Supporting Information for:

Nitrate as a Redox Co-Catalyst for the Aerobic Pd-Catalyzed Oxygenation of Unactivated sp^3-C–H Bonds

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1. General Information

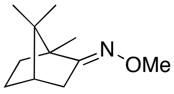
NMR spectra were obtained on a Varian Inova 500 (499.90 MHz for ^1H; 125.70 MHz for ^{13}C) or a Varian vnmrs 500 (499.90 MHz for ^1H; 125.70 MHz for ^{13}C) or a Varian MR400 (400.53 MHz for ^1H; 100.71 MHz for ^{13}C; 375.94 MHz for ^{19}F) spectrometer. ^1H NMR chemical shifts are reported in parts per million (ppm) relative to TMS, with the residual solvent peak used as an internal reference. The chloroform reference peak is set to 7.23 ppm for ^1H and 77.23 ppm for ^{13}C. In the case of benzene, the reference peak is set to 7.16 ppm. Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), doublet of doublets of doublets (ddd), doublet of triplets (dt), triplet (t), quartet (q), quintet (quin), multiplet (m), and broad resonance (br). IR spectra were obtained on a Perkin-Elmer spectrum BX FT-IR spectrometer. Melting points were determined with a Mel-Temp 3.0 (Laboratory Devices Inc) and are uncorrected. HRMS data were obtained on a Micromass AutoSpec Ultima Magnetic Sector mass spectrometer.

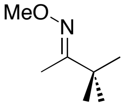
2. Materials and Methods

$Pd(OAc)_2$ was obtained from Pressure Chemical and used as received. $NaNO_3$ was obtained from Fisher Scientific and used as received. 4 Å molecular sieves were dried in Precision Economy Oven at 200 ºC for 48 h. Solvents were obtained from Fisher Chemical and used without further purification. Flash chromatography was performed on EM Science silica gel 60 (0.040–0.063 mm particle size, 230–400 mesh) and thin layer chromatography was performed on Merck TLC plates pre-coated with silica gel 60 F254. HPLC purification of **13-15** was performed on a Varian ProStar 210 HPLC using Waters *μ*-Porasil 10*μ*m silica (19 x 300 mm) columns.

3. Synthesis and Characterization of Substrates 1, S3-S11

The oxime ether substrates **1, S3-S6** were prepared via oximation of the corresponding ketones according to a procedure previously reported by our group.[1] ^{1}H and ^{13}C NMR spectral data for **1**, **S3**, **S5**, and **S6** matched that previously reported in the literature for these compounds.[1]


(**1**)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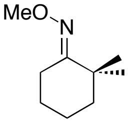
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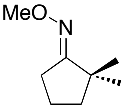
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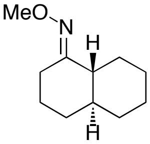
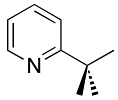
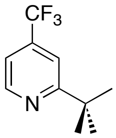

(**S6**)

The pyridine substrates **S7, S8** and **S10** were prepared via Cu-catalyzed coupling between 2-bromopyridine derivatives and the corresponding alkyl magnesium chloride (purchased from Aldrich and used as received) using a procedure previously reported by our group.[2] Substrate **S9** was synthesized as described below using a procedure from a patent.[3] Substrate **S11** was obtained from Sigma-Aldrich and used as received. ^{1}H and ^{13}C NMR spectral data for **S7-S10** matched that previously reported in the literature for these compounds.


(**S7**)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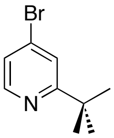
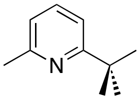

(**S9**)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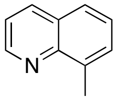
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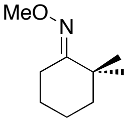

(**S4**)

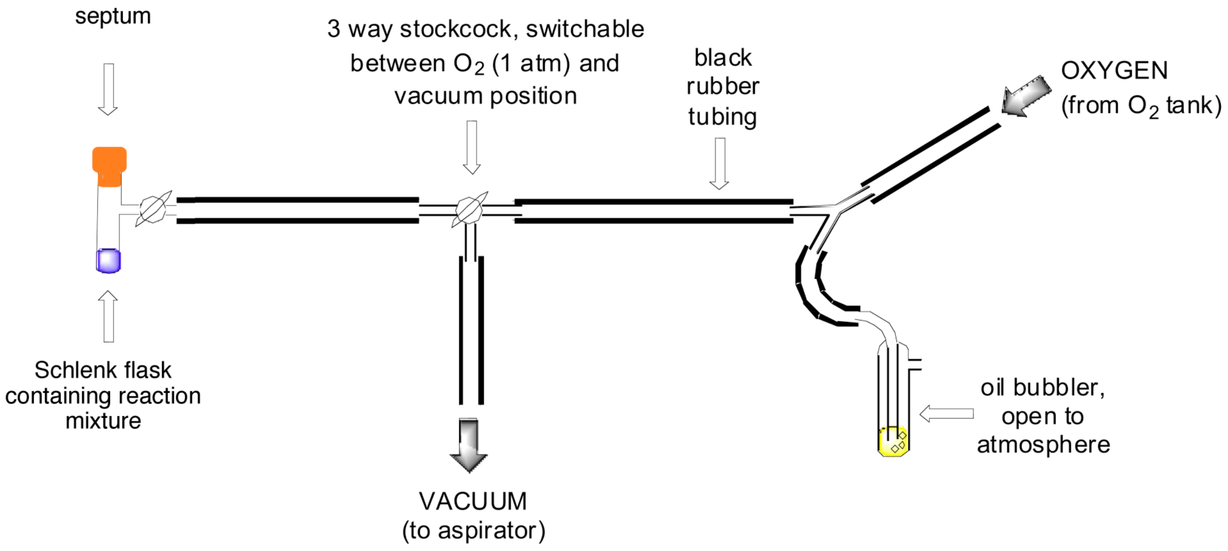
Substrate **S4** was obtained via oximation of the corresponding ketone according to a literature procedure.[1] It was obtained as a colorless oil in 80% isolated yield (R_f = 0.41 in 1:19 ethyl acetate/hexanes). ^{1}H NMR (500 MHz, C_6D_6): δ 3.78 (s, 3H), 2.59 (m, 2H), 1.61-1.65 (multiple peaks, 4H), 1.30 (m, 2H), 1.10 (s, 6H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 165.08, 67.50, 60.98, 41.36, 37.24, 26.77, 26.20, 21.73, 21.23. HRMS EI (m/z): $[M]^+$ calcd for $C_9H_{17}NO$ predicted: 155.1310, measured: 155.1315. IR (thin film) 1625, 1050 cm^{-1}.

4. Apparatus Set-Up and Optimization Table

General procedure for screening (Table 1 in manuscript)

$Pd(OAc)_2$ (2.2 mg, 0.0025 mmol, 0.05 equiv) and the appropriate redox co-catalyst were weighed into a 25 mL Schlenk flask. The solids were dissolved in Ac_2O (0.2 mL). Substrate **1** (36 mg, 0.2 mmol, 1 equiv) was added to the Schlenk flask as a solution in AcOH (1.4 mL). The top of the Schlenk flask was sealed with a rubber septum. The flask was charged with O_2 through the side arm using the set-up shown in Figure S1. The flask was evacuated (aspirator vacuum) and backfilled with oxygen (1 atm) three times through the side arm to achieve 1 atm of O_2. The flask was sealed at the side arm with a glass stopcock and then heated at the desired temperature in an oil bath for 18 h. The reaction was then cooled to room temperature, and 1 M nitrobenzene in $CDCl_3$ (50 µL, 0.5 mmol, 0.25 equiv) was added as a standard. The crude reaction mixtures were analyzed by ^1H NMR spectroscopy using nitrobenzene as an internal standard.

Figure S1. Schematic setup for filling reaction vessels with 1 atm of O_2.



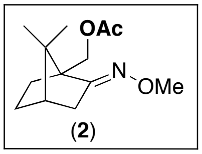
The air-free reaction (Table 1, entry 6) was set up using the same setup as shown in Figure S1 but with N_2 instead of O_2.

The reactions under an air atmosphere (Table 1, entries 1-5) were set up in air and sealed directly.

5. Synthesis and Characterization of Products 2-12

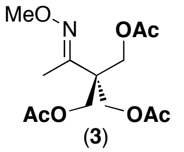
Standard Procedure

$Pd(OAc)_2$ (5.6 mg, 0.025 mmol, 0.05 equiv) and $NaNO_3$ (10.6 mg, 0.125 mmol, 0.25 equiv) were weighed into a 50 mL resealable Schlenk flask. Substrate (0.5 mmol, 1 equiv) was added to the Schlenk flask as a solution in $AcOH/Ac_2O$ (AcOH : Ac_2O = 7 : 1; overall concentration = 0.125 M in substrate). The Schlenk flask was charged with 1 atm of O_2 using the method described above (see Figure S1). The flask was heated at 110 °C in an oil bath for 18 h (unless otherwise noted). The reaction was cooled to rt, filtered through a plug of Celite, and then concentrated under reduced pressure to remove the solvent. The resulting residue was neutralized with a saturated solution of $NaHCO_3$, and the organic products were extracted into either diethyl ether or ethyl acetate. The organic extracts were washed with brine, combined, and then dried over $MgSO_4$. The products were purified by column chromatography on silica gel.



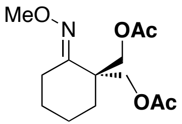
(**2**)

This reaction was conducted with substrate **1** according to the standard procedure. Product **2** was obtained as a pale yellow oil (95 mg, 80% yield, R_f = 0.25 in 1:9 ethyl acetate/hexanes). Spectral data [^{1}H NMR ($CDCl_3$) and $^{13}C\{^1H\}$ NMR ($CDCl_3$)] matched that reported in the literature for this compound.[1]



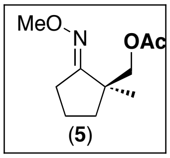
(**3**)

This reaction was conducted with substrate **S3** according to the standard procedure. Product **3** was obtained as a colorless oil (126 mg, 83% yield, R_f = 0.25 in 1:9 ethyl acetate/hexanes). Spectral data [^{1}H NMR ($CDCl_3$) and $^{13}C\{^1H\}$ NMR ($CDCl_3$)] matched that reported in the literature for this compound.[1]



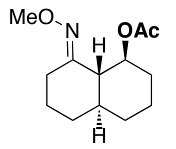
(**4**)

This reaction was conducted with substrate **S4** according to the standard procedure, except using 50 mol % of $NaNO_3$ (0.25 mmol, 0.5 equiv) at 100 °C. Product **4** was obtained as a pale yellow oil (81 mg, 60% yield, R_f = 0.25 in 1:4 ethyl acetate/ hexanes). ^{1}H NMR (500 MHz, C_6D_6): δ 4.64 (d, J = 11.0 Hz, 2H), 4.19 (d, J = 11.0 Hz, 2H), 3.70 (s, 3H), 2.51 (t, J = 6.0 Hz, 2H), 1.65 (two peaks, s, 6H), 1.42 (t, J = 6.5 Hz, 2H), 1.20 (m, 2H), 1.13 (m, 2H). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6): δ 169.97, 157.98, 64.90, 61.37, 44.16, 32.37, 25.32, 21.66, 21.06, 20.32. HRMS electrospray (m/z): $[M+H]^+$ calcd for $C_{13}H_{22}NO_5$ predicted: 272.1492, measured: 272.1491. IR (thin film) 1739 cm^{-1}.



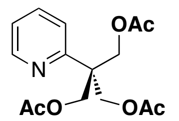
(**5**)

This reaction was conducted with substrate **S5** according to the standard procedure, except using 20 mol % of $Pd(OAc)_2$ (0.1 mmol, 0.2 equiv) at 100 °C. Product **5** was obtained as a pale yellow oil (51 mg, 51% yield, R_f = 0.25 in 3:7 diethyl ether/pentanes). Spectral data [^{1}H NMR ($CDCl_3$) and $^{13}C\{^1H\}$ NMR ($CDCl_3$)] matched that reported in the literature for this compound.[1]



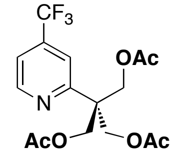
(**6**)

This reaction was conducted with substrate **S6** according to the standard procedure, except using 1 equiv of $NaNO_3$ (0.5 mmol, 1 equiv) under air. Product **6** was obtained as a yellow oil in (49 mg, 41% yield, R_f = 0.25 in 1:4 ethyl acetate/hexanes). Spectral data [^{1}H NMR ($CDCl_3$) and $^{13}C\{^1H\}$ NMR ($CDCl_3$)] matched that reported in the literature for this compound.[1]



(**7**)

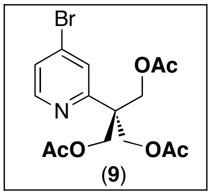
This reaction was conducted with substrate **S7** according to the standard procedure, except that 4 Å molecular sieves (270 mg) were added. Product **7** was obtained as a colorless oil (122 mg, 79% yield, R_f = 0.2 in 3:7 ethyl acetate/hexanes). Spectral data [^{1}H NMR ($CDCl_3$) and $^{13}C\{^1H\}$ NMR ($CDCl_3$)] that reported in the literature for this compound.[1]



(**8**)

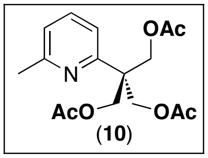
This reaction was conducted with substrate **S8** according to the standard procedure, except using 50 mol % of $NaNO_3$ (0.25 mmol, 0.5 equiv) along with 4 Å molecular sieves (270 mg). Product **8** was obtained as a colorless oil in (147 mg, 78% yield, R_f = 0.2 in 1:9 ethyl acetate/hexanes). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.74 (d, *J* = 4.8 Hz, 1H), 7.44 (s, 1H), 7.41 (d, *J* = 4.8 Hz, 1H), 4.52 (s, 6H), 1.96 (s, 9H). $^{13}C\{^1H\}$ (125 MHz) NMR

(CDCl$_3$): δ 170.61, 160.06, 150.49, 138.82 (q, *J* = 33.7 Hz), 122.95 (q, *J* = 271.8 Hz), 118.26 (q, *J* = 3.4 Hz) 117.53 (q, *J* = 3.5 Hz), 64.12, 48.50, 20.84. ^{19}F NMR (375 MHz, CDCl$_3$): δ –64.77. HRMS electrospray (m/z): [M+H]$^+$ calcd for $C_{16}H_{19}F_3NO_6$ predicted: 378.1159, measured: 378.1163. IR (thin film) 1733 cm^{-1}.



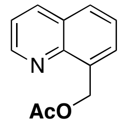
(**9**)

This reaction was conducted with substrate **S9** according to the standard procedure, except using 50 mol % of NaNO$_3$ (0.25 mmol, 0.5 equiv) along with 4 Å molecular sieves (270 mg). Product **9** was obtained as a colorless oil (149 mg, 77% yield, R$_f$ = 0.2 in 3:7 ethyl acetate/hexanes). ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.41 (d, *J* = 5.2 Hz, 1H), 7.45 (d, *J* = 2.0 Hz, 1H), 7.39 (dd, *J* = 5.2, 2.0 Hz, 1H), 4.52 (s, 6H), 2.02 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 170.53, 159.75, 150.04, 133.12, 125.81, 125.09, 64.00, 48.01, 20.77. HRMS electrospray (m/z): [M+H]$^+$ calcd for $C_{15}H_{18}BrNO_6$ predicted: 388.0390, measured: 388.0396. IR (thin film) 1739 cm^{-1}.



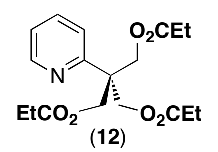
(**10**)

This reaction was conducted with substrate **S10** according to the standard procedure, except using 1 equiv of NaNO$_3$ (0.5 mmol, 1 equiv) along with 4 Å molecular sieves (270 mg). Product **10** was obtained as a colorless oil (110 mg, 68% yield, R$_f$ = 0.2 in 3:7 ethyl acetate/hexanes). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.50 (app t, *J* = 7.6 Hz, 1H), 7.01 (d, *J* = 7.6 Hz, 1H), 6.99 (d, *J* = 7.6 Hz, 1H), 4.51 (s, 6H), 2.47 (s, 3H), 1.96 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 170.88, 158.33, 157.39, 136.50, 121.92, 118.39, 64.79, 47.92, 24.73, 21.00. HRMS electrospray (m/z): [M+H]$^+$ calcd for $C_{16}H_{22}NO_6$ predicted: 324.1442, measured: 324.1446. IR (thin film) 1734 cm^{-1}.



(**11**)

This reaction was conducted with substrate **S11** according to the standard procedure, except using 1 equiv of NaNO$_3$ (0.5 mmol, 1 equiv) along with air as the oxidant. Product **11** was obtained as a colorless oil (80 mg, 80% yield, R$_f$ = 0.25 in 1:9 ethyl acetate/hexanes). Spectral data [^{1}H NMR (CDCl$_3$) and ^{13}C{^{1}H} NMR (CDCl$_3$)] matched that reported in the literature for this compound.[4]

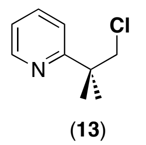


(12)

This reaction was conducted with substrate **S7** according to the standard procedure, except that 4 Å molecular sieves (270 mg) were added and $EtCO_2H/(EtCO)_2O$ was used as the solvent. Product **12** was obtained as a colorless oil (141 mg, 80% yield, $R_f = 0.32$ in 3:7 ethyl acetate/hexanes). ^1H NMR (500 MHz, $CDCl_3$): δ 8.58 (m, 1H), 7.66 (m, 1H), 7.27 (m, 1H), 7.19 (m, 1H), 4.55 (d, *J* = 2.0 Hz, 6H), 2.26 (dq, *J* = 2.0, 8.0 Hz, 6H), 1.05 (dt, *J* = 2.0, 8.0 Hz, 9H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 173.93, 158.21, 149.25, 136.14, 122.22, 121.42, 64.18, 48.13, 27.44, 9.00. HRMS electrospray (m/z): $[M+H]^+$ calcd for $C_{18}H_{26}NO_6$ predicted: 352.1755, measured: 352.1755. IR (thin film) 1737 cm^{-1}.

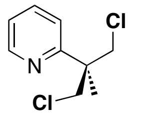
6. Synthesis and Characterization of Chlorinated Products 13-15

Under air, $Pd(OAc)_2$ (5.6 mg, 0.025 mmol, 0.05 equiv), NaCl (14.6 mg, 0.25 mmol, 10 equiv) and $NaNO_3$ (2.1 mg, 0.025 mmol, 0.10 equiv) were weighed into a 20 mL scintillation vial. Substrate **S7** (68 mg, 0.5 mmol, 1 equiv) was added as a 0.125 M solution in AcOH. The vial was sealed with a Teflon-lined cap then heated at 80 ºC for 24 h. The reaction was cooled to room temperature, filtered through a plug of Celite, and then concentrated under reduced pressure to remove the solvent. The resulting residue was neutralized with a saturated solution of $NaHCO_3$, and the organic products were extracted into ether. NMR analysis of the crude reaction mixture showed 80% conversion of the starting material, and 67% total yield of the mono-, di-, and tri-chlorinated products. The remaining 13% of the material was a mixture of the mono-, di-, and triacetoxylated products. The organic extracts were washed with brine, combined, and then dried over $MgSO_4$. A clean mixture of the three chlorinated products **13-15** was obtained by silica gel column chromatography (all three chlorinated products elute together with R_f = 0.20 in 1:9 ethyl acetate/hexanes). The yields reported below are based on the proportion of each product in the material isolated by column chromatography. Pure samples of **13**-**15** for HRMS and NMR analysis were obtained after by purification by HPLC (97:3% hexanes/ethyl acetate, 20 mL/min, Waters *µ*-porasil 19.1 mm). Using this solvent system, the products elute in the following order: **15** then **14** then **13**.



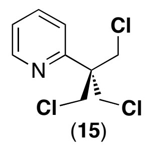
(**13**)

Product **13** was obtained as a colorless oil (11% yield). Peak #3 from HPLC purification. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.56 (dd, *J* = 4.6, 1.4 Hz, 1H), 7.62 (app td, *J* = 7.6, 1.4 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.11 (dd, *J* = 7.6, 4.6 Hz, 1H), 3.84 (s, 2H), 1.43 (s, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 164.94, 149.11, 136.55, 121.62, 120.47, 55.61, 42.67, 25.97. HRMS electrospray (m/z): $[M+H]^+$ calcd for $C_9H_{13}ClN$ predicted: 170.0731, measured: 170.0730.



(**14**)

Product **14** was obtained as a colorless oil (45% yield). Peak #2 from HPLC purification. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.55 (td, *J* = 3.6, 1.2 Hz, 1H), 7.64 (app td, *J* = 6.0, 1.2 Hz, 1H), 7.28 (d, *J* = 6.4 Hz, 1H), 7.14 (dd, *J* = 6.0, 3.6 Hz, 1H), 3.96 (app q, *J* = 8.9 Hz, 4H), 1.51 (s, 3H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 161.36, 149.37, 136.64, 122.32, 121.29, 51.25, 47.42, 21.67. HRMS electrospray (m/z): $[M+H]^+$ calcd for $C_9H_{12}Cl_2N$ predicted: 204.0341, measured: 204.0341.



(**15**)

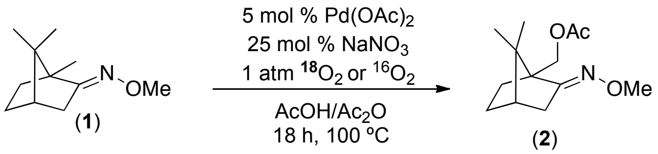
Product **15** was obtained as a colorless oil (12% yield). Peak #1 from HPLC purification. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.60 (dd, *J* = 4.4, 0.8 Hz, 1H), 7.64 (m, 1H), 7.28-7.21 (multiple peaks, 2H), 4.18 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 157.44, 149.72, 136.48, 122.92, 122.44, 52.15, 47.01. HRMS electrospray (m/z): [M+H]$^+$ calcd for $C_9H_{11}Cl_3N$ predicted: 237.9952, measured: 237.9952.

7. Reaction in the Presence of BHT

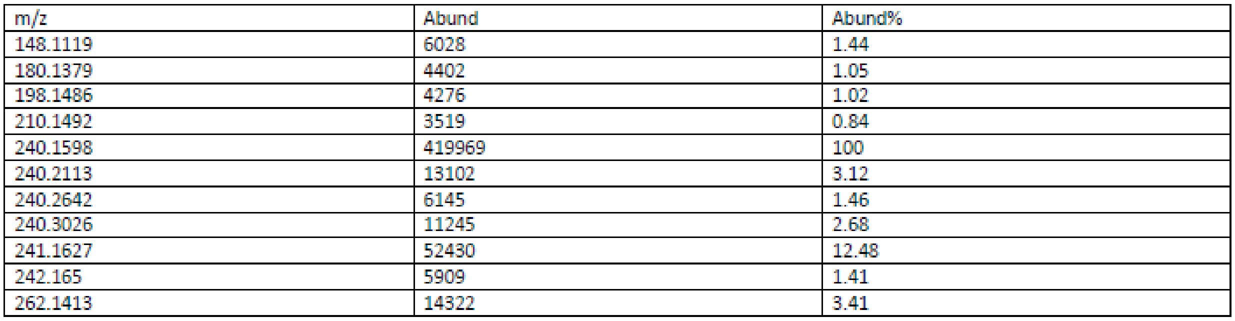
$Pd(OAc)_2$ (2.2 mg, 0.01 mmol, 0.05 equiv), $NaNO_3$ (4.3 mg, 0.05 mmol, 0.25 equiv), and BHT (11 mg, 0.05 mmol, 0.25 equiv) were weighed into a 25 mL Schlenk flask (14/20 top opening with glass side arm that can be sealed with a glass stopcock) containing a stir bar. Ac_2O (0.2 mL) was added. A solution of substrate **1** (36 mg, 0.2 mmol, 1 equiv) in AcOH (1.4 mL) was then added to the Schlenk flask. The top of the Schlenk flask was sealed with a rubber septum. The flask was charged with O_2 through the side arm using the set-up shown in Figure S1. The flask was evacuated (aspirator vacuum) and backfilled with oxygen (1 atm) three times to achieve 1 atm of O_2. The flask was sealed at the side arm with a glass stopcock and then heated at 110 °C in an oil bath for 30 min. The reaction was cooled to room temperature, and 1 M nitrobenzene in $CDCl_3$ (50 µL, 0.5 mmol, 0.25 equiv) was added as a standard. The crude reaction mixture was analyzed by ^1H NMR spectroscopy. The yield of 2,6-di-*tert*-butyl-4-methyl-4-nitrosocyclohexa-2,5-dienone[5] in the crude reaction mixture was determined by integration of a diagnostic singlet associated with this product (at 6.6 ppm) versus the internal standard.

8. Reaction with $^{16}O_2$ vs $^{18}O_2$

$Pd(OAc)_2$ (2.2 mg, 0.001 mmol, 0.05 equiv) and $NaNO_3$ (4.3 mg, 0.05 mmol, 0.25 equiv) were weighed into a 25 mL resealable Schlenk flask. A solution of substrate **1** (36 mg, 0.2 mmol, 1 equiv) in AcOH (1.4 mL) was then added to the Schlenk flask. The top of the Schlenk flask was sealed with a rubber septum. The Schlenk flask was evacuated and refilled with N_2 twice using the set-up shown in Figure S1. The flask was then evacuated a third time and sealed at the side arm by a glass stopcock. A balloon filled with either O_2 or $^{18}O_2$ (99% Aldrich) was inserted through the rubber septum using a needle in order to allow 1 atm of dioxygen to enter the reaction vessel. The flask was then heated at 110 °C in an oil bath for 18 h. The reaction was cooled to rt, diluted with ethyl acetate, and neutralized with a saturated solution of $NaHCO_3$. The organic layer was washed saturated $NaHCO_3$ (X 2) and brine then dried over $MgSO_4$. The products were purified by column chromatography on silica gel (1:9 ethyl acetate/hexanes). The isolated products were submitted for HRMS and analyzed by ESI.

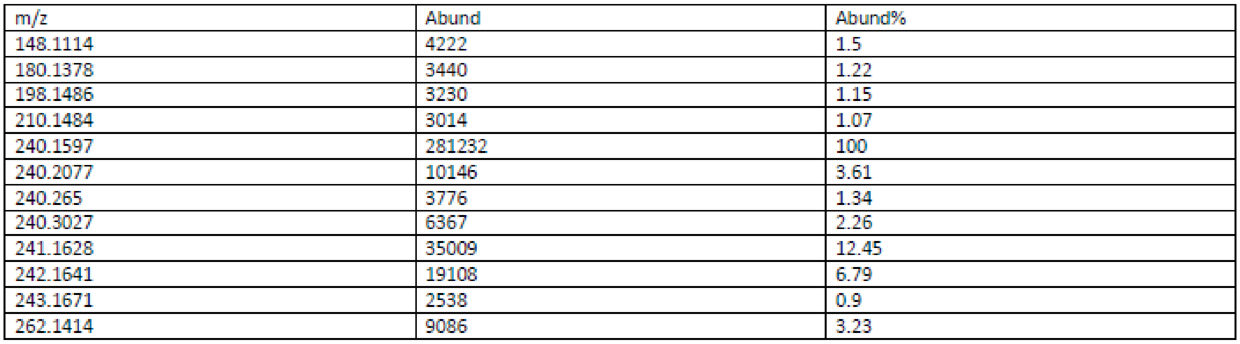


HRMS data for the molecular ion region: reaction with $^{16}O_2$



m/z	Abund	Abund%
148.1119	6028	1.44
180.1379	4402	1.05
198.1486	4276	1.02
210.1492	3519	0.84
240.1598	419969	100
240.2113	13102	3.12
240.2642	6145	1.46
240.3026	11245	2.68
241.1627	52430	12.48
242.165	5909	1.41
262.1413	14322	3.41

HRMS data for the molecular ion region: reaction with $^{18}O_2$

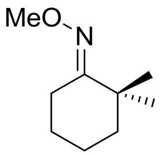


m/z	Abund	Abund%
148.1114	4222	1.5
180.1378	3440	1.22
198.1486	3230	1.15
210.1484	3014	1.07
240.1597	281232	100
240.2077	10146	3.61
240.265	3776	1.34
240.3027	6367	2.26
241.1628	35009	12.45
242.1641	19108	6.79
243.1671	2538	0.9
262.1414	9086	3.23

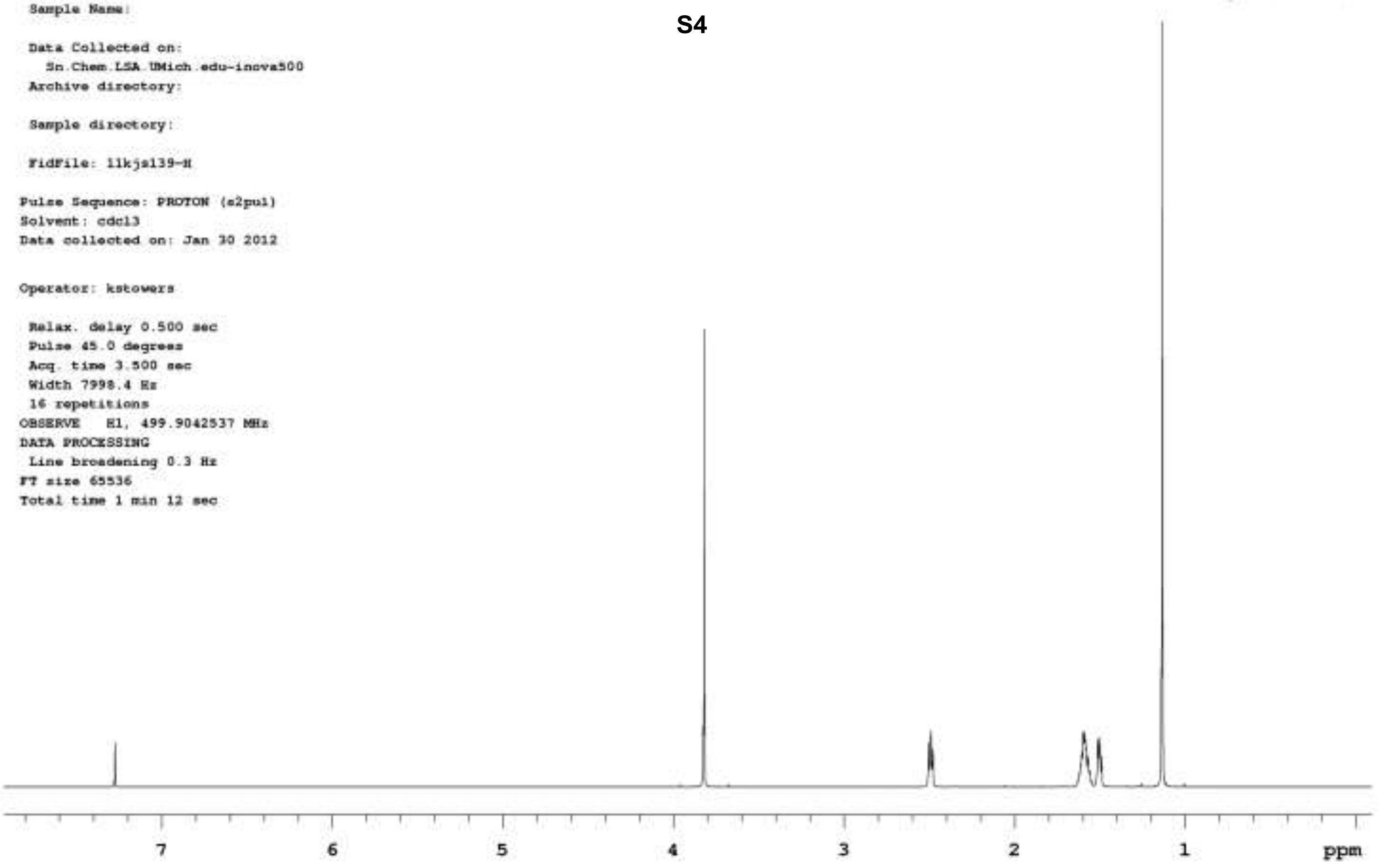
Using the published deconvolution mass spreadsheet[6] it was determined that 5% of product in the reaction with $^{18}O_2$ contained a ^{18}O in product **2**.

9. References

1. Desai, L. V.; Hull, K. L.; Sanford, M. S. *J. Am. Chem. Soc.* **2004**, *126*, 9542.
2. Stowers, K. J.; Fortner, K. F.; Sanford, M. S. *J. Am. Chem. Soc.* **2011**, *133*, 6541.
3. NOVARTIS, AG; Caravatti, G.; Fairhurst, R. A.; Furet, P; Guagano, V.; Imbach, P. WO2010/29082; (2010); (A1) English.
4. Dick, A. R.; Hull, K. L.; Sanford, M. S. *J. Am. Chem. Soc.* **2004**, *126*, 2300.
5. Janzen, E. G.; Wilcox, A. L.; Manoharan, V. *J. Org. Chem.* **1993**, *58*, 3597.
6. Gruber, C. C.; Oberdorfer, G.; Voss, C. V.; Kremsner, J. M.; Kappe, C. O. Kroutil, W. *J. Org. Chem.* **2007**, *72*, 5778.



S4



```
11kjs139-H

 Sample Name:

 Data Collected on:
   Sn.Chem.LSA.UMich.edu-inova500
 Archive directory:

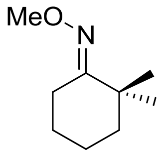
 Sample directory:

 FidFile: 11kjs139-H

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Jan 30 2012

Operator: kstowers

 Relax. delay 0.500 sec
 Pulse 45.0 degrees
 Acq. time 3.500 sec
 Width 7998.4 Hz
 16 repetitions
OBSERVE   H1, 499.9042537 MHz
DATA PROCESSING
 Line broadening 0.3 Hz
FT size 65536
Total time 1 min 12 sec
```



S4

```
11kjs139-C

 Sample Name:

 Data Collected on:
   Sn.Chem.LSA.UMich.edu-inova500
 Archive directory:

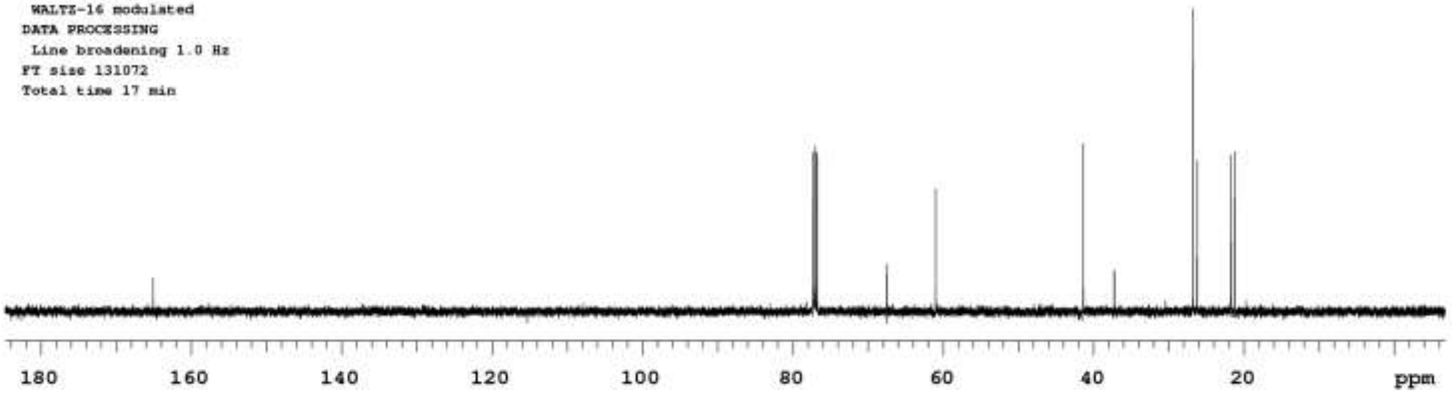
 Sample directory:

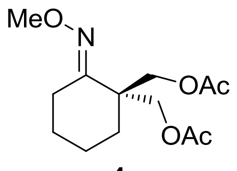
 FidFile: 11kjs139-C

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Jan 30 2012

Operator: kstowers

 Relax. delay 0.100 sec
 Pulse 45.0 degrees
 Acq. time 2.086 sec
 Width 31421.8 Hz
 480 repetitions
OBSERVE  C13, 125.7010246 MHz
DECOUPLE  H1, 499.9067532 MHz
 Power 32 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 1.0 Hz
FT size 131072
Total time 17 min
```





4

```
11kjs86-H

 Sample Name:

 Data Collected on:
   Sn.Chem.LSA.UMich.edu-inova500
 Archive directory:

 Sample directory:

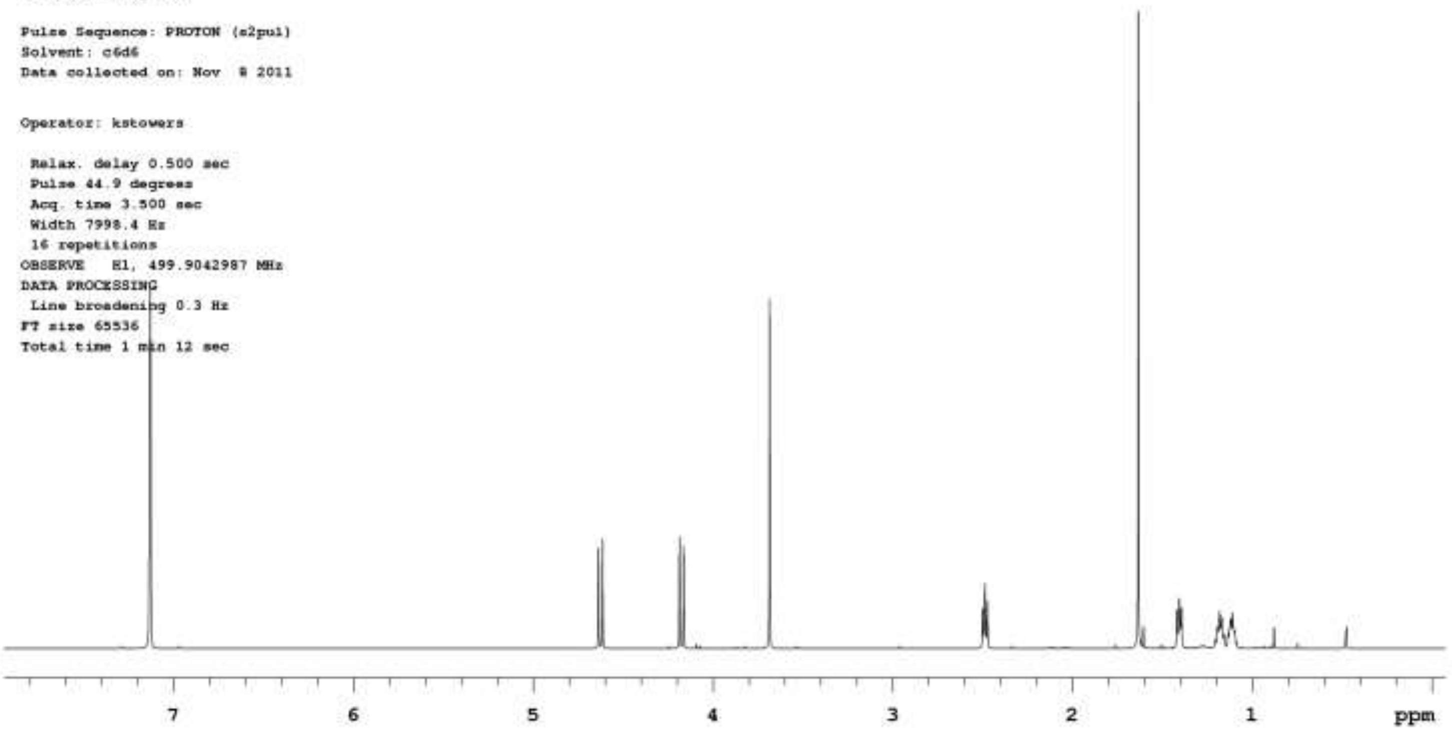
 FidFile: 11kjs86-H

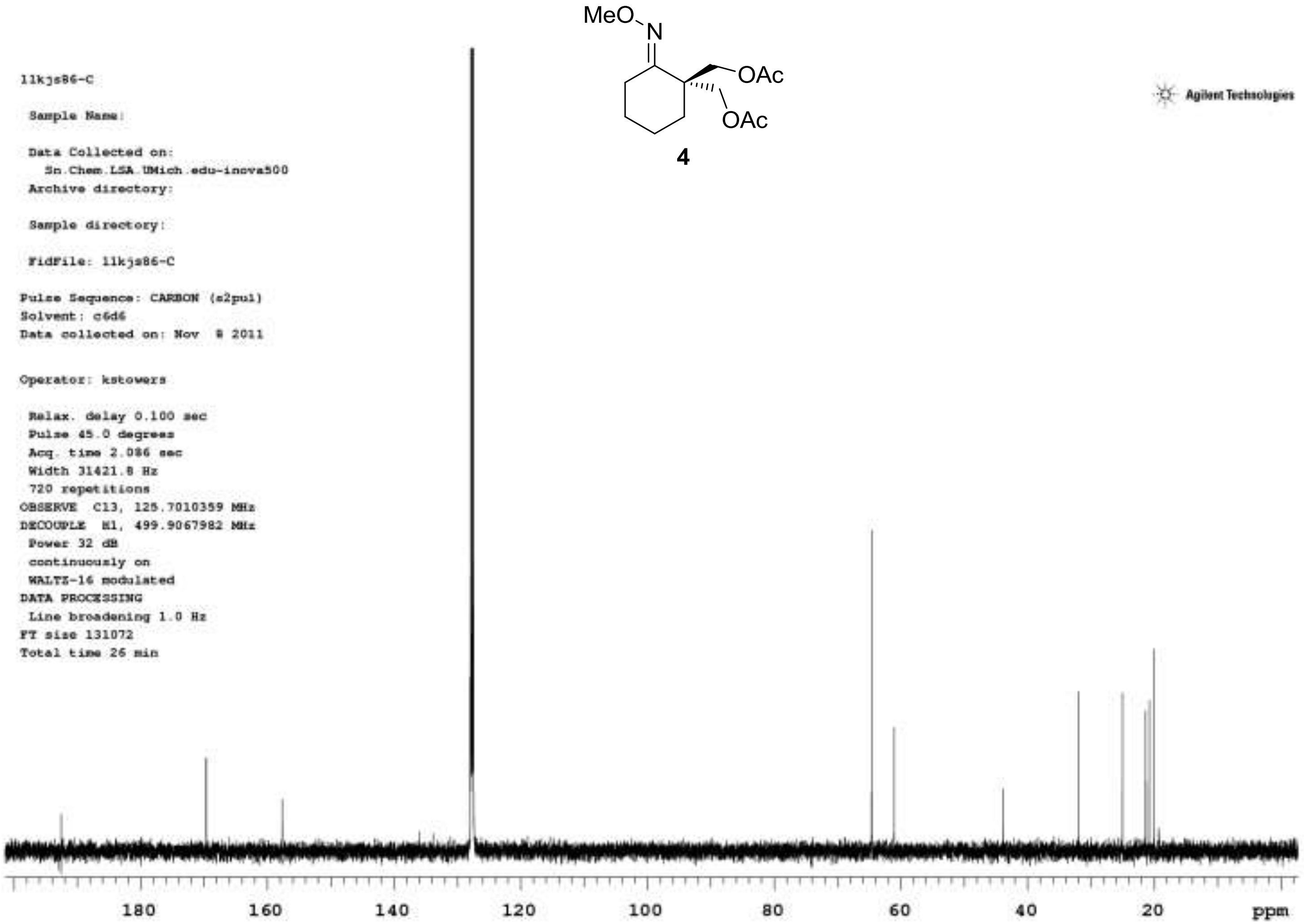
Pulse Sequence: PROTON (s2pul)
Solvent: c6d6
Data collected on: Nov  8 2011


Operator: kstowers

 Relax. delay 0.500 sec
 Pulse 44.9 degrees
 Acq. time 3.500 sec
 Width 7998.4 Hz
 16 repetitions
OBSERVE   H1, 499.9042987 MHz
DATA PROCESSING
 Line broadening 0.3 Hz
FT size 65536
Total time 1 min 12 sec
```

Agilent Technologies





4

```
11kjs86-C

 Sample Name:

 Data Collected on:
   Sn.Chem.LSA.UMich.edu-inova500
 Archive directory:

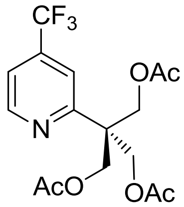
 Sample directory:

 FidFile: 11kjs86-C

Pulse Sequence: CARBON (s2pul)
Solvent: c6d6
Data collected on: Nov  8 2011


Operator: kstowers

 Relax. delay 0.100 sec
 Pulse 45.0 degrees
 Acq. time 2.086 sec
 Width 31421.8 Hz
 720 repetitions
OBSERVE  C13, 125.7010359 MHz
DECOUPLE  H1, 499.9067982 MHz
 Power 32 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 1.0 Hz
FT size 131072
Total time 26 min
```



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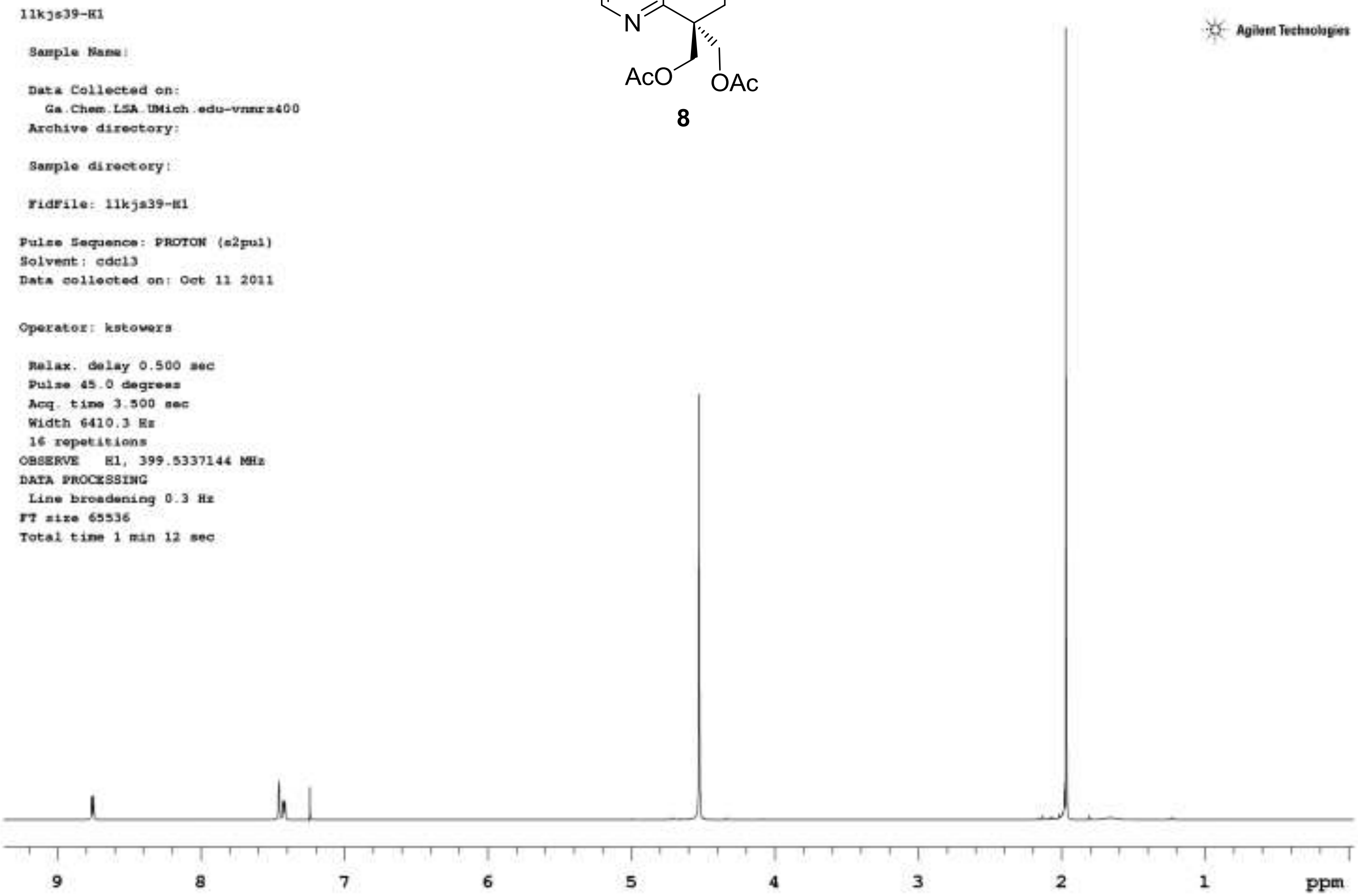


11kjs39-H1

Sample Name:

Data Collected on:
Ga.Chem.LSA.UMich.edu-vnmrs400
Archive directory:

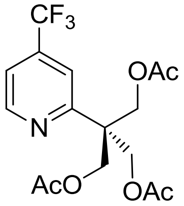
Sample directory:

FidFile: 11kjs39-H1

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Oct 11 2011

Operator: kstowers

Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6410.3 Hz
16 repetitions
OBSERVE H1, 399.5337144 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 1 min 12 sec



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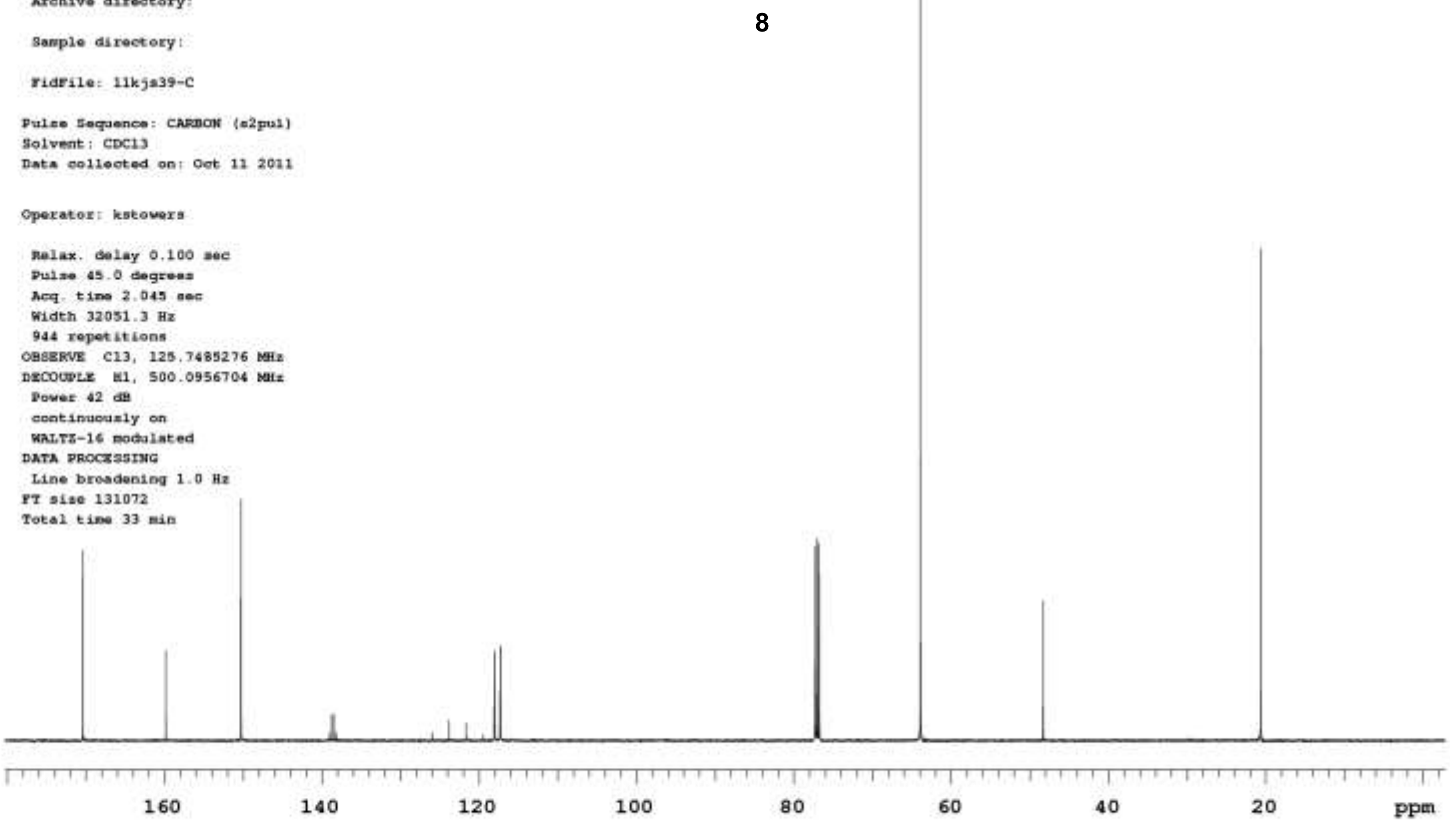

```
11kjs39-C

 Sample Name:

 Data Collected on:
   Te-vnmrs500
 Archive directory:

 Sample directory:

 FidFile: 11kjs39-C

Pulse Sequence: CARBON (s2pul)
Solvent: CDCl3
Data collected on: Oct 11 2011

Operator: kstowers

 Relax. delay 0.100 sec
 Pulse 45.0 degrees
 Acq. time 2.045 sec
 Width 32051.3 Hz
 944 repetitions
OBSERVE  C13, 125.7485276 MHz
DECOUPLE  H1, 500.0956704 MHz
 Power 42 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 1.0 Hz
FT size 131072
Total time 33 min
```

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```
11kjs39-F19

 Sample Name:

 Data Collected on:
   Ga.Chem.LSA.UMich.edu-vnmrs400
 Archive directory:

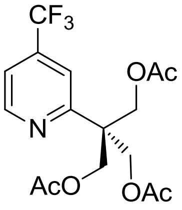
 Sample directory:

 FidFile: 11kjs39-F19

Pulse Sequence: FLUORINE (s2pul)
Solvent: cdcl3
Data collected on: Oct 11 2011

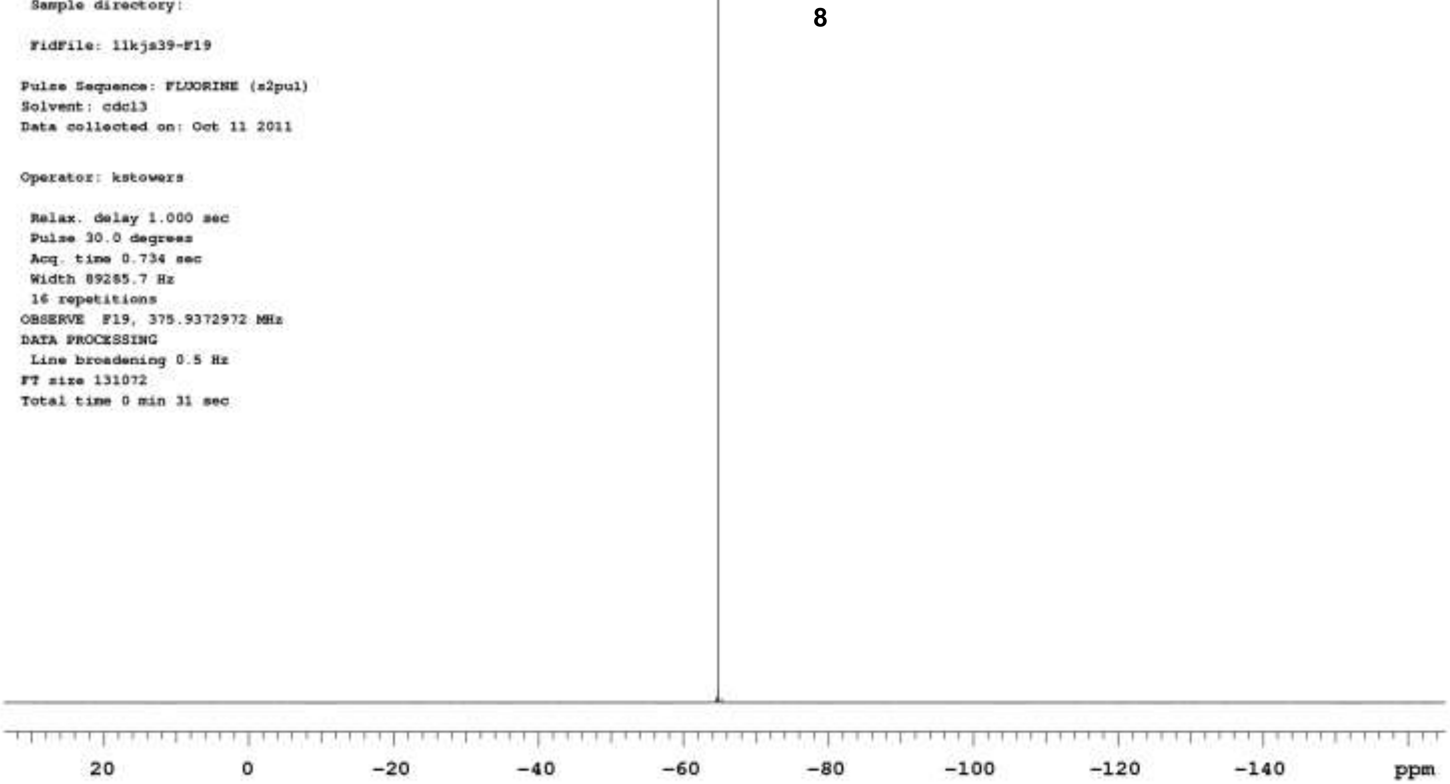

Operator: kstowers

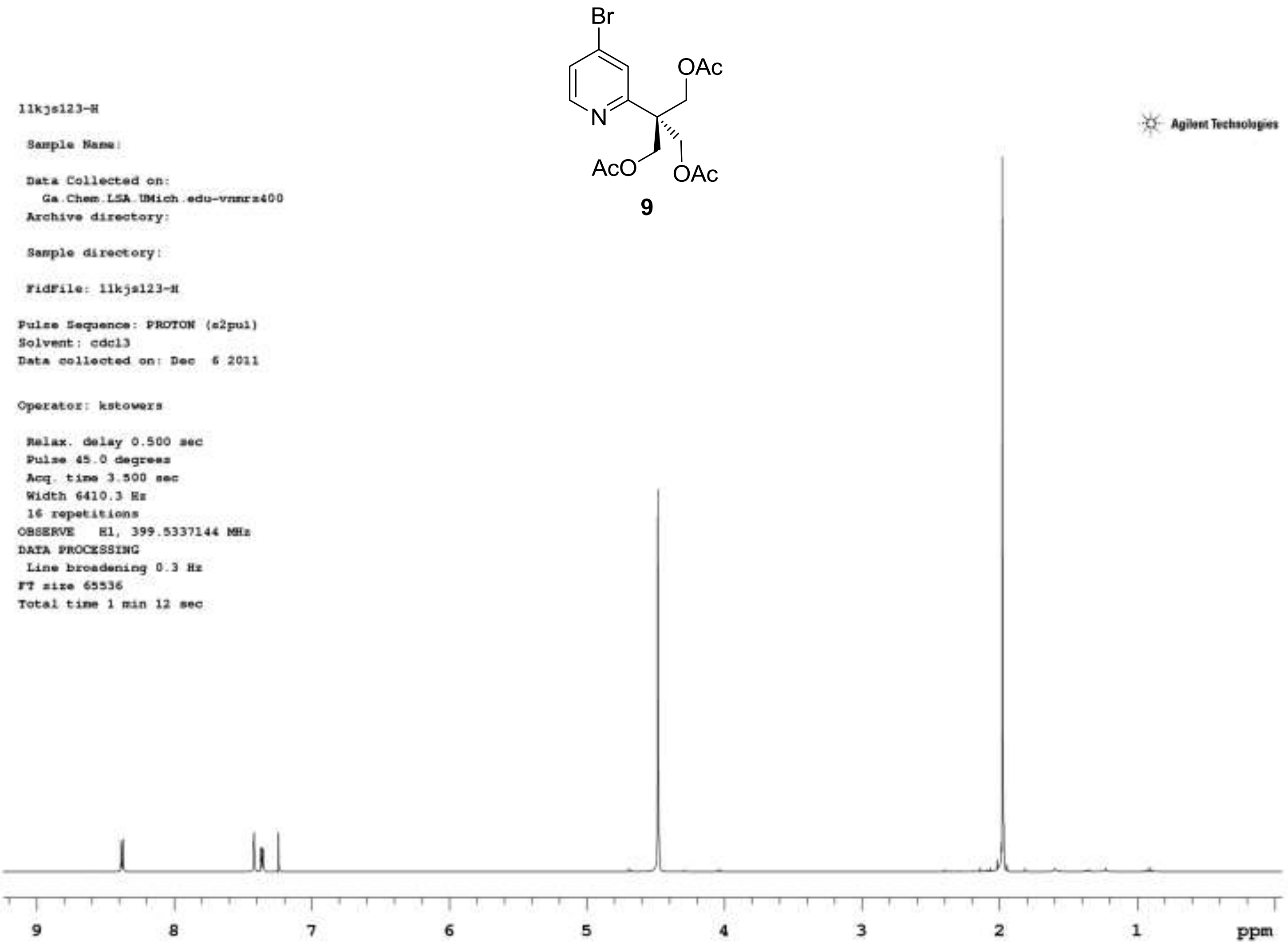
 Relax. delay 1.000 sec
 Pulse 30.0 degrees
 Acq. time 0.734 sec
 Width 89285.7 Hz
 16 repetitions
OBSERVE  F19, 375.9372972 MHz
DATA PROCESSING
 Line broadening 0.5 Hz
FT size 131072
Total time 0 min 31 sec
```



8

Agilent Technologies





9

```
11kjs123-H

 Sample Name:

 Data Collected on:
   Ga.Chem.LSA.UMich.edu-vnmrs400
 Archive directory:

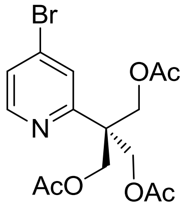
 Sample directory:

 FidFile: 11kjs123-H

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Dec  6 2011

Operator: kstowers

 Relax. delay 0.500 sec
 Pulse 45.0 degrees
 Acq. time 3.500 sec
 Width 6410.3 Hz
 16 repetitions
OBSERVE   H1, 399.5337144 MHz
DATA PROCESSING
 Line broadening 0.3 Hz
FT size 65536
Total time 1 min 12 sec
```



9

```
11kjs140-C

 Sample Name:

 Data Collected on:
   Ga.Chem.LSA.UMich.edu-vnmrs400
 Archive directory:

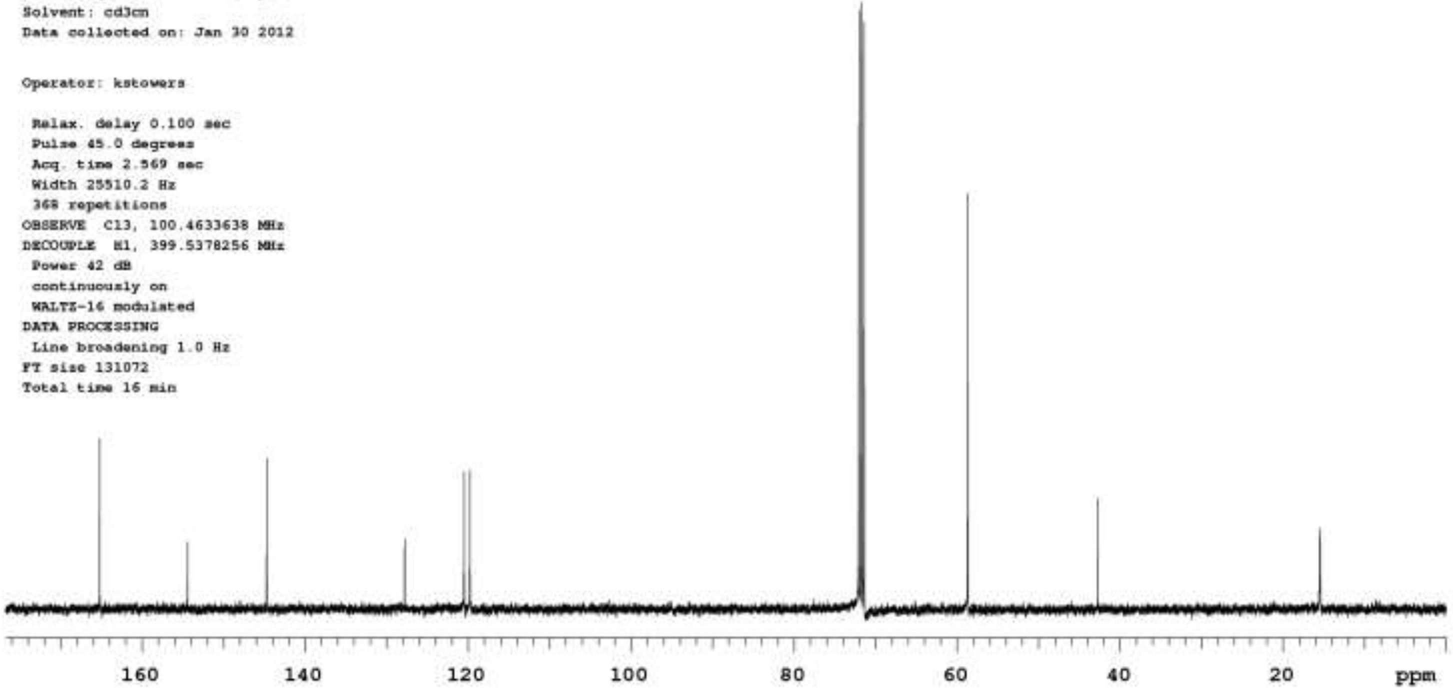
 Sample directory:

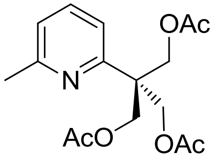
 FidFile: 11kjs140-C

Pulse Sequence: CARBON (s2pul)
Solvent: cd3cn
Data collected on: Jan 30 2012

Operator: kstowers

 Relax. delay 0.100 sec
 Pulse 45.0 degrees
 Acq. time 2.569 sec
 Width 25510.2 Hz
 368 repetitions
OBSERVE  C13, 100.4633638 MHz
DECOUPLE  H1, 399.5378256 MHz
 Power 42 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 1.0 Hz
FT size 131072
Total time 16 min
```





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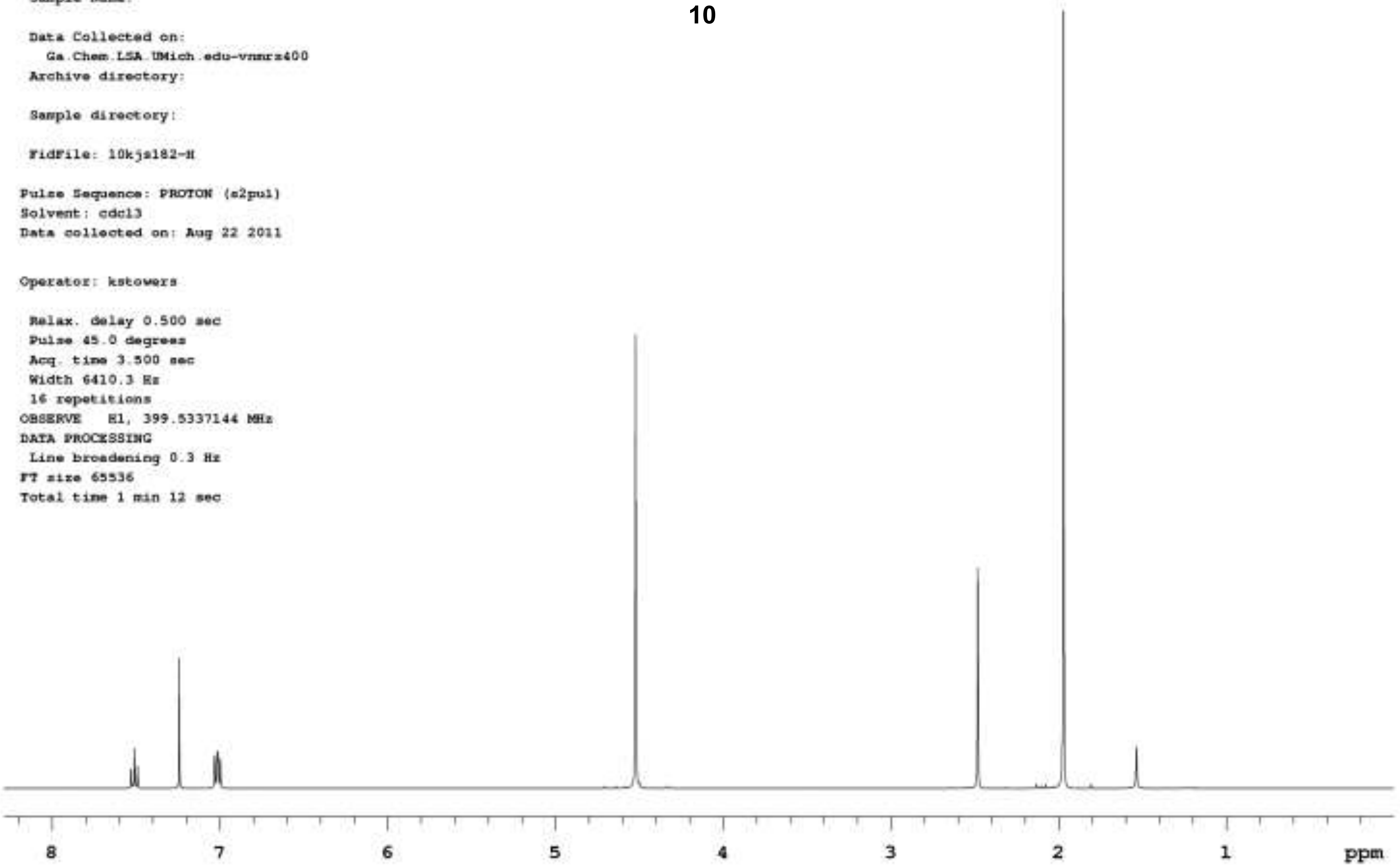


```
10kjs182-H

 Sample Name:

 Data Collected on:
   Ga.Chem.LSA.UMich.edu-vnmrs400
 Archive directory:

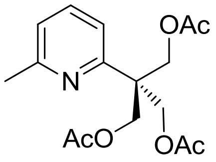
 Sample directory:

 FidFile: 10kjs182-H

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Aug 22 2011


Operator: kstowers

 Relax. delay 0.500 sec
 Pulse 45.0 degrees
 Acq. time 3.500 sec
 Width 6410.3 Hz
 16 repetitions
OBSERVE   H1, 399.5337144 MHz
DATA PROCESSING
 Line broadening 0.3 Hz
FT size 65536
Total time 1 min 12 sec
```



10

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10kjs182-C

 Sample Name:

 Data Collected on:
   Ga.Chem.LSA.UMich.edu-vnmrs400
 Archive directory:

 Sample directory:

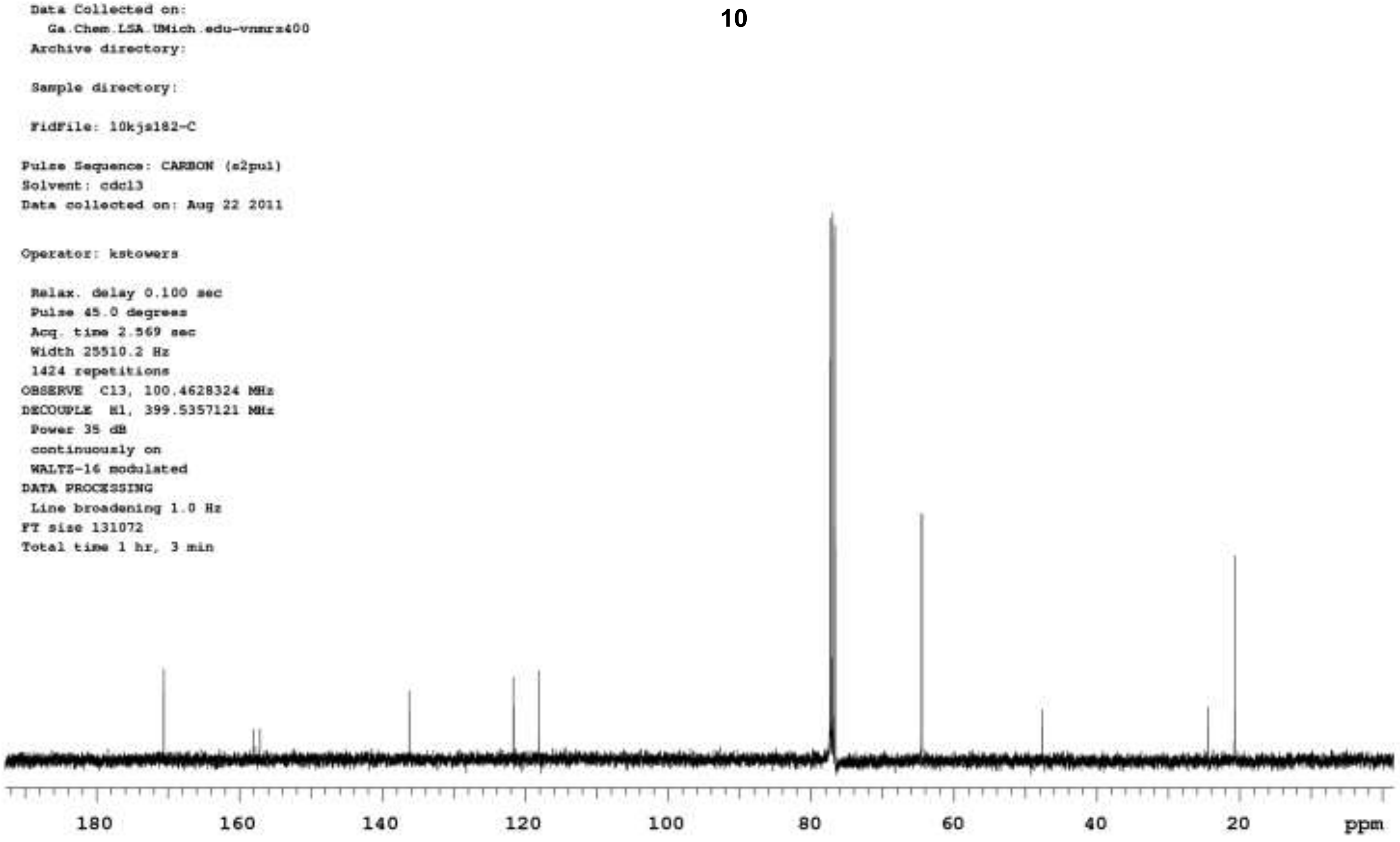
 FidFile: 10kjs182-C

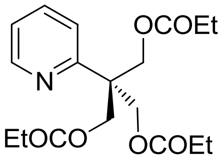
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Aug 22 2011

Operator: kstowers

 Relax. delay 0.100 sec
 Pulse 45.0 degrees
 Acq. time 2.569 sec
 Width 25510.2 Hz
 1424 repetitions
OBSERVE  C13, 100.4628324 MHz
DECOUPLE  H1, 399.5357121 MHz
 Power 35 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 1.0 Hz
FT size 131072
Total time 1 hr, 3 min
```

Agilent Technologies





12

```
AK8-102-f15-17

 Sample Name:

 Data Collected on:
   Te-vnmrs500
 Archive directory:

 Sample directory:

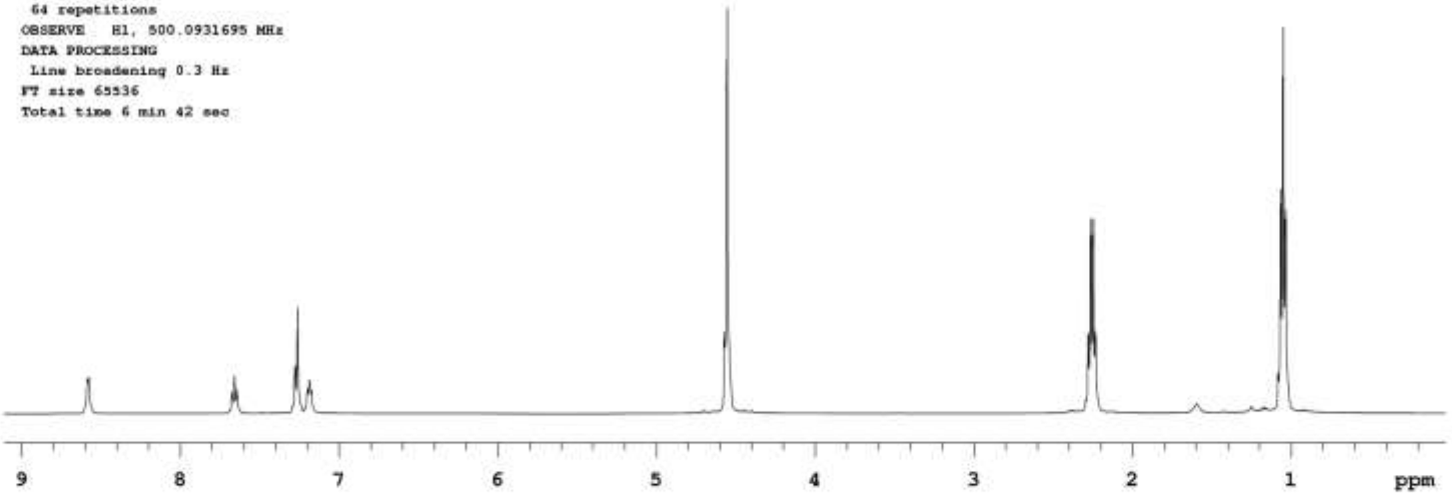
 FidFile: AK8-102-f15-17-H

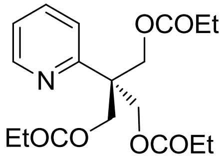
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Apr 17 2012

Operator: akubota

 Relax. delay 2.000 sec
 Pulse 45.0 degrees
 Acq. time 4.089 sec
 Width 8012.8 Hz
 64 repetitions
OBSERVE   H1, 500.0931695 MHz
DATA PROCESSING
 Line broadening 0.3 Hz
FT size 65536
Total time 6 min 42 sec
```

Agilent Technologies





12

```
AK8-102-f15-17

 Sample Name:

 Data Collected on:
   Te-vnmrs500
 Archive directory:

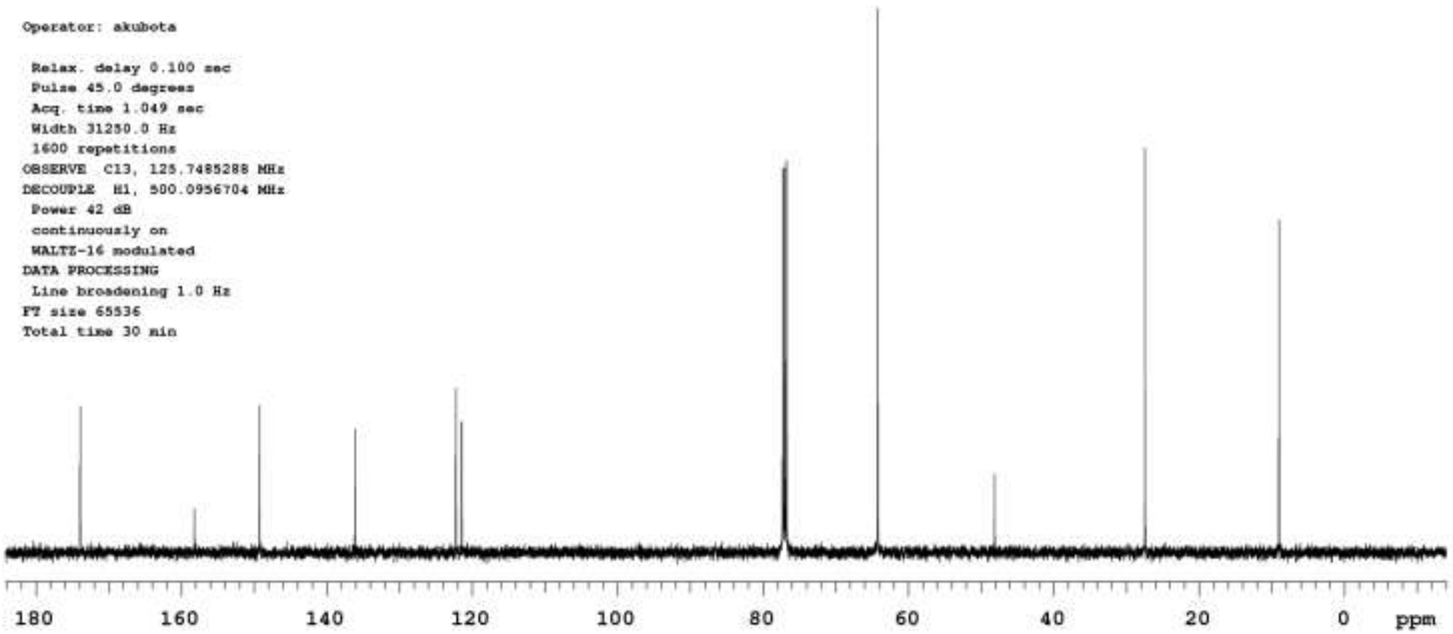
 Sample directory:

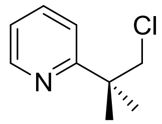
 FidFile: AK8-102-f15-17-hv-C

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Apr 17 2012

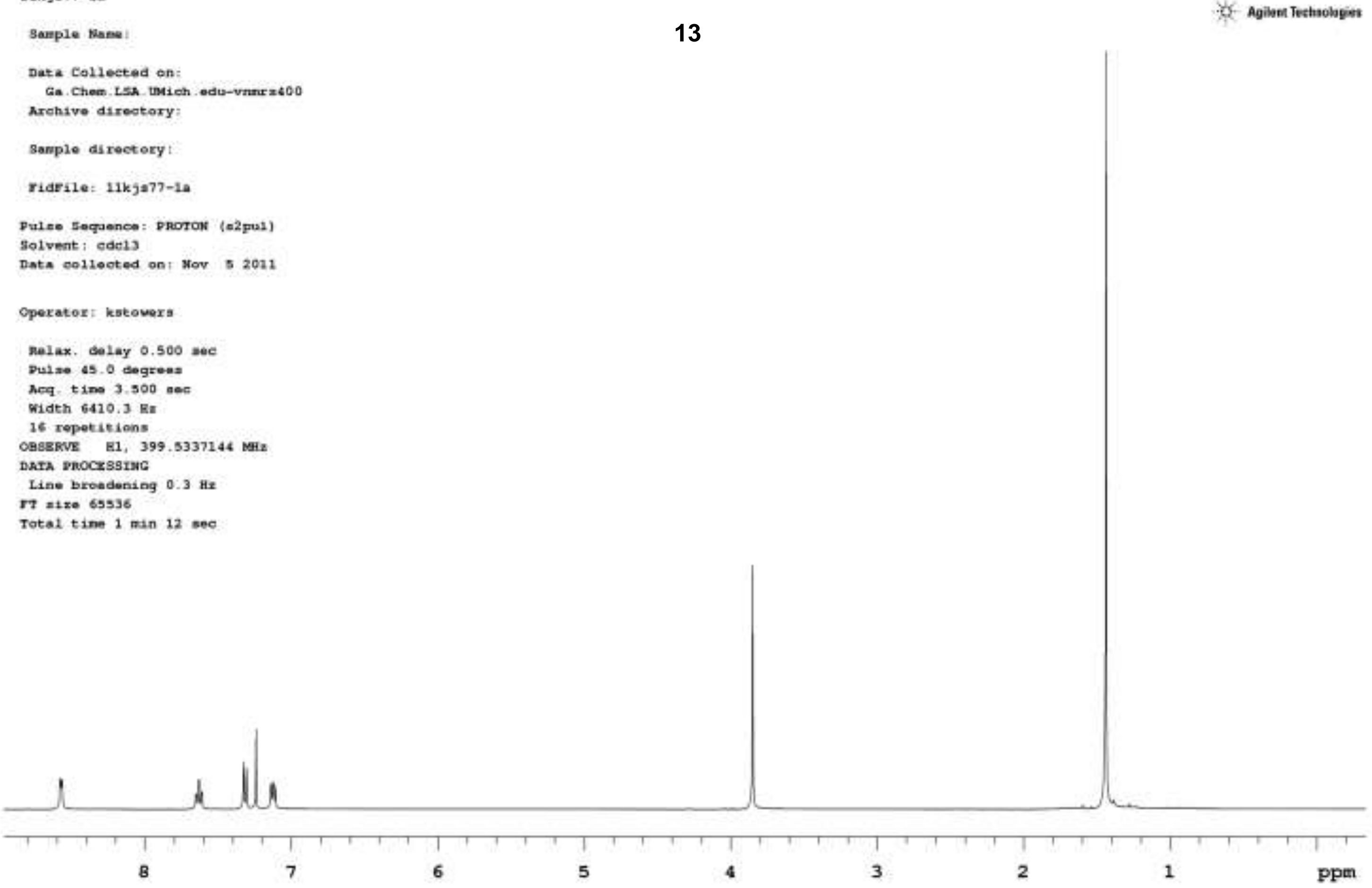
Operator: akubota

 Relax. delay 0.100 sec
 Pulse 45.0 degrees
 Acq. time 1.049 sec
 Width 31250.0 Hz
 1600 repetitions
OBSERVE  C13, 125.7485288 MHz
DECOUPLE  H1, 500.0956704 MHz
 Power 42 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 1.0 Hz
FT size 65536
Total time 30 min
```





13



```
11kjs77-1a

 Sample Name:

 Data Collected on:
   Ga.Chem.LSA.UMich.edu-vnmrs400
 Archive directory:

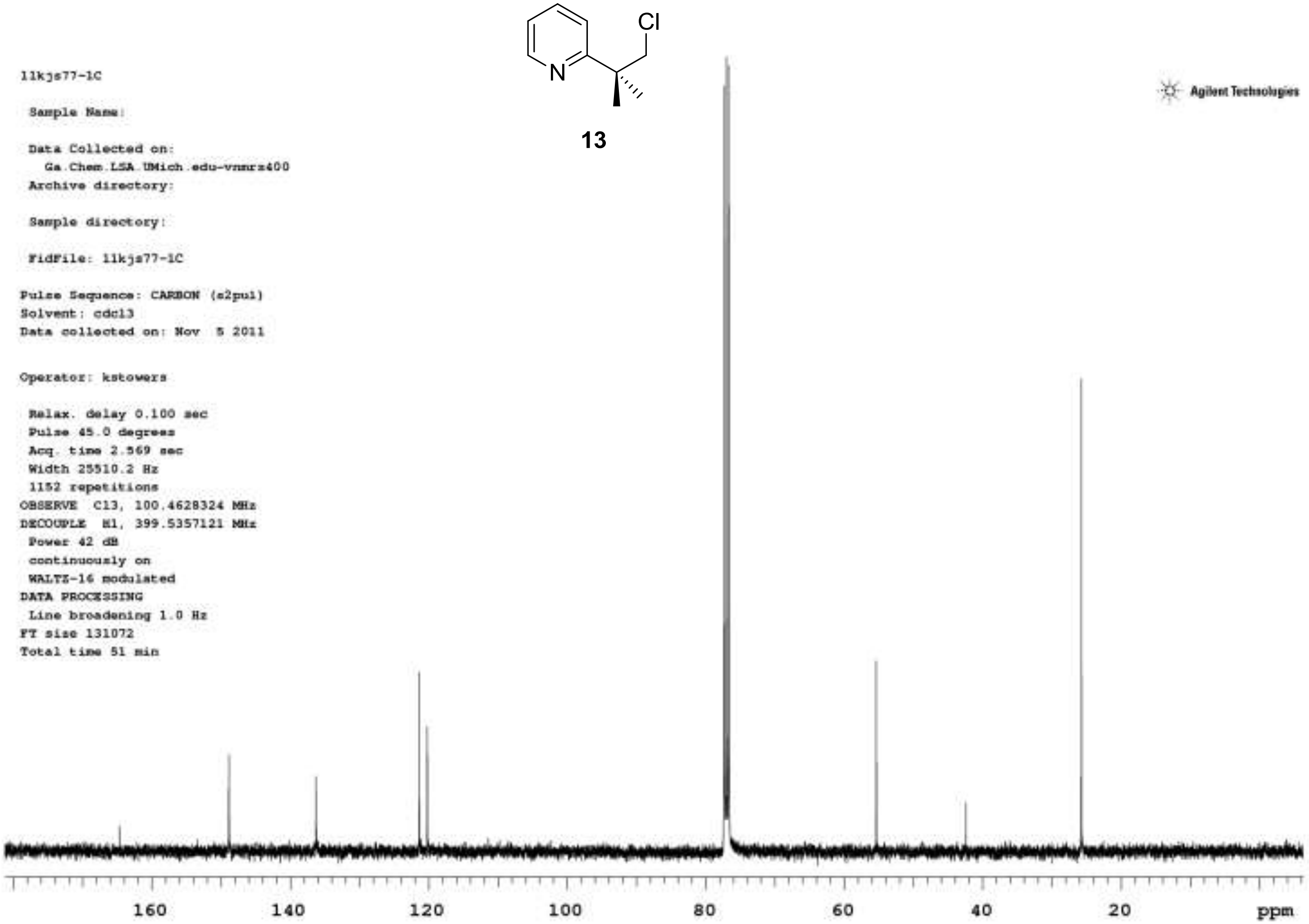
 Sample directory:

 FidFile: 11kjs77-1a

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Nov  5 2011

Operator: kstowers

 Relax. delay 0.500 sec
 Pulse 45.0 degrees
 Acq. time 3.500 sec
 Width 6410.3 Hz
 16 repetitions
OBSERVE   H1, 399.5337144 MHz
DATA PROCESSING
 Line broadening 0.3 Hz
FT size 65536
Total time 1 min 12 sec
```



13

```
11kjs77-1C

 Sample Name:

 Data Collected on:
   Ga.Chem.LSA.UMich.edu-vnmrs400
 Archive directory:

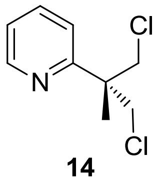
 Sample directory:

 FidFile: 11kjs77-1C

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Nov  5 2011

Operator: kstowers

 Relax. delay 0.100 sec
 Pulse 45.0 degrees
 Acq. time 2.569 sec
 Width 25510.2 Hz
 1152 repetitions
OBSERVE  C13, 100.4628324 MHz
DECOUPLE  H1, 399.5357121 MHz
 Power 42 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 1.0 Hz
FT size 131072
Total time 51 min
```



14

```
11kjs40-2H

 Sample Name:

 Data Collected on:
   Sn.Chem.LSA.UMich.edu-inova500
 Archive directory:

 Sample directory:

 FidFile: 11kjs40-2H

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Oct  7 2011

Operator: kstowers

 Relax. delay 0.500 sec
 Pulse 45.0 degrees
 Acq. time 3.500 sec
 Width 7998.4 Hz
 16 repetitions
OBSERVE   H1, 499.9042537 MHz
DATA PROCESSING
 Line broadening 0.3 Hz
FT size 65536
Total time 1 min 12 sec
```

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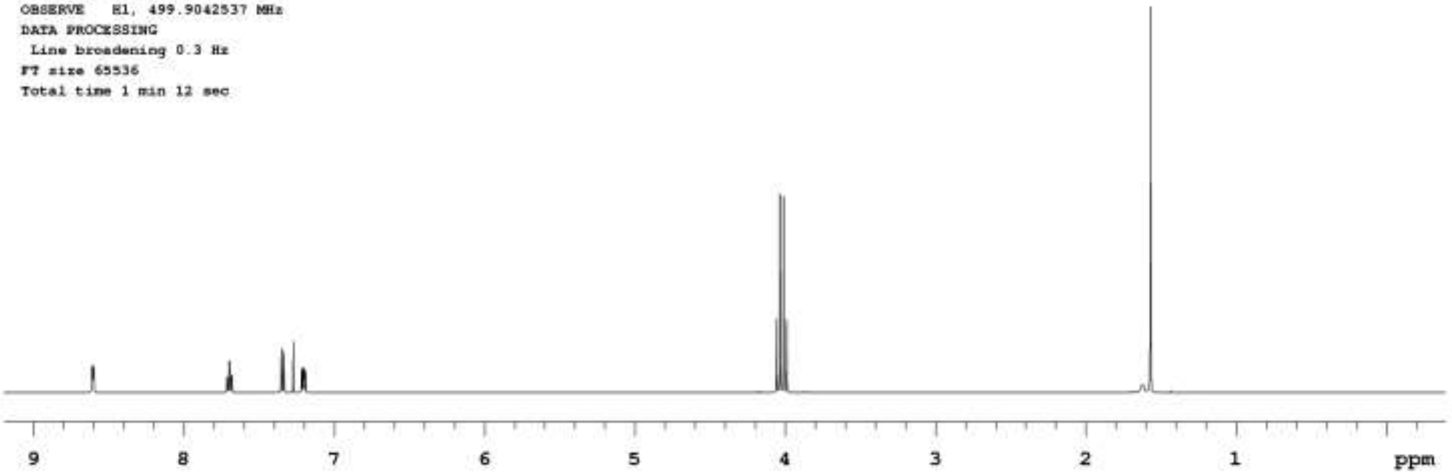

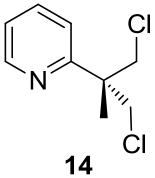

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```
11kjs40-2C

 Sample Name:

 Data Collected on:
   Sn.Chem.LSA.UMich.edu-inova500
 Archive directory:

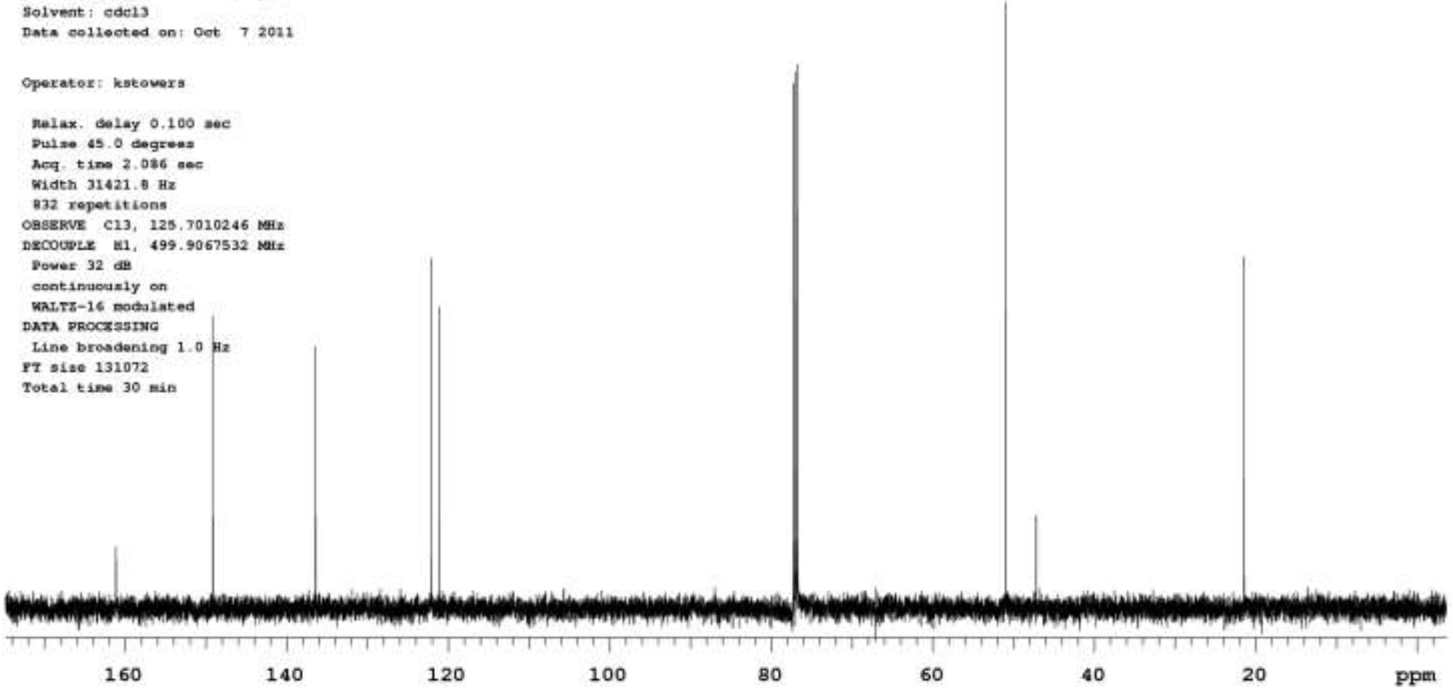
 Sample directory:

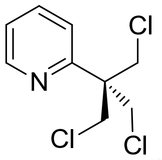
 FidFile: 11kjs40-2C

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Oct  7 2011

Operator: kstowers

 Relax. delay 0.100 sec
 Pulse 45.0 degrees
 Acq. time 2.086 sec
 Width 31421.8 Hz
 832 repetitions
OBSERVE  C13, 125.7010246 MHz
DECOUPLE  H1, 499.9067532 MHz
 Power 32 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 1.0 Hz
FT size 131072
Total time 30 min
```





15

```
11kjs77-3a

 Sample Name:

 Data Collected on:
   Ga.Chem.LSA.UMich.edu-vnmrs400
 Archive directory:

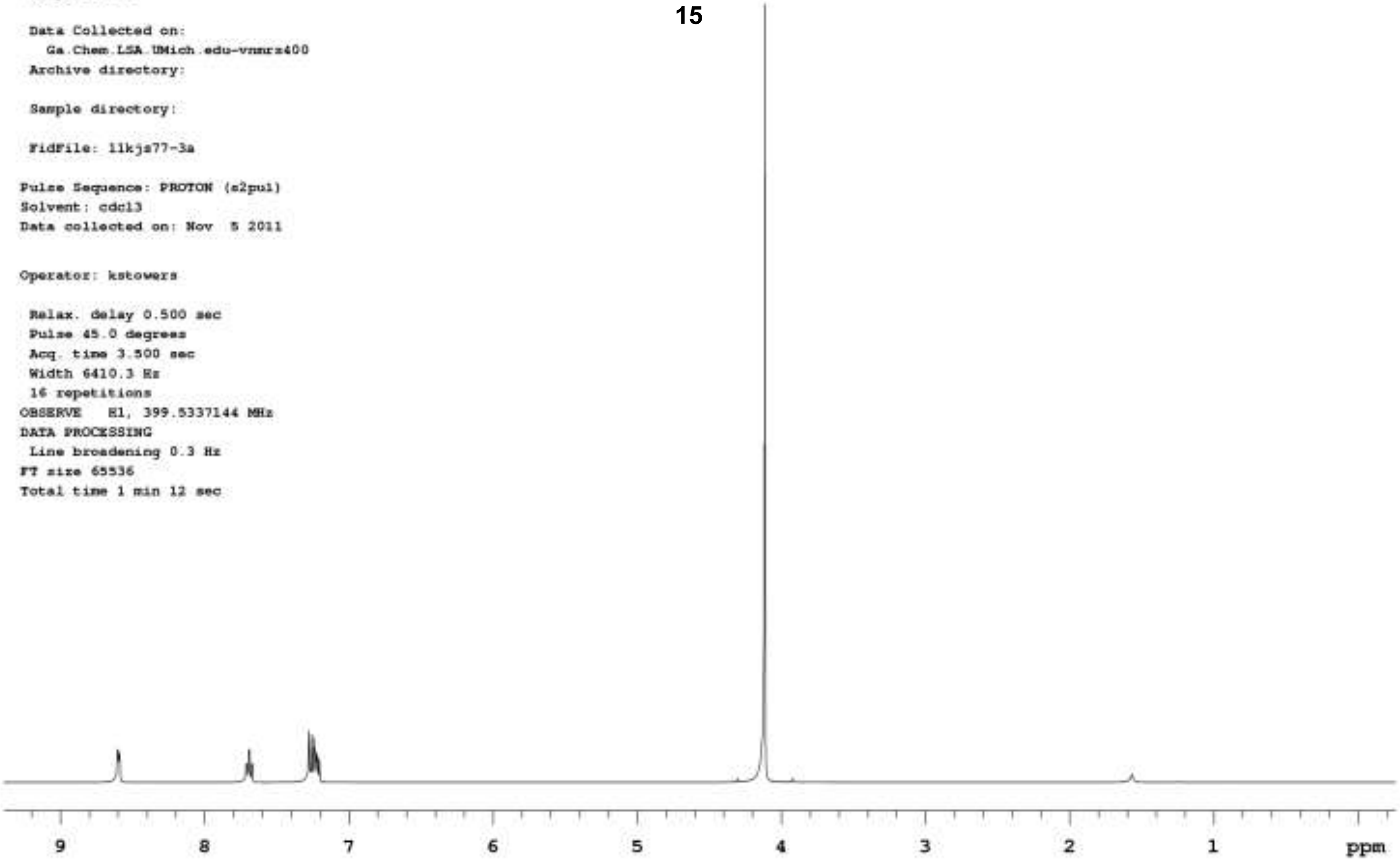
 Sample directory:

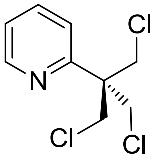
 FidFile: 11kjs77-3a

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Nov  5 2011


Operator: kstowers

 Relax. delay 0.500 sec
 Pulse 45.0 degrees
 Acq. time 3.500 sec
 Width 6410.3 Hz
 16 repetitions
OBSERVE   H1, 399.5337144 MHz
DATA PROCESSING
 Line broadening 0.3 Hz
FT size 65536
Total time 1 min 12 sec
```





15

```
11kjs77-3C

 Sample Name:

 Data Collected on:
   Ga.Chem.LSA.UMich.edu-vnmrs400
 Archive directory:

 Sample directory:

 FidFile: 11kjs77-3C

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Nov  5 2011


Operator: kstowers

 Relax. delay 0.100 sec
 Pulse 45.0 degrees
 Acq. time 2.569 sec
 Width 25510.2 Hz
 560 repetitions
OBSERVE  C13, 100.4628324 MHz
DECOUPLE  H1, 399.5357121 MHz
 Power 42 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 1.0 Hz
FT size 131072
Total time 24 min
```

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