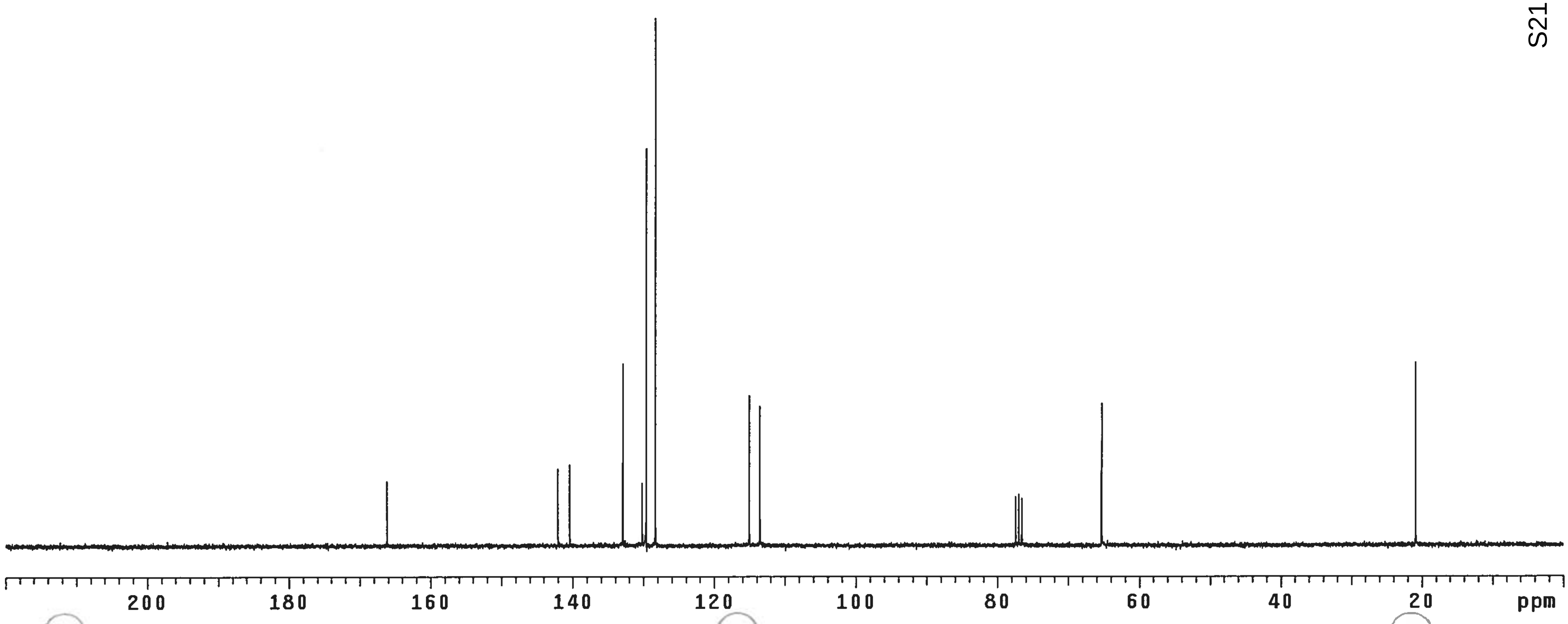
 Temp. 25.0 C / 298.1 K
Operator: Diver

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 0.868 sec
 Width 18867.9 Hz
 256 repetitions
OBSERVE  C13,  75.4536423 MHz
DECOUPLE  H1, 300.0754430 MHz
 Power 38 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 0.5 Hz
FT size 32768
Total time 8 min 15 sec
```

INDEX	FREQUENCY	PPM	HEIGHT
1	12537.6	166.163	10.3
2	10718.1	142.049	12.3
3	10593.7	140.400	13.0
4	10028.3	132.906	29.2
5	9821.0	130.159	10.1
6	9778.4	129.594	63.6
7	9681.6	128.312	84.5
8	8680.9	115.049	24.2
9	8565.7	113.523	22.4
10	5842.2	77.427	7.8
11	5809.9	77.000	8.2
12	5777.7	76.573	7.5
13	4927.8	65.309	22.8
14	1576.6	20.895	29.3



2b



STANDARD PROTON PARAMETERS

Sample Name:
tmg1108b
Data Collected on:
roesy.chem.buffalo.edu-mercury300
Archive directory:

Sample directory:

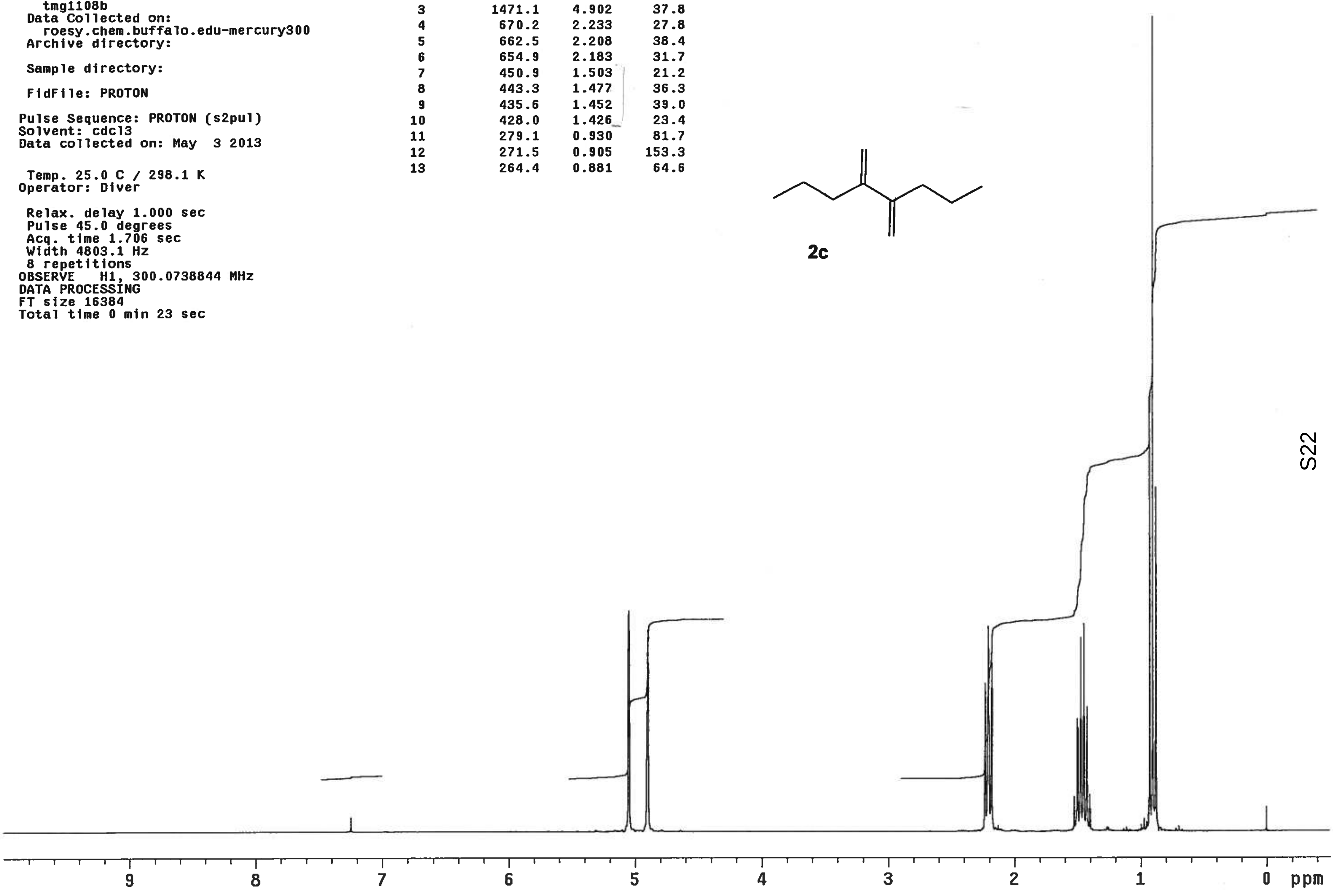
FidFile: PROTON

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: May 3 2013

Temp. 25.0 C / 298.1 K
Operator: Diver

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.706 sec
Width 4803.1 Hz
8 repetitions
OBSERVE H1, 300.0738844 MHz
DATA PROCESSING
FT size 16384
Total time 0 min 23 sec

INDEX	FREQUENCY	PPM	HEIGHT
1	1516.2	5.053	40.8
2	1515.0	5.049	41.4
3	1471.1	4.902	37.8
4	670.2	2.233	27.8
5	662.5	2.208	38.4
6	654.9	2.183	31.7
7	450.9	1.503	21.2
8	443.3	1.477	36.3
9	435.6	1.452	39.0
10	428.0	1.426	23.4
11	279.1	0.930	81.7
12	271.5	0.905	153.3
13	264.4	0.881	64.6


2c

STANDARD CARBON PARAMETERS

Sample Name:
  tmg1108b
Data Collected on:
  roesy.chem.buffalo.edu-mercury300
Archive directory:

Sample directory:

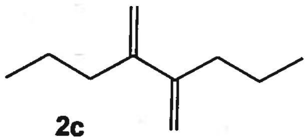
FidFile: CARBON

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: May 3 2013

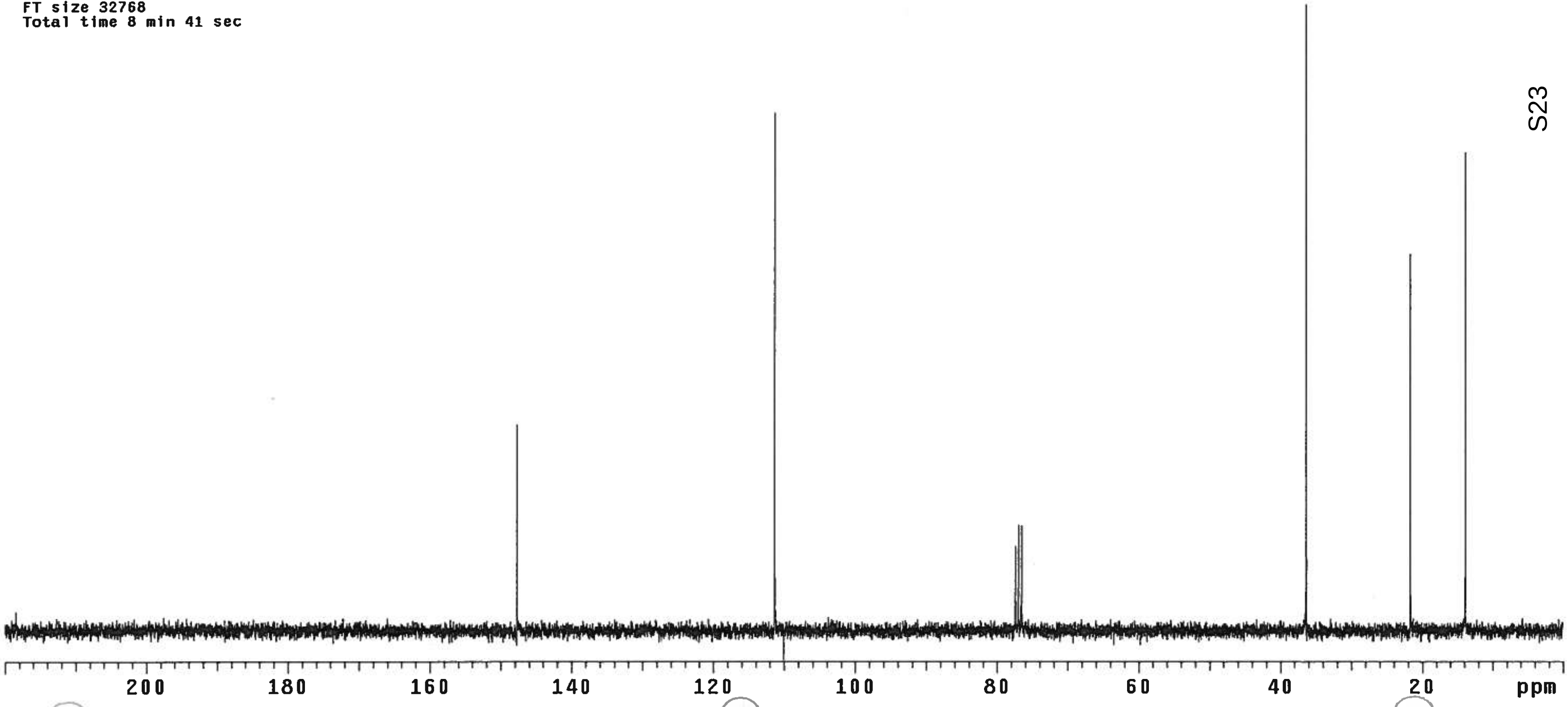
Temp. 25.0 C / 298.1 K
Operator: Diver

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 0.868 sec
Width 18867.9 Hz
64 repetitions
OBSERVE C13, 75.4536366 MHz
DECOUPLE H1, 300.0754430 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 8 min 41 sec

INDEX	FREQUENCY	PPM	HEIGHT
1	11147.6	147.741	33.0
2	8403.3	111.371	82.8
3	5841.0	77.412	13.5
4	5809.9	77.000	16.8
5	5777.7	76.573	16.7
6	2745.5	36.387	100.0
7	1638.8	21.719	60.0
8	1050.3	13.920	76.2



2c



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STANDARD PROTON PARAMETERS

 Sample Name:
   tmg1104b
 Data Collected on:
   roesy.chem.buffalo.edu-mercury300
 Archive directory:

 Sample directory:

 FidFile: tmg1104b

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: May  1 2013

 Temp. 25.0 C / 298.1 K
Operator: Diver

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 1.706 sec
 Width 4803.1 Hz
 8 repetitions
OBSERVE   H1, 300.0738838 MHz
DATA PROCESSING
FT size 16384
Total time 0 min 23 sec
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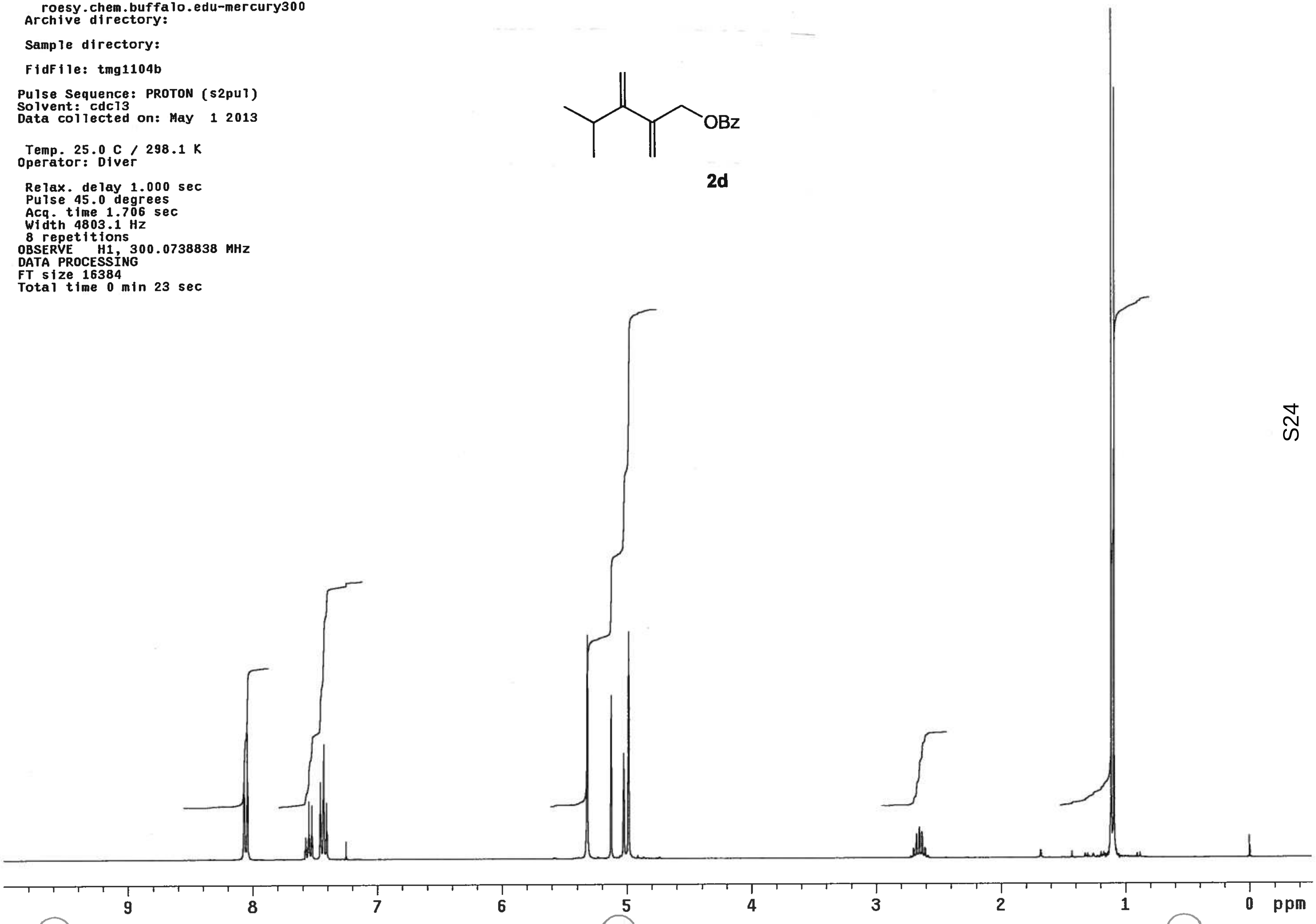


2d

```
STANDARD CARBON PARAMETERS

 Sample Name:
   tmg1104b
 Data Collected on:
   roesy.chem.buffalo.edu-mercury300
 Archive directory:

 Sample directory:

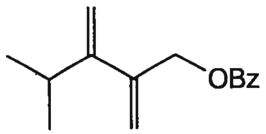
 FidFile: CARBON

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: May  1 2013

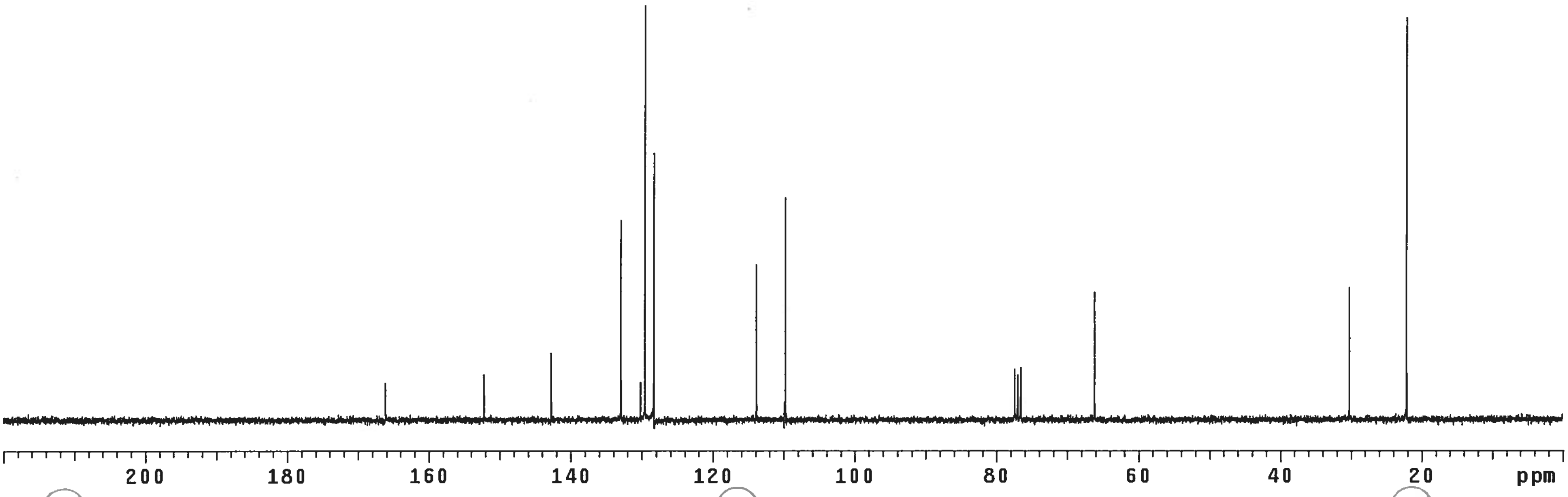
 Temp. 25.0 C / 298.1 K
Operator: Diver

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 0.868 sec
 Width 18867.9 Hz
 128 repetitions
OBSERVE  C13,  75.4536400 MHz
DECOUPLE  H1, 300.0754430 MHz
 Power 38 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 0.5 Hz
FT size 32768
Total time 8 min 15 sec
```

INDEX	FREQUENCY	PPM	HEIGHT
1	12537.6	166.163	5.8
2	11487.4	152.244	7.2
3	10772.2	142.766	10.7
4	10029.4	132.922	32.0
5	9824.4	130.205	5.9
6	9778.4	129.594	66.3
7	9683.9	128.343	42.7
8	8595.7	113.920	24.9
9	8284.7	109.799	35.6
10	5842.2	77.427	8.0
11	5809.9	77.000	7.1
12	5778.8	76.588	8.3
13	4992.3	66.164	20.5
14	2281.4	30.236	21.3
15	1669.9	22.132	64.2



2d



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STANDARD PROTON PARAMETERS

 Sample Name:
   tmg1101b
 Data Collected on:
   roesy.chem.buffalo.edu-mercury300
 Archive directory:

 Sample directory:

 FidFile: tmg1101b

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Apr 29 2013

 Temp. 25.0 C / 298.1 K
Operator: Diver

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 1.706 sec
 Width 4803.1 Hz
 8 repetitions
OBSERVE   H1, 300.0738844 MHz
DATA PROCESSING
FT size 16384
Total time 0 min 23 sec
```
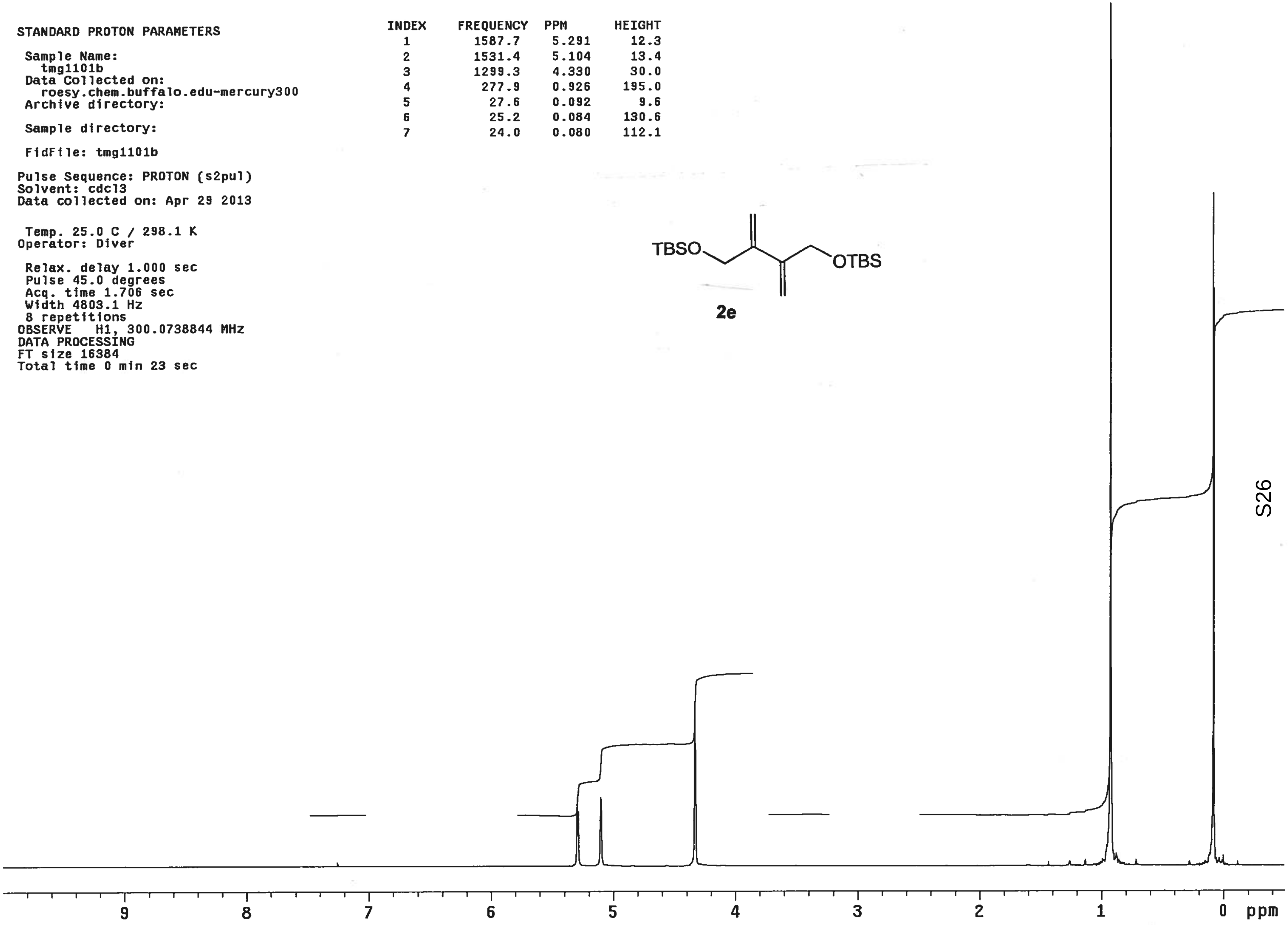
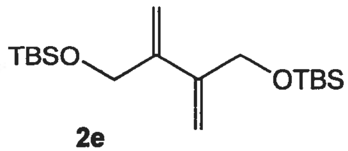

```
INDEX    FREQUENCY   PPM      HEIGHT
  1        1587.7    5.291     12.3
  2        1531.4    5.104     13.4
  3        1299.3    4.330     30.0
  4         277.9    0.926    195.0
  5          27.6    0.092      9.6
  6          25.2    0.084    130.6
  7          24.0    0.080    112.1
```



2e

```
STANDARD CARBON PARAMETERS

 Sample Name:
   tmg1101b
 Data Collected on:
   roesy.chem.buffalo.edu-mercury300
 Archive directory:

 Sample directory:

 FidFile: CARBON

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Apr 29 2013

 Temp. 25.0 C / 298.1 K
Operator: Diver

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 0.868 sec
 Width 18867.9 Hz
 64 repetitions
OBSERVE  C13,  75.4536377 MHz
DECOUPLE  H1, 300.0754430 MHz
 Power 38 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 0.5 Hz
FT size 32768
Total time 8 min 41 sec
```

```
INDEX   FREQUENCY   PPM      HEIGHT
  1      10870.1  144.063     13.9
  2       8297.4  109.967     24.4
  3       4812.6   63.783     41.9
  4       1954.4   25.901    100.0
  5       1385.5   18.362     20.3
```



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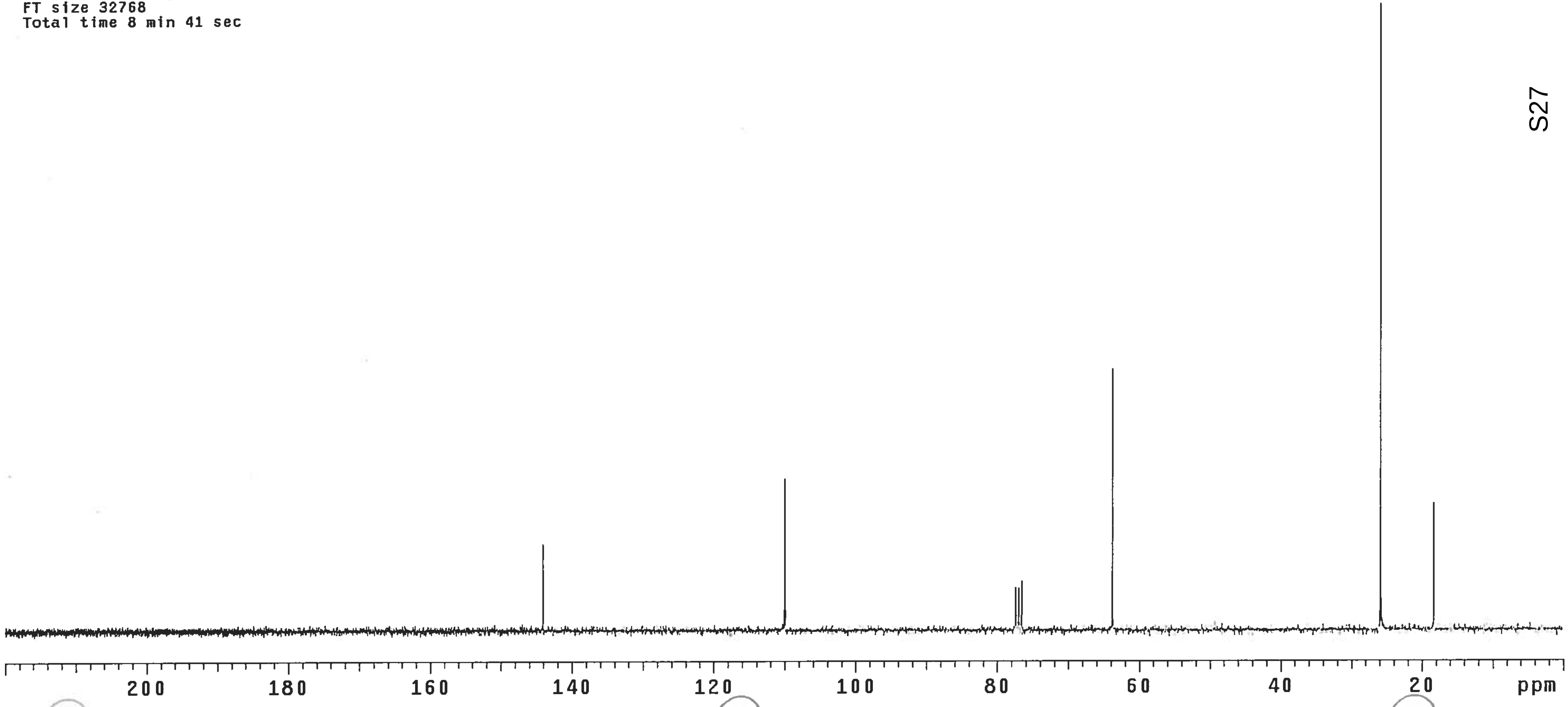


STANDARD PROTON PARAMETERS

Sample Name:
tmg1102b
Data Collected on:
roesy.chem.buffalo.edu-mercury300
Archive directory:

Sample directory:

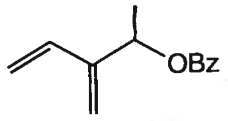
FidFile: PROTON

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Apr 30 2013

Temp. 25.0 C / 298.1 K
Operator: Diver

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.706 sec
Width 4803.1 Hz
8 repetitions
OBSERVE H1, 300.0738844 MHz
DATA PROCESSING
FT size 16384
Total time 0 min 23 sec

INDEX	FREQUENCY	PPM	HEIGHT
1	2426.2	8.085	27.2
2	2425.0	8.081	27.6
3	2423.2	8.075	12.3
4	2419.7	8.064	8.2
5	2418.0	8.058	36.8
6	2416.2	8.052	26.7
7	2267.9	7.558	5.4
8	2265.5	7.550	16.7
9	2259.6	7.530	9.8
10	2257.9	7.524	10.4
11	2256.7	7.521	9.6
12	2240.3	7.466	5.3
13	2238.5	7.460	19.3
14	2236.8	7.454	11.8
15	2232.1	7.438	19.5
16	2230.9	7.435	28.1
17	2225.1	7.415	7.4
18	2223.3	7.409	17.4
19	2222.1	7.405	6.4
20	2175.2	7.249	6.2
21	1927.8	6.424	7.7
22	1916.1	6.385	8.3
23	1909.6	6.364	10.6
24	1898.5	6.327	10.8
25	1760.1	5.866	10.2
26	1758.9	5.862	12.3
27	1752.5	5.840	11.7
28	1629.9	5.432	21.0
29	1611.8	5.371	20.8
30	1600.6	5.334	25.8
31	1599.5	5.330	25.6
32	1558.4	5.193	31.0
33	1554.3	5.180	17.4
34	1543.2	5.143	15.3
35	464.9	1.549	162.0
36	458.5	1.528	151.0
37	-0.0	-0.000	11.5



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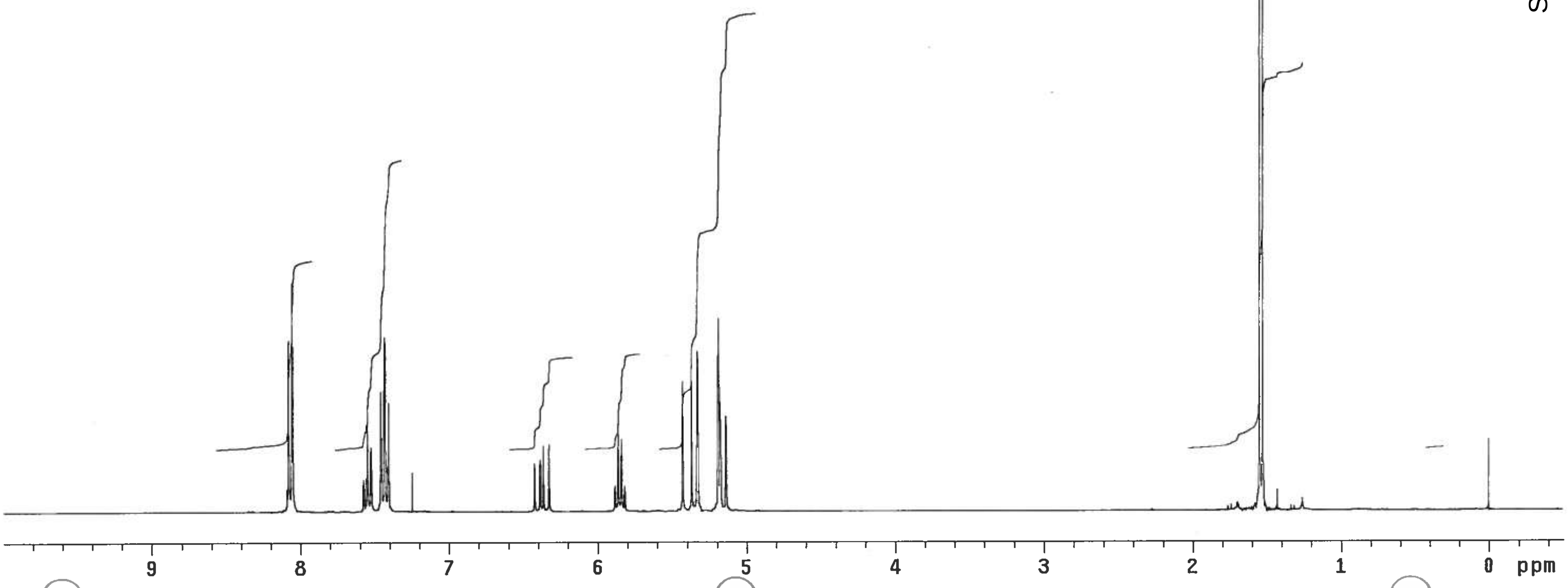
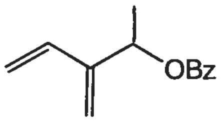


```
STANDARD CARBON PARAMETERS

 Sample Name:
   tmg102b
 Data Collected on:
   roesy.chem.buffalo.edu-mercury300
 Archive directory:

 Sample directory:

 FidFile: CARBON

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Apr 30 2013

 Temp. 25.0 C / 298.1 K
Operator: Diver

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 0.868 sec
 Width 18867.9 Hz
 192 repetitions
OBSERVE  C13,  75.4536412 MHz
DECOUPLE  H1, 300.0754430 MHz
 Power 38 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 0.5 Hz
FT size 32768
Total time 8 min 41 sec
```

```
INDEX    FREQUENCY   PPM      HEIGHT
  1       12496.2  165.614     10.8
  2       11052.0  146.475     31.1
  3       10239.0  135.699     41.0
  4       10024.8  132.861     71.3
  5        9844.0  130.464     15.7
  6        9774.9  129.549     58.4
  7        9680.5  128.297    100.0
  8        8663.6  114.820     77.0
  9        8655.6  114.713     61.8
 10        5842.2   77.427     16.6
 11        5809.9   77.000     15.2
 12        5778.8   76.588     13.0
 13        5282.5   70.010     45.4
 14        1531.7   20.300     73.7
```



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