Synthesis of α,β-Unsaturated Carbonyl Compounds via a Visible-Light-Promoted Organocatalytic Aerobic Oxidation

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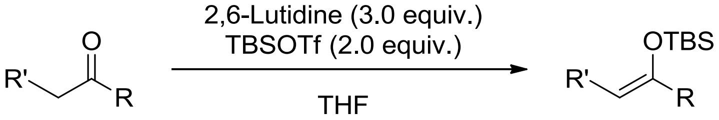
General methods and materials

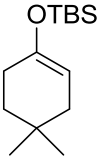
All the solvents were distilled under a nitrogen atmosphere prior to use. Anhydrous DMF was distilled from calcium hydride powder and anhydrous THF was distilled from sodium-benzophenone. EtOH was pre-dried with small amount of sodium and distilled. All glassware was flame-dried prior to use. TBSOTf and 2,6-lutidine were distilled from commercial reagents. Other chemical reagents were purchased and used as received. Thin-layer chromatography (TLC) was performed on 0.25 mm Tsingdao silica gel plates (60F-254). Gas chromatograph was recorded on a SHIMADZU GC-2014 spectrometer. TLC visualization was achieved by exposure to UV light (254 nm) and then stained with $KMnO_4$. Chromatographic purification was carried out by using Tsingdao silica gel (particle size 0.040–0.063 mm). ^{1}H NMR spectra were recorded on Bruker spectrometers (400 or 500 MHz) and are reported relative to the deuterated solvent signals. Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity, coupling constants (Hz) and integration. Multiplicities are described as: s (singlet), br (broad singlet), d (doublet), t (triplet), q (quartet), m (multiplet). ^{13}C NMR spectra were recorded on Bruker spectrometers (100 or 125 MHz) with total proton decoupling. HRMS (ESI-TOF) and X-ray analysis were performed by The Analytical Instrument Center at Shenzhen Graduate School of Peking University. HRMS data were reported as the ratio of ion mass/charge (m/z) in atomic mass unit. IR spectra were measured as dry films (KBr) and are reported in terms of frequency (cm^{-1}) and intensity of absorption.

General procedure for silyl enol ethers



To a solution of the corresponding carbonyl compound (10.0 mmol, 1.0 eq.) in dry THF (10 mL, 1 M) was added 2,6-Lutidine (30.0 mmol, 3.0 equiv.) at room temperature. The reaction vessel was cooled to 0 °C and stirred for 5 min before TBSOTf (20.0 mmol, 2.0 equiv.) was added slowly via a syringe. The mixture was stirred for 1 hr and was quenched by addition of saturated aqueous NH_4Cl solution. The aqueous layer was extracted three times using EtOAc. The combined organic layer was dried over $MgSO_4$, filtered, concentrated and purified by flash chromatography on silica gel (pre-treated with Et_3N) to yield the desired TBS-silyl enol ether.

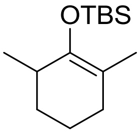
Characterization of silyl enol ethers



1a

tert-Butyl((4,4-dimethylcyclohex-1-en-1-yl)oxy)dimethylsilane, **1a** (2.28 g, 95% yield, 10 mmol scale)

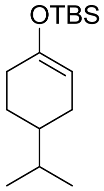
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.78 (t, *J* = 4.0 Hz, 1H), 2.01-1.99 (m, 2H), 1.83-1.81 (m, 2H), 1.42 (t, 1.5Hz, 2H), 0.93 (s, 15H), 0.14 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.4, 103.1, 37.9, 35.9, 28.6, 28.0, 27.5, 25.7, 18.0, -4.4; HRMS-ESI calcd. for $C_{14}H_{29}OSi$ [M + H$^+$]: 241.1988; Found: 241.1972. IR (KBr, thin film) 2957, 2932, 2860, 1684, 1198 cm^{-1}.



1b

tert-Butyl((2,6-dimethylcyclohex-1-en-1-yl)oxy)dimethylsilane, **1b** (1.92 g, 80% yield, 10 mmol scale)

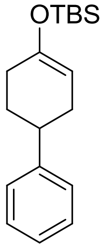
^{1}H NMR (500 MHz, $CDCl_3$) 2.20-2.10 (m, 1H), 2.00-1.88 (br, 2H), 1.82-1.74 (m, 1H), 1.66-1.59 (m, 1H), 1.57 (s, 3H), 1.51-1.42 (m, 1H), 1.06 (d, J = 6.9 Hz, 3H), 0.97 (s, 9H), 0.14-1.09 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.1, 111.6, 33.8, 32.1, 31.0, 25.9, 20.1, 19.0, 18.3, 16.9, -3.8, -4.2; HRMS-ESI calcd. for $C_{14}H_{29}OSi$ [M + H$^+$]: 241.1988; Found: 241.1982. IR (KBr, thin film) 2959, 2930, 2859, 1682, 1254, 1167 cm^{-1}.



1c

tert-butyl((4-isopropylcyclohex-1-en-1-yl)oxy)dimethylsilane, **1c** (2.46 g, 97% yield, 10 mmol scale)

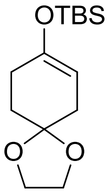
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.85-4.84 (m, 1H), 2.10-1.97 (m, 3H), 1.80-1.75 (m, 2H), 1.51-1.47 (m, 1H), 1.31-1.22 (m, 2H), 0.92 (s, 9H), 0.90-0.87 (m, 6H), 0.127 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.5, 103.8, 40.1, 32.0, 30.3, 27.3, 26.5, 25.7, 20.1, 19.8, 18.0, -4.3(-4.5); HRMS-ESI calcd. for $C_{15}H_{31}OSi$ [M + H$^+$]: 255.2144; Found: 255.2140. IR (KBr, thin film) 2957, 2930, 2886, 2858, 1672, 1256 cm^{-1}.



1d

tert-Butyldimethyl((1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-yl)oxy)silane, **1d** (2.07 g, 72% yield, 10 mmol scale)

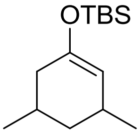
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33-7.20 (m, 5H), 4.97 (d, *J* = 4.0 Hz, 1H), 2.77 (t, *J* = 10.5 Hz, 1H), 2.32-2.22 (m, 3H), 2.08 (d, *J* = 16.0 Hz, 1H), 1.97 (d, *J* = 13.5 Hz, 1H), 1.88 (dd, *J* = 11.5 Hz, 6.0 Hz, 1H), 0.96 (s, 9H), 0.18 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.4, 146.7, 128.3, 126.9, 126.0, 103.7, 40.0, 32.0, 30.2, 30.1, 18.0, -4.3, -4.4; HRMS-ESI calcd. for $C_{18}H_{29}OSi$ [M + H$^+$]: 289.1943; Found: 289.1977. IR (KBr, thin film) 3084, 3061, 3026, 2955, 2928, 2893, 2857, 1670 cm^{-1}.



1e

(1,4-dioxaspiro[4.5]dec-7-en-8-yloxy)(tert-butyl)dimethylsilane, **1e** (2.48 g, 92% yield, 10 mmol scale)

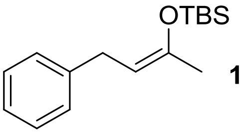
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.72 (t, *J* = 4.0 Hz, 1H), 3.98-3.95 (m, 4H), 2.60 (dd, *J* = 16.5, 1.5 Hz, 2H), 2.21 (dd, *J* = 6.5 Hz, 1.0 Hz, 2H), 1.80 (t, *J* = 6.5 Hz, 2H), 0.91 (s, 9H), 0.13 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.0, 107.7, 100.7, 64.4, 34.0, 31.2, 28.5, 25.6, 18.0, -4.5; HRMS-ESI calcd. for $C_{14}H_{27}O_3Si$ [M + H$^+$]: 271.1729 ; Found: 271.1730 . IR (KBr, thin film) 2957, 2930, 2887, 2859, 1676, 1246 cm^{-1}.



1f

tert-Butyl((3,5-dimethylcyclohex-1-en-1-yl)oxy)dimethylsilane, **1f** (2.16 g, 92% yield, 10 mmol scale)

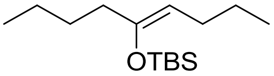
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.72 (s, 1H), 2.31-2.26 (m, 1H), 1.99 (dt, *J* = 16.5 Hz, 2.5 Hz, 1H), 1.78-1.72 (m, 1H), 1.71-1.64 (m, 2H), 0.99-0.95(m, 6H), 0.947(s, 9H), 0.76-0.69 (m, 1H), 0.15 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.0, 110.8, 40.9, 38.5, 30.3, 29.7, 26.0, 22.7, 22.0, 18.0, -4.4, -4.5; HRMS-ESI calcd. for $C_{14}H_{29}OSi$ [M + H$^+$]: 241.1988; Found: 241.1972. IR (KBr, thin film) 2957, 2932, 2860, 1684, 1653, 1198 cm^{-1}.



1g

(Z)-tert-butyldimethyl((4-phenylbut-2-en-2-yl)oxy)silane, **1g** (1.83 g, 70% yield, 10 mmol scale)

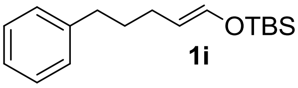
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30-7.27 (m, 2H), 7.23-7.17 (m, 3H), 4.63 (t, *J* = 7.0 Hz, 1H), 3.40 (d, *J* = 7.5 Hz, 2H), 1.85 (s, 3H), 0.99 (s, 9H), 0.19 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.4, 142.4, 128.4, 128.3, 125.6, 107.2, 31.7, 25.9, 22.8, 18.3, -3.6; HRMS-ESI calcd. for $C_{16}H_{27}OSi$ [M + H$^+$]: 263.1831; Found: 263.1840. IR (KBr, thin film) 3084, 3063, 3028, 2957, 2930, 2887, 2858, 1676, 1603, 1495, 1454, 1256 cm^{-1}.



1h

(Z)-tert-butyldimethyl(non-4-en-5-yloxy)silane, **1h** (2.27 g, 89% yield, 10 mmol scale)

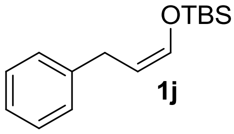
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.43 (t, *J* = 7.0 Hz, 1H), 2.08-1.92 (m, 4H), 1.49-1.43 (m, 2H), 1.37-1.31 (m, 4H), 0.92 (s, 9H), 0.89 (t, *J* = 8.0 Hz, 6H), 0.13 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ150.5, 103.8, 40.1, 31.9, 30.2, 27.3, 26.5, 25.7, 20.6, 19.8, 18.0, -4.3, -4.5; MS-EI calcd. for $C_{15}H_{32}OSi$ [M $^+$]: 256.2; Found: 256.2. IR (KBr, thin film) 2959, 2932, 2897, 2860, 1674, 1253 cm^{-1}.



1i

(E)-tert-butyldimethyl((5-phenylpent-1-en-1-yl)oxy)silane, **1i** (2.43 g, 88% yield, 10 mmol scale)

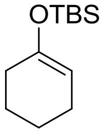
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29-7.26 (m, 2H), 7.20-7.16 (m, 3H), 6.22 (d, *J* = 6.0 Hz, 1H), 4.49 (dd, *J* = 13.5 Hz, 7.5 Hz, 1H), 2.64 (t, *J* = 7.5 Hz, 2H), 2.16 (t, *J* = 7.5 Hz, 1H), 2.13 (t, *J* = 7.5 Hz, 1H), 1.68 (q, *J* = 7.5 Hz, 2H), 0.93 (s, 9H), 0.13 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ142.8, 138.8, 128.4, 128.2, 125.5, 110.2, 35.6, 31.5, 25.6, 23.4, 18.3, -5.4; HRMS-ESI calcd. for $C_{17}H_{29}OSi$ [M + H$^+$]: 277.1988; Found: 277.1979. IR (KBr, thin film) 2955, 2920, 2850, 1655, 1651, 1255 cm^{-1}.



1j

(Z)-tert-butyldimethyl((3-phenylprop-1-en-1-yl)oxy)silane, **1j** (2.18 g, 88% yield, 10 mmol scale)

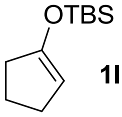
^{1}H NMR (500 MHz, CDCl$_3$) δ7.32-7.27 (m, 4H), 7.23 (m, H), 6.37 (d, *J* = 5.5 Hz, 1H), 4.73 (d, *J* = 6.0 Hz, 3H), 3.51 (d, *J* = 6.5 Hz, 2H), 1.01 (s, 9H), 0.22 (s, 6H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 142.0, 139.1, 128.4, 128.3, 125.6, 126.4, 109.2, 30.0, 25.7, 18.3, -5.3; HRMS-ESI calcd. for $C_{15}H_{25}OSi$ [M + H$^+$]: 249.1675 ; Found: 249.1664 . IR (KBr, thin film) 3084, 3063, 3030, 2957, 2930, 2855, 1654, 1494, 1255 cm^{-1}.



1k

tert-butyl(cyclohex-1-en-1-yloxy)dimethylsilane, **1k** (1.97 g, 92% yield, 10 mmol scale)

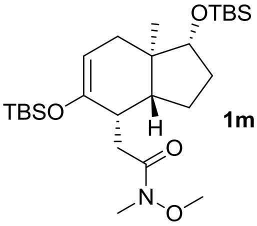
^{1}H NMR (400 MHz, CDCl$_3$) δ 4.87 (m, 1H), 2.03-1.99 (m, 4H), 1.69-1.63 (m, 2H), 1.56-1.48 (m, 2H), 0.93 (s, 9H), 0.13 (s, 6H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 150.4, 104.3, 29.9, 25.7, 23.8, 23.2, 22.3, 18.0, -4.5; HRMS-ESI calcd. for $C_{12}H_{25}OSi$ [M + H$^+$]: 215.1596; Found:215.1593. IR (KBr, thin film) 2930, 2895, 2886, 2859, 1670, 1651, 1256 cm^{-1}.



1l

tert-butyl(cyclopent-1-en-1-yloxy)dimethylsilane, **1l** (1.41 g, 71% yield, 10 mmol scale)

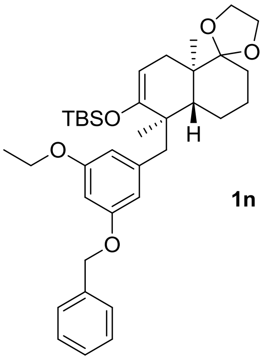
^{1}H NMR (400 MHz, CDCl$_3$) δ 4.65-4.60 (m, 1H), 2.30-2.20 (m, 4H), 1.90-1.80 (m, 2H), 0.93 (s, 9H), 0.15 (s, 6H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 155.3, 102.3, 33.4, 28.6, 25.6, 21.3, 18.0, -4.5; HRMS-ESI calcd. for $C_{11}H_{23}OSi$ [M + H$^+$]: 199.1518; Found:199.1521. IR (KBr, thin film) 2956, 2987, 2856, 1647, 1473, 1342, 1251, 1070, 923, 718 cm^{-1}.



1m

2-((1*R*,3a*R*,4*S*,7a*R*)-1,5-bis((tert-butyldimethylsilyl)oxy)-7a-methyl-2,3,3a,4,7,7a-hexahydro-1*H*-inden-4-yl)-N-methoxy-N-methylacetamide, **1m** (0.239 g, 96% yield, 0.5 mmol scale)

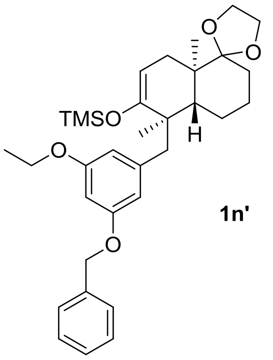
^{1}H NMR (500 MHz, CDCl$_3$) δ 4.80 (m, 1H), 3.67 (s, 3H, O-CH$_3$), 3.63 (d, *J* = 8.5 Hz, 1H), 3.15 (s, 3H, N-CH$_3$), 2.87 (dd, *J* = 15.5 Hz, 4.0 Hz, 1H), 2.61 (m, 1H), 2.34 (dd, *J* = 15.5 Hz, 9.0 Hz, 1H), 1.93 (ddd, J = 16.0 Hz, 5.5 Hz, 1.0 Hz, 1H), 1.87-1.83 (m, 2H), 1.54-1.45 (m, 3H), 1.43-1.35 (m, 1H), 0.91 (s, 9H), 0.87 (s, 9H), 0.81 (s, 3H), 0.14 (s, 6H), 0.00 (s, 6H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 174.2, 151.8, 103.4, 81.2, 61.1, 47.6, 42.9, 39.1, 36.3, 33.1, 32.4, 31.3, 25.9, 25.8, 24.3, 18.1, 18.0, 11.0, -4.2, -4.5, -4.8, -4.9; HRMS-ESI calcd. for $C_{26}H_{52}NO_4Si_2$ [M + H$^+$]: 498.3435; Found: 498.3429. IR (KBr, thin film) 2957, 2930, 2884, 2857, 1672, 1651, 1258 cm^{-1}.



1n

(((4a'*R*,5'*R*,8a'*R*)-5'-(3-(benzyloxy)-5-ethoxybenzyl)-5',8a'-dimethyl-3',4',4a',5',8',8a'-hexahydro-2'*H*-spiro[[1,3]dioxolane-2,1'-naphthalen]-6'-yl)oxy)(tert-butyl)dimethylsilane, **1n** (0.224 g, 90% yield, 0.42 mmol scale)

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.45-7.32 (m, 5H), 6.48 (s, 1H), 6.40 (s, 2H), 5.03 (s, 2H), 4.71 (dd, *J* = 6.5 Hz, 2.0 Hz, 1H), 3.99 (q, *J* = 7.0 Hz, 2H), 3.84-3.80 (m, 2H), 3.77-3.74 (m, 2H), 2.94 (d, *J* = 13.0 Hz, 1H), 2.41 (d, *J* = 13.0 Hz, 1H), 1.98-1.94 (m, 2H), 1.64 (m, 1H), 1.61-1.49 (m, 4H), 1.47-1.41 (m, 2H), 1.39 (t, *J* = 7.0 Hz, 3H), 1.08 (s, 3H), 1.06 (s, 3H), 1.01 (s, 9H), 0.26 (s, 3H), 0.18 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.3, 151.7, 141.8, 137.6, 128.5, 127.7, 127.3, 112.7, 109.4, 109.3, 102.2, 100.8, 70.2, 65.0, 64.6, 63.5, 44.3, 43.4, 41.9, 40.5, 30.6, 29.2, 26.0, 22.7, 22.3, 21.0, 18.4, 16.9, 14.9, -3.3, -5.3; HRMS-ESI calcd. for $C_{36}H_{53}O_5Si$ [M + H$^+$]:593.3662 ; Found: 593.3655. IR (KBr, thin film) 2978, 2953, 2930, 2882, 2860, 1668, 1595, 1454, 1254, 1166, 1058 cm^{-1}.



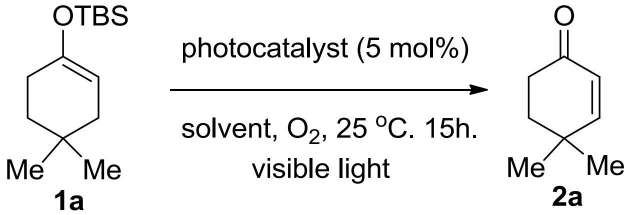
1n'

To a solution of the substrate ketone (114 mg，1.0 eq.) in dry THF (5 mL) was added 2,6-Lutidine(78 mg, 3.0 eq.) at room temperature. The reaction vessel was cooled to 0 °C and stirred for 5 min before TMSOTf (106 mg, 2.0 equiv.) was added slowly via a syringe. The mixture was stirred for 1 hr and was quenched by the addition of saturated aqueous NH_4Cl solution. The aqueous layer was extracted three times using EtOAc. The combined organic layer was dried over $MgSO_4$, filtered, concentrated and purified by flash chromatography on silica gel (pre-treated with Et_3N) to yield the desired TMS-silyl enol ether (120 mg, 92% yield).

(((4a'*R*,5'*R*,8a'*R*)-5'-(3-(benzyloxy)-5-ethoxybenzyl)-5',8a'-dimethyl-3',4',4a',5',8',8a'-hexahydro-2'*H*-spiro[[1,3]dioxolane-2,1'-naphthalen]-6'-yl)oxy)trimethylsilane, **1n’**

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45-7.32 (m, 5H), 6.48 (s, 1H), 6.40 (s, 2H), 5.03 (s, 2H), 4.70 (dd, *J* = 6.5 Hz, 2.0 Hz, 1H), 4.03-3.87 (m, 2H), 3.86-3.81 (m, 2H), 3.77-3.75 (m, 2H), 2.98 (d, *J* = 13.0 Hz, 1H), 2.42 (d, *J* = 13.0 Hz, 1H), 1.99-1.94 (m, 2H), 1.63 (m, 1H), 1.54-1.45 (m, 6H), 1.39 (t, *J* = 7.0 Hz, 3H), 1.08 (s, 3H), 1.02 (s, 3H), 0.25 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.2, 151.9, 141.8, 137.6, 128.5, 127.7, 127.4, 112.7, 109.5, 109.4, 102.2, 100.6, 70.1, 65.0, 64.6, 63.4, 44.5, 43.1, 41.9, 40.7, 30.6, 29.1, 22.7, 22.3, 20.1, 16.8, 14.9, 0.49; HRMS-ESI calcd. for $C_{36}H_{53}O_5Si$ [M + H^+]:551.3193 ; Found: 551.3171. IR (KBr, thin film) 2978, 2945, 2932, 2879, 1701, 1670, 1593, 1452, 1251, 1161, 1056 cm^{-1}.

Procedure for reaction investigation and optimization



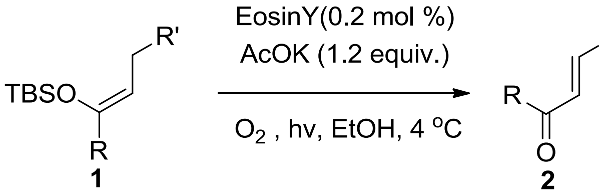
An oven-dried 10mm × 100 mm test tube containing a magnetic stir bar was charged a photocatalyst (0.05 mmol, 0.05 equiv.), the TBS-silyl enol ether (240 mg, 1.0 mmol, 1.0 equiv.), biphenyl (as internal standard, 154 mg, 1.0 mmol), and a solvent (5 mL). The reaction mixture was degassed/backfilled with oxygen three times and placed in a half cut plastic rack. The rack was placed next to (2 cm) a household light bulb. The reaction was stirred slowly under an oxygen balloon for 15 hrs. A small aliquot was taken, filtered through a plug of silica gel, diluted with ether and analyzed by GC.

Condition screening table:

Catalyst	solvent	additives	Light source	temperature	time	conv	SM
$[Ru(bpy)_3]^{2+}Cl^{2-}$ (5 mol%)	DMF	--	LED Corn 12W	RT	12h	9 %	8 %
$[Ru(bpy)_3]^{2+}Cl^{2-}$ (5 mol%)	DMF	--	LED Green 9W	RT	12h	13 %	55 %
$[Ru(bpy)_3]^{2+}Cl^{2-}$ (5 mol%)	DMF	--	Tornado 24W	RT	12h	41 %	0 %
TPP (5 mol%)	DMF	--	Tornado 24W	RT	12h	32 %	0 %
Rhodamine B (5 mol%)	DMF	--	Tornado 24W	RT	12h	0.3 %	44 %
		--			24h	13 %	17 %
Aliazrin (5 mol%)	DMF	--	Tornado 24W	RT	12h	0 %	100 %
		--			24h	3 %	70 %
Eosin B (5 mol%)	DMF	--	Tornado 24W	RT	12h	33 %	24 %
Eosin Y Na_2 (5 mol%)	DMF	--	Tornado 24W	RT	12h	45 %	0 %
--	DMF	--	Tornado 24W	RT	12h	0 %	100 %
Eosin Y Na_2 (5 mol%)	PhMe	--	Tornado 24W	RT	12h	5 %	0 %
Eosin Y Na_2 (5 mol%)	DCM	--	Tornado 24W	RT	12h	10 %	0 %
Eosin Y Na_2 (5 mol%)	DCE	--	Tornado 24W	RT	12h	12 %	0 %
Eosin Y Na_2 (5 mol%)	1,4-Dioxane	--	Tornado 24W	RT	12h	16 %	0 %
Eosin Y Na_2 (5 mol%)	THF	--	Tornado 24W	RT	12h	19 %	0 %
Eosin Y Na_2 (5 mol%)	acetone	--	Tornado 24W	RT	12h	20 %	0 %
Eosin Y Na_2 (5 mol%)	CH_3CN	--	Tornado 24W	RT	12h	35 %	0 %

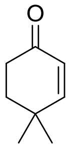
Eosin Y Na$_2$ (5 mol%)	DMSO	--	Tornado 24W	RT	12h	52 %	0 %
Eosin Y Na$_2$ (5 mol%)	MeOH	--	Tornado 24W	RT	12h	59 %	0 %
Eosin Y Na$_2$ (10 mol%)	MeOH	--	Tornado 24W	RT	12h	59 %	0 %
Eosin Y Na$_2$ (8 mol%)	MeOH	--	Tornado 24W	RT	12h	58 %	0 %
Eosin Y Na$_2$ (6 mol%)	MeOH	--	Tornado 24W	RT	12h	58 %	0 %
Eosin Y Na$_2$ (4 mol%)	MeOH	--	Tornado 24W	RT	12h	61 %	0 %
Eosin Y Na$_2$ (2 mol%)	MeOH	--	Tornado 24W	RT	12h	59 %	0 %
Eosin Y Na$_2$ (1 mol%)	MeOH	--	Tornado 24W	RT	12h	59 %	0 %
Eosin Y Na$_2$ (0.5 mol%)	MeOH	--	Tornado 24W	RT	12h	59 %	0 %
Eosin Y Na$_2$ (0.2 mol%)	MeOH	--	Tornado 24W	RT	12h	56 %	0 %
Eosin Y Na$_2$ (0.2 mol%)	MeOH	--	Tornado 24W	RT	1h	35 %	36 %
Eosin Y Na$_2$ (0.2 mol%)	MeOH	--	Tornado 24W	RT	2h	49 %	5 %
Eosin Y (0.2 mol%)	MeOH	--	Tornado 24W	RT	4h	51 %	0 %
Eosin Y Na$_2$ (0.2 mol%)	MeOH	--	Tornado 24W	RT	8h	54 %	0 %
Eosin Y Na$_2$ (0.2 mol%)	MeOH	4A-MS	Tornado 24W	RT	12h	59 %	0 %
Eosin Y Na$_2$ (0.2 mol%)	MeOH	NaHCO$_3$ 5 mol%	Tornado 24W	RT	12h	59 %	0 %
Eosin Y Na$_2$ (0.2 mol%)	MeOH	Cs$_2$CO$_3$ 5 mol%	Tornado 24W	RT	12h	61 %	0 %
Eosin Y Na$_2$ (0.2 mol%)	MeOH	K$_2$CO$_3$ 5 mol%	Tornado 24W	RT	12h	59 %	0 %
Eosin Y Na$_2$ (0.2 mol%)	MeOH	Et$_3$N 5 mol%	Tornado 24W	RT	12h	59 %	0 %
Eosin Y Na$_2$ (0.2 mol%)	MeOH	DMAP 5 mol%	Tornado 24W	RT	12h	52 %	0 %
Eosin Y Na$_2$ (0.2 mol%)	MeOH	Pyridine 5 mol%	Tornado 24W	RT	12h	61 %	0 %
Eosin Y Na$_2$ (0.2 mol%)	EtOH	--	Tornado 24W	RT	15h	59 %	0 %
Eosin Y Na$_2$ (0.2 mol%)	EtOH	PTSA 1.5equiv.	Tornado 24W	RT	15h	1 %	0 %
Eosin Y Na$_2$ (0.2 mol%)	EtOH	AcOH 1.5equiv.	Tornado 24W	RT	15h	45 %	0 %
Eosin Y Na$_2$ (0.2 mol%)	EtOH	NaOH 1.5equiv.	Tornado 24W	RT	15h	1 %	0 %
Eosin Y Na$_2$ (0.2 mol%)	EtOH	Imidazole 1.5equiv.	Tornado 24W	RT	15h	45 %	0 %
Eosin Y Na$_2$ (0.2 mol%)	EtOH	AcOH 1.5equiv.	Tornado 24W	RT	15h	61 %	0 %
Eosin Y Na$_2$ (0.2 mol%)	EtOH	AcOK 1.5equiv.	Tornado 24W	4 °C	15h	65 %	0 %

General synthesis of α,β-Unsaturated carbonyl compounds



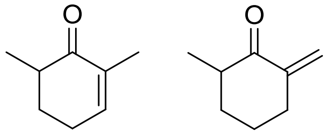
An oven-dried 10mm × 100 mm test tube containing a magnetic stir bar was charged Eosin Y (1.4 mg, 2.0 umol, 0.2 mol %), the corresponding TBS-silyl enol ether (1.0 mmol, 1.0 eq.), AcOK (118 mg, 1.20 mmol, 1.2 eq.) and EtOH (2.0 mL). The reaction mixture was degassed/backfilled with oxygen three times and placed in a half cut plastic rack. The rack was placed next to (2 cm) a household florescent bulb (Philip, Torado-24W) in a 4 °C cold room. The reaction was stirred slowly under an oxygen balloon. Upon complete consumption of the starting material as judged by TLC, solvent was removed and the residue was purified by flash silica gel chromatography using ether/hexanes. Extra care was taken during rotorvap (ice bath) to avoid loss of volatile products.

Product characterization


2a

4,4-dimethylcyclohex-2-enone, **2a** (0.081 g, 65% yield, 1.0 mmol scale)

^{1}H NMR (400 MHz, CDCl$_3$) δ 6.66 (d, *J* = 10.4 Hz, 1H), 5.85 (dd, *J* = 10.4 Hz, 2.0 Hz, 1H), 2.46 (td, *J* = 7.2 Hz, 1.6Hz, 2H), 1.88 (td, *J* = 6.8 Hz, 1.6Hz, 2H), 1.17 (d, *J*= 2.0 Hz, 6H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 199.6, 159.8, 126.8, 36.0, 34.3, 32.7, 27.6; HRMS-ESI calcd. for $C_8H_{13}O$ [M + H$^+$]: 125.0966; Found: 125.0959. IR (KBr, thin film) 2960, 2928, 2870, 1676 cm^{-1}.

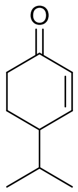


2b **2b'**

The product was formed as a 1:1.6 mixture of region isomers (0.081 g, 65% yield, 1.0 mmol scale). The exo-olefinic isomer **2b'** slowly converted to the cyclohexenone isomer **2b** during flash column.

Cyclohexenone isomer, 2,6-dimethylcyclohex-2-enone, **2b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.72-6.65 (m, 1H), 2.51-2.29 (m, 2H), 2.10-1.98 (m, 1H), 1.77-1.75(m, 3H), 1.74-1.67(m, 2H), 1.13 (d, *J*=6.8); ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.6, 144.5, 134.9, 41.5, 31.2, 25.2, 16.1, 15.2;

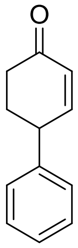
Exo-olefinic isomer, 2-methyl-6-methylenecyclohexanone, **2b'**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.70 (br, 1H), 5.07 (dd, *J* = 3.28Hz, 2.12Hz, 1H), 2.77-2.62 (m, 1H), 2.51-2.29 (m, 2H), 2.12-1.81 (m, 3H), 1.62-1.48 (m, 1H), 1.12 (d, *J*=10.5); ^{13}C NMR (125 MHz, $CDCl_3$) δ 204.8, 146.0, 119.0, 44.8, 33.5, 32.7, 23.6,15.4; HRMS-ESI calcd. for $C_8H_{13}O$ [M + H$^+$]: 125.0966; Found: 125.0959. IR (KBr, thin film) 2961, 2932, 1666, 1607, 1371, 1213, 878 cm^{-1}.



2c

4-*I*sopropylcyclohex-2-enone, **2c** (0.086 g, 62% yield, 1.0 mmol scale)

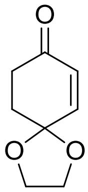
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.89 (d, *J* = 10.0 Hz, 1H), 6.00 (dd, *J* = 10.0 Hz, 2.0 Hz, 1H), 2.53-2.48 (m, 1H), 2.37-2.27 (m, 2H), 2.02-1.98 (m, 1H), 1.85-1.78 (m, 2H), 0.92-0.99 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.0, 154.3, 129.7, 42.5, 37.4, 31.5, 25.3, 19.6, 19.5; HRMS-ESI calcd. for $C_9H_{15}O$ [M + H$^+$]: 139.1123; Found: 139.1121. IR (KBr, thin film) 2959, 2932, 2874, 1682, 912, 744 cm^{-1}.



2d

2,3-dihydro-[1,1'-biphenyl]-4(1H)-one, **2d** (0.125 g, 73% yield, 1.0 mmol scale)

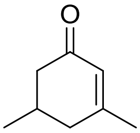
^{1}H NMR (500 MHz, CDCl$_3$) δ 7.31-7.29 (m, 2H), 7.28-7.26 (m, 1H), 7.24-7.22 (m, 2H), 7.01-6.98 (m, 1H), 6.19-6.16 (dd, *J* = 10.0 Hz, 2.5 Hz, 1H), 3.75-3.72 (m, 1H), 2.58-2.45 (m, 2H), 2.39-2.35 (m, 1H), 2.10-2.05 (m, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 199.1, 152.7, 142.8, 130.0, 128.9, 127.5, 127.1, 42.6, 36.9, 32.4; HRMS-ESI calcd. for $C_{12}H_{13}O$ [M + H$^+$]: 173.0966; Found: 173.0959. IR (KBr, thin film) 3061, 3028, 2951, 2928, 2864, 1684, 1603, 762, 700 cm^{-1}



2e

1,4-Dioxaspiro[4.5]dec-6-en-8-one, **2e** (0.120 g, 78% yield, 1.0 mmol scale)

^{1}H NMR (400 MHz, CDCl$_3$) δ 6.60 (d, *J* = 10.2 Hz, 1H), 5.99 (d, *J* = 10.2 Hz, 1H), 4.05 (d, *J* = 13.8 Hz, 2H), 4.01 (d, *J* = 13.8 Hz, 2H), 2.61 (t, *J* = 6.4 Hz, 2H), 2.18 (t, *J* = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 198.7, 146.4, 130.5, 103.9, 65.0, 35.2, 32.9; HRMS-ESI calcd. for $C_8H_{11}O_3$ [M + H$^+$]: 155.0708; Found: 155.0701. IR (KBr, thin film) 2961, 2889, 1684, 1220 cm^{-1}.

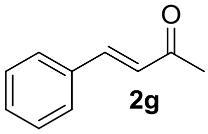


2f

3,5-Dimethylcyclohex-2-enone, **2f** (0.079 g, 64% yield, 1.0 mmol scale)

^{1}H NMR (500 MHz, CDCl$_3$) δ 5.88 (s, 1H), 2.42 (dd, *J* = 16.5 Hz, 4.0 Hz, 1H), 2.30 (dd, *J*

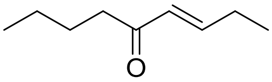
= 17.5 Hz, 4.0 Hz, 1H), 2.23-2.16 (m, 1H), 2.05-1.99 (m, 2H), 1.96 (s, 3H), 1.07 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 199.8, 161.7, 126.4, 45.2, 39.4, 30.0, 24.3, 21.1; HRMS-ESI calcd. for $C_8H_{13}O$ [M + H$^+$]: 125.0966; Found: 125.0962. IR (KBr, thin film) 2957, 2928, 1668, 1654, 912, 743 cm^{-1}.



2g

(E)-4-phenylbut-3-en-2-one, **2g** (0.096 g, 66% yield, 1.0 mmol scale)

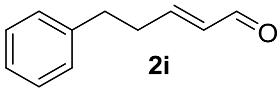
^{1}H NMR (400 MHz, CDCl$_3$) δ 7.57-7.56 (m, 2H), 7.53 (d, *J* = 16.4 Hz, 1H), 7.42-7.40 (m, 3H), 6.73 (d, *J* = 16.4 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 198.4, 143.4, 134.4, 130.5, 128.9, 128.2, 127.1, 27.5; HRMS-ESI calcd. for $C_{10}H_{11}O$ [M + H$^+$]: 147.0810; Found: 147.0804 . IR (KBr, thin film) 3061, 3028, 3003, 2960, 2926, 1690, 1668, 1625, 1609, 1576, 1495, 1450, 1258 cm^{-1}.



2h

(E)-Non-3-en-5-one, **2h** (0.085 g, 61% yield, 1.0 mmol scale)

^{1}H NMR (400 MHz, CDCl$_3$) δ 6.88(dt, *J* = 16.0 Hz, 6.4 Hz, 1H), 6.09 (dt, *J* = 16.0 Hz, 1.6 Hz, 1H), 2.54 (t, *J* = 7.6 Hz, 2H), 2.25 (dt, *J* = 7.6 Hz, 1.6 Hz, 2H), 1.60 (q, *J* = 7.6 Hz, 2H), 1.39-1.29 (s, *J* = 7.6 Hz, 2H), 1.08 (t, *J* = 7.6 Hz, 3H), 0.92 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 201.1, 148.5, 129.4, 39.7, 26.4, 25.4, 22.4, 13.8, 12.2; HRMS-ESI calcd. for $C_9H_{17}O$ [M + H$^+$]: 141.1279; Found: 141.1274. IR (KBr, thin film) 2960, 2934, 2874, 1716, 1458 cm^{-1}.

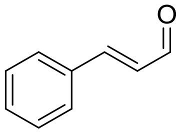


2i

(*E*)-5-Phenylpent-2-enal, **2i** (0.102 g, 64% yield, 1.0 mmol scale, containing a minor *Z*-isomer: *E*/*Z* > 20/1)

^{1}H NMR (400 MHz, CDCl$_3$) δ 9.50 (d, *J* = 8 Hz, 1H), 7.34-7.30 (m, 2H), 7.25-7.19 (m, 3H), 6.87 (dt, *J* = 15.6 Hz, 6.8 Hz, 1H), 6.15 (ddt, *J* = 15.6 Hz, 8.0 Hz, 1.2 Hz, 1H), 2.85

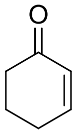
(t, *J* = 7.2 Hz, 2H), 2.69 (t, *J* = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.0, 157.4, 140.3, 133.4, 128.6, 128.3, 126.4, 34.2, 34.0; HRMS-EI calcd. for $C_{11}H_{13}O$ [M $^{+}$]: 160.0888; Found: 160.0877. IR (KBr, thin film) 3028, 2930, 2818, 1693, 1682, 1124 cm^{-1}.



2j

Cinnamaldehyde, **2j** (0.116 g, 88% yield, 1.0 mmol scale)

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.70 (d, *J* = 8 Hz, 1H), 7.58-7.55 (m, 2H), 7.47 (d, *J* = 16 Hz, 1H), 7.45-7.41 (m, 3H), 6.72 (dd, *J* = 16 Hz, 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.7, 152.8, 133.9, 131.2, 129.1, 128.5; HRMS-ESI calcd. for C_9H_9O [M + H^{+}]: 133.0653; Found: 133.0650. IR (KBr, thin film) 3061, 3028, 2816, 2743, 1670, 1626, 1450 cm^{-1}.

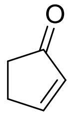


2k

Cyclohex-2-enone, **2k** (0.053 g, 56% yield, 1.0 mmol scale).

A large scale experiment was performed using 20 mmol of **1k** and 1.0 mol% of Eosin Y under otherwise identical conditions. The desired cyclohexenone was isolated in 53% yield, 1.02 g).

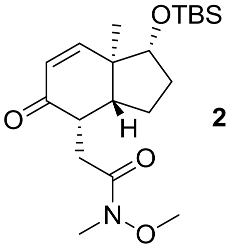
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00-6.95 (dt, *J* = 10.1 Hz, 4.1 Hz, 1H), 6.05-5.95 (dt, *J* = 10.1 Hz, 1.9 Hz, 1H), 2.50-2.35 (t, *J* = 8.0 Hz, 2H), 2.35-2.25 (m, 2H), 2.05-1.95 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.7, 150.7, 129.8, 38.0, 25.6, 22.6; MS-EI calcd. for C_6H_8O [M $^{+}$]: 96.1; Found: 96.1. IR (KBr, thin film) 3341, 3034, 2951, 1685, 1340, 1123, 876, 672 cm^{-1}



2l

Cyclopent-2-enone, **2l** (0.020 g, 25% yield, 1.0 mmol scale)

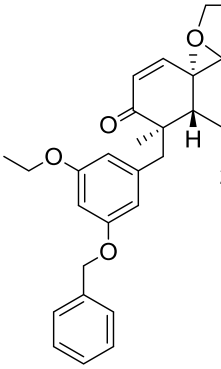
^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.75-7.65 (dt, *J*=8.0 Hz, 2.5 Hz, 1H), 6.20-6.10 (dt, *J*=6.0 Hz, 2.0 Hz, 1H), 2.75-2.60 (m, 2H), 2.35-2.25 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 210.4, 164.8, 134.4, 33.9, 28.9; MS-EI calcd. for C_5H_6O [M $^+$]: 82.0; Found: 82.1. IR (KBr, thin film) 3406, 2924, 1710, 1348, 915, 752 cm^{-1}.



2m

2-((1*R*,3a*R*,4*S*,7a*R*)-1-((tert-butyldimethylsilyl)oxy)-7a-methyl-5-oxo-2,3,3a,4,5,7a-hexahydro-1*H*-inden-4-yl)-N-methoxy-N-methylacetamide, **2m** (0.029 g, 74% yield, 0.1 mmol scale)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.07(d, *J* = 9.5 Hz, 1H), 5.90 (d, *J* = 9.5 Hz, 1H), 3.75 (s, 3H, O-CH_3), 3.90 (dd, *J* = 7.5 Hz, 9.0 Hz, 1H), 3.18 (s, 3H, N-CH_3), 2.97 (dt, *J* = 13.0 Hz, 5.5 Hz, 1H), 2.86 (dd, *J* = 17.0 Hz, 4.5 Hz, 1H), 2.61 (dd, *J* = 17.0 Hz, 4.5 Hz, 1H), 2.09-1.99 (m, 2H), 1.62-1.51 (m, 4H), 1.01 (s, 3H), 0.91 (s, 9H), 0.06 (s, 3H), 0.04 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 201.2, 173.4, 155.7, 126.2, 76.5, 61.1, 46.6, 45.5, 44.5, 30.1, 29.9, 25.8, 23.6, 18.0, 12.6, -4.4, -4.9; HRMS-ESI calcd. for $C_{20}H_{36}NO_4Si$ [M + H$^+$]: 382.2414; Found: 382.2403. IR (KBr, thin film) 2955, 2930, 2886, 2857, 1672, 1250 cm^{-1}.



2n

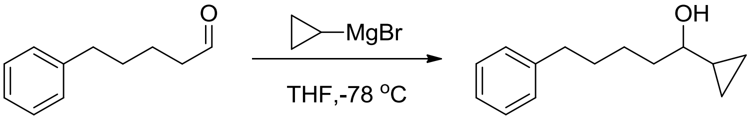
(4a'*R*,5'*R*,8a'*R*)-5'-(3-(benzyloxy)-5-ethoxybenzyl)-5',8a'-dimethyl-3',4',4a',5'-tetrahydro-2'*H*-spiro[[1,3]dioxolane-2,1'-naphthalen]-6'(8a'*H*)-one, **2n** (0.056 g, 61% yield, 0.2 mmol scale; the reaction using the corresponding TMS substrate **1n'** resulted 64% yield.)

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.43-7.32 (m, 5H), 6.94 (d, *J* = 10.0 Hz, 1H), 6.37 (s, 1H), 6.29 (s, 1H), 6.22 (s, 1H), 5.85 (d, *J* = 10.0 Hz, 1H), 5.0 (s, 2H), 3.98-3.83 (m, 6H), 3.23 (d, *J* = 13.5 Hz, 1H), 2.55 (d, *J* = 13.5 Hz, 1H), 2.49 (dd, *J* = 10.5 Hz, 2.0 Hz, 1H), 1.72 (dd, *J* = 12.0 Hz, 2.0 Hz, 1H), 1.65-1.58 (m, 4H), 1.50 (dd, *J* = 13.0 Hz, 3.0 Hz, 1H), 1.37 (t, *J* = 7.0 Hz, 3H), 1.25 (s, 3H), 1.19 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 204.1, 159.5, 155.9, 140.4, 137.1, 128.5, 127.8, 127.5, 127.4, 111.7, 109.2, 100.6, 70.0, 65.0, 64.6, 63.4, 49.6, 45.2, 40.6, 29.5, 22.5, 21.1, 19.6, 14.8; HRMS-ESI calcd. for $C_{30}H_{37}O_5$ [M + H$^+$]: 477.2641; Found: 477.2635. IR (KBr, thin film) 2980, 2940, 2884, 1665, 1593, 1450, 1166, 1055 cm^{-1}.

Mechanistic studies:

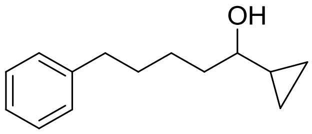
Radical clock experiments:

Substrate preparation



1o-precursor-1 **1o-precursor-2**

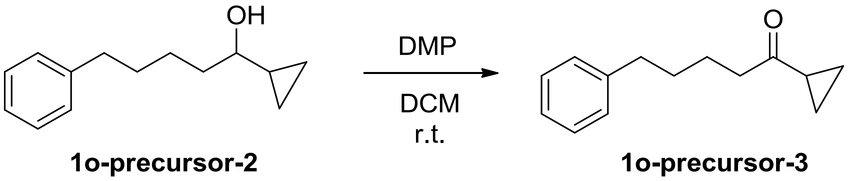
To a solution of **1o-precursor-1** (164 mg, 1.01 mmol) in THF (5 mL) was added Cyclopropylmagnesium Bromide (0.5 M in THF, 4.0 mL) slowly at -78 ^{o}C. The mixture was allowed to stir for 1 hr and quenched carefully with saturated aqueous NH_4Cl solution. The aqueous layer was extracted with EtOAc (3 x 10 mL) and the combined organic layer was dried over $MgSO_4$, filtered, and the solvent was removed under vacuum. The residue was purified by flash chromatography on silica gel (EtOAc/hexane = 1/4) to give the product alcohol **1o-precursor-2** (155 mg, 75%).



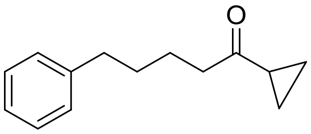
1o-precursor-2

1-Cyclopropyl-5-phenylpentan-1-ol, **1o-precursor-2**

1H NMR (500 MHz, $CDCl_3$) δ 7.32-7.27 (m, 2H), 7.21-7.18 (m, 3H), 2.90-2.85 (m, 1H), 2.65 (t, J = 7.7 Hz, 2H), 1.72-1.63 (m, 4H), 1.59-1.43 (m, 2H), 0.94-0.87 (m, 1H), 0.56-0.47 (m, 2H), 0.30-0.26 (m, 1H), 0.24-0.19 (m, 1H); 13C NMR (125 MHz, $CDCl_3$) δ 142.7, 128.4, 128.3, 125.6, 100.0, 37.1, 36.0, 31.6, 25.4, 18.0, 2.8, 2.4; HRMS-ESI calcd. for $C_{14}H_{20}ONa$ [M + Na^+]: 227.1412; Found: 227.1404. IR (KBr, thin film) 2997, 2934, 2857, 1771, 1759, 1242, 1049, 746, 698 cm^{-1}.



To a solution of **1o-precursor-2** (150 mg, 0.73 mmol) in DCM (3 mL) was added DMP (2.0 equiv.) in one-pot at room temperature. The mixture was allowed to stir for 10 mins and quenched with saturated NH_4Cl solution. The aqueous layer was extracted by DCM (3 x 10 mL) and the combined organic layer was dried over $MgSO_4$, filtered, and the solvent was removed under vacuum. The residue was purified by flash chromatography on silica gel (EtOAc/hexane = 1/6) to give the product **1o-precursor-3** (131 mg, 89%).

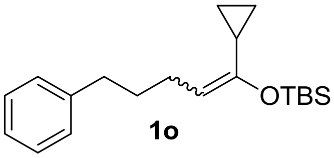


1o-precursor-3

1-Cyclopropyl-5-phenylpentan-1-one, **1o-precursor-3**

1H NMR (500 MHz, $CDCl_3$) δ 7.32-7.26 (m, 2H), 7.22-7.16 (m, 3H), 2.67-2.61 (t, J=7.2 Hz, 2H), 2.60-2.54 (t, J = 6.8 Hz, 2H), 1.95-1.88 (m, 1H), 1.72-1.62 (m, 4H), 1.05-0.98 (m, 2H), 0.88-0.82 (m, 2H), 13C NMR (125 MHz, $CDCl_3$) δ 201.7, 142.2 128.4, 128.3, 125.7, 43.2, 35.7, 31.0, 23.7, 20.3, 10.4; HRMS-ESI calcd. for $C_{14}H_{19}O$ [M + H^+]: 203.1436; Found: 203.1431. IR (KBr, thin film) 2995, 2937, 2859, 1771, 1759, 1697, 744, 698 cm^{-1}.

The silyl enol ether **1o** was synthesized as a mixture of *E*/*Z* isomers from **1o-precursor-3** using the procedure described in page 3.



1o

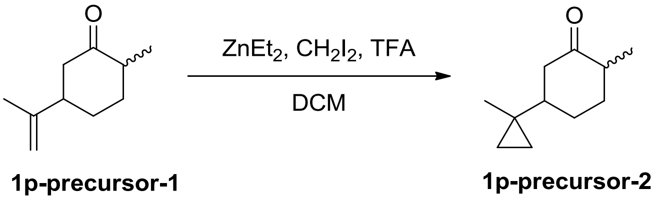
(0.52 g, 82% yield, 2.0 mmol scale)

Z-isomer: (*Z*)-tert-butyl((1-cyclopropyl-5-phenylpent-1-en-1-yl)oxy)dimethylsilane, **1o-*Z***

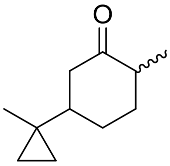
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35-7.27 (m, 2H), 7.26-7.18 (m, 3H), 4.69 (t, *J* = 7.5 Hz, 1H), 2.70 (t, *J* = 7.6 Hz, 2H), 2.08 (dd, *J* = 14.5 Hz, 7.2 Hz, 2H), 1.82-1.73 (m, 2H), 1.75-1.61 (m, 1H), 0.96 (s, 9H), 0.77-0.73 (m, 1H), 0.69-0.64 (m, 1H), 0.60-0.55 (m, 2H), 0.20 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.7, 142.7, 128.4, 128.2, 125.6, 104.8, 35.5, 32.6, 25.8, 18.3, 16.0, 11.1, 6.2, 3.9, -4.4;

E-isomer: (*E*)-tert-butyl((1-cyclopropyl-5-phenylpent-1-en-1-yl)oxy)dimethylsilane, **1o-*E***

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35-7.27 (m, 2H), 7.26-7.18 (m, 3H), 4.44 (t, *J* = 7.0 Hz, 1H), 2.64 (t, *J* = 7.8 Hz, 2H), 2.18 (dd, *J* = 17.7 Hz, 7.4 Hz, 2H), 1.71-1.63 (m, 2H), 1.37-1.27 (m, 1H), 1.00 (s, 9H), 0.77-0.73 (m, 1H), 0.69-0.64 (m, 1H), 0.56-0.50 (m,2H), 0.20 (s, 6H); 13C NMR (125 MHz, CDCl3) δ 152.3, 142.8, 128.5, 128.2, 125.6, 104.9, 35.8, 31.7, 25.9, 24.9, 18.2, 16.0, 11.1, 6.2, 3.9, -4.4; HRMS-ESI calcd. for $C_{20}H_{33}OSi$ [M + H+]: 317.2301; Found: 317.2290. IR (KBr, thin film) 3026, 3011, 2955, 2930, 2857, 1651, 1253, 746, 698 cm-1.



Et_2Zn (1.0 M in hexanes, 5 mL, 5 mmol) was added to freshly distilled DCM (5 mL) and the resulting colorless solution was cooled to 0 °C. TFA (0.38 mL, 5 mmol) was added dropwise via a gas-tight micro-syringe. The mixture was stirred for 30min before CH_2I_2 (0.41 ml, 5mmol) was added. After stirred for another 30 min, a solution of **1p-precursor-1** (380 mg, 2.5 mmol) in DCM (5 mL) was added and the reaction mixture was allowed to warm to room temperature. The mixture was allowed to stir for 1 hr and quenched carefully with saturated aqueous NH_4Cl solution. The aqueous layer was extracted by EtOAc (3 x 15 mL) and the combined organic layer was dried over $MgSO_4$, filtered, and the solvent was removed under vacuum. The residue was purified by flash chromatography on silica gel (EtOAc/hexane = 1/10) to give **1p-precursor-2** (298 mg, 72%).

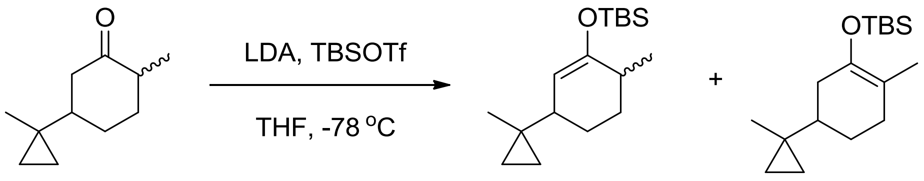


1p-precursor-2

2-Methyl-5-(1-methylcyclopropyl)cyclohexanone, **1p-precursor-2**

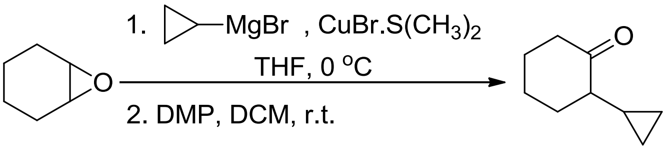
^{1}H NMR (500 MHz, $CDCl_3$) δ 2.36-2.20 (m, 3H), 2.12-2.03 (m, 1H), 1.82-1.75 (m, 1H), 1.56-1.66 (m, 1H), 1.27-1.16 (qd, *J* = 13.1 Hz, *J* = 3.6 Hz, 1H), 1.01-0.95 (m, 4H), 0.94

(d, 1H), 0.30-0.17 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 213.2, 48.9, 45.6, 44.8, 34.9, 29.0, 18.8, 18.6, 14.3, 12.8, 12.7; HRMS-ESI calcd. for $C_{11}H_{19}O$ [M + H$^+$]: 167.1436; Found:167.1426. IR (KBr, thin film) 2982, 2961, 2932, 1771, 1759, 1713, 1240, 1055 cm^{-1}.



1p-precursor-2 **1p** **1p'**

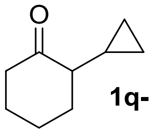
To a solution of the **1p-precursor-2** (250 mg, 1.5 mmol) in THF (5 mL) was added LDA (2M in THF, 2.0 mL) at -78 °C. After stirred for 2 hs, TBSOTf (0.69 mL, 3.0 mmol) was added dropwise via a gas-tight microsyringe. The mixture was quenched using saturated NH_4Cl aqueous solution 10 min later. The aqueous layer was extracted by EtOAc (3 x 10 mL) and the combined organic layer was dried over $MgSO_4$, filtered, and the solvent was removed under vacuum. The product was directly used for the photosensized aerobic oxidation directly without further purification.



1q-precursor-1 **1q-precusor-2**

To a solution of CuBr•SMe_2 (203 mg, 0.99 mmol) in THF (5 mL) was added Cyclopropylmagnesium Bromide (0.5 M in THF, 4.0 mL) at 0 °C. After stirred for 30 mins, Cyclohexene oxide (98 mg, 1.0 mmol, 0.1 mL) was added. The mixture was quenched using saturated aqueous NH_4Cl solution 1hr later. The aqueous layer was extracted by EtOAc (3 x 10 mL) and the combined organic layer was dried over $MgSO_4$, filtered, and the solvent was removed under vacuum. The residue was dissolved in DCM (5mL). DMP (840 mg) was carefully added at room temperature. The mixture was allowed to stir for 10 min and quenched with saturated aqueous NH_4Cl solution.

The aqueous layer was extracted by DCM (3 x 10mL) and the combined organic layer was dried over $MgSO_4$, filtered, and the solvent was removed under vacuum. The residue was purified by flash chromatography on silica gel (EtOAc/hexane = 1/4) to give the product (108 mg, 78%).

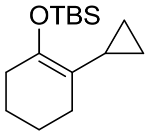


1q-precursor-2

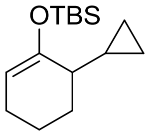
2-Cyclopropylcyclohexanone, **1q-precursor-2**

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.45-2.36 (m, 1H), 2.27-2.18 (m, 1H), 2.12-2.02 (m, 1H), 1.99-1.91 (m, 1H), 1.88-1.78 (m, 1H), 1.76-1.46 (m, 4H), 0.94-0.78 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 213.1, 56.1, 41.6, 33.6, 27.8, 24.4, 11.1, 4.2, 2.5; HRMS-ESI calcd. for $C_9H_{14}ONa$ [M + Na$^+$]: 161.0942; Found: 161.0949. IR (KBr, thin film) 2995, 1771, 1759, 1373, 1242, 1053 cm^{-1}.

The silyl enol ether **1q and 1q'** were synthesized as an inseparable mixture of regio isomers from **1q-precursor-2** using the procedure described in page 3.



1q

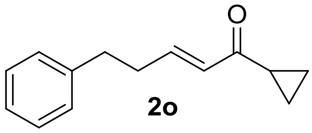


1q'

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.81 (t, *J*=3.0Hz, 1H), 2.05-1.98 (m, 2H), 1.75-1.55 (m, 5H), 0.96-0.93 (s, 9H), 0.60-0.45 (m, 2H), 0.45-0.35(m, 2H),0.17-0.16 (s, 3H), 0.14-0.13 (s, 3H), 0.51-0.00 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.6, 103.2, 43.5, 29.4, 25.8, 24.2, 19.9, 15.1, 5.66, 2.87, -3.83; ^{1}H NMR (400 MHz, $CDCl_3$) 2.10-2.05 (m, 2H), 2.05-1.90 (m,1H), 1.45-1.55 (m,4H), 1.35-1.25(m,1H), 1.00-0.95 (s, 9H), 0.80-0.75 (m, 2H), 0.35-0.25(m, 2H), 0.16-0.15 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.4, 114.6, 30.8, 25.9, 23.4, 22.7, 18.2, 18.0, 10.62,1.85,-2.97; IR (KBr, thin film) 2959, 2930, 2859, 1682, 1254, 1167 cm^{-1}

General Procedures for the Radical Clock Experiments:

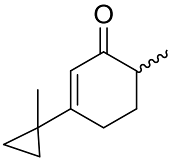
An oven-dried 10mm × 100 mm test tube containing a magnetic stir bar was charged Eosin Y (0.35 mg, 0.50 umol, 0.2 mol %), the corresponding TBS-silyl enol ether (0.25 mmol, 1.0 eq.), AcOK (29 mg, 0.30 mmol, 1.2 eq.) and EtOH (0.5 mL). The reaction mixture was degassed/backfilled with oxygen three times and placed in a half cut plastic rack. The rack was placed next to (2 cm) a household florescent bulb (Philip, Torado-24W) in a 4°C cold room. The reaction was stirred slowly under an oxygen balloon. Upon complete consumption of the starting material as judged by TLC, solvent was removed and the residue was purified by flash silica gel chromatography using ether/hexanes. Extra care was taken during rotorvap (ice bath) to avoid loss of volatile products.



2o

(*E*)-1-Cyclopropyl-5-phenylpent-2-en-1-one, **2o** (36 mg, 72% yield)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34-7.28 (m, 2H), 7.26-7.18 (m, 3H), 6.98-6.89 (m, 1H), 6.26 (dt, *J* = 15.8 Hz, 1.5Hz, 1H), 2.84-2.79 (t, *J* = 7.5 Hz, 2H), 2.61-2.54 (m, 2H), 2.14-2.17 (m, 1H), 1.10-1.05 (m, 2H), 0.93-0.88 (m, 2H), ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.1, 145.5, 140.8, 130.8, 128.4, 128.2, 126.1, 34.4, 34.1, 18.7, 10.9; HRMS-ESI calcd. for $C_{14}H_{17}O$ [M + H$^+$]: 201.1279; Found: 201.1274. IR (KBr, thin film) 3005, 2936, 2859, 1771, 1759, 1737, 1684, 1662, 1626, 748, 700 cm^{-1}.



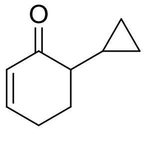
2p

6-Methyl-3-(1-methylcyclopropyl)cyclohex-2-enone, **2p** (27 mg, 65% yield)

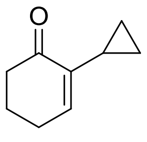
^{1}H NMR (500 MHz, $CDCl_3$) δ5.91-5.89 (d, *J* =1.48 Hz,1H), 2.32-2.20 (m,1H), 2.15-1.97 (m, 3H), 1.66-1.53 (m, 1H), 1.12-1.08 (d, *J* =6.88 Hz ,3H), 0.95-0.85 (m, 2H), 0.70-0.60 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 201.9, 168.8, 123.5, 40.6, 30.8, 25.3, 22.6, 20.8, 15.2, 15.1, 15.0; HRMS-ESI calcd. for $C_{11}H_{18}O$ [M + H$^+$]: 165.1279; Found:165.1274. IR

(KBr, thin film) 2961, 2932, 2872, 1665, 1607, 1213, 878 cm^{-1}.

Product **2q** and **2q'** were obtained as an inseparable mixture (23 mg, 68% yield)



2q



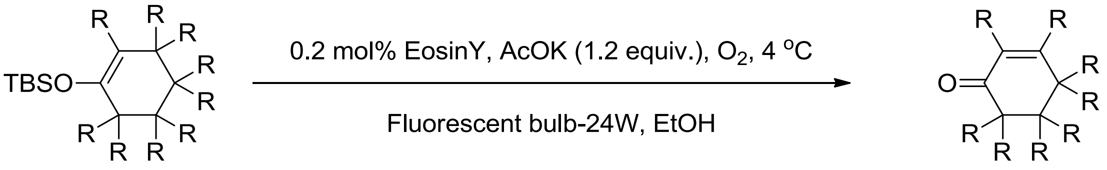
2q'

GC-MS calcd. for $C_9H_{12}O$ [M $^+$]: 137.1; Found: 137.1. IR (KBr, thin film) 3005, 2929, 2893, 2337, 1678, 1388, 1022, 796cm^{-1}.

6-Cyclopropylcyclohex-2-enone, **2q**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.94-6.88 (dt, *J*=10 Hz, 1H), 5.96-6.02 (dt, *J*=10Hz, 1.5Hz, 1H), 2.50-2.40 (m, 1H), 2.35-2.25 (m, 1H), 2.15-2.05 (m, 1H), 2.0-1.85 (m, 1H), 1.65-1.61 (m, 1H), 1.00-0.90 (m, 1H), 0.50-0.40 (m, 1H), 0.40-0.30 (m, 1H), 0.15-0.00 (m, 2H); ^{13}C NMR (400 MHz, $CDCl_3$) δ: 201.5, 149.4, 129.4, 51.4, 28.2, 24.8, 11.4, 4.3, 2.2.

2-Cyclopropylcyclohex-2-enone, **2q'**: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 6.44-6.41 (t, *J*=4.5 Hz, 1H), 2.50-2.40 (m, 2H), 2.38-2.28 (m, 2H), 2.15-2.05 (m, 2H), 0.95-0.85 (m, 1H), 0.75-0.70 (m, 2H), 0.40-0.30 (m, 1H), 0.15-0.00 (m, 1H); ^{13}C NMR (400 MHz, $CDCl_3$) δ: 199.5, 141.0, 140.7, 38.5, 25.7, 25.6, 22.8, 9.3, 6.1.

Kinetics and Isotope effect:



1k: R=H,
1k': R=D.

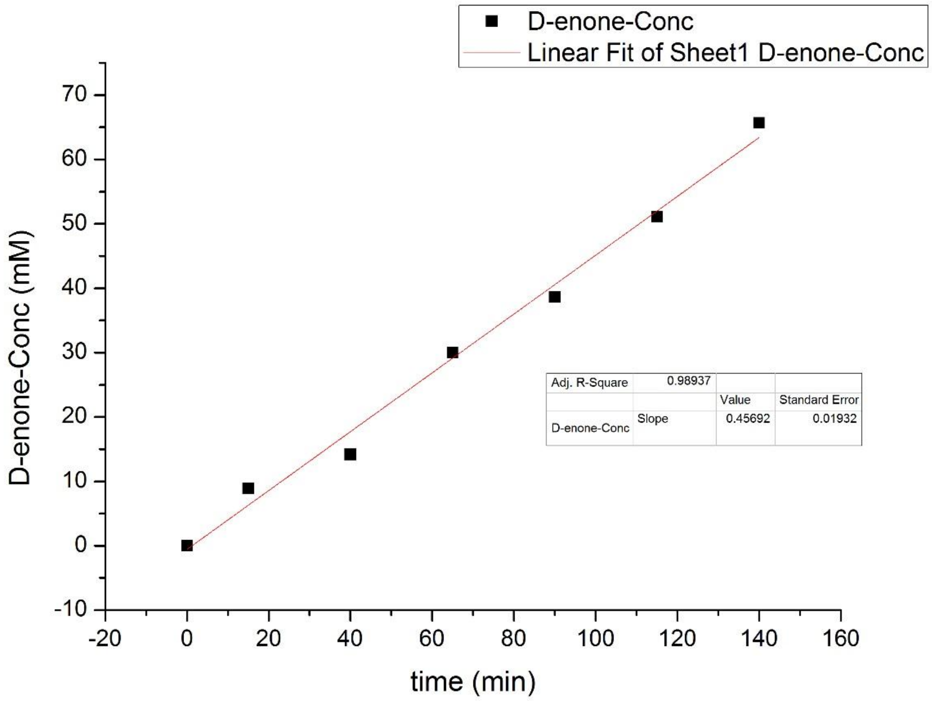
$K_{H/D}$=1.27

2k: R=H,
2k': R=D.

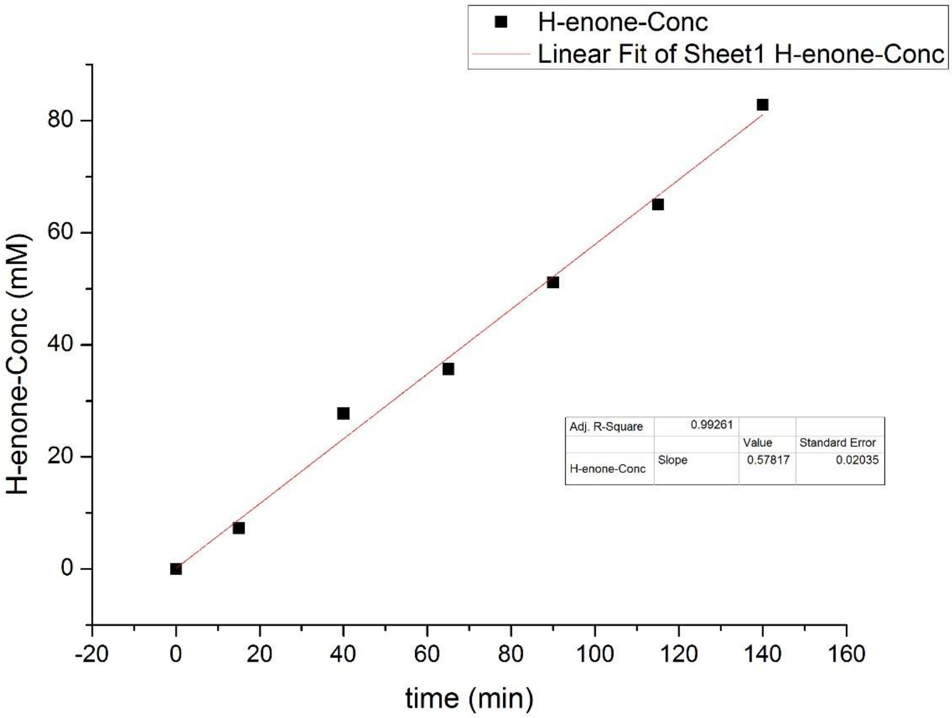
(Note: The preparation of the TBS-silyl enol ethers followed the general procedure in page 3) Two oven-dried 10mm × 100 mm test tubes were equipped with magnetic stir bars and charged with **1k** (182 mg, 0.86 mmol) and **1k'** (190 mg, 0.86 mmol) respectively. EtOH (2.6 mL), AcOK (103 mg, 1.03 mmol, 1.2 eq.), biphenyl (132.6 mg, 0.86 mmol), and Eosin Y (1.2 mg, 0.2 mol %) were added to each tube. The reaction mixture was degassed/backfilled with oxygen three times and placed in a half cut plastic rack. The rack was placed next to (2 cm) a household florescent bulb (Philip, Torado-24W) in a 4^{o}C cold room. The reaction was stirred slowly under an oxygen balloon. After 15mins, 40mins, 65mins, 90mins, 115mins, 140mins, 165mins and 195mins, aliquots of 0.1 mL of the crude reactions were taken, filtered through a plug of silica gel, diluted and analyzed by GC.

Raw data of conversion vs time

time	GC-yield of **2k**	GC-yield of **2k'**
15min	2.2%	3.1%
+25=40min	8.4%	4.3%
+25=65min	10.8%	9.1%
+25=90min	15.5%	11.7%
+25=115min	19.7%	15.5%
+25=140min	25.1%	19.9%
+25=165min	27.9%	25.9%
+30=195min	33.4%	28.6%



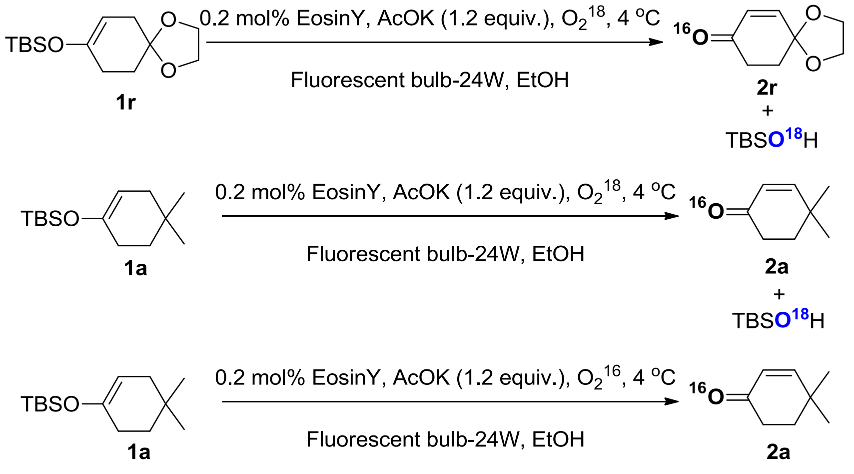
Adj R^2=0.98937, slope=0.45692



Adj R^2=0.99261, slope=0.57817

K_H/K_D=1.27

Experimental Details for $^{18}O_2$ Experiments:



$K_{16O/18O}=1.05$

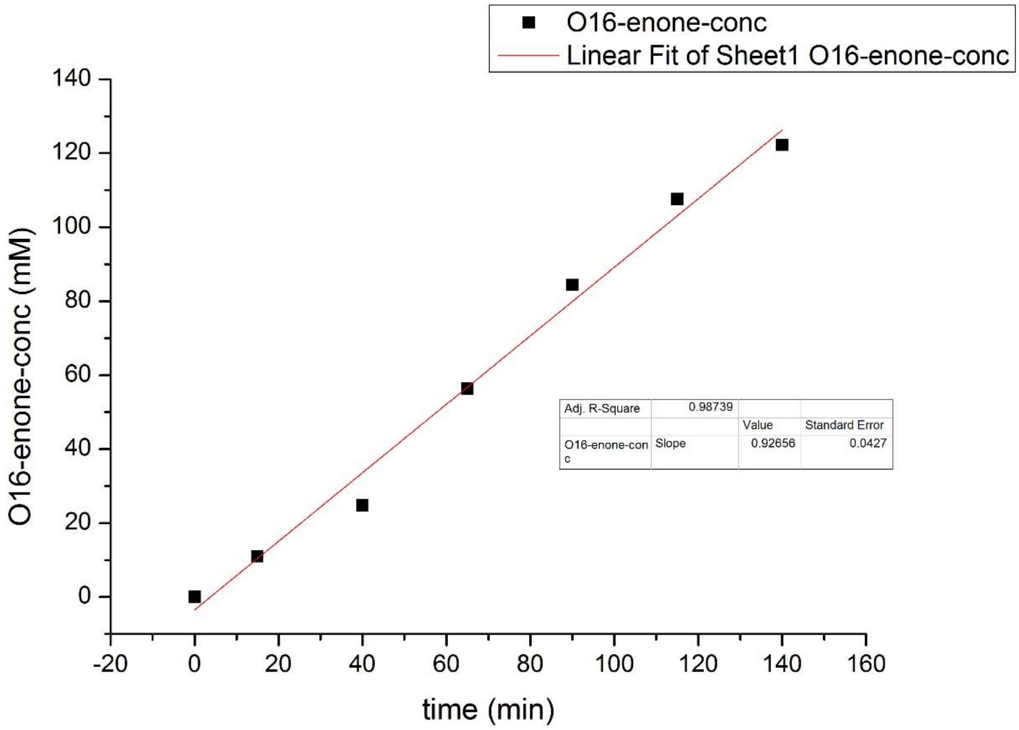
Two oven-dried 10mm × 100 mm test tubes were equipped with magnetic stir bars and charged with the same amount of **1a** (173 mg, 0.72 mmol), AcOK (85 mg, 0.85 mmol, 1.2 eq.), biphenyl (internal standard, 111 mg, 0.72 mmol) and Eosin Y (1.0 mg, 0.2 mol %) respectively. The reaction vessels were degassed/backfilled with nitrogen carefully and placed in a glovebox. Oxygen free EtOH (3.6 mL) was added to each tube in the glovebox. The test tubes were taken out of the glovebox, degassed/backfilled with $^{18}O_2$ and $^{16}O_2$, respectively. The reaction vessels were placed in a 4°C cold room next to a household fluorescent light bulb (24 W) under $^{18}O_2$ and $^{16}O_2$ balloons respectively. After 15mins, 40mins, 65mins, 90mins, 115mins, 140mins, 165mins and 195mins, aliquots of 0.1 mL of the crude reactions were taken, filtered through a plug of silica gel, diluted and analyzed by GC. At the end of the reaction, the crude mixture was analyzed by GC-MS and HRMS.

A separate reaction using substrate **1r** was carried out similarly to further confirm the result.

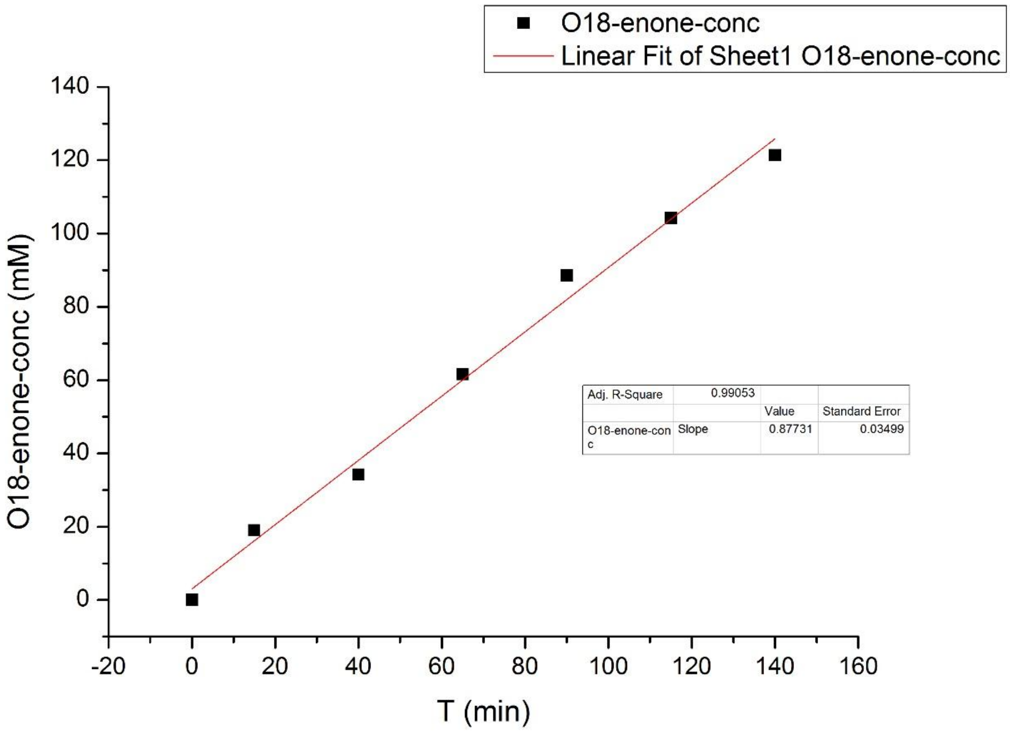
Raw data of conversion vs time

time	GC-yield of **2r** for O_2^{16} system	GC-yield of **2a** for O_2^{18} system

15min	5.5 %	9.5 %
+25=40min	12.4 %	17.1 %
+25=65min	28.2 %	30.8 %
+25=90min	42.2 %	44.3 %
+25=115min	53.8 %	52.1 %
+25=140min	61.1 %	60.7 %
+30=170min	62.5 %	61.2 %
+30=200min	62.7 %	61.6 %

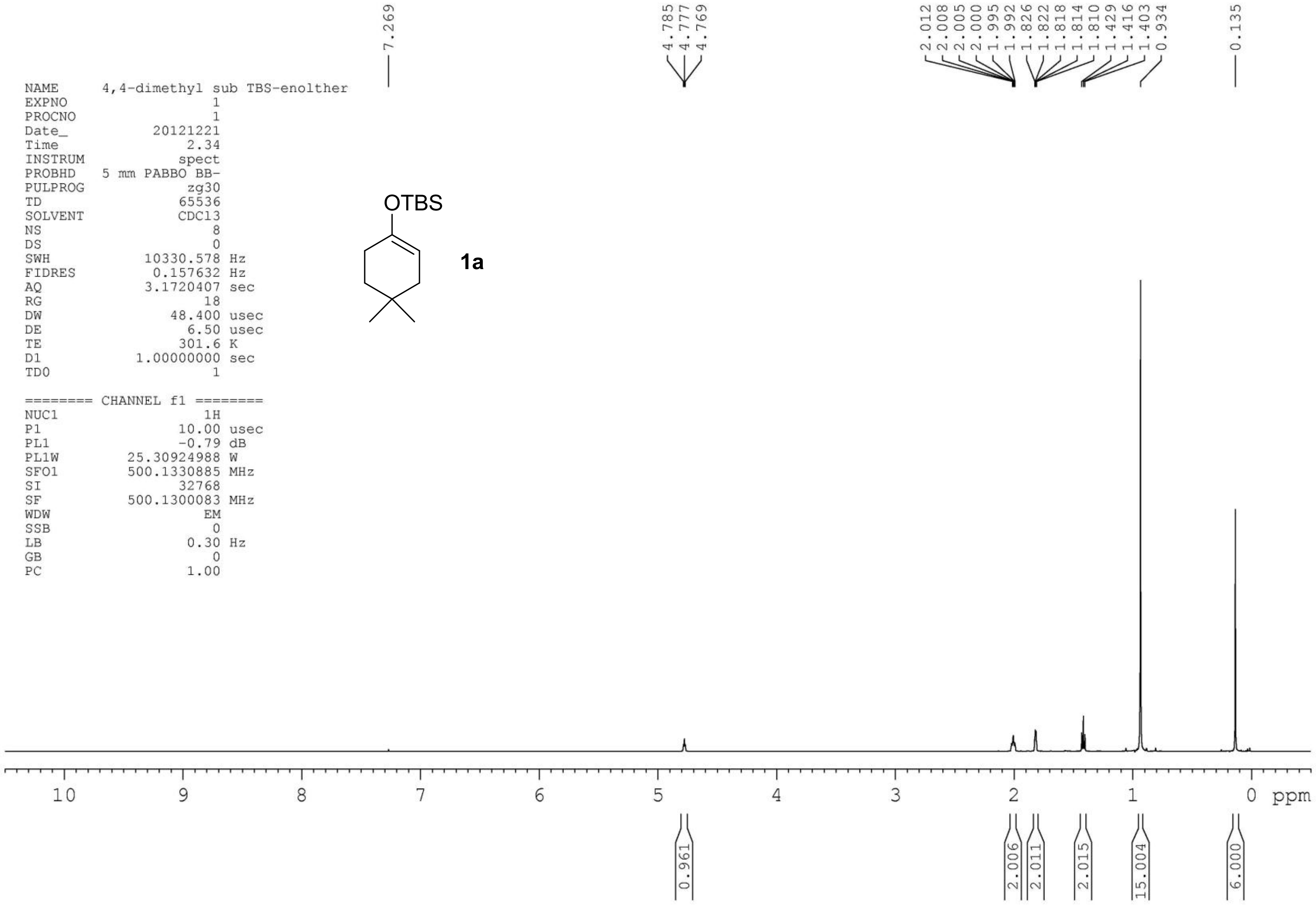


Adj R^2=0.98739, slope=0.92656



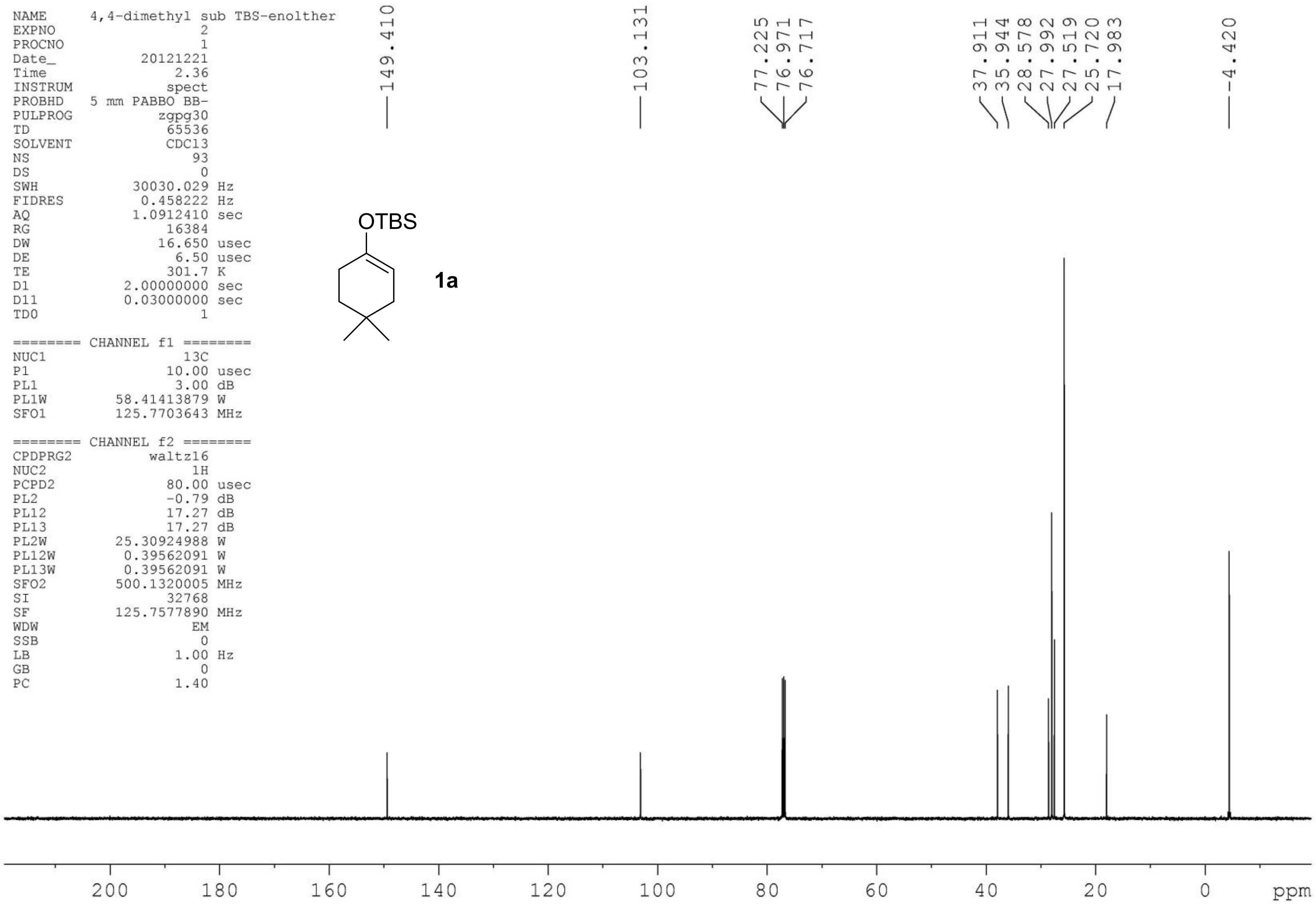
Adj R^2=0.99053, slope=0.87731

$K_{O16}/K_{O18}=1.05$



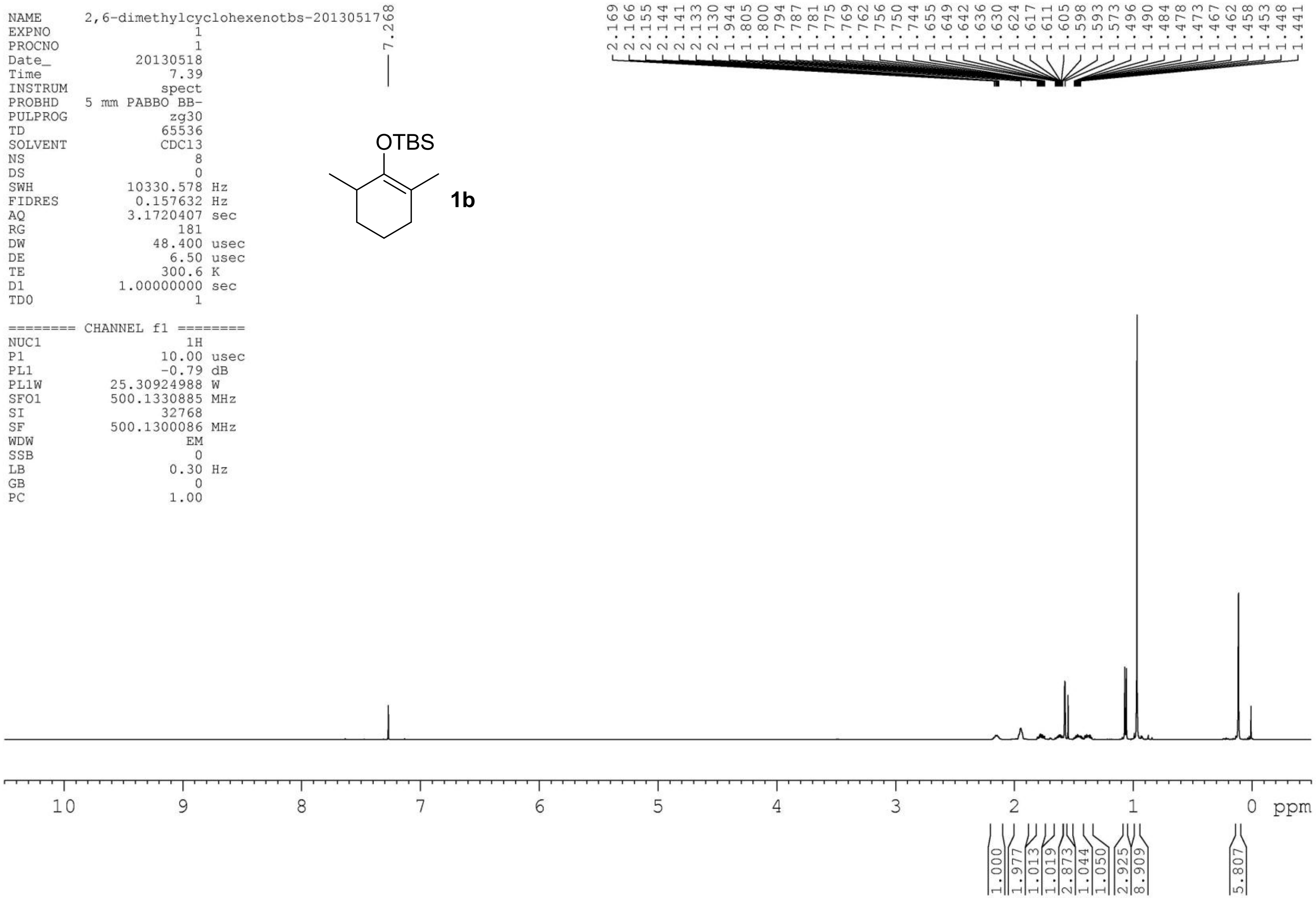
```
NAME      4,4-dimethyl sub TBS-enolther
EXPNO                  1
PROCNO                 1
Date_           20121221
Time                2.34
INSTRUM            spect
PROBHD    5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     0
SWH            10330.578 Hz
FIDRES          0.157632 Hz
AQ             3.1720407 sec
RG                    18
DW                48.400 usec
DE                  6.50 usec
TE                 301.6 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 10.00 usec
PL1                -0.79 dB
PL1W         25.30924988 W
SFO1         500.1330885 MHz
SI                 32768
SF           500.1300083 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

^{1}H NMR



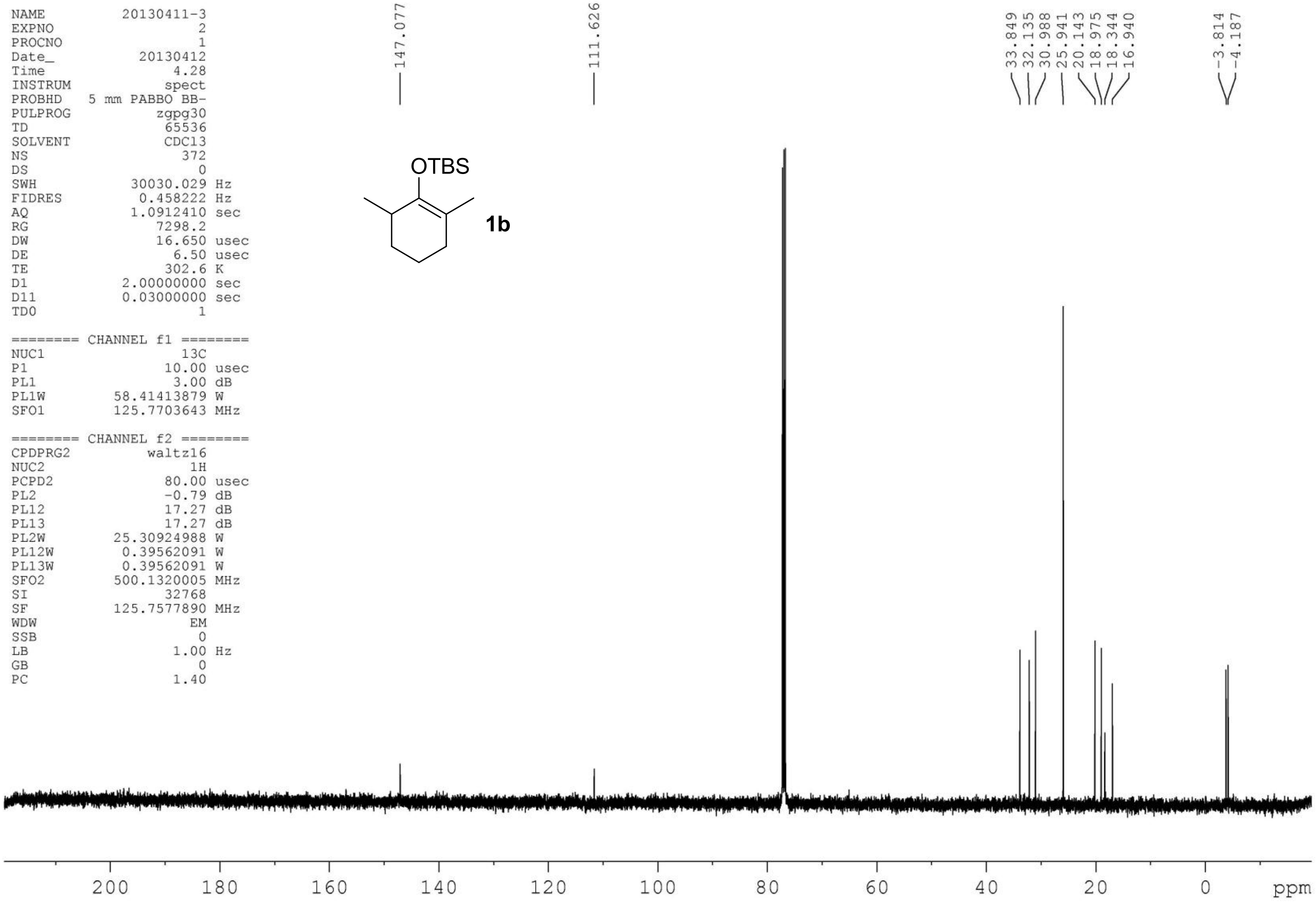
```
NAME     4,4-dimethyl sub TBS-enolther
EXPNO                   2
PROCNO                  1
Date_            20121221
Time                 2.36
INSTRUM             spect
PROBHD    5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    93
DS                     0
SWH            30030.029 Hz
FIDRES          0.458222 Hz
AQ             1.0912410 sec
RG                 16384
DW                16.650 usec
DE                  6.50 usec
TE                 301.7 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 10.00 usec
PL1                 3.00 dB
PL1W         58.41413879 W
SFO1         125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -0.79 dB
PL12               17.27 dB
PL13               17.27 dB
PL2W         25.30924988 W
PL12W         0.39562091 W
PL13W         0.39562091 W
SFO2         500.1320005 MHz
SI                 32768
SF           125.7577890 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

^{13}C NMR



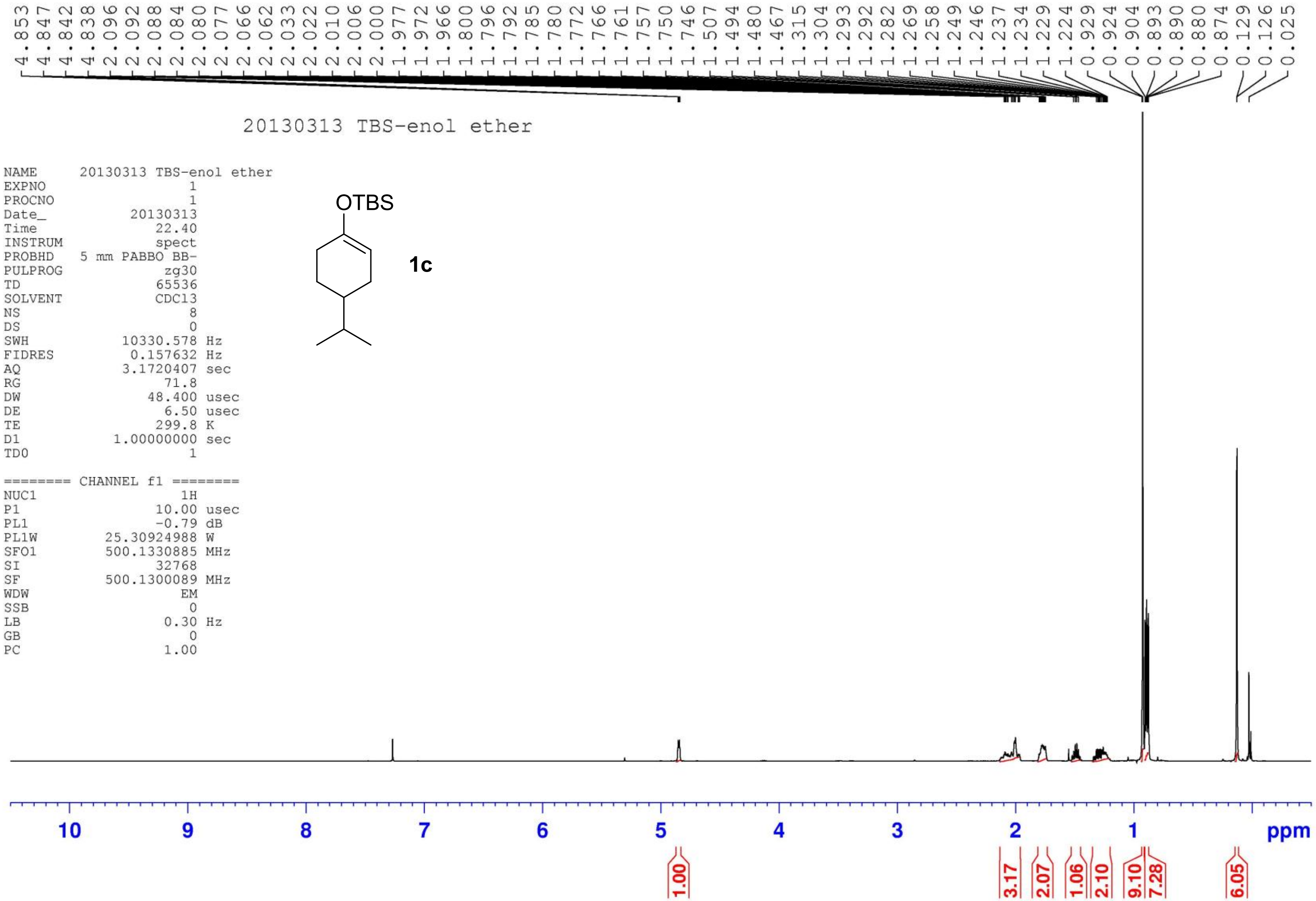
```
NAME      2,6-dimethylcyclohexenotbs-20130517
EXPNO                    1
PROCNO                   1
Date_             20130518
Time                  7.39
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                       8
DS                       0
SWH              10330.578 Hz
FIDRES            0.157632 Hz
AQ               3.1720407 sec
RG                     181
DW                  48.400 usec
DE                    6.50 usec
TE                   300.6 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   10.00 usec
PL1                  -0.79 dB
PL1W           25.30924988 W
SFO1           500.1330885 MHz
SI                   32768
SF             500.1300086 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

^{1}H NMR



```
NAME          20130411-3
EXPNO                  2
PROCNO                 1
Date_           20130412
Time                4.28
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  372
DS                    0
SWH           30030.029 Hz
FIDRES         0.458222 Hz
AQ            1.0912410 sec
RG               7298.2
DW               16.650 usec
DE                 6.50 usec
TE                302.6 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                10.00 usec
PL1                3.00 dB
PL1W        58.41413879 W
SFO1        125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             80.00 usec
PL2               -0.79 dB
PL12              17.27 dB
PL13              17.27 dB
PL2W        25.30924988 W
PL12W        0.39562091 W
PL13W        0.39562091 W
SFO2        500.1320005 MHz
SI                32768
SF          125.7577890 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

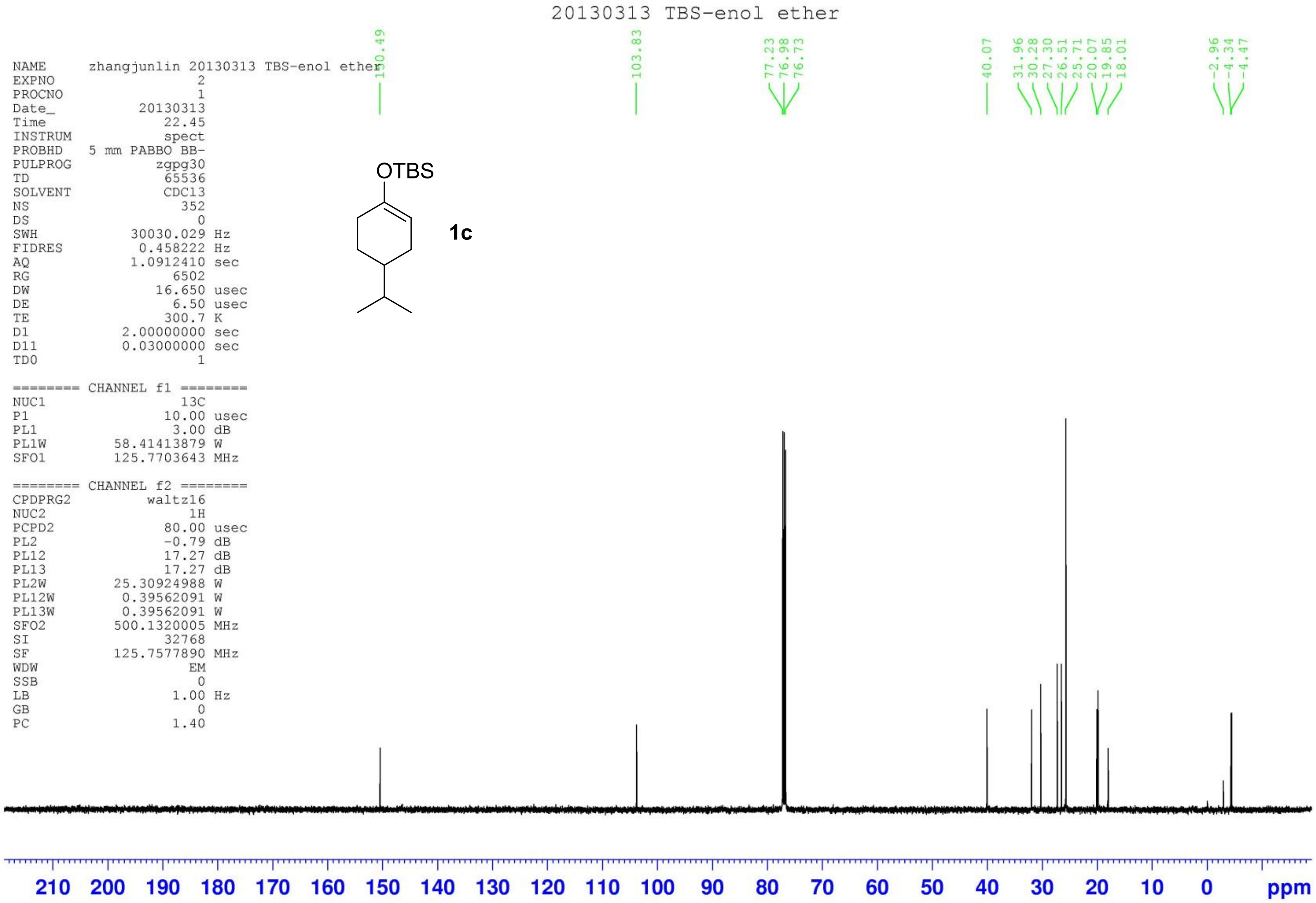
^{13}C NMR



1c

```
NAME       20130313 TBS-enol ether
EXPNO                    1
PROCNO                   1
Date_             20130313
Time                 22.40
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                       8
DS                       0
SWH              10330.578 Hz
FIDRES            0.157632 Hz
AQ               3.1720407 sec
RG                    71.8
DW                  48.400 usec
DE                    6.50 usec
TE                   299.8 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   10.00 usec
PL1                  -0.79 dB
PL1W           25.30924988 W
SFO1           500.1330885 MHz
SI                   32768
SF             500.1300089 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

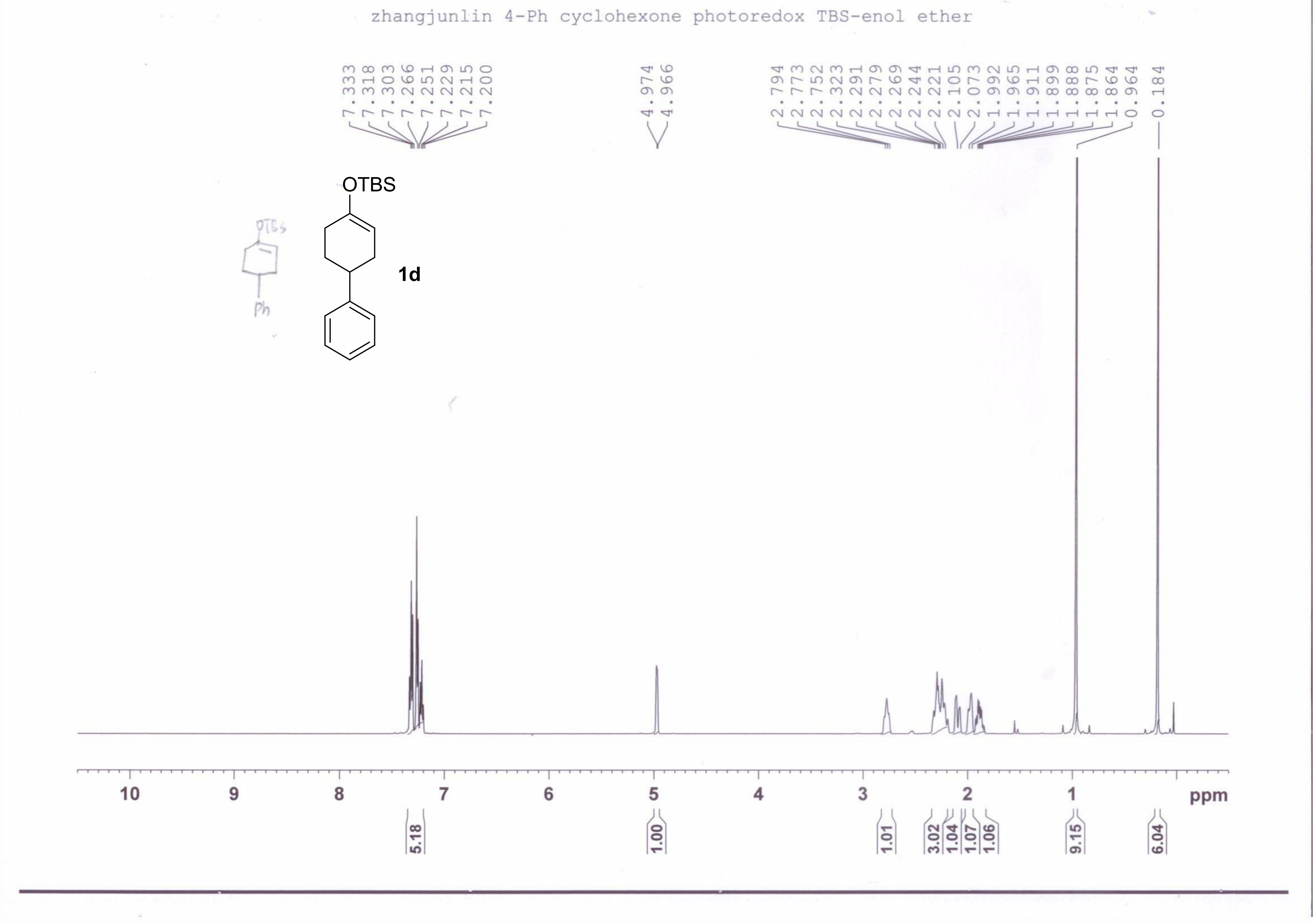
^{1}H NMR



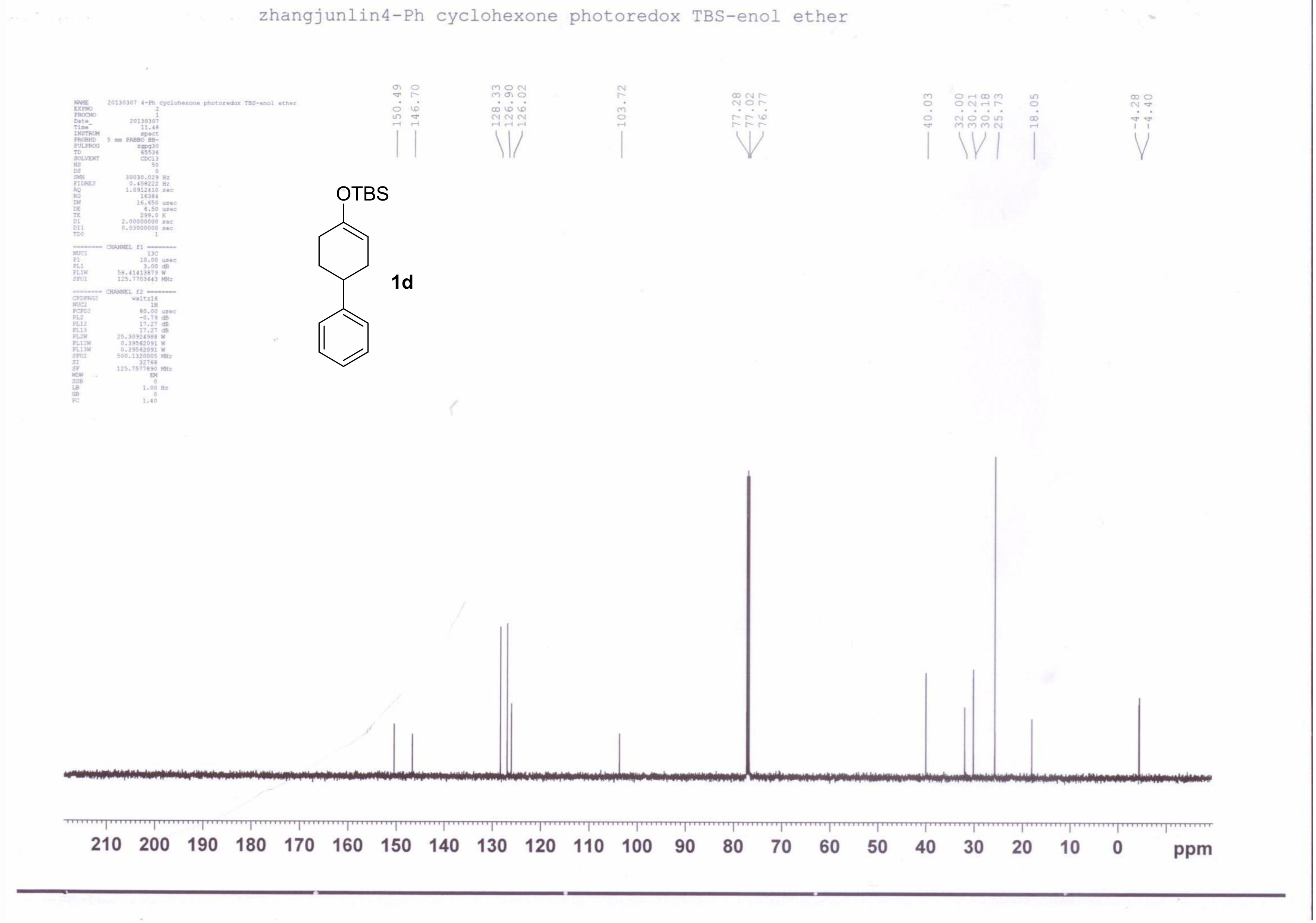
20130313 TBS-enol ether

```
NAME       zhangjunlin 20130313 TBS-enol ether
EXPNO                     2
PROCNO                    1
Date_              20130313
Time                  22.45
INSTRUM               spect
PROBHD     5 mm PABBO BB-
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      352
DS                        0
SWH               30030.029 Hz
FIDRES             0.458222 Hz
AQ                1.0912410 sec
RG                     6502
DW                   16.650 usec
DE                     6.50 usec
TE                    300.7 K
D1               2.00000000 sec
D11              0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    13C
P1                    10.00 usec
PL1                    3.00 dB
PL1W            58.41413879 W
SFO1            125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                 80.00 usec
PL2                   -0.79 dB
PL12                  17.27 dB
PL13                  17.27 dB
PL2W            25.30924988 W
PL12W            0.39562091 W
PL13W            0.39562091 W
SFO2            500.1320005 MHz
SI                    32768
SF              125.7577890 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.40
```

^{13}C NMR

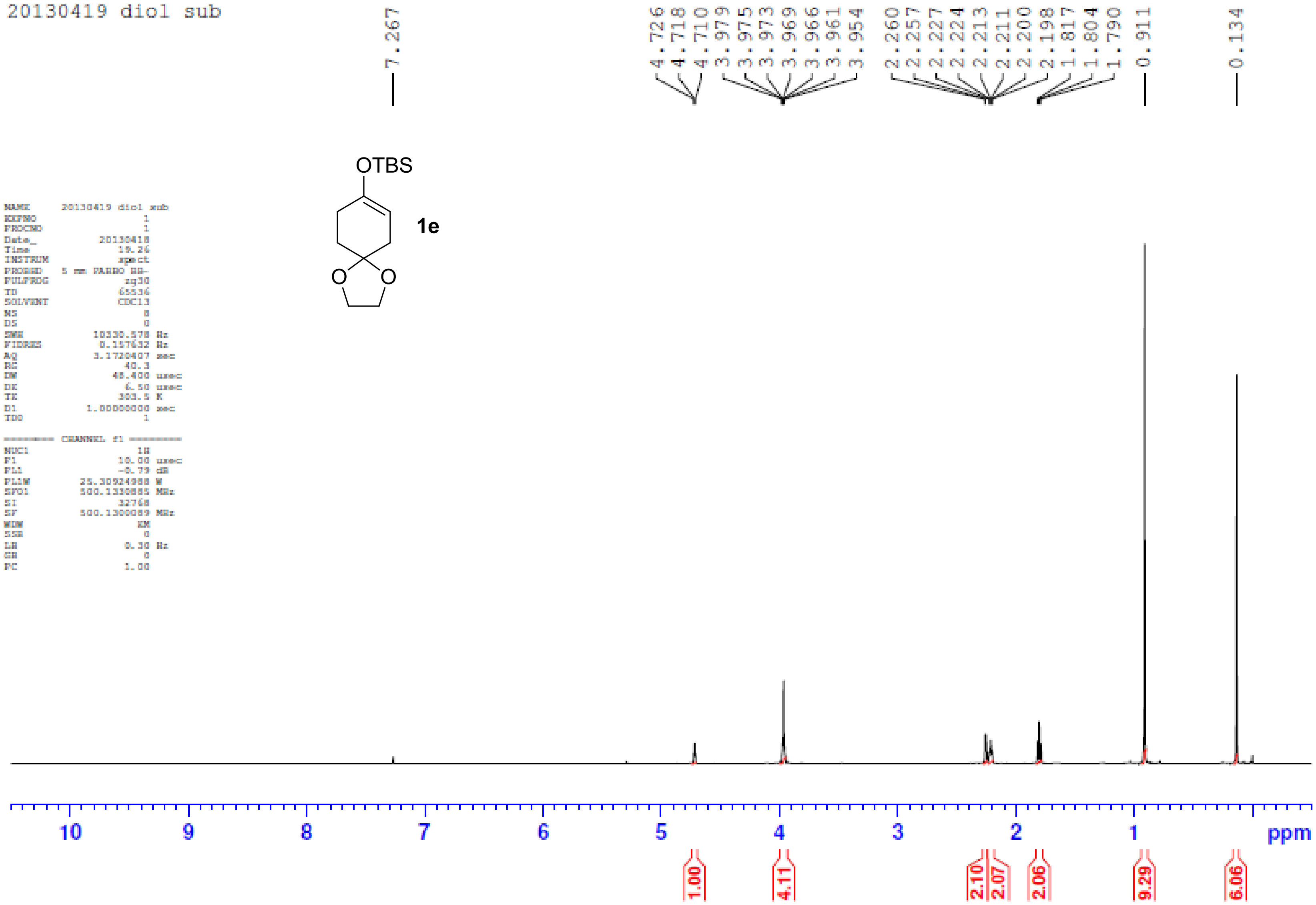

zhangjunlin 4-Ph cyclohexone photoredox TBS-enol ether
7.333
7.318
7.303
7.266
7.251
7.229
7.215
7.200
4.974
4.966
2.794
2.773
2.752
2.323
2.291
2.279
2.269
2.244
2.221
2.105
2.073
1.992
1.965
1.911
1.899
1.888
1.875
1.864
0.964
0.184
OTBS
1d
OTBS
Ph
10
9
8
7
6
5
4
3
2
1
ppm
5.18
1.00
1.01
3.02
1.04
1.07
1.06
9.15
6.04

^{1}H NMR

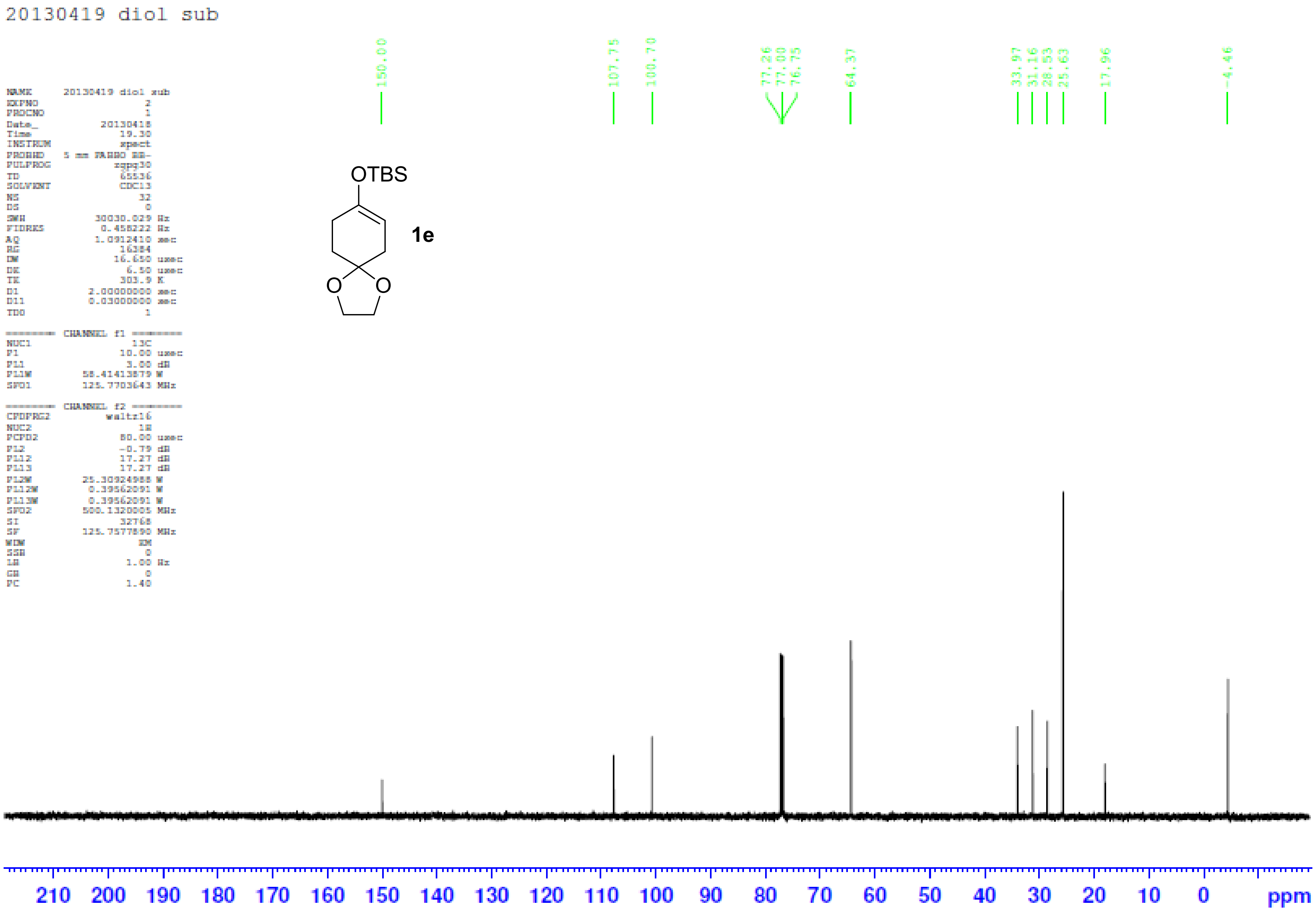

zhangjunlin4-Ph cyclohexone photoredox TBS-enol ether
150.49
146.70
128.33
126.90
126.02
103.72
77.28
77.02
76.77
40.03
32.00
30.21
30.18
25.73
18.05
-4.28
-4.40
OTBS
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

1d

^{13}C NMR


20130419 diol sub
7.267
4.726
4.718
4.710
3.979
3.975
3.973
3.969
3.966
3.961
3.954
2.260
2.257
2.227
2.224
2.213
2.211
2.200
2.198
1.817
1.804
1.790
0.911
0.134
OTBS
O
O
1e
NAME 20130419 diol sub
EXPNO 1
PROCNO 1
Date_ 20130418
Time 19.26
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1720407 sec
RG 40.3
DW 48.400 usec
DE 6.50 usec
TE 303.5 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.00 usec
PL1 -0.79 dB
PL1W 25.30924988 W
SFO1 500.1330885 MHz
SI 32768
SF 500.1300089 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
10
9
8
7
6
5
4
3
2
1
ppm
1.00
4.11
2.10
2.07
2.06
9.29
6.06

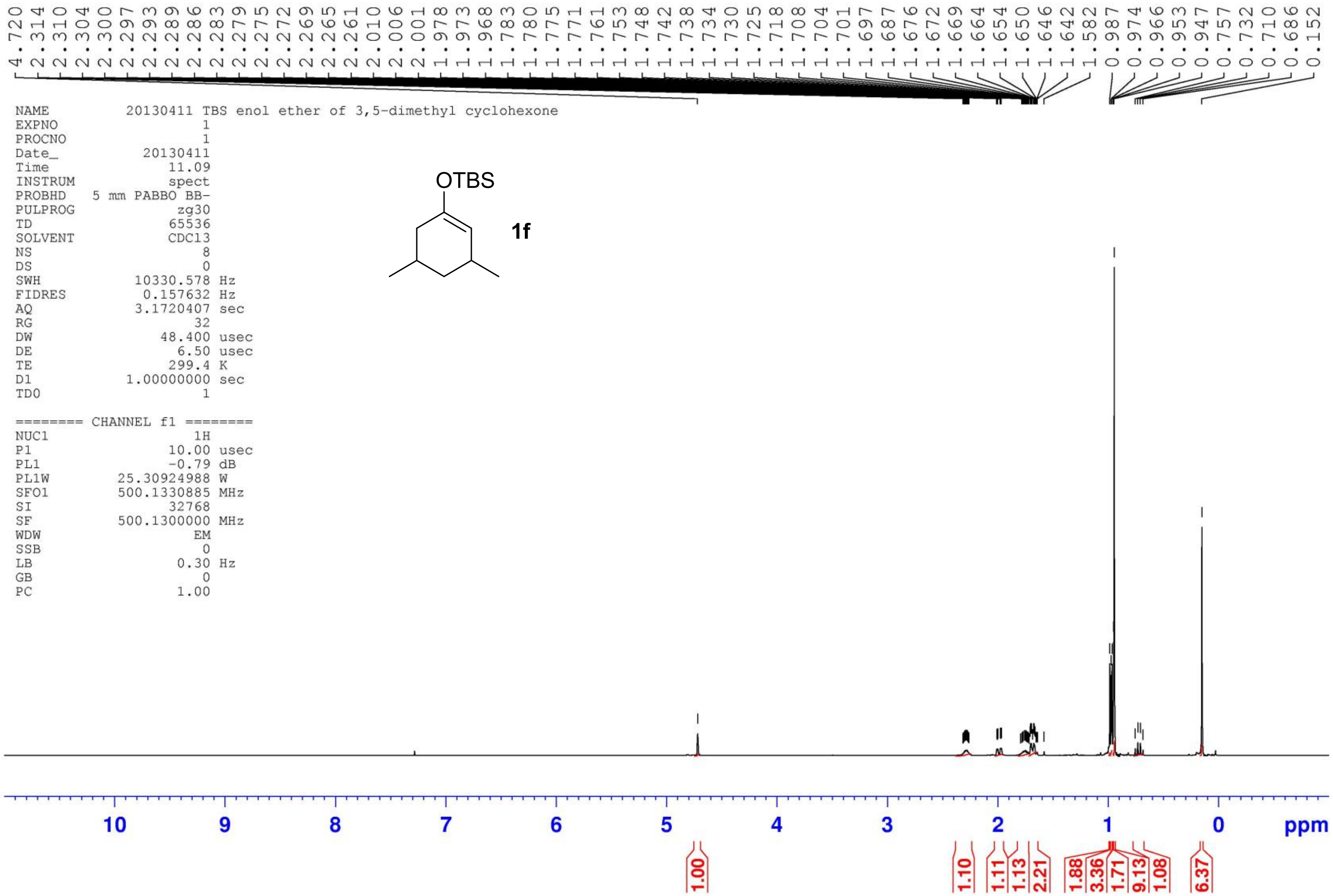
^{1}H NMR



1e

```
NAME     20130419 diol sub
EXPNO                    2
PROCNO                   1
Date_             20130418
Time                 19.30
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG            zgpg30
TD                   65536
SOLVENT              CDCl3
NS                      32
DS                       0
SWH           30030.029 Hz
FIDRES         0.458222 Hz
AQ            1.0912410 sec
RG                   16384
DW               16.650 usec
DE                 6.50 usec
TE                303.9 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                 10.00 usec
PL1                 3.00 dB
PL1W         58.41413879 W
SFO1         125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2              80.00 usec
PL2                -0.79 dB
PL12               17.27 dB
PL13               17.27 dB
PL2W         25.30924988 W
PL12W         0.39562091 W
PL13W         0.39562091 W
SFO2         500.1320005 MHz
SI                   32768
SF           125.7577890 MHz
WDW                     EM
SSB                      0
LB                  1.00 Hz
GB                       0
PC                    1.40
```

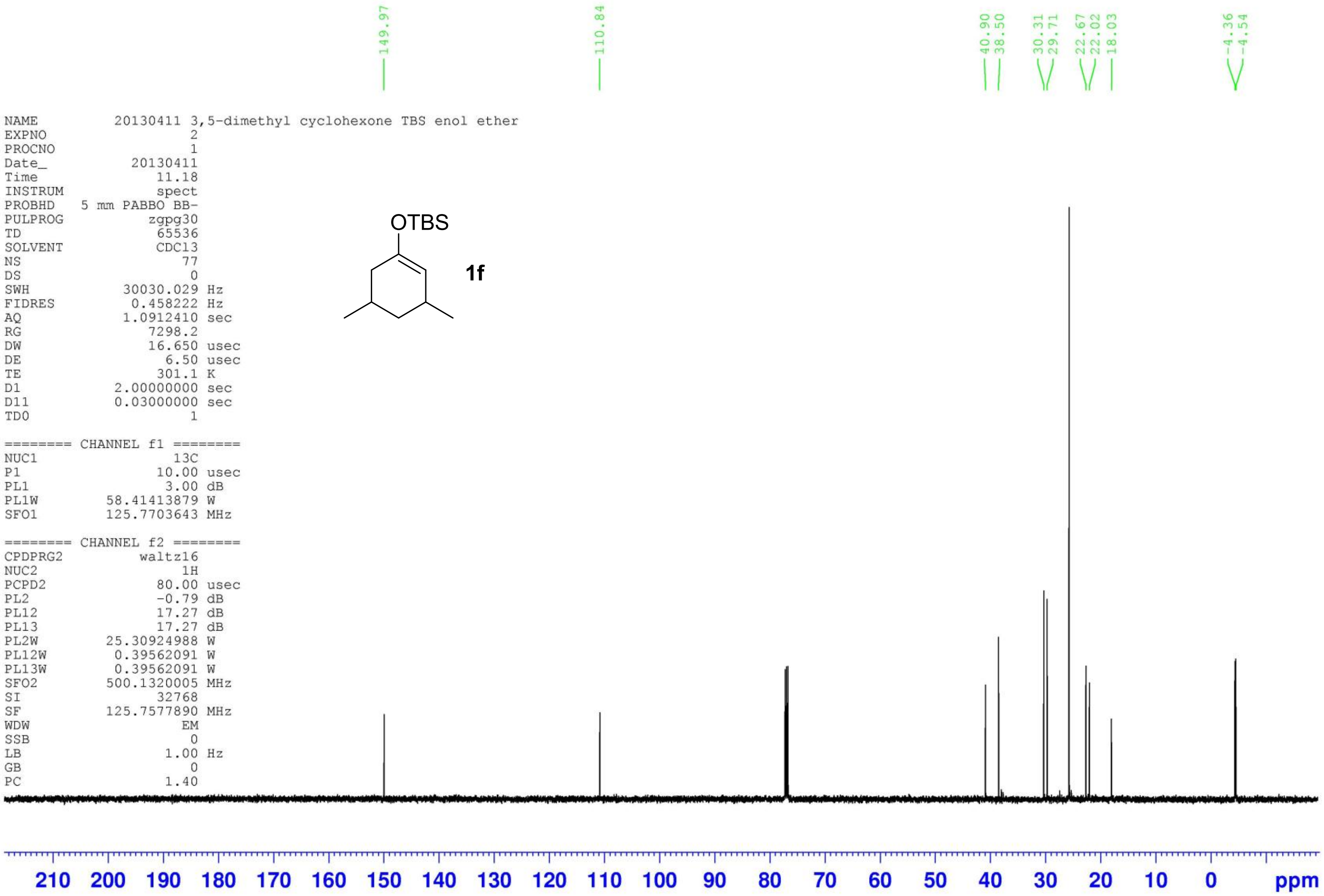
^{13}C NMR



```
NAME         20130411 TBS enol ether of 3,5-dimethyl cyclohexone
EXPNO                 1
PROCNO                1
Date_          20130411
Time              11.09
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    8
DS                    0
SWH           10330.578 Hz
FIDRES         0.157632 Hz
AQ            3.1720407 sec
RG                   32
DW               48.400 usec
DE                 6.50 usec
TE                299.4 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                10.00 usec
PL1               -0.79 dB
PL1W        25.30924988 W
SFO1        500.1330885 MHz
SI                32768
SF          500.1300000 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

1f

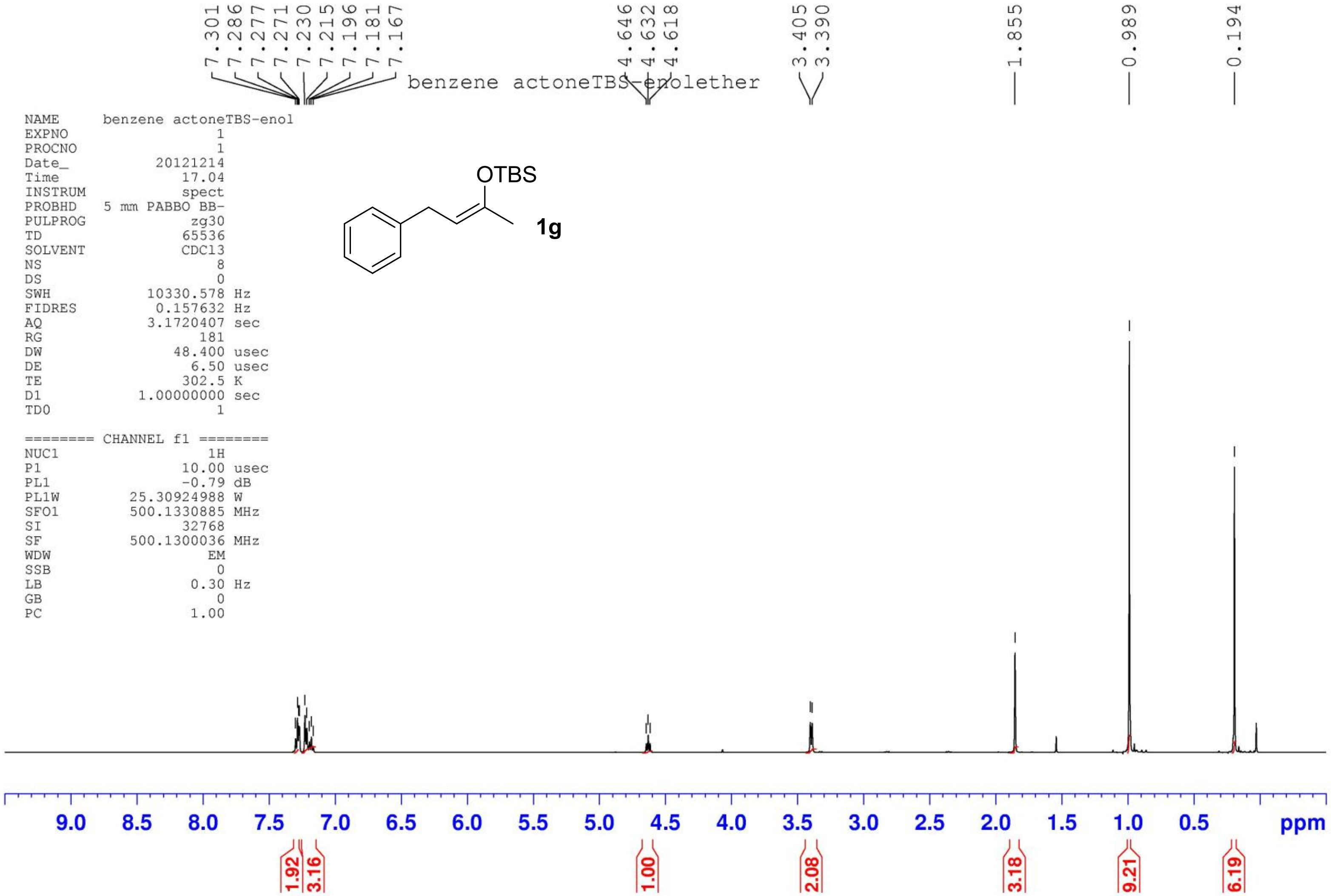
^{1}H NMR



1f

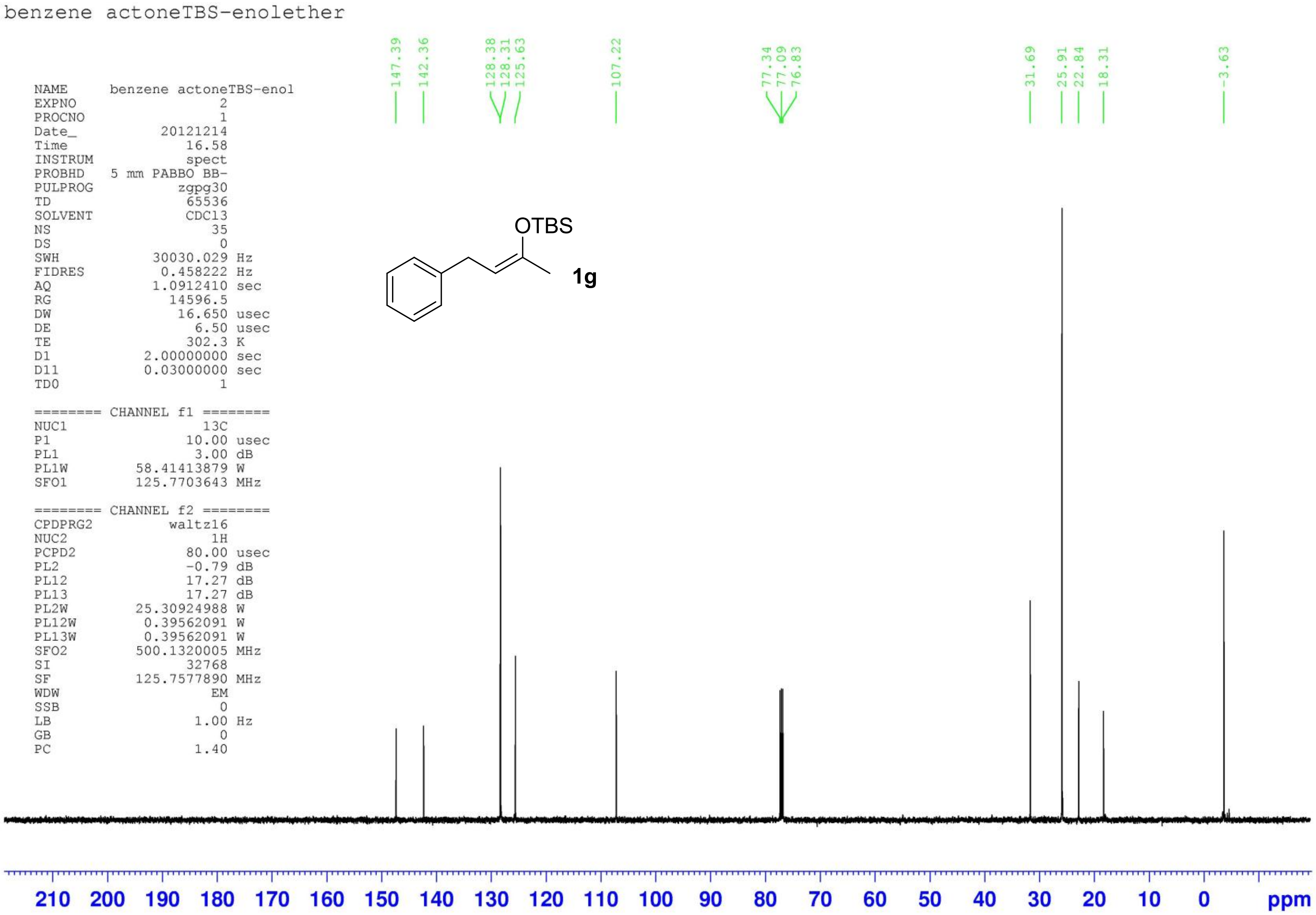
```
NAME         20130411 3,5-dimethyl cyclohexone TBS enol ether
EXPNO                   2
PROCNO                  1
Date_            20130411
Time                11.18
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    77
DS                     0
SWH            30030.029 Hz
FIDRES          0.458222 Hz
AQ             1.0912410 sec
RG                7298.2
DW                16.650 usec
DE                  6.50 usec
TE                 301.1 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 10.00 usec
PL1                 3.00 dB
PL1W         58.41413879 W
SFO1        125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -0.79 dB
PL12               17.27 dB
PL13               17.27 dB
PL2W         25.30924988 W
PL12W         0.39562091 W
PL13W         0.39562091 W
SFO2        500.1320005 MHz
SI                 32768
SF          125.7577890 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

^{13}C NMR



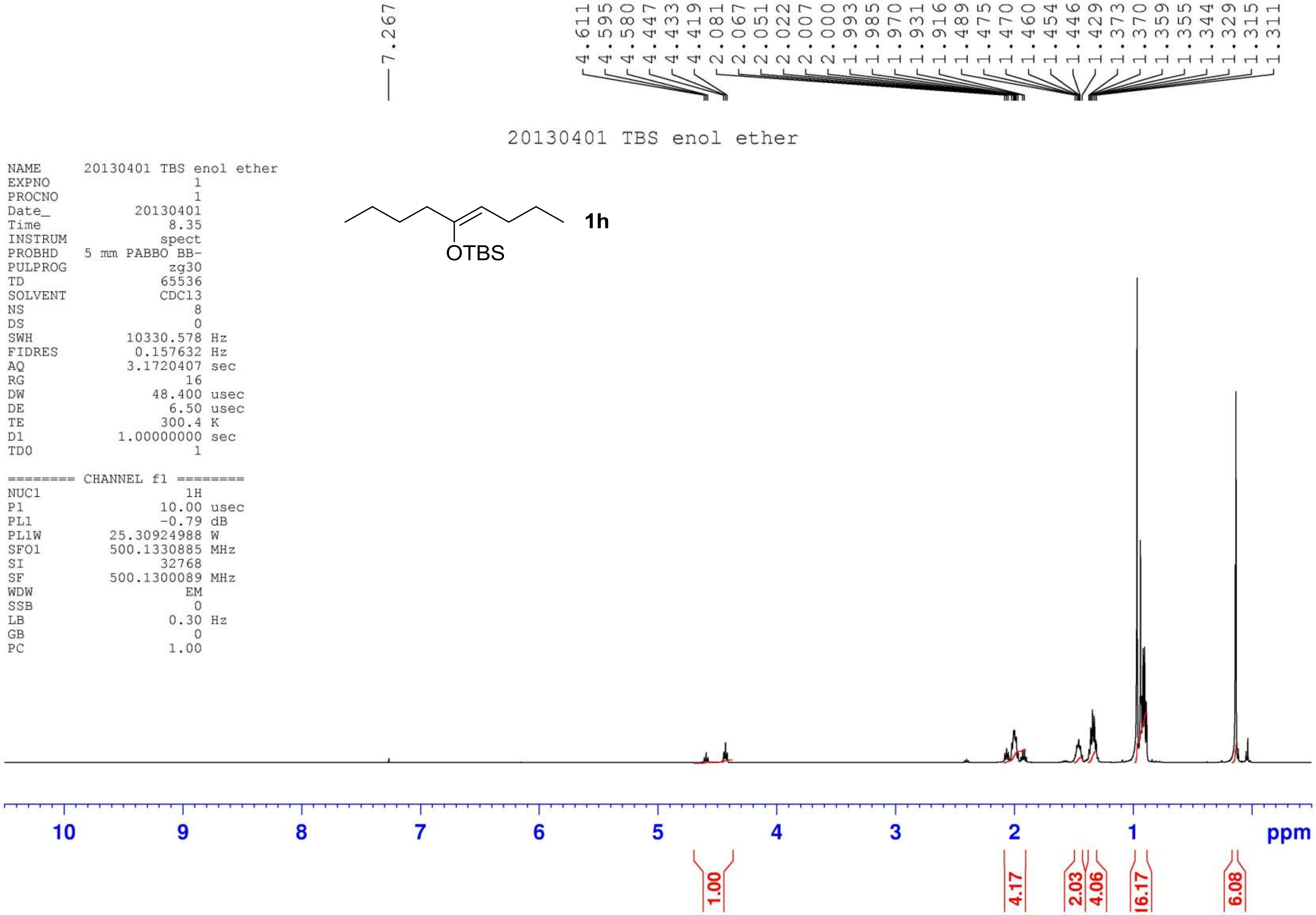
```
NAME      benzene actoneTBS-enol
EXPNO                1
PROCNO               1
Date_         20121214
Time             17.04
INSTRUM          spect
PROBHD   5 mm PABBO BB-
PULPROG           zg30
TD               65536
SOLVENT          CDCl3
NS                   8
DS                   0
SWH          10330.578 Hz
FIDRES        0.157632 Hz
AQ           3.1720407 sec
RG                 181
DW              48.400 usec
DE                6.50 usec
TE               302.5 K
D1          1.00000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1                1H
P1               10.00 usec
PL1              -0.79 dB
PL1W       25.30924988 W
SFO1       500.1330885 MHz
SI               32768
SF         500.1300036 MHz
WDW                 EM
SSB                  0
LB                0.30 Hz
GB                   0
PC                1.00
```

^{1}H NMR



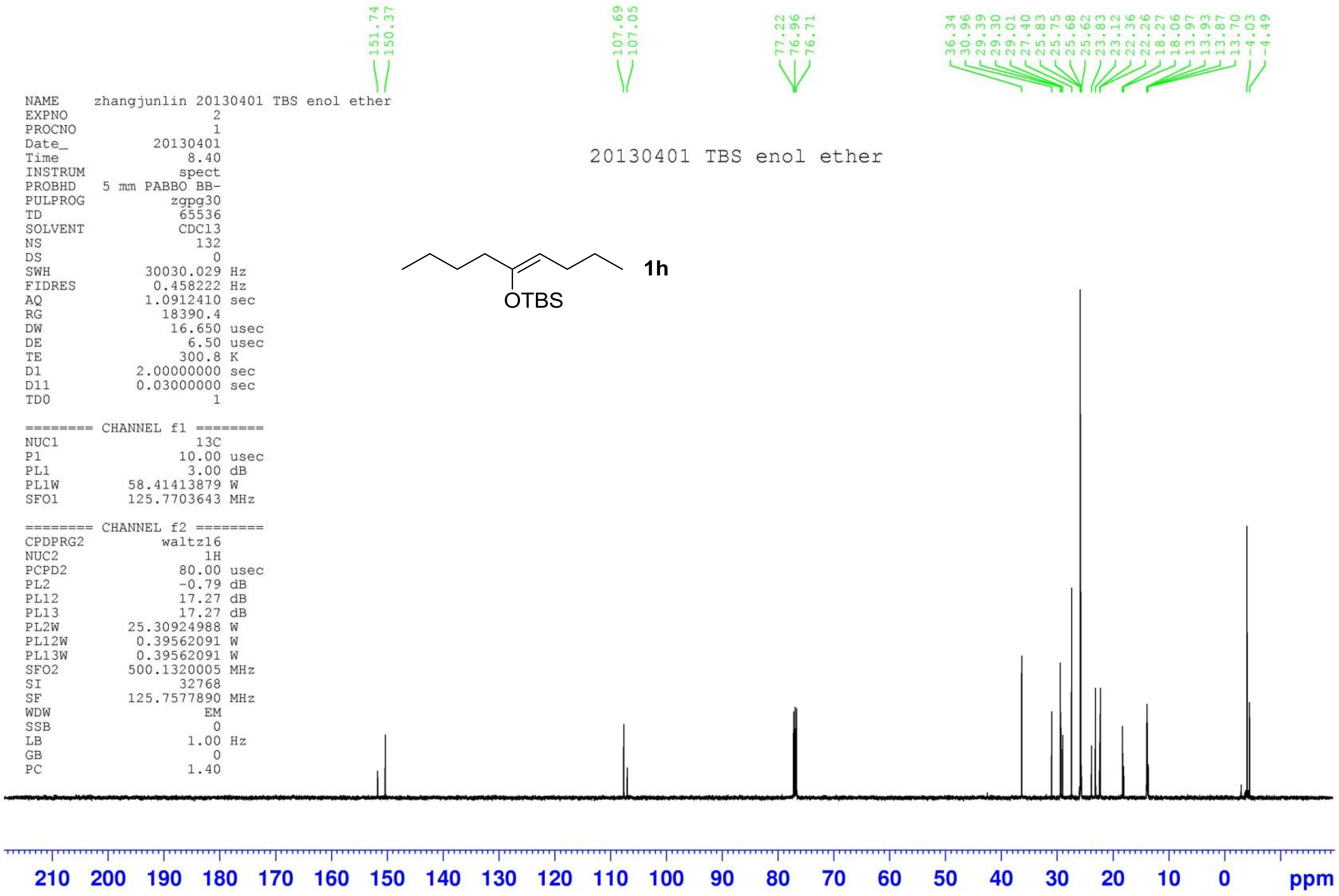
```
NAME      benzene actoneTBS-enol
EXPNO                     2
PROCNO                    1
Date_              20121214
Time                  16.58
INSTRUM               spect
PROBHD   5 mm PABBO BB-
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                       35
DS                        0
SWH               30030.029 Hz
FIDRES             0.458222 Hz
AQ                1.0912410 sec
RG                  14596.5
DW                   16.650 usec
DE                     6.50 usec
TE                    302.3 K
D1               2.00000000 sec
D11              0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    13C
P1                    10.00 usec
PL1                    3.00 dB
PL1W            58.41413879 W
SFO1            125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                 80.00 usec
PL2                   -0.79 dB
PL12                  17.27 dB
PL13                  17.27 dB
PL2W            25.30924988 W
PL12W            0.39562091 W
PL13W            0.39562091 W
SFO2            500.1320005 MHz
SI                    32768
SF              125.7577890 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.40
```

^{13}C NMR



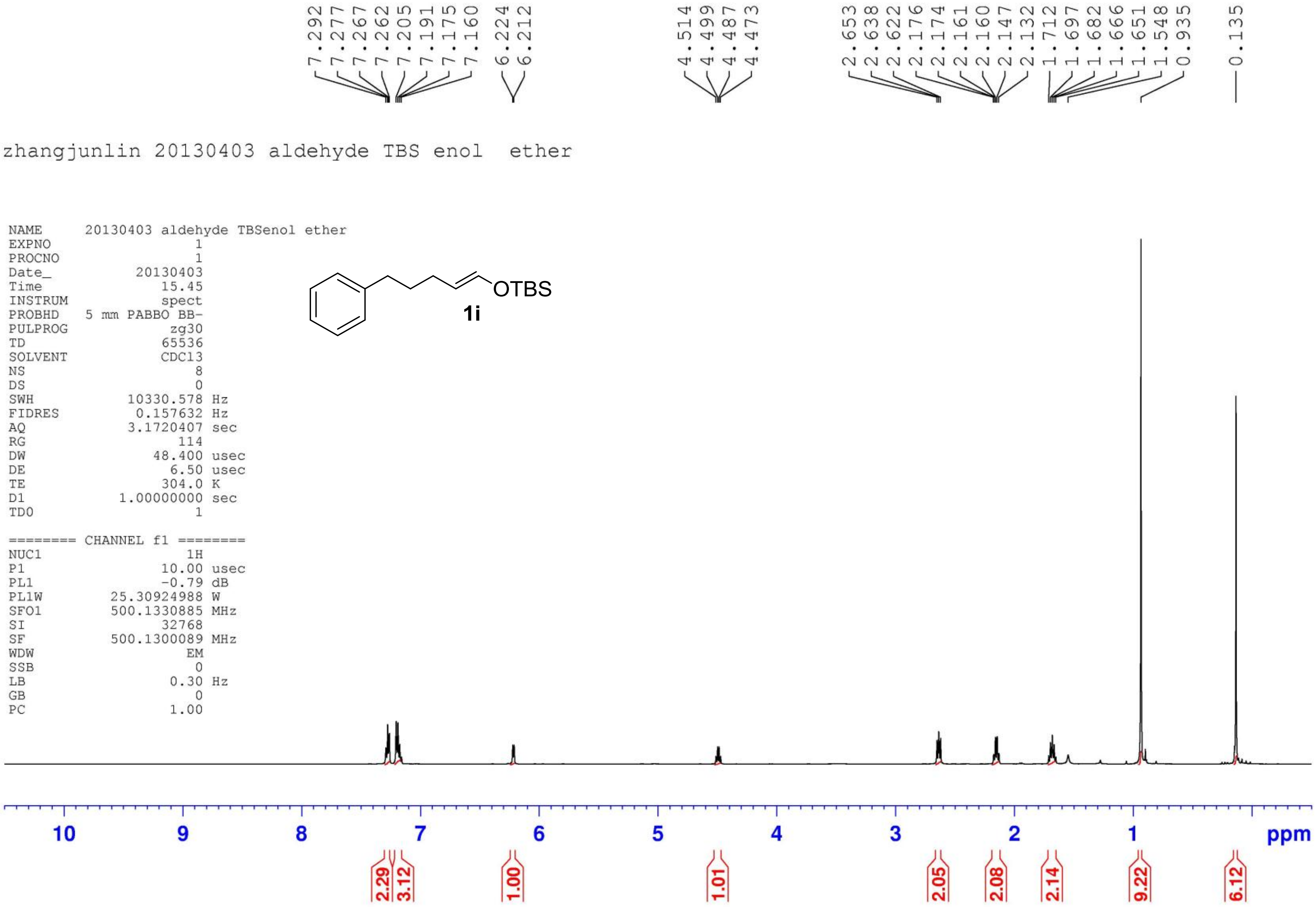
```
NAME       20130401 TBS enol ether
EXPNO                    1
PROCNO                   1
Date_             20130401
Time                  8.35
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                       8
DS                       0
SWH             10330.578 Hz
FIDRES           0.157632 Hz
AQ              3.1720407 sec
RG                      16
DW                  48.400 usec
DE                    6.50 usec
TE                   300.4 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   10.00 usec
PL1                  -0.79 dB
PL1W           25.30924988 W
SFO1           500.1330885 MHz
SI                   32768
SF             500.1300089 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

^{1}H NMR



```
NAME     zhangjunlin 20130401 TBS enol ether
EXPNO                  2
PROCNO                 1
Date_           20130401
Time                8.40
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   132
DS                     0
SWH            30030.029 Hz
FIDRES          0.458222 Hz
AQ             1.0912410 sec
RG               18390.4
DW                16.650 usec
DE                  6.50 usec
TE                 300.8 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 10.00 usec
PL1                 3.00 dB
PL1W         58.41413879 W
SFO1         125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -0.79 dB
PL12               17.27 dB
PL13               17.27 dB
PL2W         25.30924988 W
PL12W         0.39562091 W
PL13W         0.39562091 W
SFO2         500.1320005 MHz
SI                 32768
SF           125.7577890 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

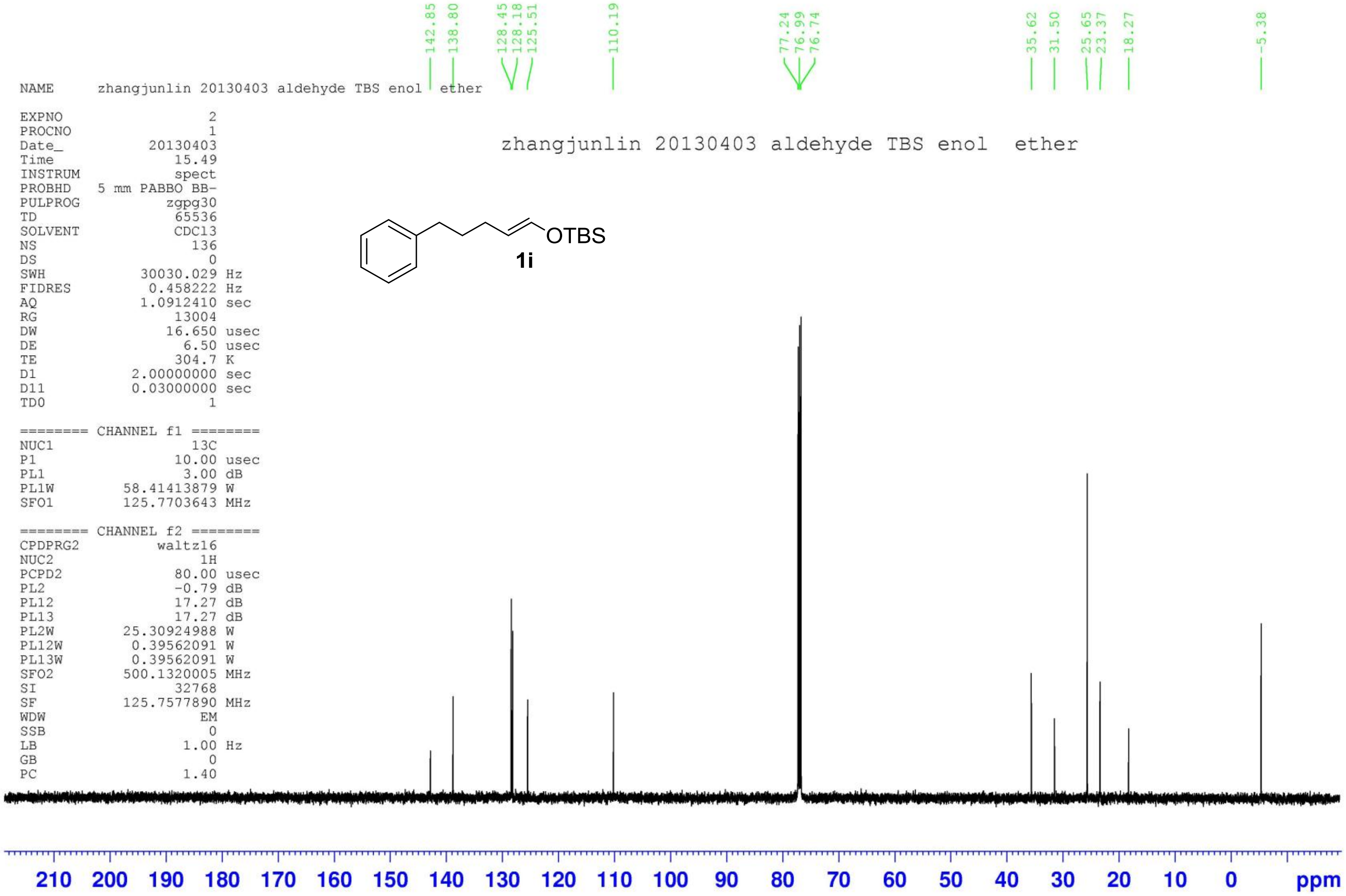
^{13}C NMR



zhangjunlin 20130403 aldehyde TBS enol ether

```
NAME     20130403 aldehyde TBSenol ether
EXPNO                 1
PROCNO                1
Date_          20130403
Time              15.45
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    8
DS                    0
SWH          10330.578 Hz
FIDRES        0.157632 Hz
AQ           3.1720407 sec
RG                  114
DW               48.400 usec
DE                 6.50 usec
TE                304.0 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                10.00 usec
PL1               -0.79 dB
PL1W        25.30924988 W
SFO1        500.1330885 MHz
SI                32768
SF          500.1300089 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

^{1}H NMR

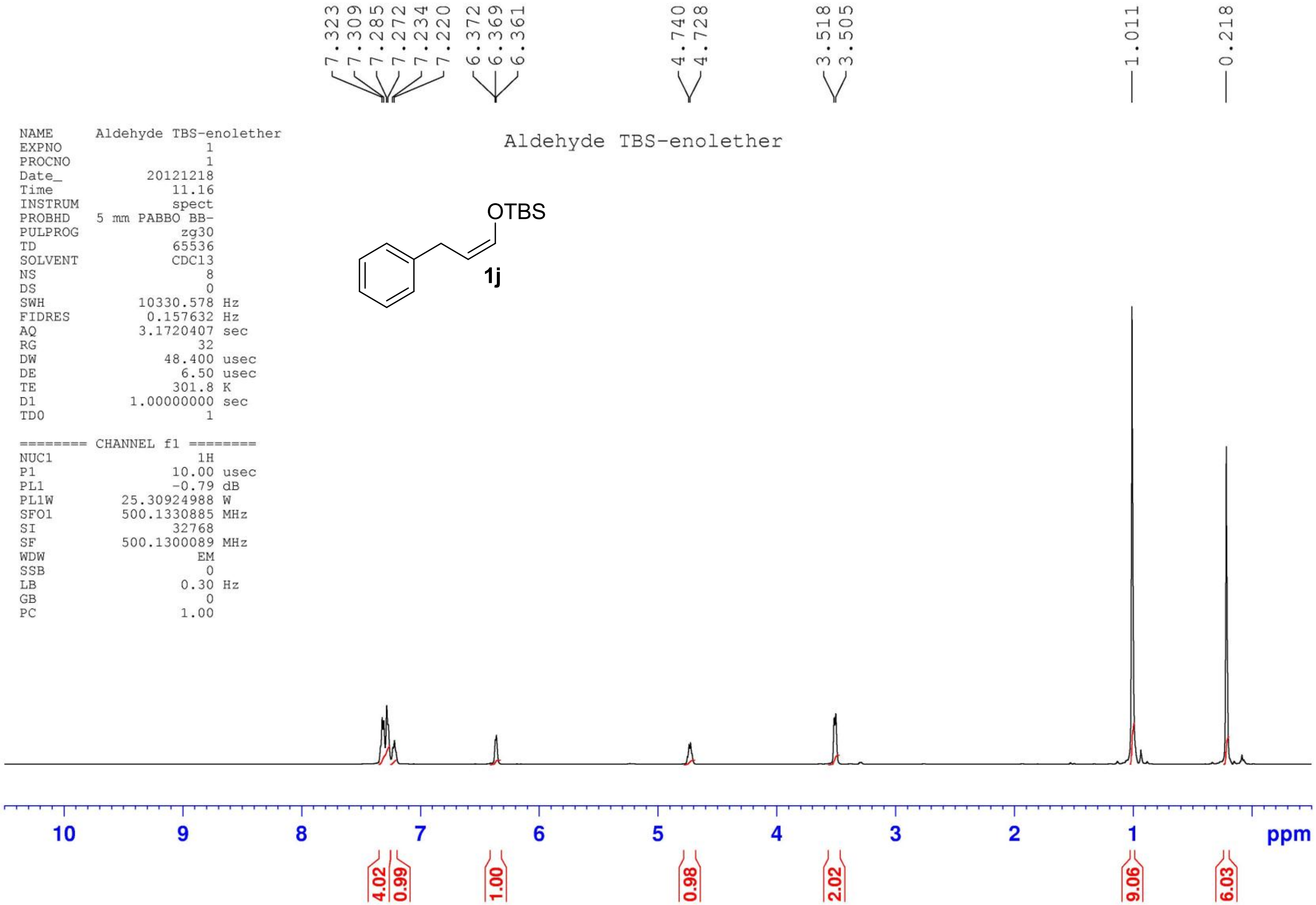


```
NAME      zhangjunlin 20130403 aldehyde TBS enol  ether

EXPNO              2
PROCNO             1
Date_       20130403
Time           15.49
INSTRUM        spect
PROBHD   5 mm PABBO BB-
PULPROG       zgpg30
TD             65536
SOLVENT        CDCl3
NS               136
DS                 0
SWH        30030.029 Hz
FIDRES      0.458222 Hz
AQ         1.0912410 sec
RG             13004
DW            16.650 usec
DE              6.50 usec
TE             304.7 K
D1        2.00000000 sec
D11       0.03000000 sec
TD0                1

======== CHANNEL f1 ========
NUC1             13C
P1             10.00 usec
PL1             3.00 dB
PL1W     58.41413879 W
SFO1     125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2      waltz16
NUC2              1H
PCPD2          80.00 usec
PL2            -0.79 dB
PL12           17.27 dB
PL13           17.27 dB
PL2W     25.30924988 W
PL12W     0.39562091 W
PL13W     0.39562091 W
SFO2     500.1320005 MHz
SI             32768
SF       125.7577890 MHz
WDW               EM
SSB                0
LB              1.00 Hz
GB                 0
PC              1.40
```

zhangjunlin 20130403 aldehyde TBS enol ether

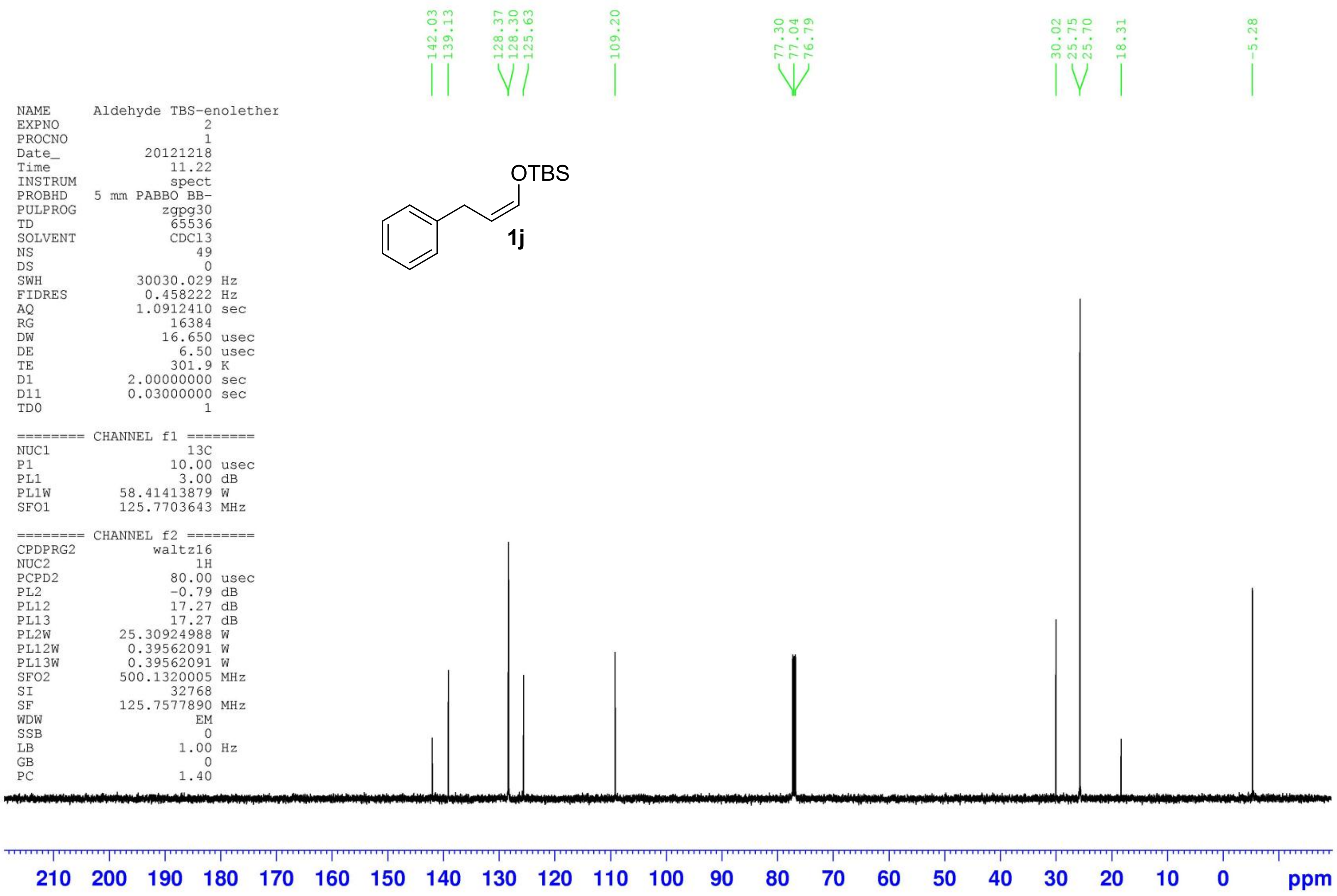
1i

^{13}C NMR


7.323
7.309
7.285
7.272
7.234
7.220
6.372
6.369
6.361
4.740
4.728
3.518
3.505
1.011
0.218
Aldehyde TBS-enolether
OTBS
1j
NAME Aldehyde TBS-enolether
EXPNO 1
PROCNO 1
Date_ 20121218
Time 11.16
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1720407 sec
RG 32
DW 48.400 usec
DE 6.50 usec
TE 301.8 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.00 usec
PL1 -0.79 dB
PL1W 25.30924988 W
SFO1 500.1330885 MHz
SI 32768
SF 500.1300089 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
10
9
8
7
6
5
4
3
2
1
ppm
4.02
0.99
1.00
0.98
2.02
9.06
6.03

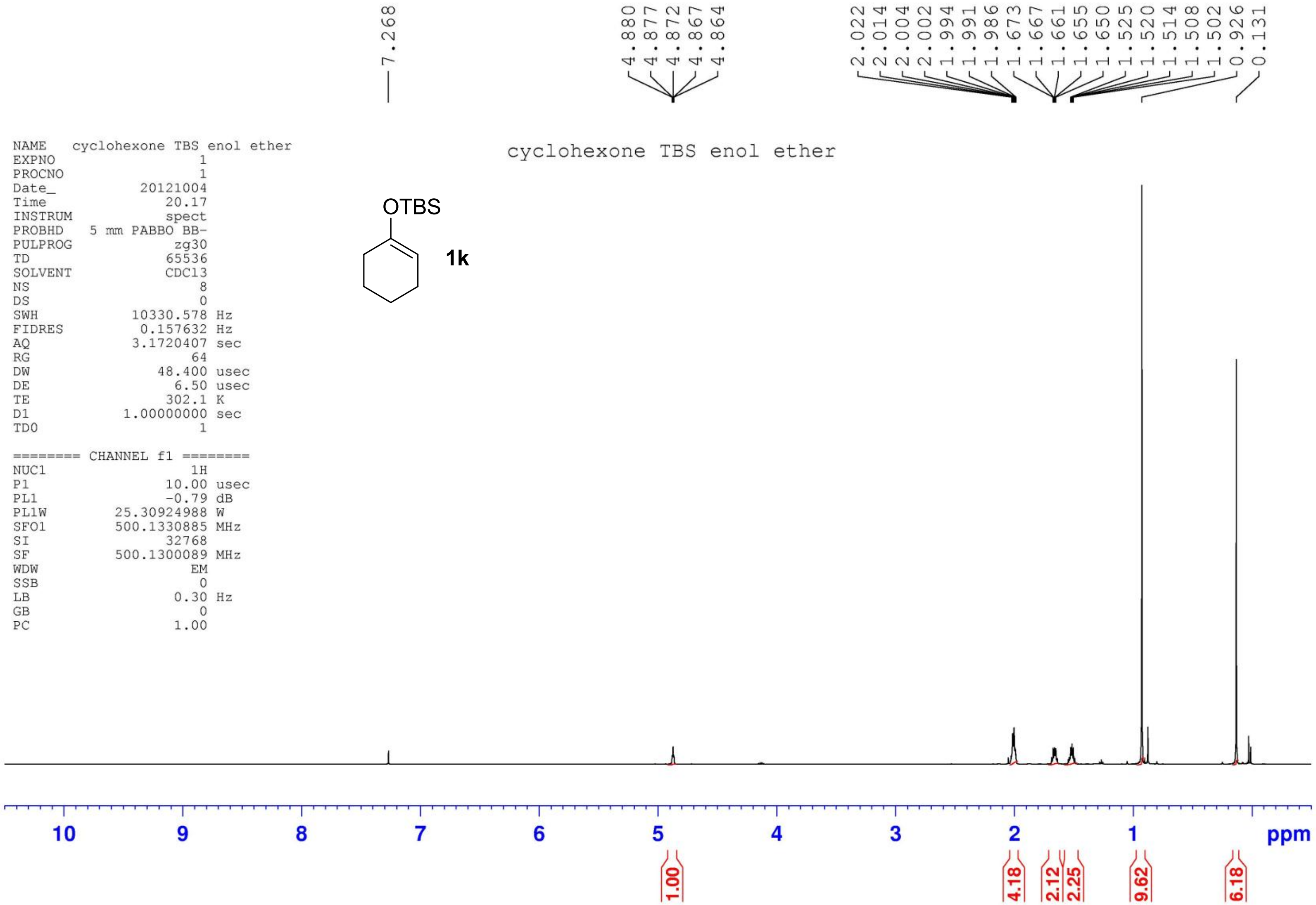
^{1}H NMR

Aldehyde TBS-enolether



```
NAME      Aldehyde TBS-enolether
EXPNO                   2
PROCNO                  1
Date_            20121218
Time                11.22
INSTRUM             spect
PROBHD    5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    49
DS                     0
SWH            30030.029 Hz
FIDRES          0.458222 Hz
AQ             1.0912410 sec
RG                 16384
DW                16.650 usec
DE                  6.50 usec
TE                 301.9 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 10.00 usec
PL1                 3.00 dB
PL1W         58.41413879 W
SFO1         125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -0.79 dB
PL12               17.27 dB
PL13               17.27 dB
PL2W         25.30924988 W
PL12W         0.39562091 W
PL13W         0.39562091 W
SFO2         500.1320005 MHz
SI                 32768
SF           125.7577890 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

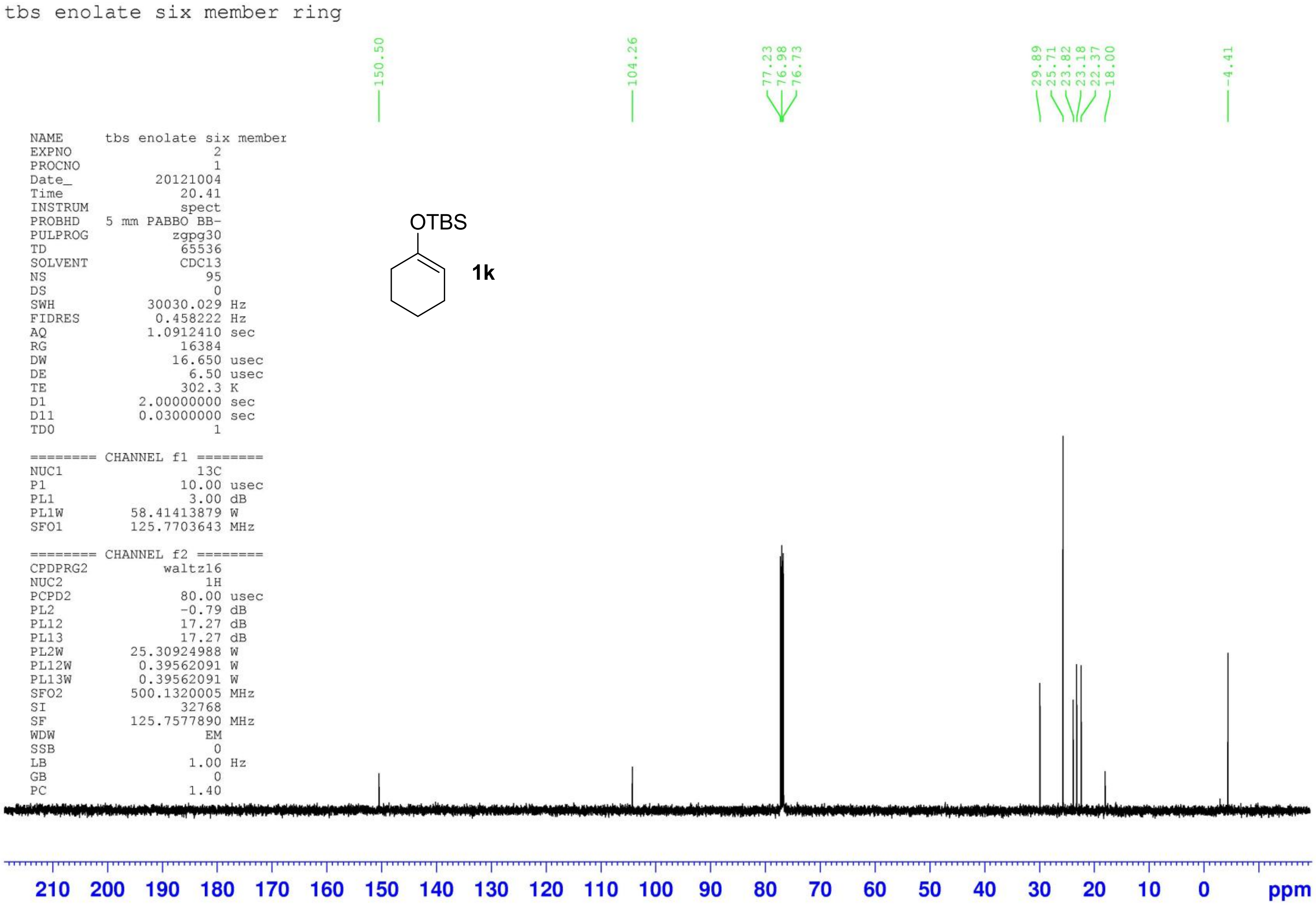
^{13}C NMR



1k

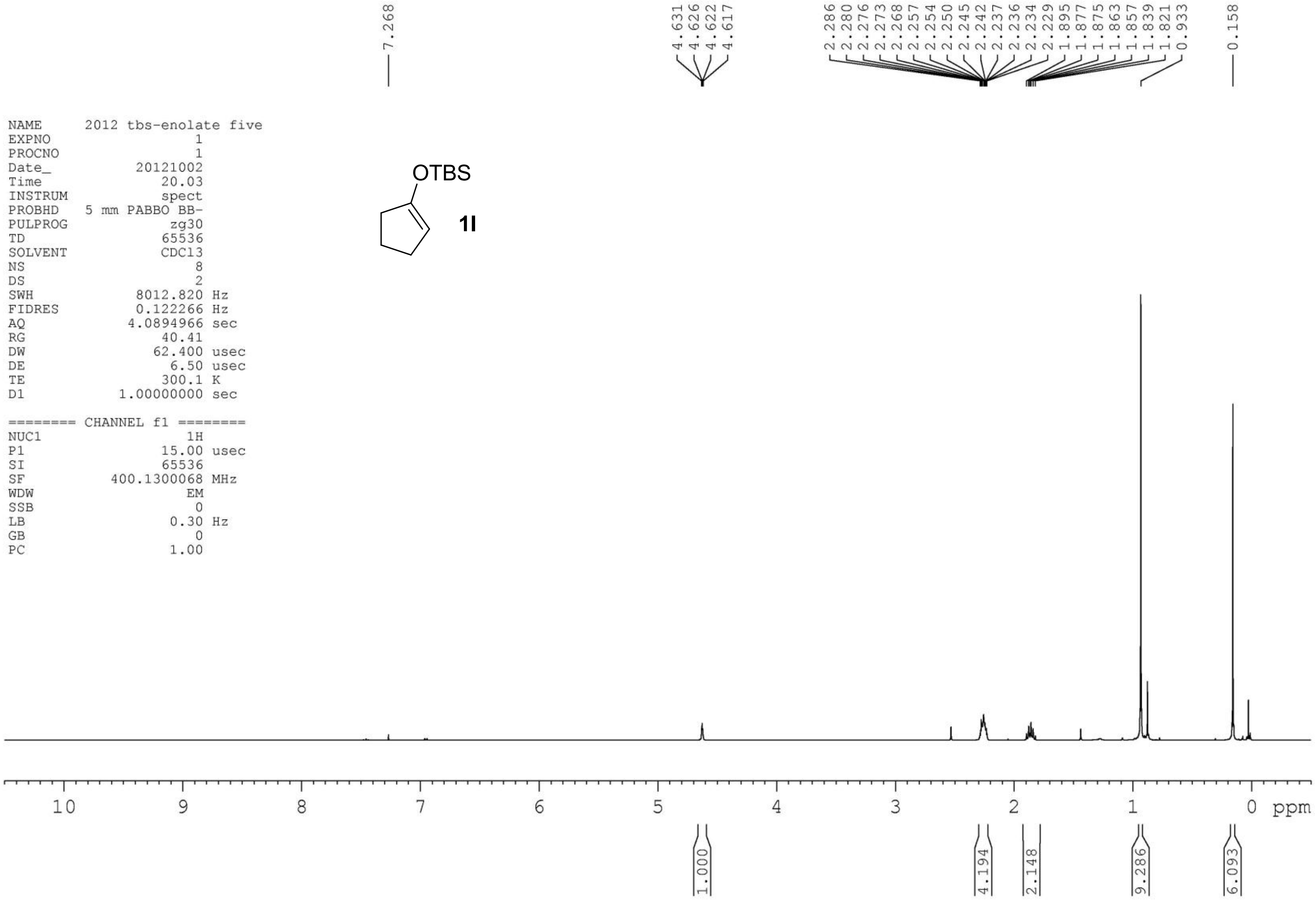
```
NAME     cyclohexone TBS enol ether
EXPNO                     1
PROCNO                    1
Date_              20121004
Time                  20.17
INSTRUM               spect
PROBHD   5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                        8
DS                        0
SWH               10330.578 Hz
FIDRES             0.157632 Hz
AQ                3.1720407 sec
RG                       64
DW                   48.400 usec
DE                     6.50 usec
TE                    302.1 K
D1               1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     1H
P1                    10.00 usec
PL1                   -0.79 dB
PL1W            25.30924988 W
SFO1            500.1330885 MHz
SI                    32768
SF              500.1300089 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00
```

^{1}H NMR



```
tbs enolate six member ring

NAME     tbs enolate six member
EXPNO                 2
PROCNO                1
Date_          20121004
Time              20.41
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG         zgpg30
TD               65536
SOLVENT          CDCl3
NS                  95
DS                   0
SWH          30030.029 Hz
FIDRES        0.458222 Hz
AQ           1.0912410 sec
RG               16384
DW              16.650 usec
DE                6.50 usec
TE               302.3 K
D1          2.00000000 sec
D11         0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1               13C
P1               10.00 usec
PL1               3.00 dB
PL1W       58.41413879 W
SFO1       125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2               -0.79 dB
PL12              17.27 dB
PL13              17.27 dB
PL2W        25.30924988 W
PL12W        0.39562091 W
PL13W        0.39562091 W
SFO2       500.1320005 MHz
SI                32768
SF         125.7577890 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

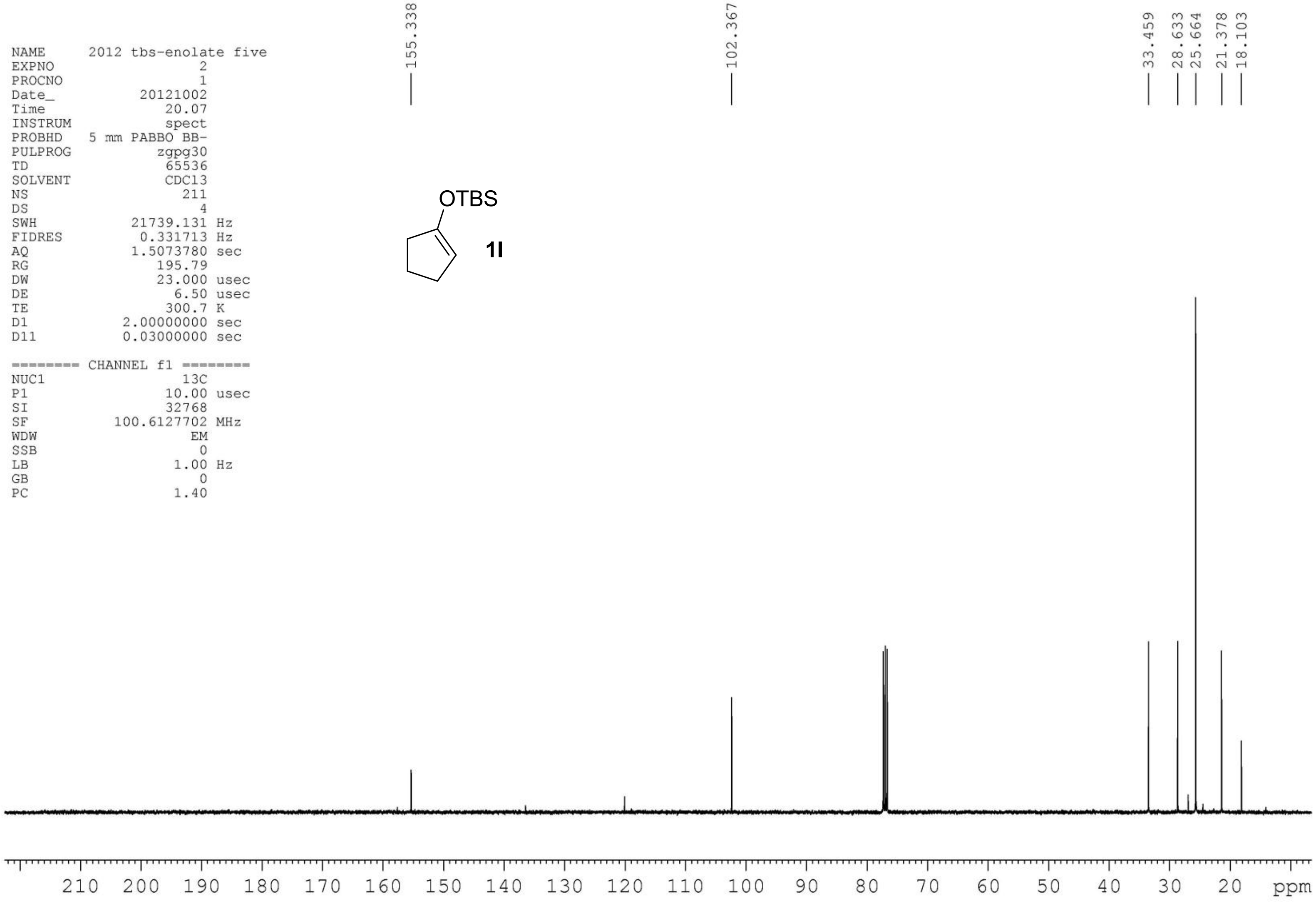
^{13}C NMR



1l

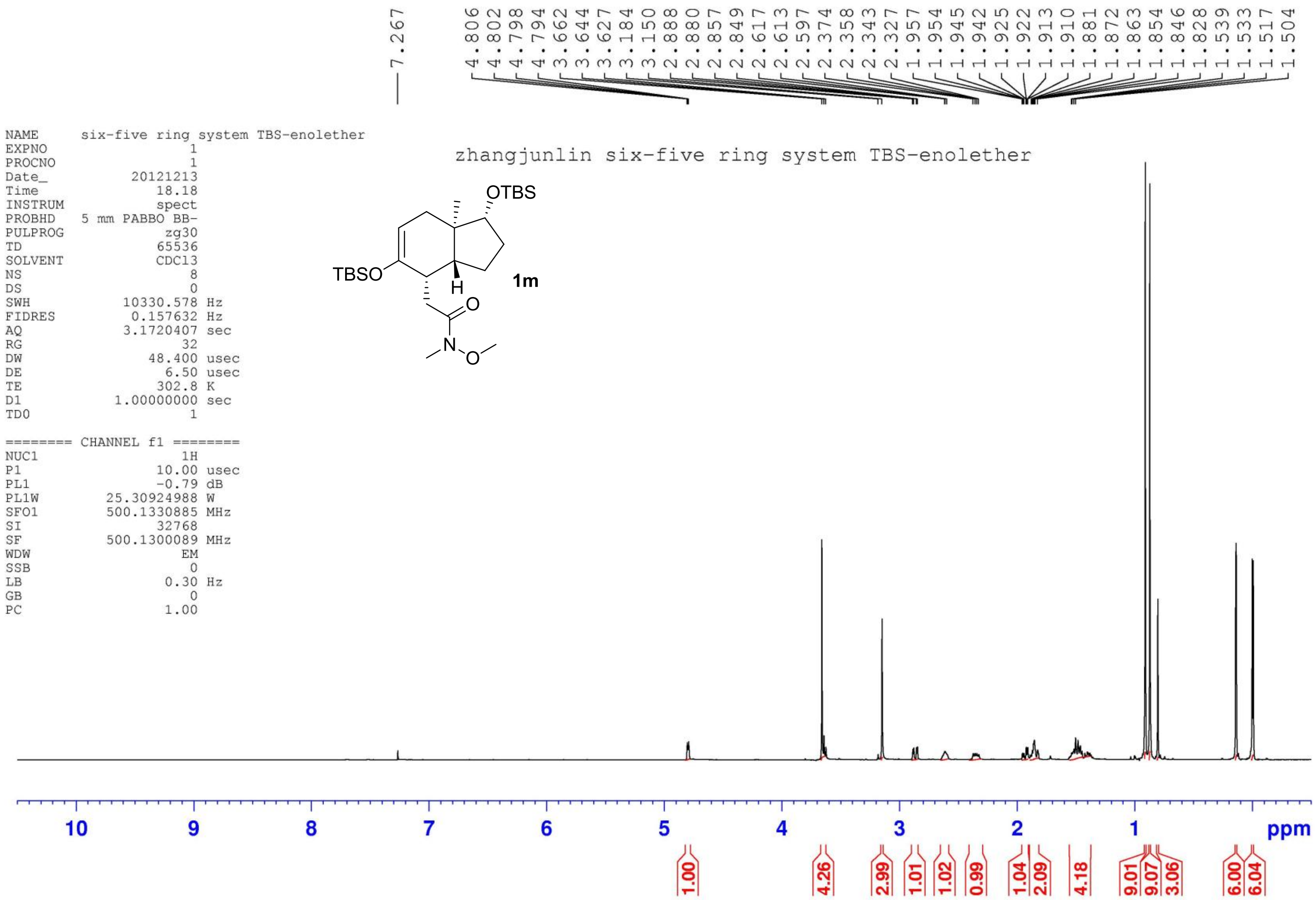
```
NAME     2012 tbs-enolate five
EXPNO                   1
PROCNO                  1
Date_            20121002
Time                20.03
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                      8
DS                      2
SWH              8012.820 Hz
FIDRES           0.122266 Hz
AQ              4.0894966 sec
RG                  40.41
DW                 62.400 usec
DE                   6.50 usec
TE                  300.1 K
D1             1.00000000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                  15.00 usec
SI                  65536
SF            400.1300068 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

^{1}H NMR



```
NAME       2012 tbs-enolate five
EXPNO                     2
PROCNO                    1
Date_              20121002
Time                  20.07
INSTRUM               spect
PROBHD   5 mm PABBO BB-
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                     211
DS                       4
SWH             21739.131 Hz
FIDRES           0.331713 Hz
AQ              1.5073780 sec
RG                  195.79
DW                  23.000 usec
DE                    6.50 usec
TE                   300.7 K
D1              2.00000000 sec
D11             0.03000000 sec

======== CHANNEL f1 ========
NUC1                   13C
P1                   10.00 usec
SI                   32768
SF             100.6127702 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

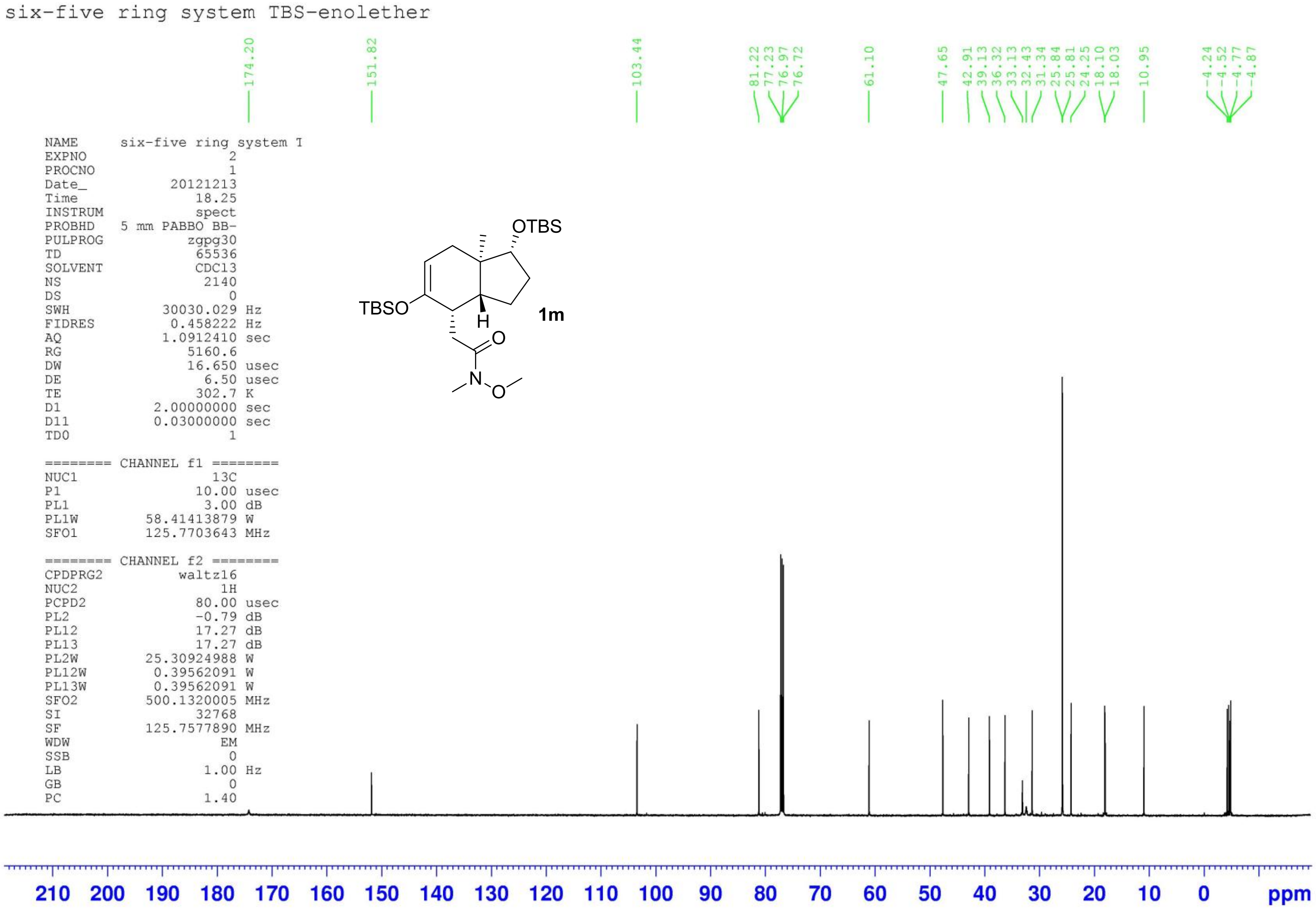
^{13}C NMR



```
NAME       six-five ring system TBS-enolether
EXPNO                    1
PROCNO                   1
Date_             20121213
Time                 18.18
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                       8
DS                       0
SWH              10330.578 Hz
FIDRES            0.157632 Hz
AQ               3.1720407 sec
RG                      32
DW                  48.400 usec
DE                    6.50 usec
TE                   302.8 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   10.00 usec
PL1                  -0.79 dB
PL1W           25.30924988 W
SFO1           500.1330885 MHz
SI                   32768
SF             500.1300089 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

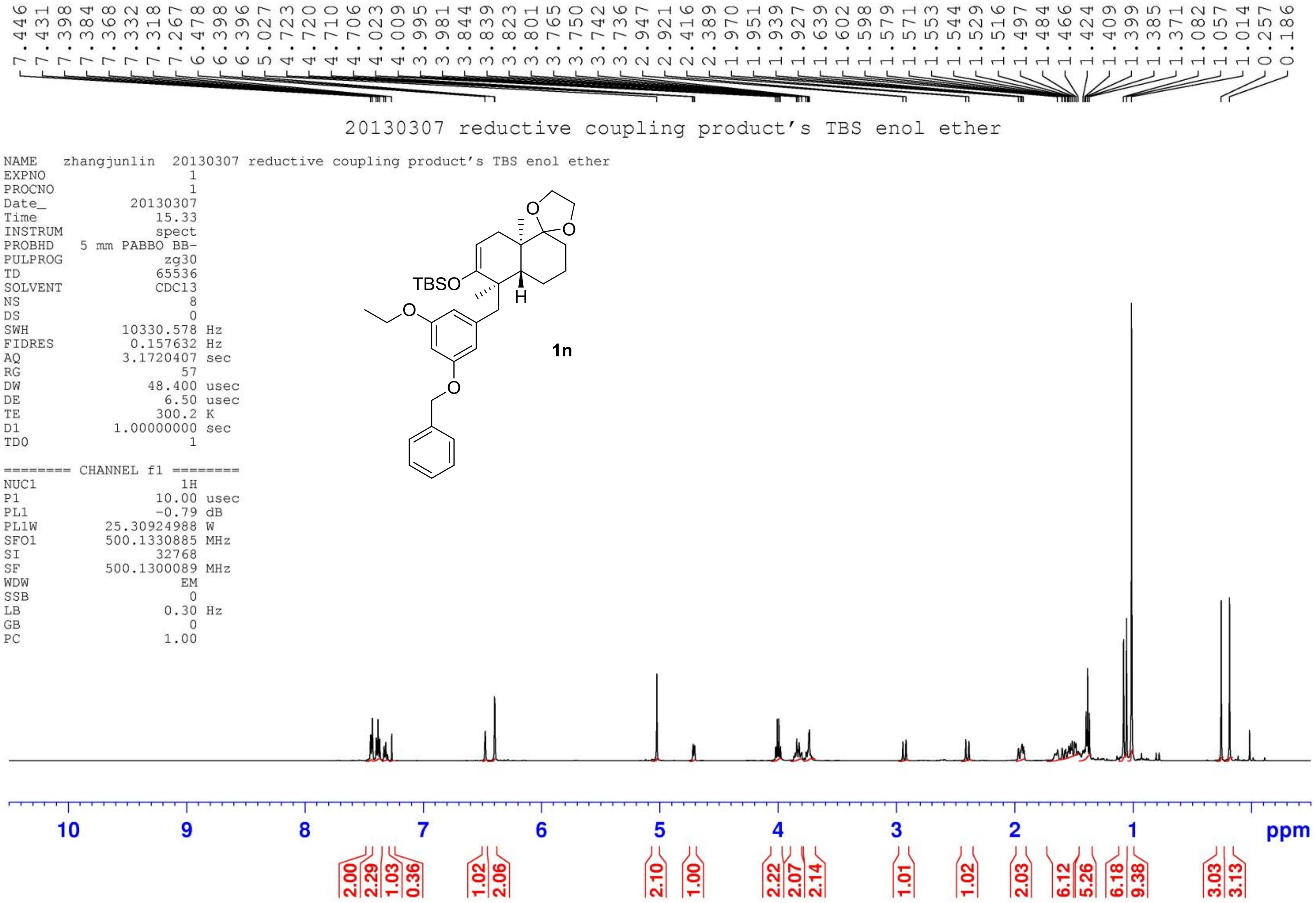
zhangjunlin six-five ring system TBS-enolether

^{1}H NMR



```
NAME       six-five ring system T
EXPNO                   2
PROCNO                  1
Date_            20121213
Time                18.25
INSTRUM             spect
PROBHD     5 mm PABBO BB-
PULPROG           zgpg30
TD                  65536
SOLVENT             CDCl3
NS                   2140
DS                      0
SWH             30030.029 Hz
FIDRES           0.458222 Hz
AQ              1.0912410 sec
RG                 5160.6
DW                 16.650 usec
DE                   6.50 usec
TE                  302.7 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                  10.00 usec
PL1                  3.00 dB
PL1W          58.41413879 W
SFO1          125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                 -0.79 dB
PL12                17.27 dB
PL13                17.27 dB
PL2W          25.30924988 W
PL12W          0.39562091 W
PL13W          0.39562091 W
SFO2          500.1320005 MHz
SI                  32768
SF            125.7577890 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

^{13}C NMR



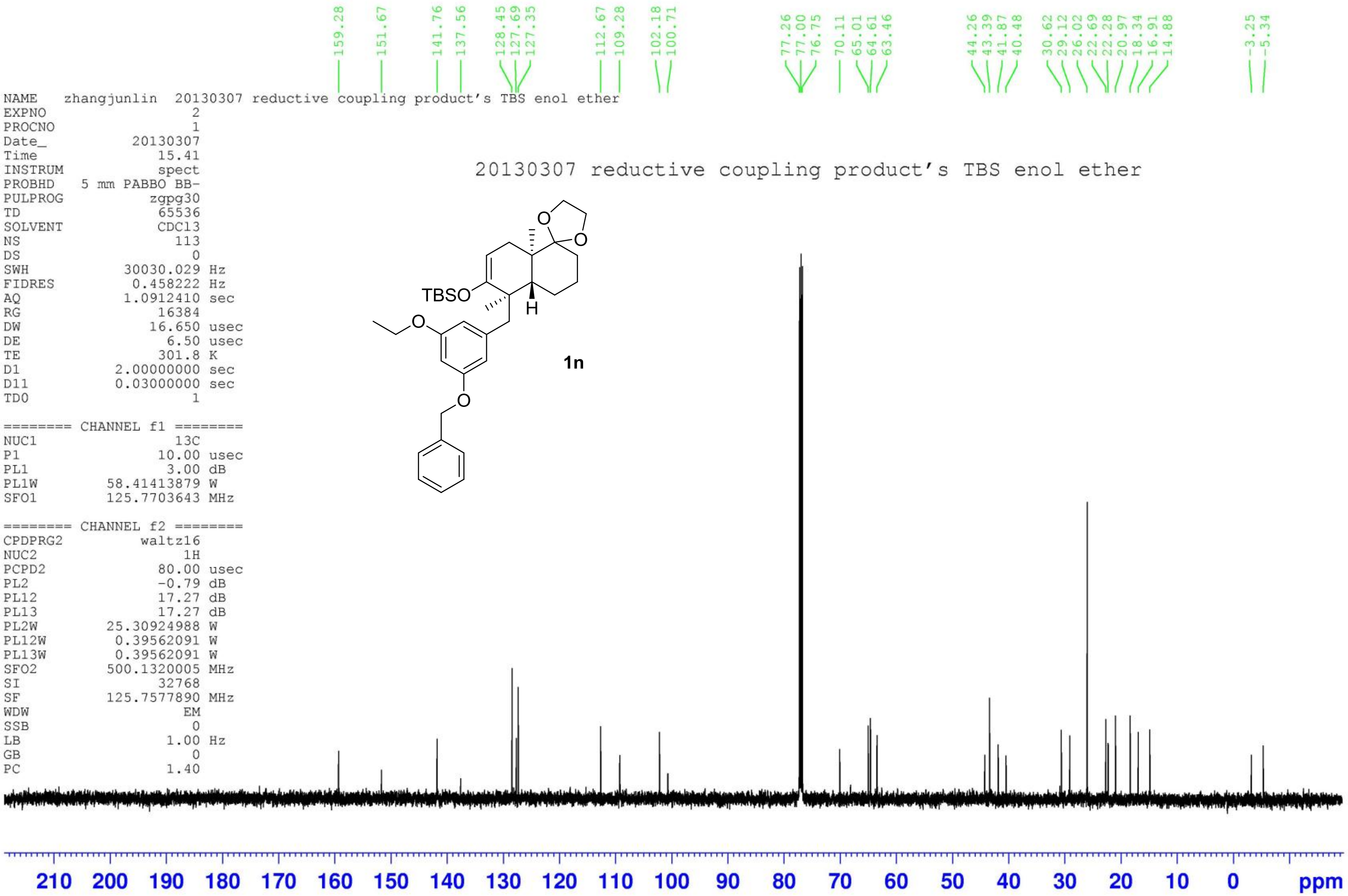
1n

```
NAME    zhangjunlin  20130307 reductive coupling product’s TBS enol ether
EXPNO                 1
PROCNO                1
Date_          20130307
Time              15.33
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    8
DS                    0
SWH           10330.578 Hz
FIDRES         0.157632 Hz
AQ            3.1720407 sec
RG                   57
DW               48.400 usec
DE                 6.50 usec
TE                300.2 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                10.00 usec
PL1               -0.79 dB
PL1W        25.30924988 W
SFO1        500.1330885 MHz
SI                32768
SF          500.1300089 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

^{1}H NMR

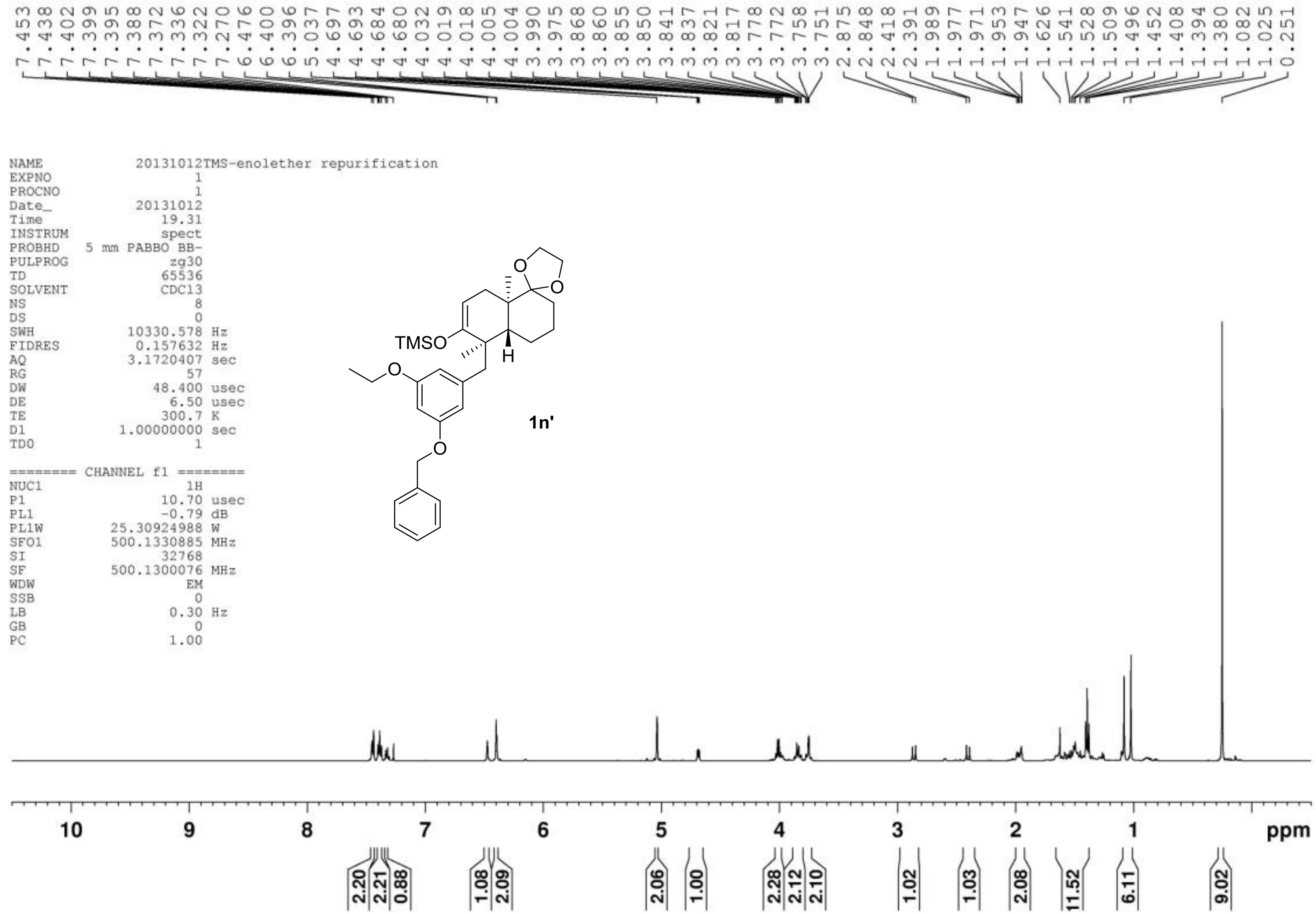
```
NAME    zhangjunlin  20130307 reductive coupling product's TBS enol ether
EXPNO                  2
PROCNO                 1
Date_           20130307
Time               15.41
INSTRUM            spect
PROBHD    5 mm PABBO BB-
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   113
DS                     0
SWH            30030.029 Hz
FIDRES          0.458222 Hz
AQ             1.0912410 sec
RG                 16384
DW                16.650 usec
DE                  6.50 usec
TE                 301.8 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 10.00 usec
PL1                 3.00 dB
PL1W         58.41413879 W
SFO1         125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -0.79 dB
PL12               17.27 dB
PL13               17.27 dB
PL2W         25.30924988 W
PL12W         0.39562091 W
PL13W         0.39562091 W
SFO2         500.1320005 MHz
SI                 32768
SF           125.7577890 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

20130307 reductive coupling product's TBS enol ether



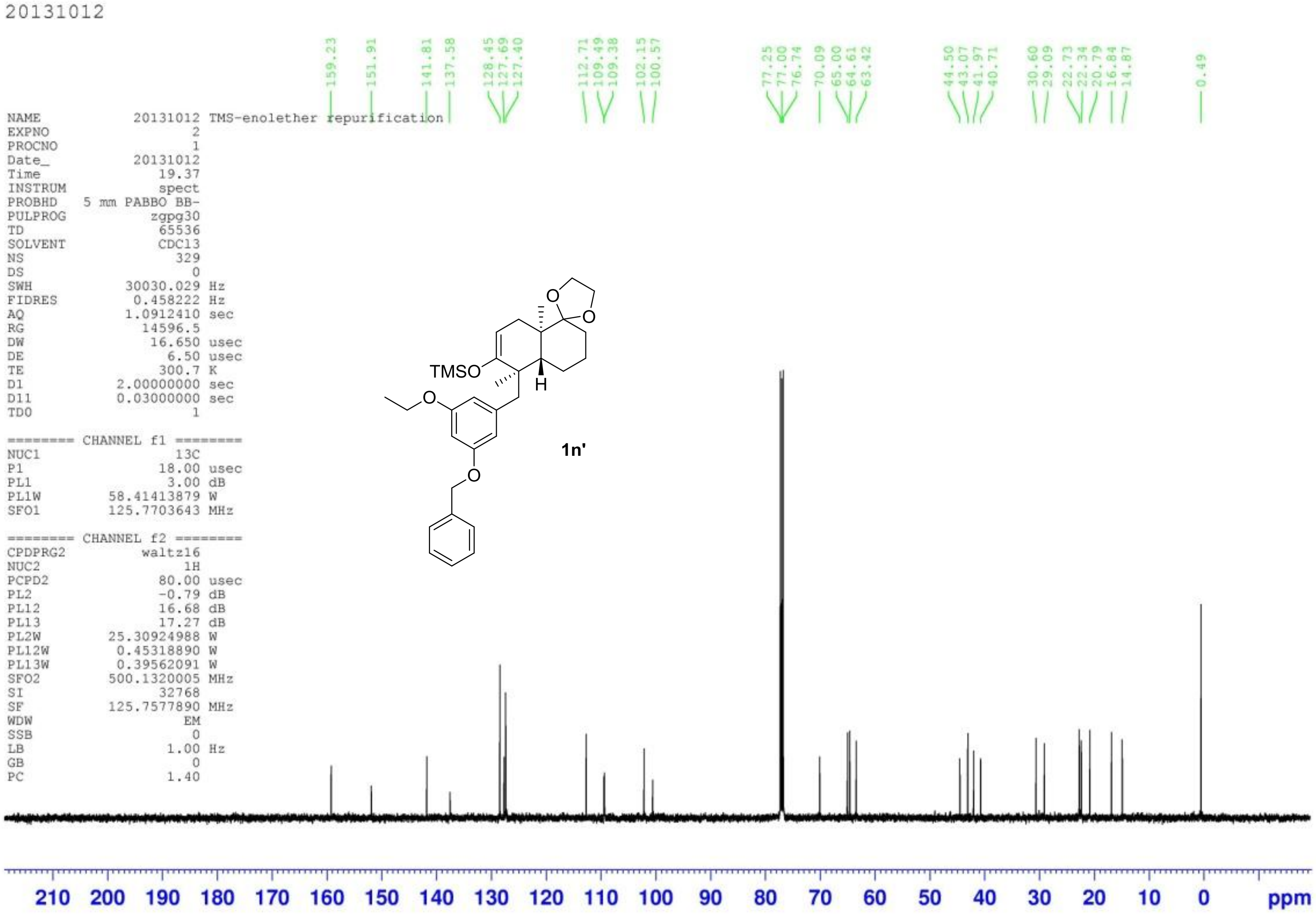
1n

^{13}C NMR



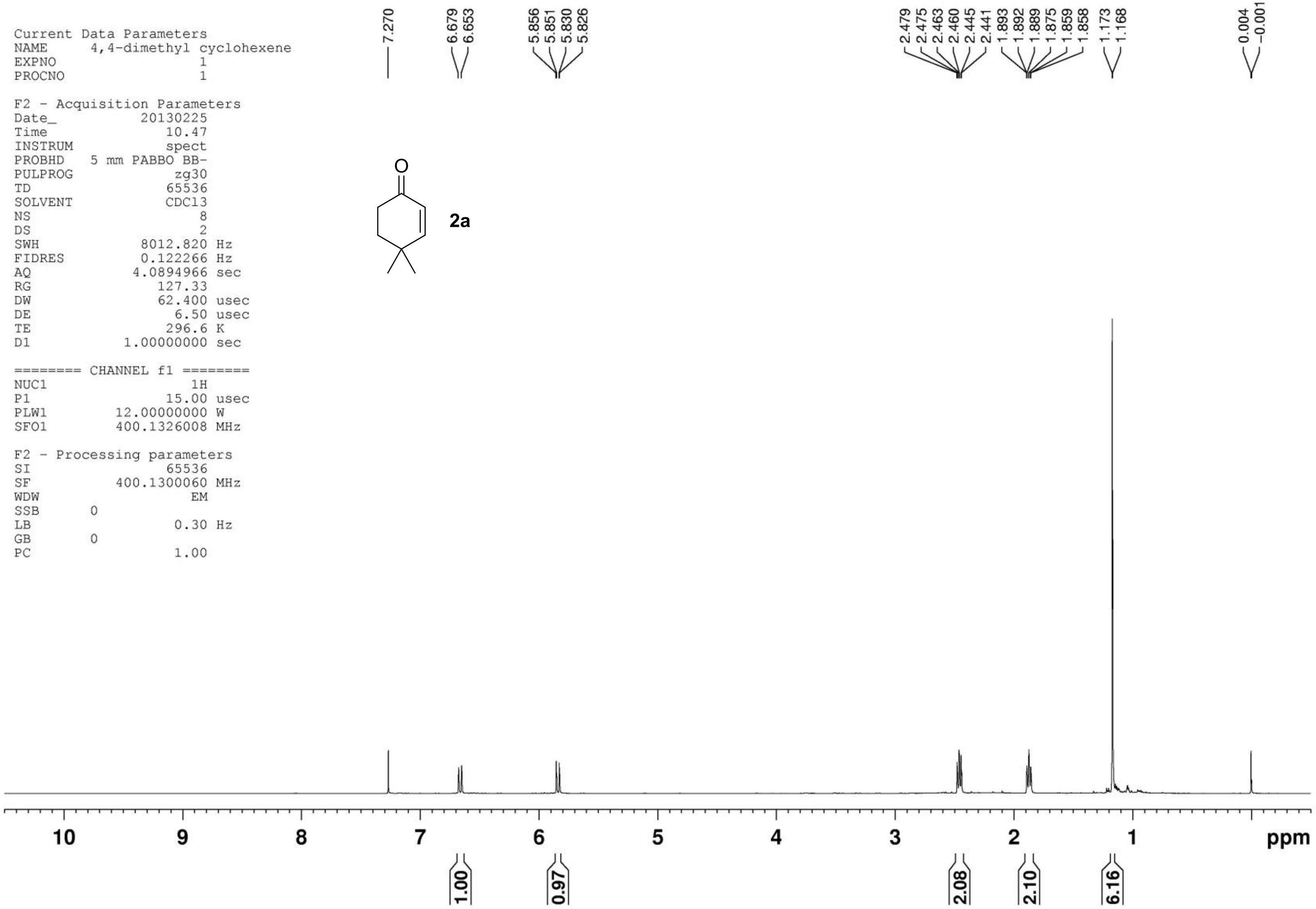
```
NAME          20131012TMS-enolether repurification
EXPNO                    1
PROCNO                   1
Date_             20131012
Time                 19.31
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                       8
DS                       0
SWH              10330.578 Hz
FIDRES            0.157632 Hz
AQ               3.1720407 sec
RG                      57
DW                  48.400 usec
DE                    6.50 usec
TE                   300.7 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   10.70 usec
PL1                  -0.79 dB
PL1W           25.30924988 W
SFO1           500.1330885 MHz
SI                   32768
SF             500.1300076 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

^{1}H NMR



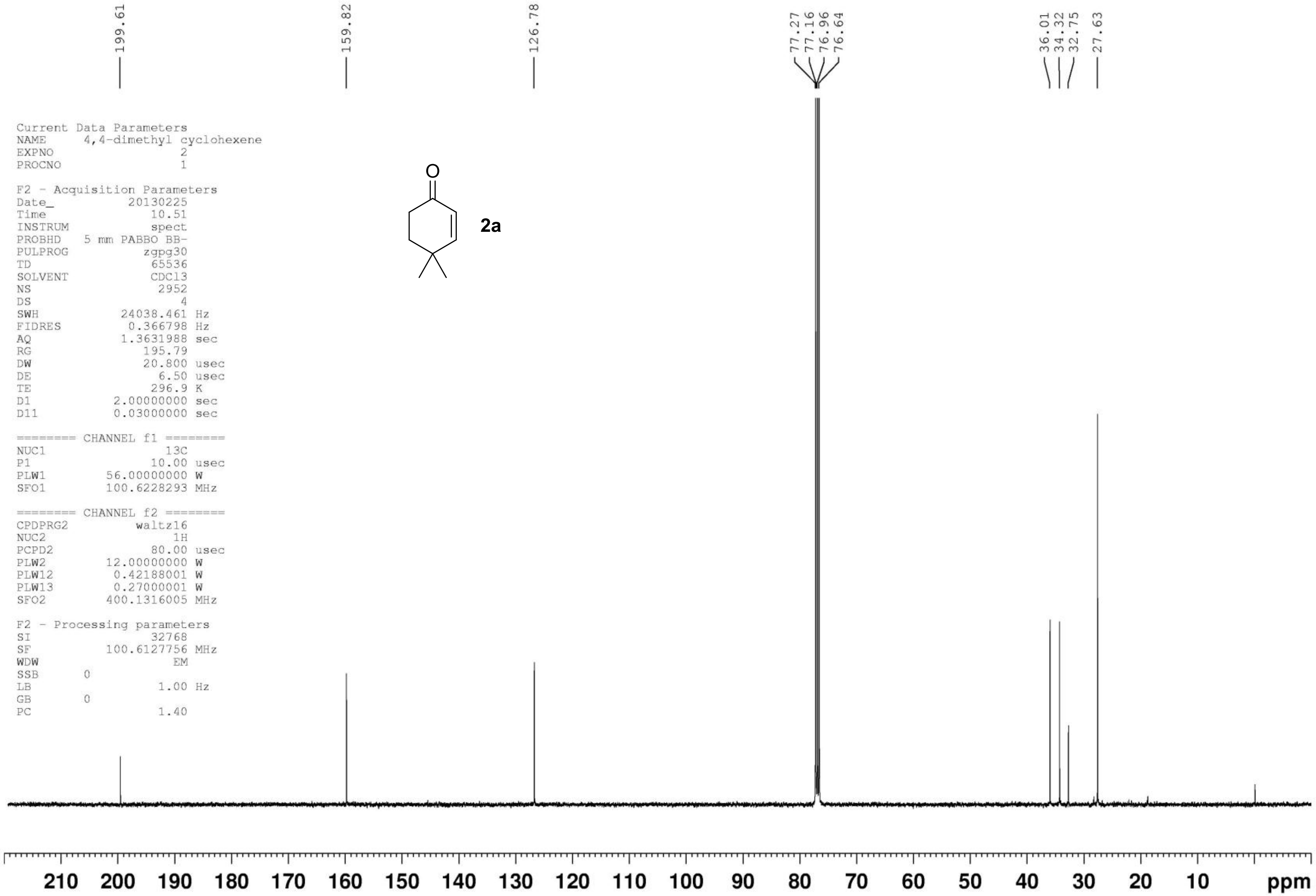
```
NAME           20131012 TMS-enolether repurification
EXPNO                 2
PROCNO                1
Date_          20131012
Time              19.37
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG         zgpg30
TD               65536
SOLVENT          CDCl3
NS                 329
DS                   0
SWH          30030.029 Hz
FIDRES        0.458222 Hz
AQ           1.0912410 sec
RG             14596.5
DW              16.650 usec
DE                6.50 usec
TE               300.7 K
D1          2.00000000 sec
D11         0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1               13C
P1               18.00 usec
PL1               3.00 dB
PL1W       58.41413879 W
SFO1       125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2            80.00 usec
PL2              -0.79 dB
PL12             16.68 dB
PL13             17.27 dB
PL2W       25.30924988 W
PL12W       0.45318890 W
PL13W       0.39562091 W
SFO2       500.1320005 MHz
SI               32768
SF         125.7577890 MHz
WDW                 EM
SSB                  0
LB                1.00 Hz
GB                   0
PC                1.40
```

^{13}C NMR



```
Current Data Parameters
NAME     4,4-dimethyl cyclohexene
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20130225
Time               10.47
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     2
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                127.33
DW                62.400 usec
DE                  6.50 usec
TE                 296.6 K
D1            1.00000000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 15.00 usec
PLW1         12.00000000 W
SFO1         400.1326008 MHz

F2 - Processing parameters
SI                 65536
SF           400.1300060 MHz
WDW                   EM
SSB       0
LB                  0.30 Hz
GB        0
PC                  1.00
```

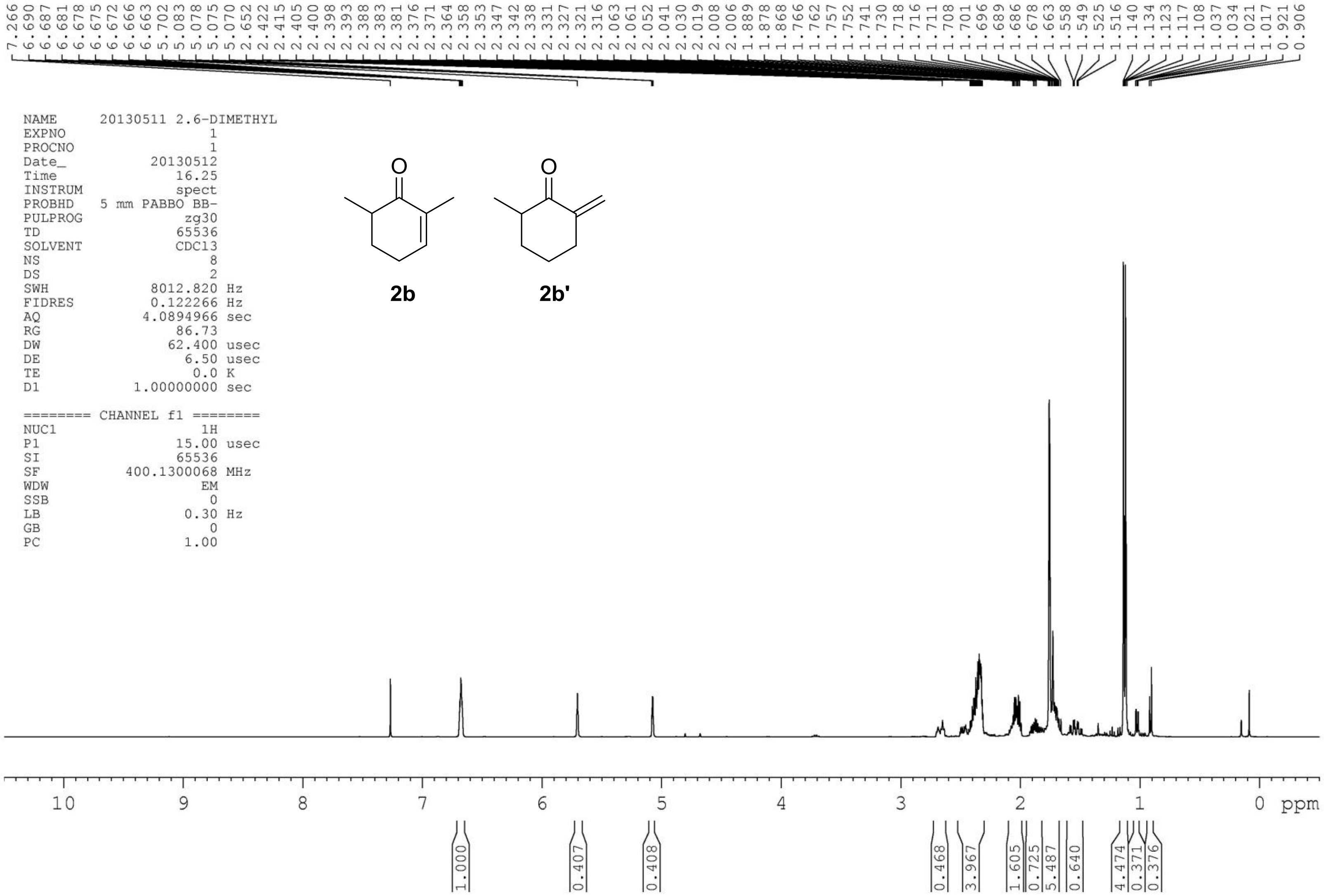
^{1}H NMR



2a

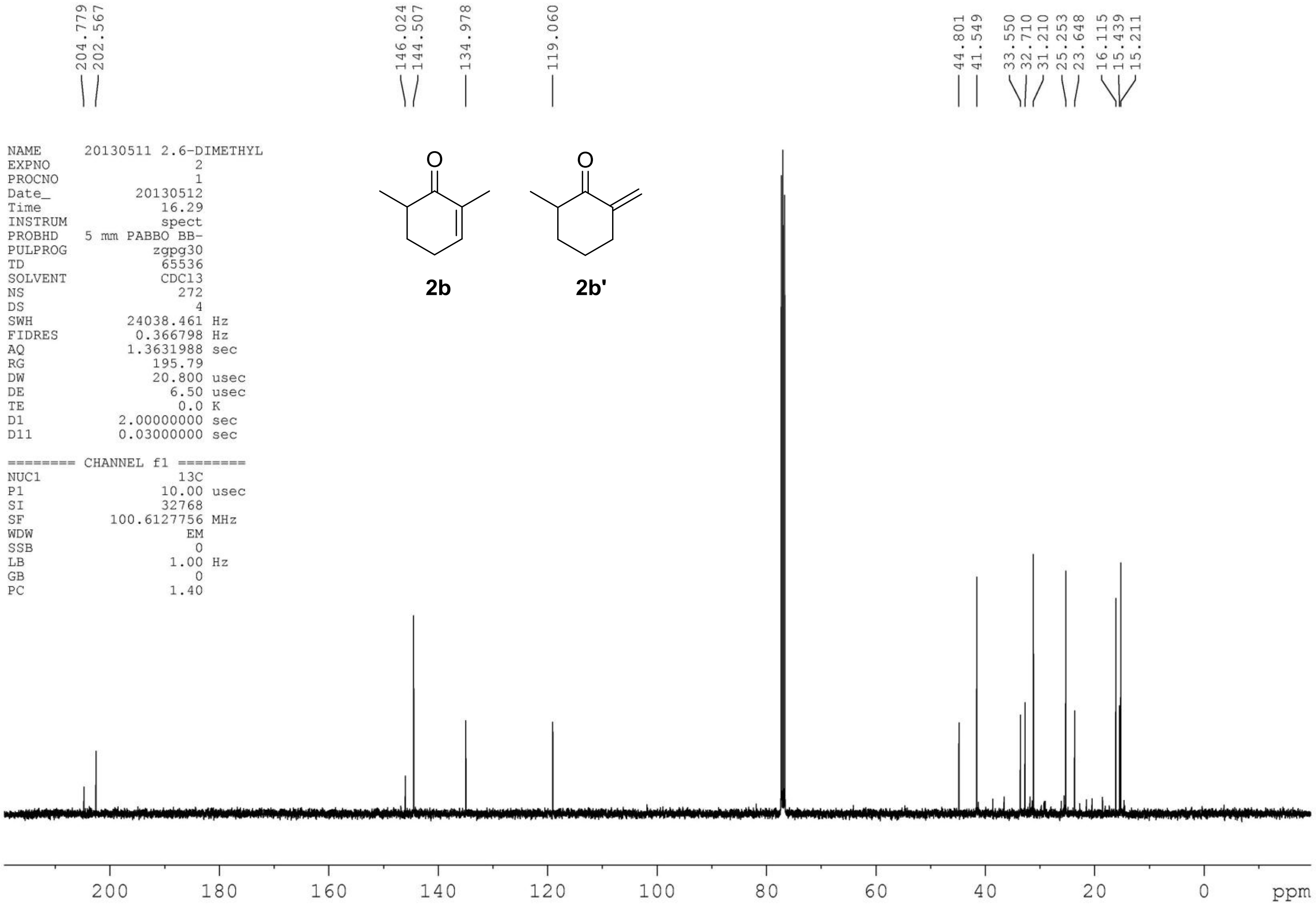
```
Current Data Parameters
NAME     4,4-dimethyl cyclohexene
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20130225
Time                10.51
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  2952
DS                     4
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                195.79
DW                20.800 usec
DE                  6.50 usec
TE                 296.9 K
D1            2.00000000 sec
D11           0.03000000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                 10.00 usec
PLW1         56.00000000 W
SFO1         100.6228293 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PLW2         12.00000000 W
PLW12         0.42188001 W
PLW13         0.27000001 W
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF           100.6127756 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  1.40
```

^{13}C NMR



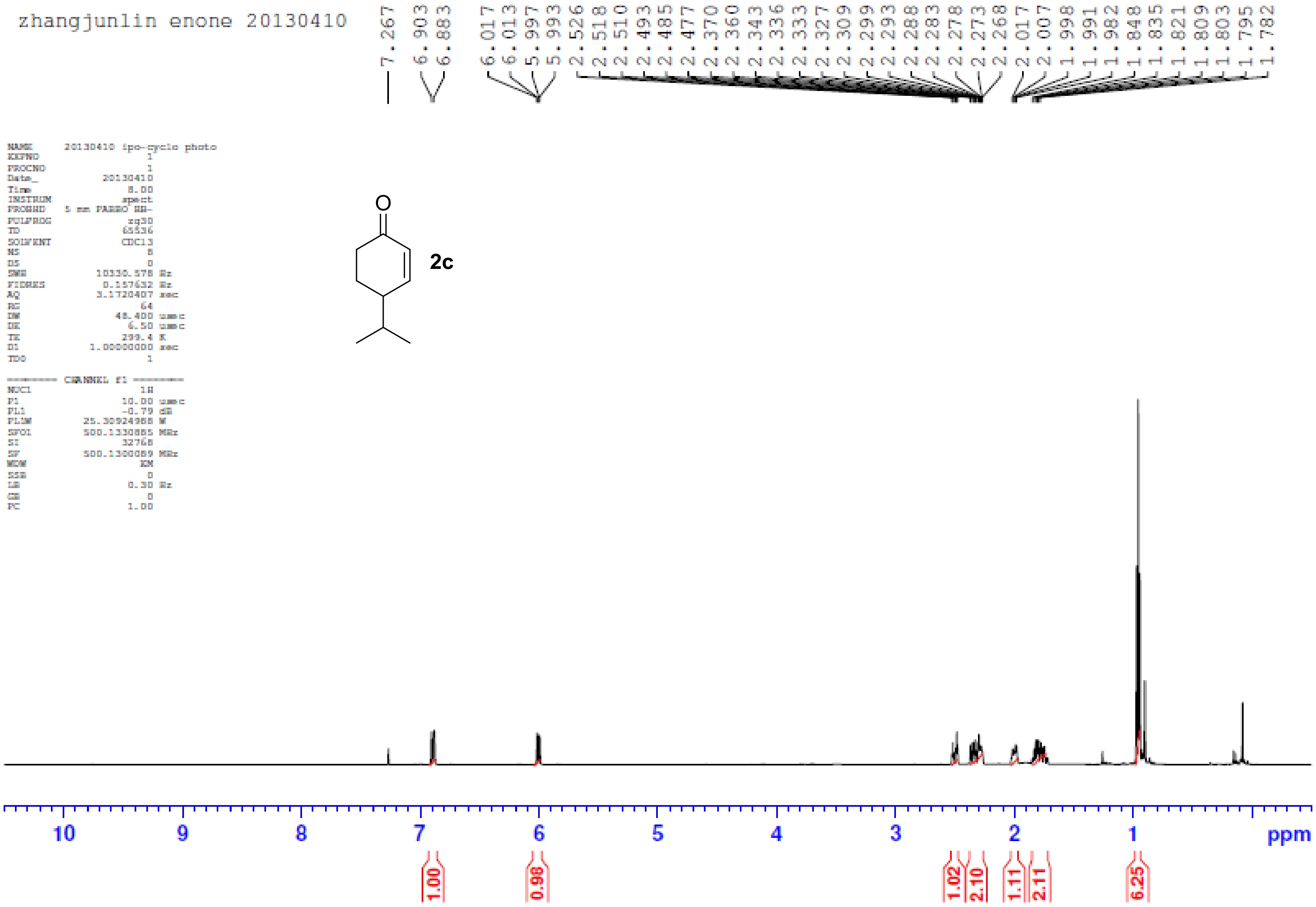
```
NAME      20130511 2.6-DIMETHYL
EXPNO                 1
PROCNO                1
Date_          20130512
Time              16.25
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.122266 Hz
AQ            4.0894966 sec
RG                86.73
DW               62.400 usec
DE                 6.50 usec
TE                  0.0 K
D1           1.00000000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                15.00 usec
SI                65536
SF          400.1300068 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

^{1}H NMR



```
NAME      20130511 2.6-DIMETHYL
EXPNO                 2
PROCNO                1
Date_          20130512
Time              16.29
INSTRUM           spect
PROBHD    5 mm PABBO BB-
PULPROG         zgpg30
TD               65536
SOLVENT          CDCl3
NS                 272
DS                   4
SWH          24038.461 Hz
FIDRES        0.366798 Hz
AQ           1.3631988 sec
RG              195.79
DW              20.800 usec
DE                6.50 usec
TE                 0.0 K
D1          2.00000000 sec
D11         0.03000000 sec

======== CHANNEL f1 ========
NUC1               13C
P1               10.00 usec
SI               32768
SF         100.6127756 MHz
WDW                 EM
SSB                  0
LB                1.00 Hz
GB                   0
PC                1.40
```

^{13}C NMR

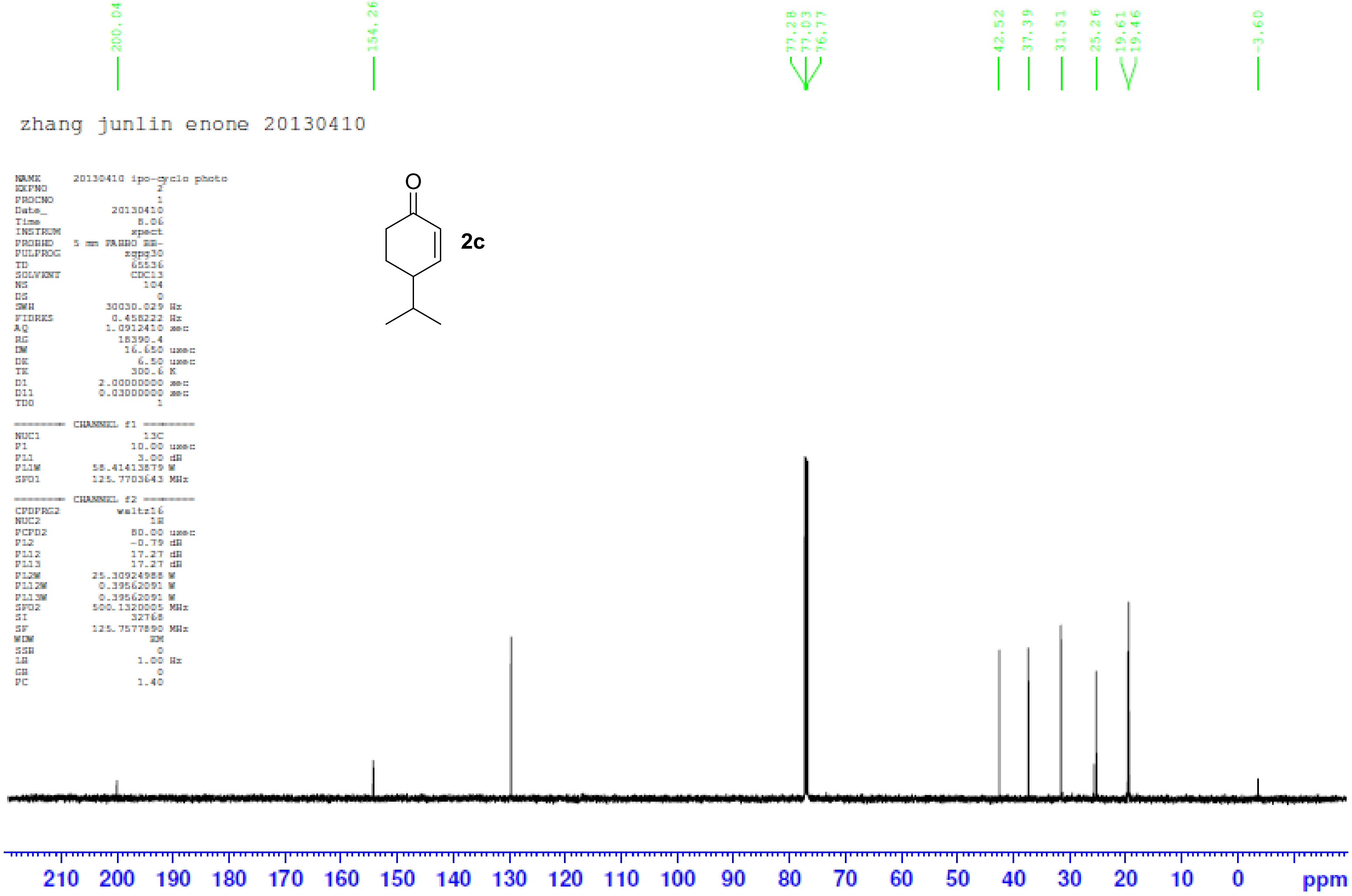


zhangjunlin enone 20130410

```
NAME       20130410 ipo-cyclo photo
EXPNO                     1
PROCNO                    1
Date_              20130410
Time                   8.00
INSTRUM               spect
PROBHD     5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                        8
DS                        0
SWH               10330.578 Hz
FIDRES             0.157632 Hz
AQ                3.1720407 sec
RG                       64
DW                   48.400 usec
DE                     6.50 usec
TE                    299.4 K
D1               1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     1H
P1                    10.00 usec
PL1                   -0.79 dB
PL1W            25.30924988 W
SFO1            500.1330885 MHz
SI                    32768
SF              500.1300089 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00
```

2c

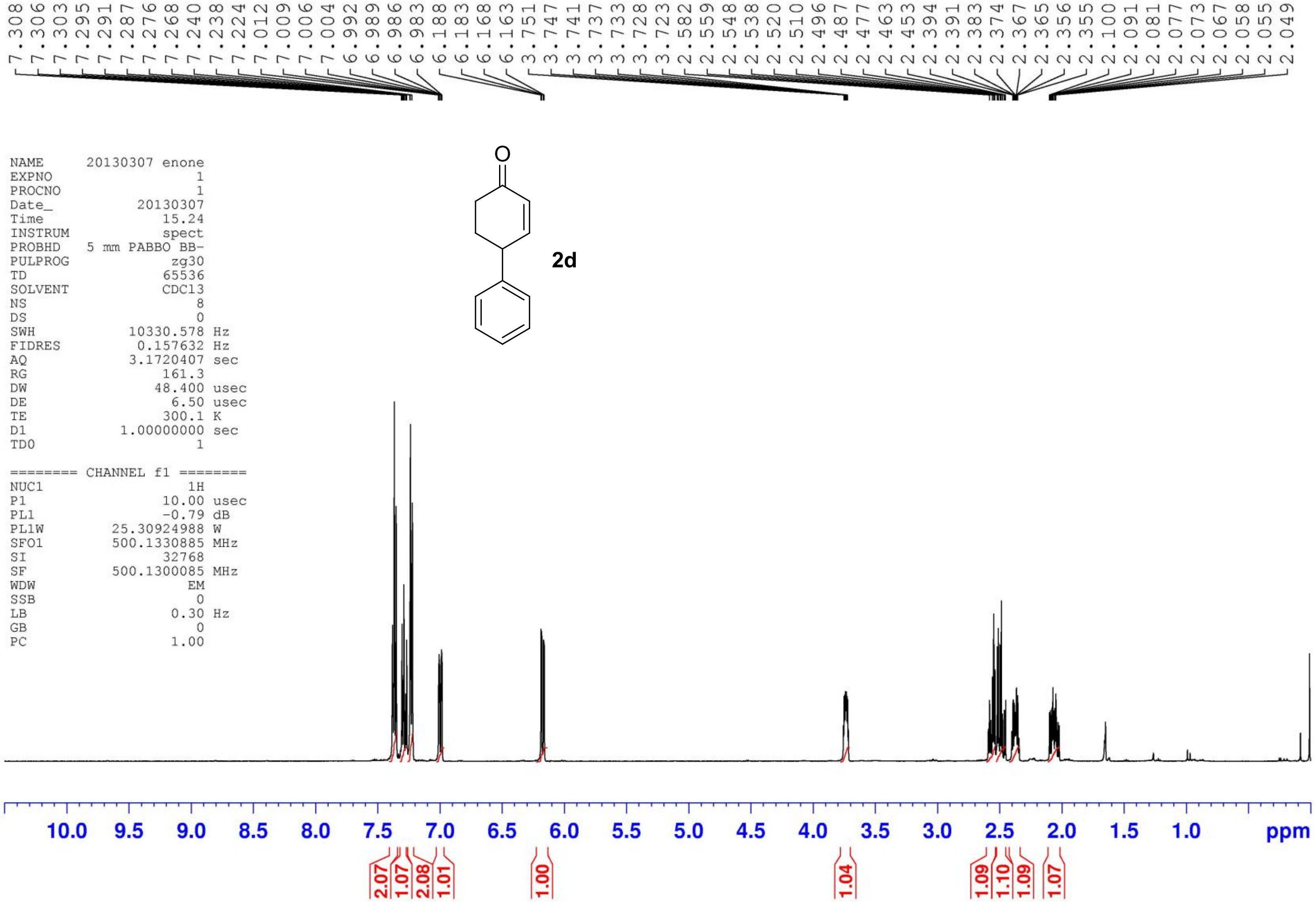
^{1}H NMR



2c

```
NAME     20130410 ipo-cyclo photo
EXPNO                   2
PROCNO                  1
Date_            20130410
Time                 8.06
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    104
DS                      0
SWH             30030.029 Hz
FIDRES           0.458222 Hz
AQ              1.0912410 sec
RG                18390.4
DW                 16.650 usec
DE                   6.50 usec
TE                  300.6 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                  10.00 usec
PL1                  3.00 dB
PL1W          58.41413879 W
SFO1          125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                 -0.79 dB
PL12                17.27 dB
PL13                17.27 dB
PL2W          25.30924988 W
PL12W          0.39562091 W
PL13W          0.39562091 W
SFO2          500.1320005 MHz
SI                  32768
SF            125.7577890 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

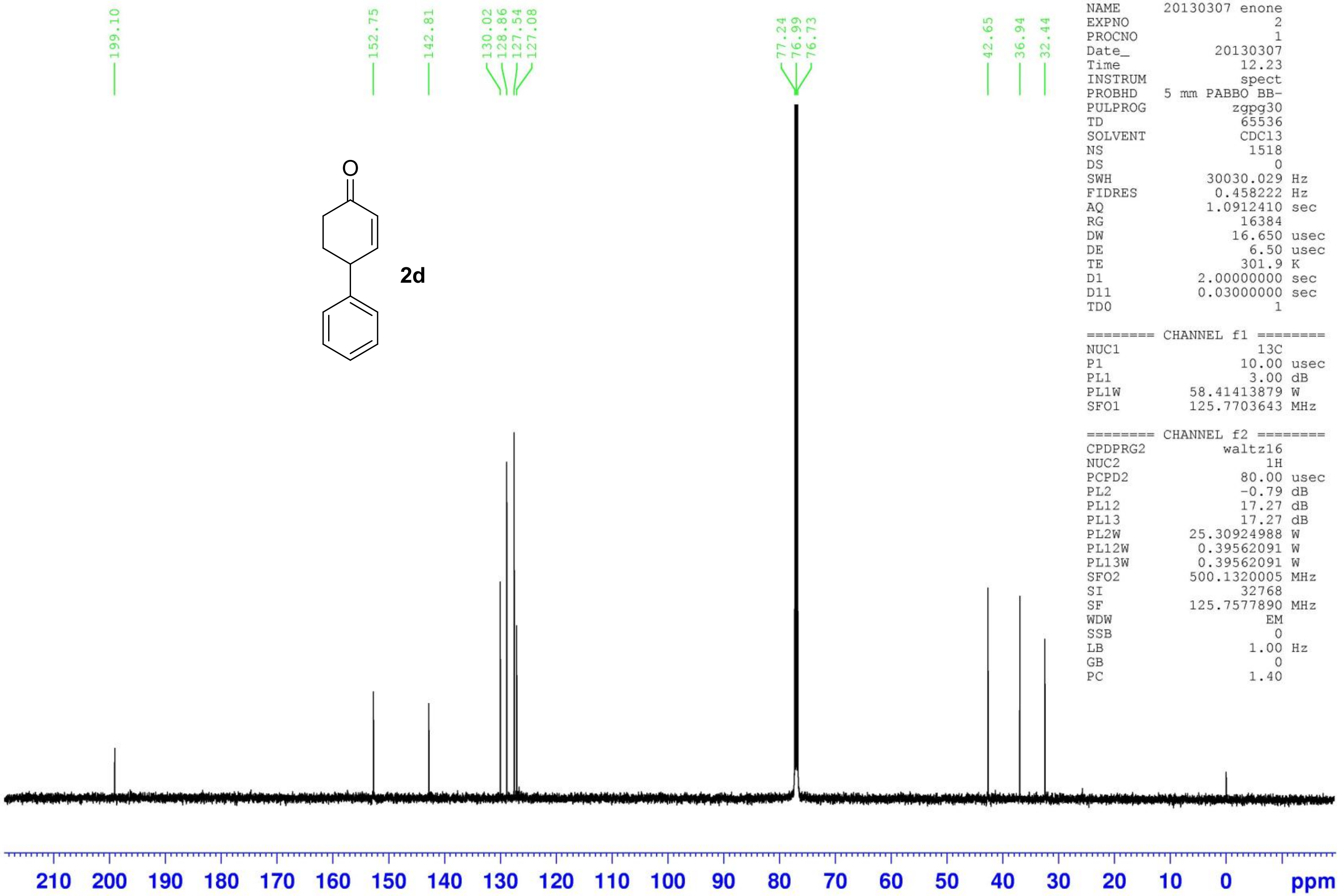
^{13}C NMR



2d

```
NAME      20130307 enone
EXPNO                  1
PROCNO                 1
Date_           20130307
Time               15.24
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     0
SWH            10330.578 Hz
FIDRES          0.157632 Hz
AQ             3.1720407 sec
RG                 161.3
DW                48.400 usec
DE                  6.50 usec
TE                 300.1 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 10.00 usec
PL1                -0.79 dB
PL1W         25.30924988 W
SFO1         500.1330885 MHz
SI                 32768
SF           500.1300085 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

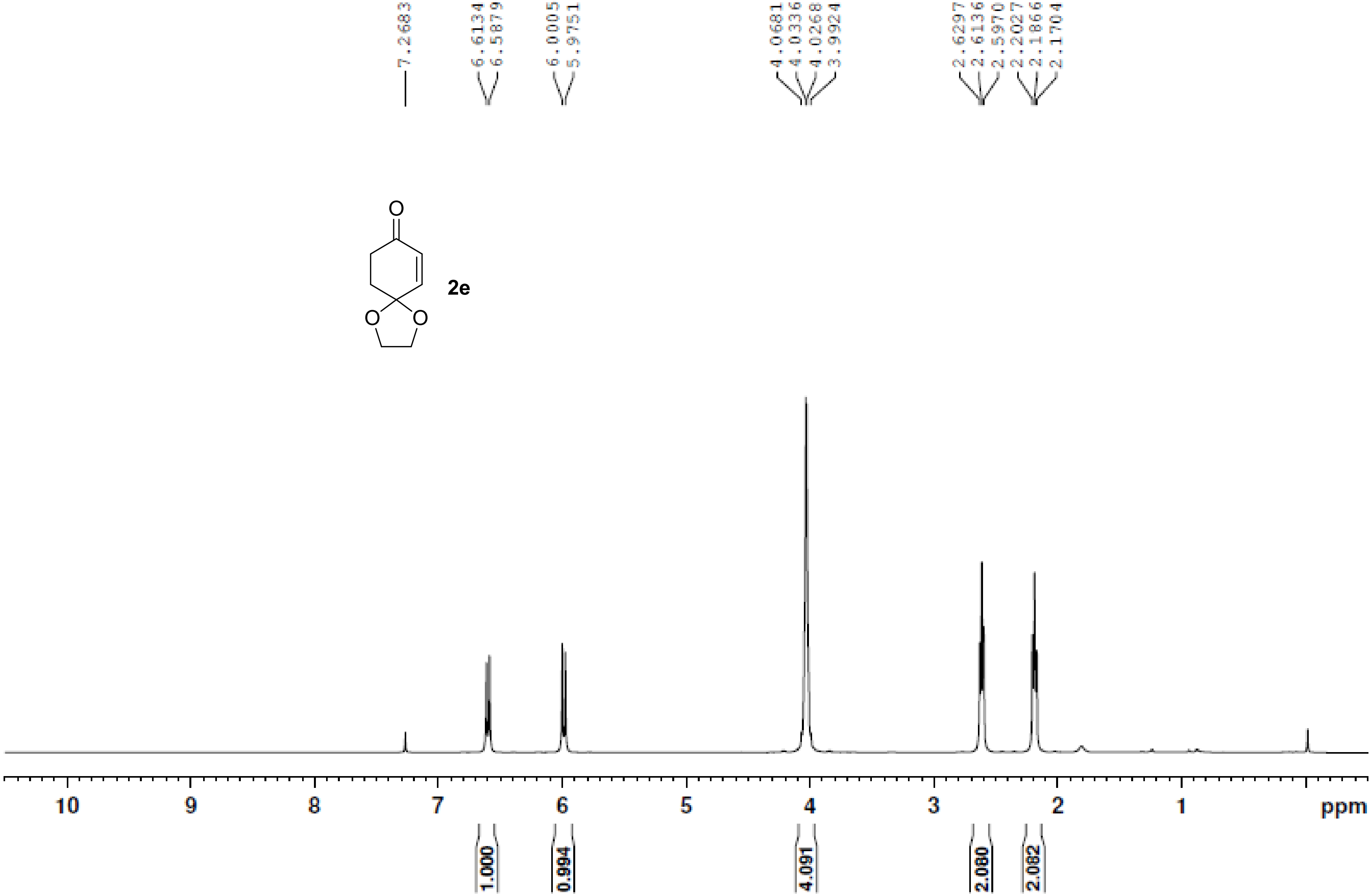
^{1}H NMR



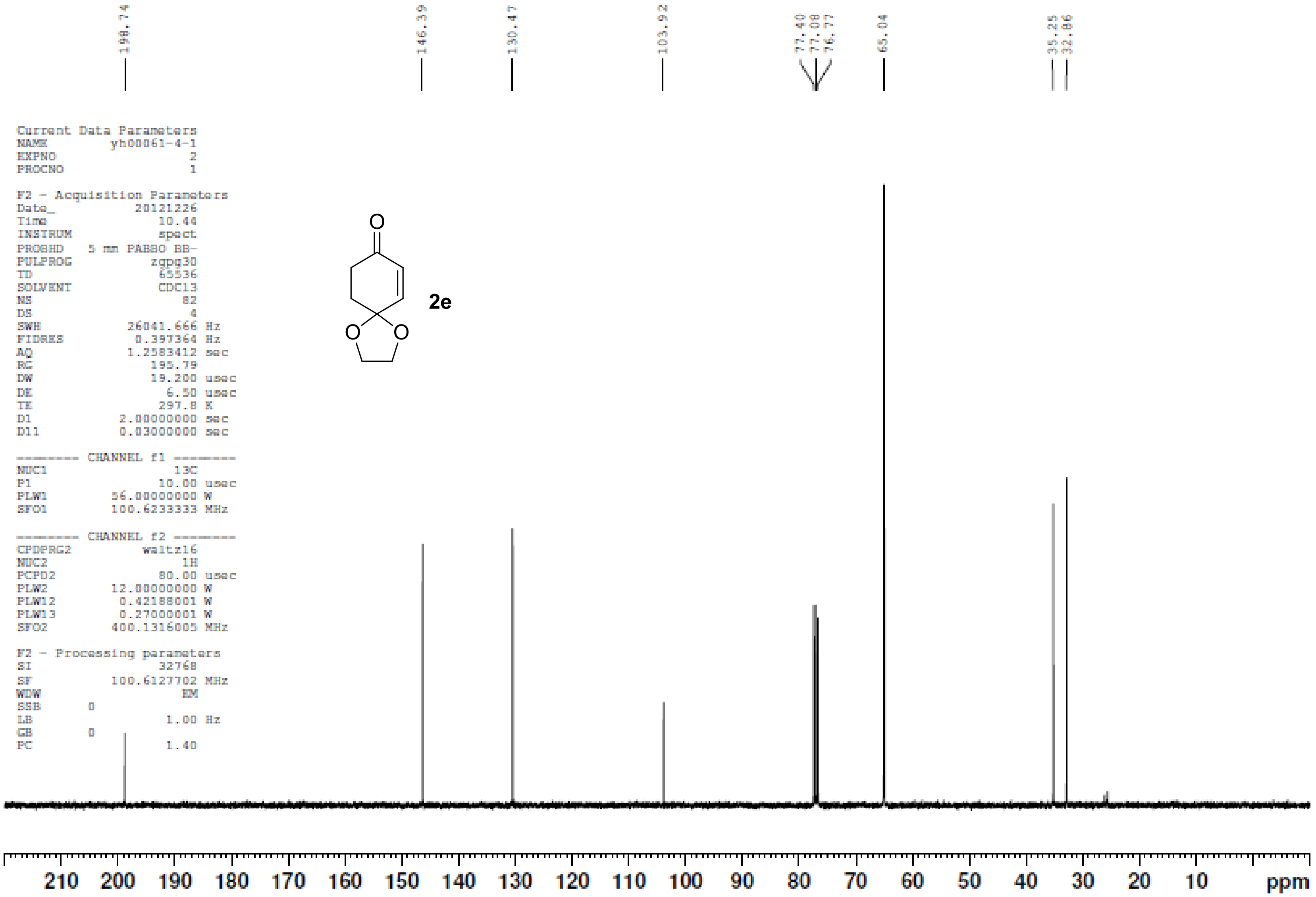
2d

```
NAME      20130307 enone
EXPNO                  2
PROCNO                 1
Date_           20130307
Time               12.23
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1518
DS                    0
SWH           30030.029 Hz
FIDRES         0.458222 Hz
AQ            1.0912410 sec
RG                16384
DW               16.650 usec
DE                 6.50 usec
TE                301.9 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                10.00 usec
PL1                3.00 dB
PL1W        58.41413879 W
SFO1        125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2               -0.79 dB
PL12              17.27 dB
PL13              17.27 dB
PL2W        25.30924988 W
PL12W        0.39562091 W
PL13W        0.39562091 W
SFO2        500.1320005 MHz
SI                32768
SF          125.7577890 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

^{13}C NMR


7.2683
6.6134
6.5879
6.0005
5.9751
4.0681
4.0336
4.0268
3.9924
2.6297
2.6136
2.5970
2.2027
2.1866
2.1704
O
O
O
2e
10
9
8
7
6
5
4
3
2
1
ppm
1.000
0.994
4.091
2.080
2.082

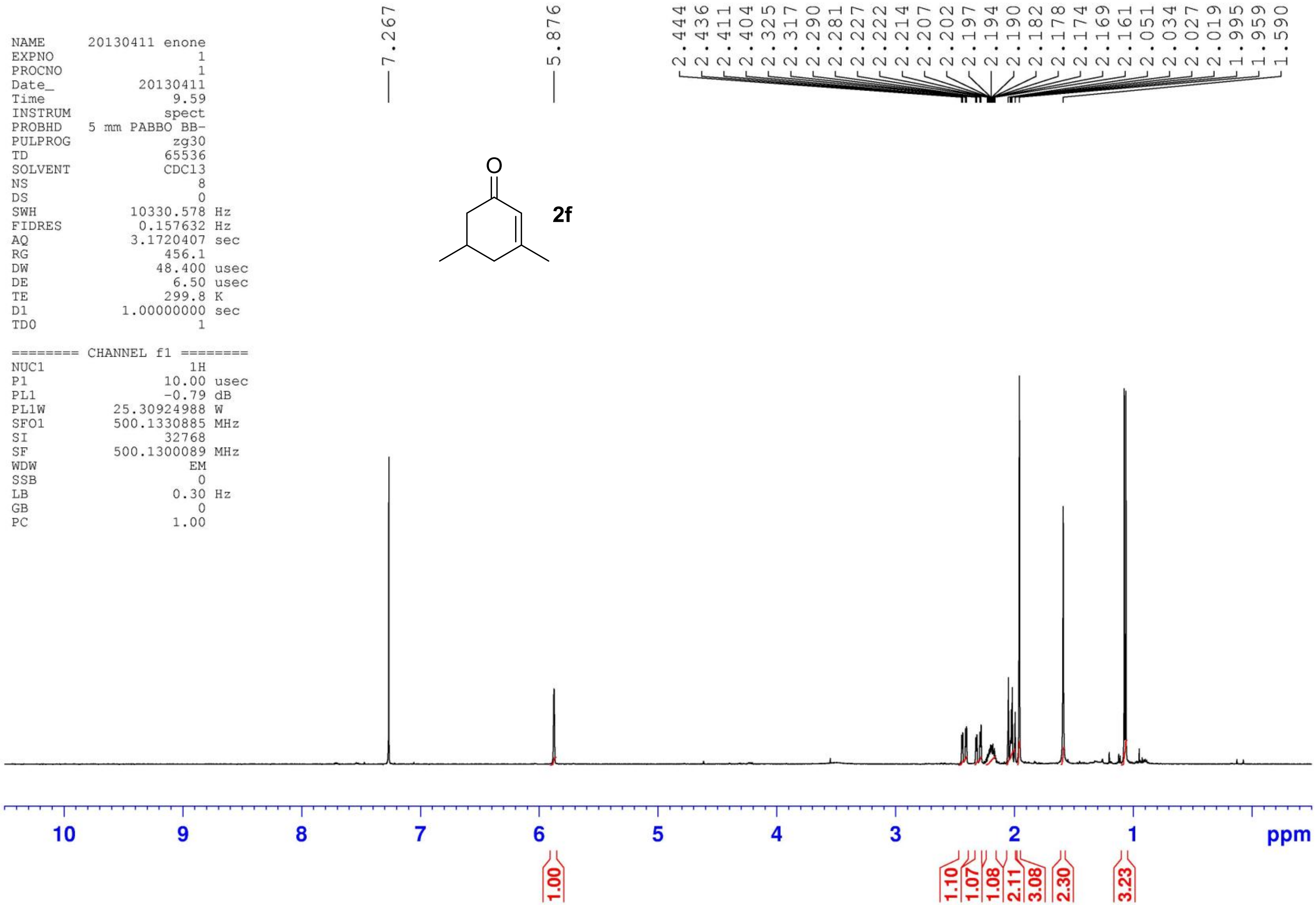
^{1}H NMR



```
Current Data Parameters
NAME           yh00061-4-1
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_             20121226
Time                 10.44
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG            zgpg30
TD                   65536
SOLVENT              CDCl3
NS                      82
DS                       4
SWH             26041.666 Hz
FIDRES           0.397364 Hz
AQ              1.2583412 sec
RG                 195.79
DW                 19.200 usec
DE                   6.50 usec
TE                  297.8 K
D1             2.00000000 sec
D11            0.03000000 sec

======== CHANNEL f1 ========
NUC1                   13C
P1                   10.00 usec
PLW1          56.00000000 W
SFO1          100.6233333 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                80.00 usec
PLW2          12.00000000 W
PLW12          0.42188001 W
PLW13          0.27000001 W
SFO2          400.1316005 MHz

F2 - Processing parameters
SI                   32768
SF            100.6127702 MHz
WDW                     EM
SSB       0
LB                    1.00 Hz
GB        0
PC                    1.40
```

2e

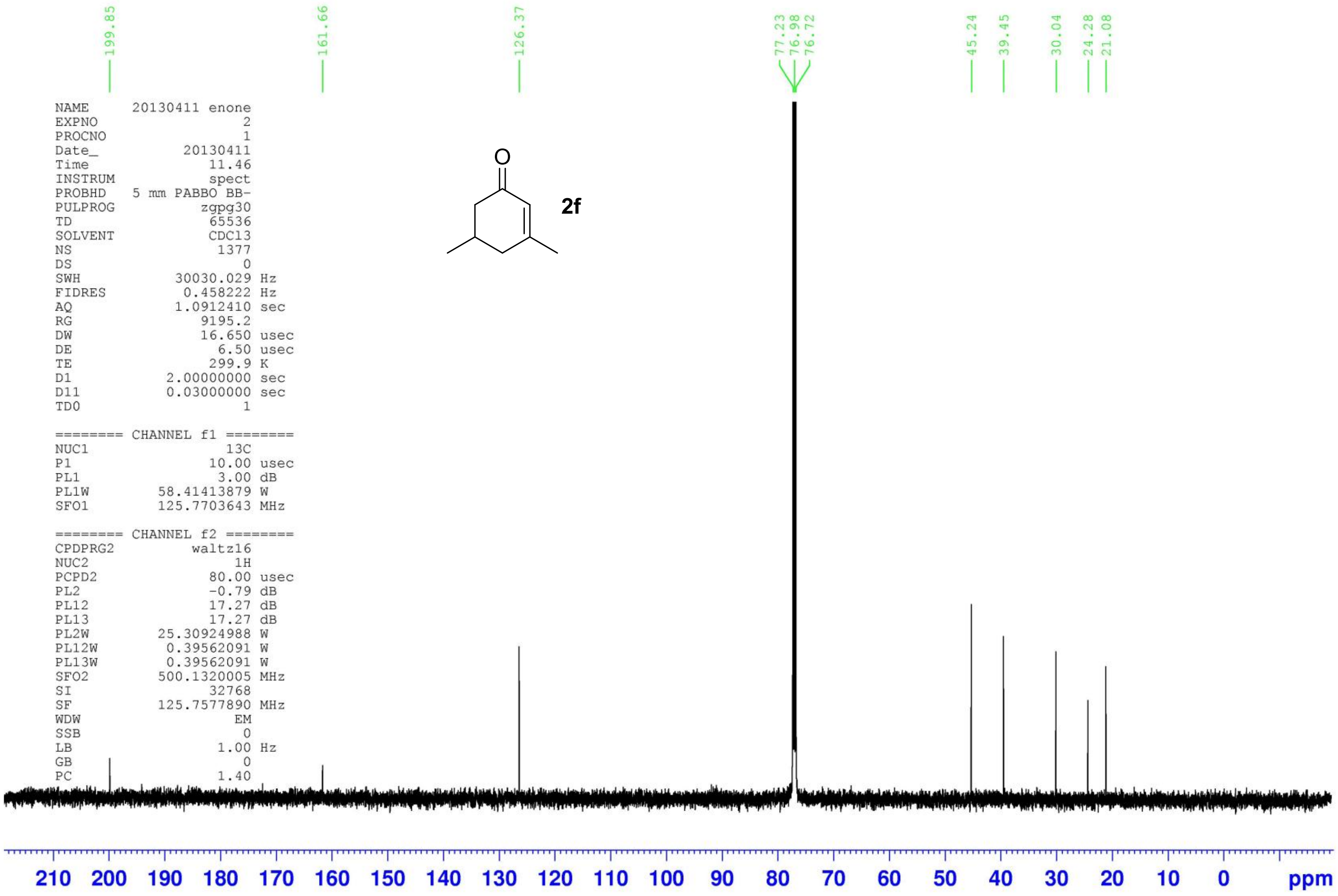
^{13}C NMR



2f

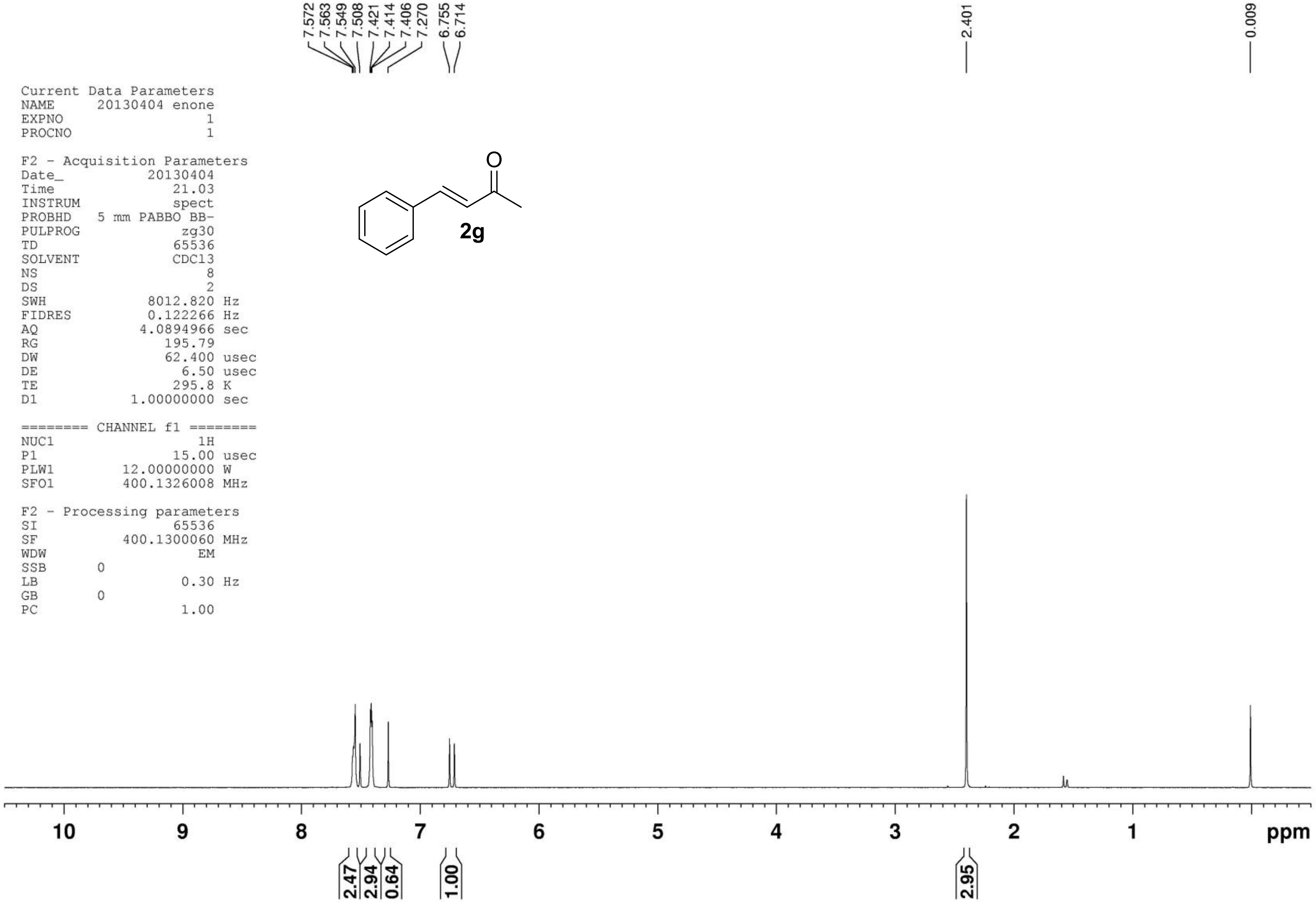
```
NAME       20130411 enone
EXPNO                   1
PROCNO                  1
Date_            20130411
Time                 9.59
INSTRUM             spect
PROBHD    5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                      8
DS                      0
SWH             10330.578 Hz
FIDRES           0.157632 Hz
AQ              3.1720407 sec
RG                  456.1
DW                 48.400 usec
DE                   6.50 usec
TE                  299.8 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  10.00 usec
PL1                 -0.79 dB
PL1W          25.30924988 W
SFO1          500.1330885 MHz
SI                  32768
SF            500.1300089 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

^{1}H NMR



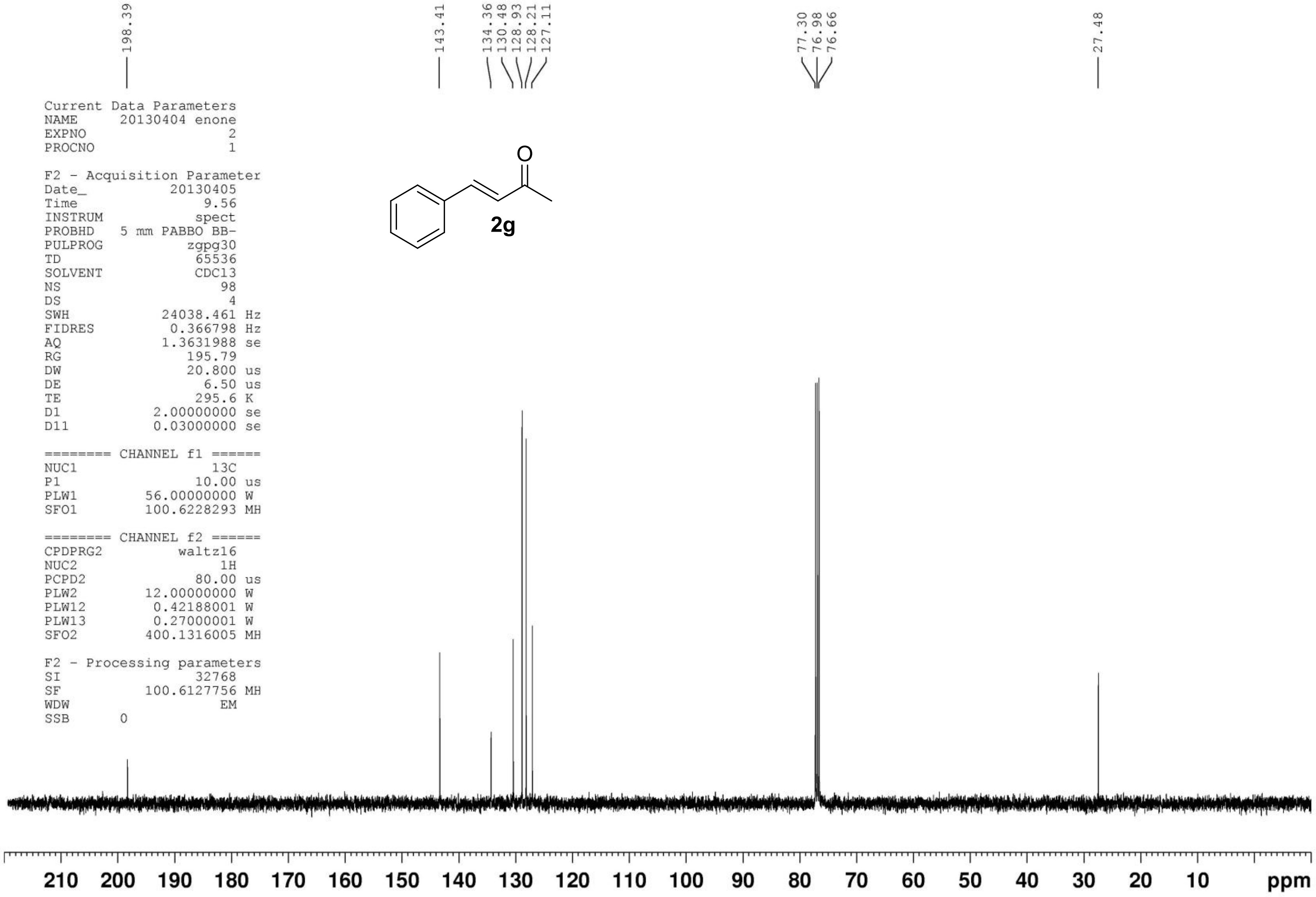
```
NAME       20130411 enone
EXPNO                   2
PROCNO                  1
Date_            20130411
Time                11.46
INSTRUM             spect
PROBHD     5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  1377
DS                     0
SWH            30030.029 Hz
FIDRES          0.458222 Hz
AQ             1.0912410 sec
RG                9195.2
DW                16.650 usec
DE                  6.50 usec
TE                 299.9 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 10.00 usec
PL1                 3.00 dB
PL1W         58.41413879 W
SFO1         125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -0.79 dB
PL12               17.27 dB
PL13               17.27 dB
PL2W         25.30924988 W
PL12W         0.39562091 W
PL13W         0.39562091 W
SFO2         500.1320005 MHz
SI                 32768
SF           125.7577890 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

^{13}C NMR



```
Current Data Parameters
NAME     20130404 enone
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20130404
Time              21.03
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.122266 Hz
AQ            4.0894966 sec
RG               195.79
DW               62.400 usec
DE                 6.50 usec
TE                295.8 K
D1           1.00000000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                15.00 usec
PLW1        12.00000000 W
SFO1        400.1326008 MHz

F2 - Processing parameters
SI                65536
SF          400.1300060 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.00
```

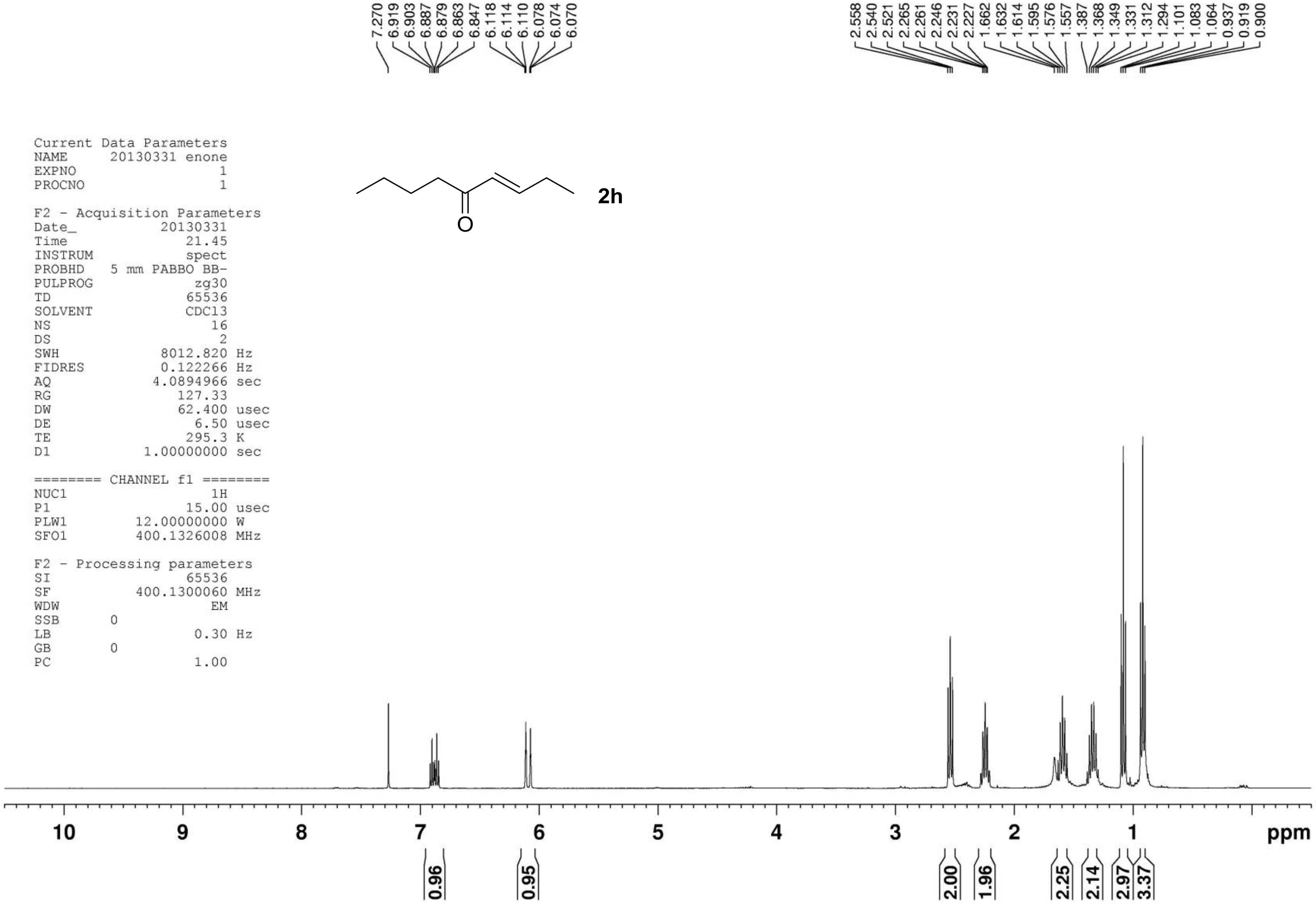
^{1}H NMR



```
Current Data Parameters
NAME      20130404 enone
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameter
Date_          20130405
Time               9.56
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG         zgpg30
TD               65536
SOLVENT          CDCl3
NS                  98
DS                   4
SWH          24038.461 Hz
FIDRES        0.366798 Hz
AQ           1.3631988 se
RG              195.79
DW              20.800 us
DE                6.50 us
TE               295.6 K
D1          2.00000000 se
D11         0.03000000 se

======== CHANNEL f1 ======
NUC1               13C
P1               10.00 us
PLW1       56.00000000 W
SFO1       100.6228293 MH

======== CHANNEL f2 ======
CPDPRG2        waltz16
NUC2                1H
PCPD2            80.00 us
PLW2       12.00000000 W
PLW12       0.42188001 W
PLW13       0.27000001 W
SFO2       400.1316005 MH

F2 - Processing parameters
SI               32768
SF         100.6127756 MH
WDW                 EM
SSB      0
```

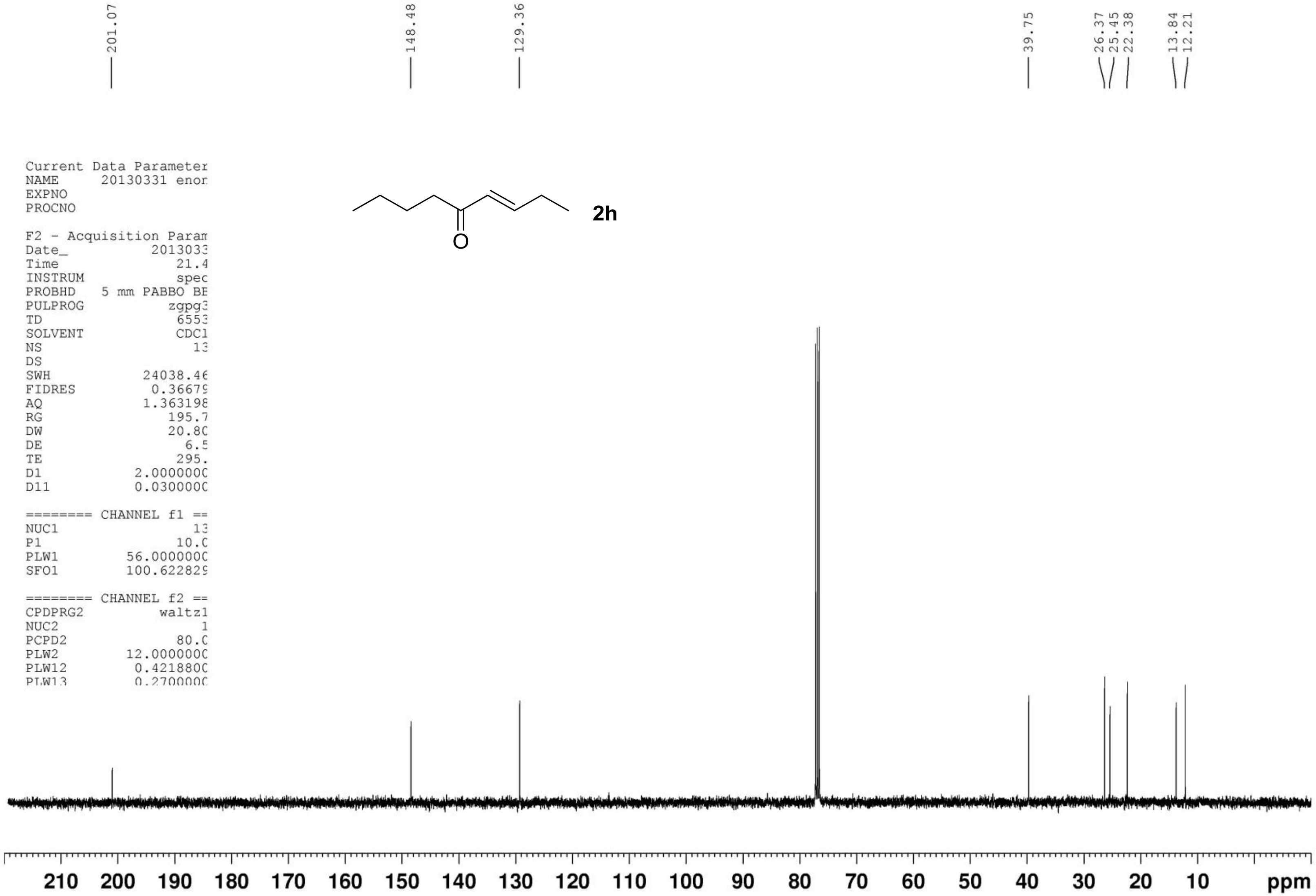
2g

^{13}C NMR



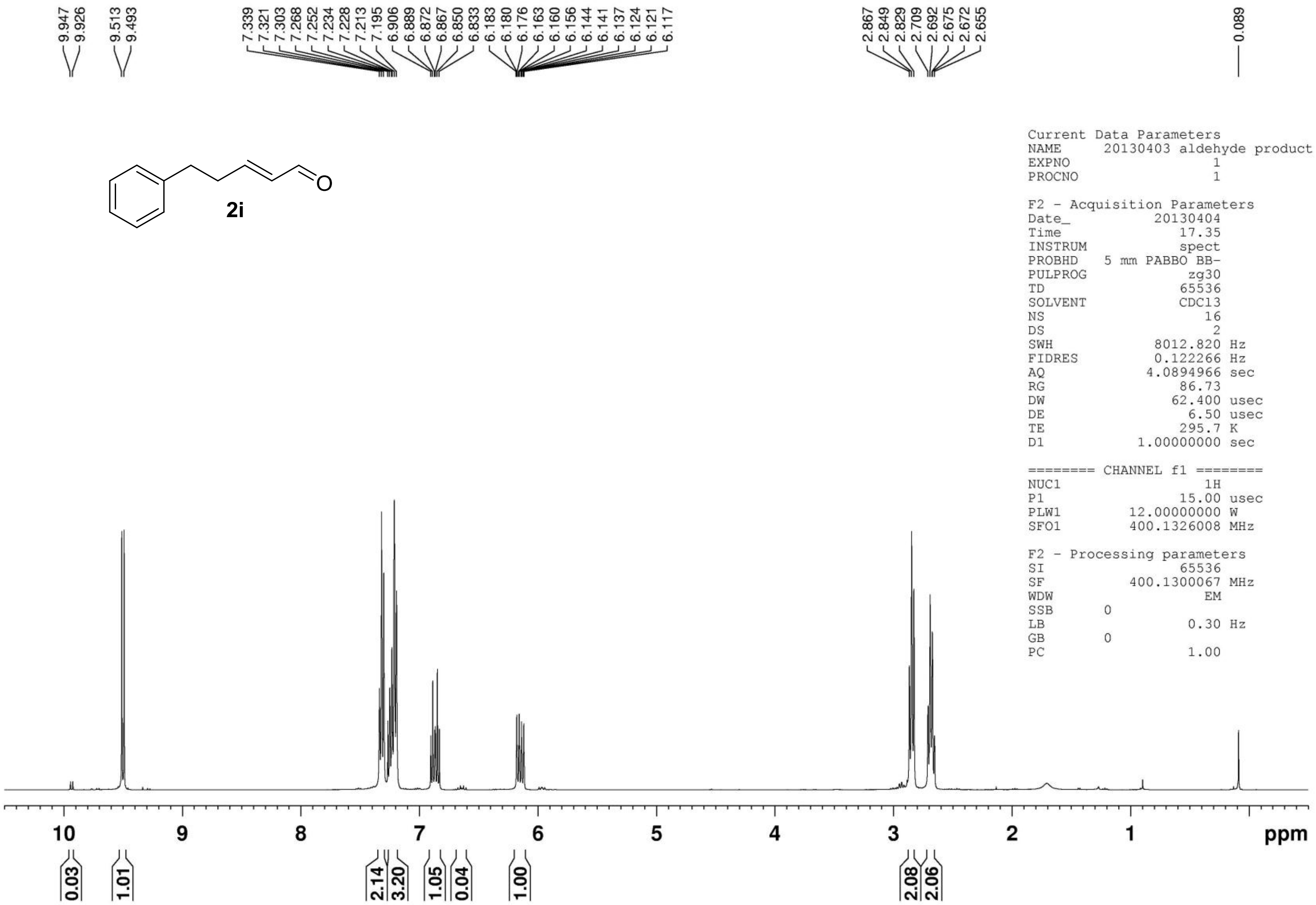
```
Current Data Parameters
NAME      20130331 enone
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_          20130331
Time              21.45
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            8012.820 Hz
FIDRES         0.122266 Hz
AQ            4.0894966 sec
RG               127.33
DW               62.400 usec
DE                 6.50 usec
TE                295.3 K
D1           1.00000000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                15.00 usec
PLW1        12.00000000 W
SFO1        400.1326008 MHz

F2 - Processing parameters
SI                65536
SF          400.1300060 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.00
```

^{1}H NMR



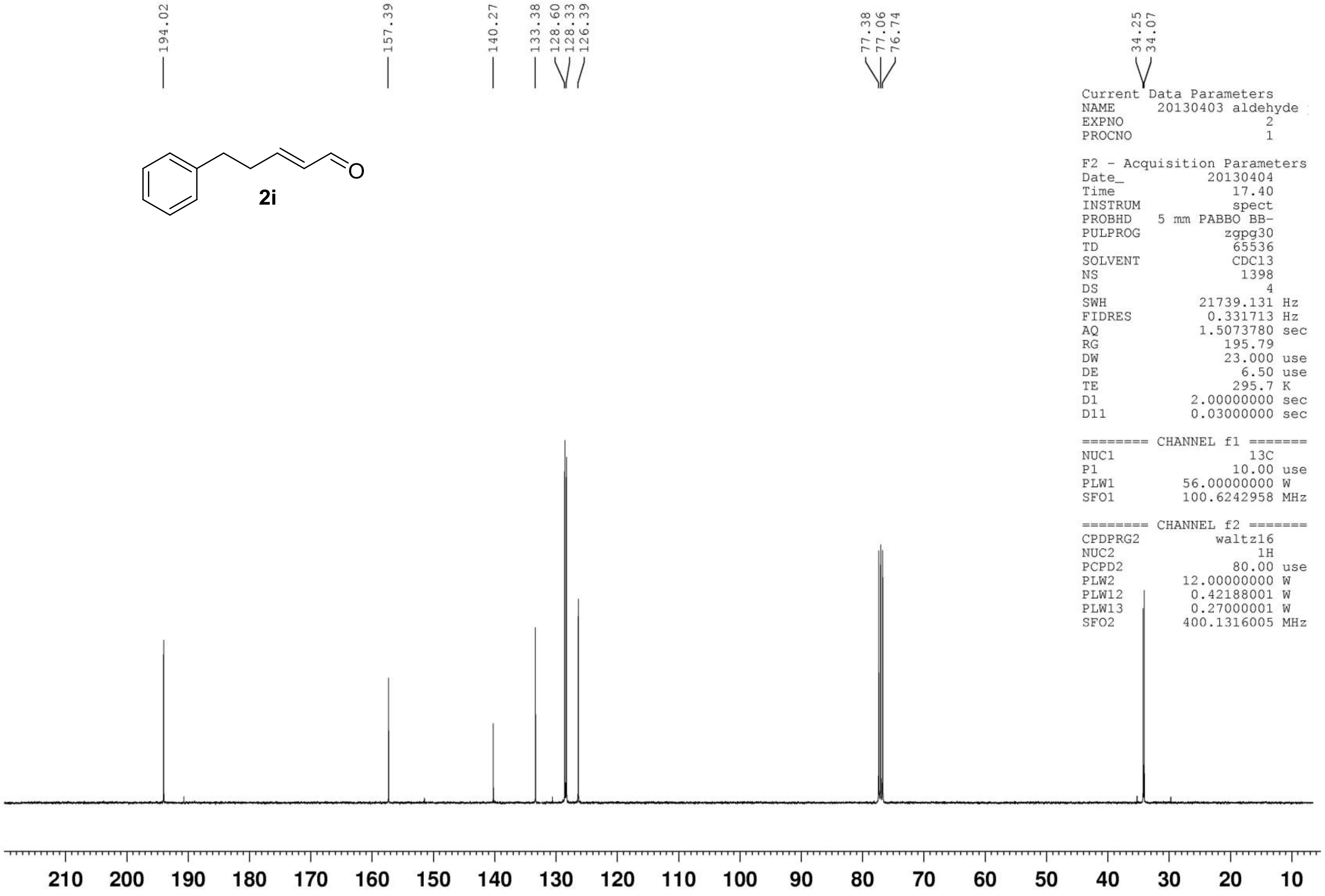
```
Current Data Parameter
NAME     20130331 enor
EXPNO
PROCNO

F2 - Acquisition Param
Date_           2013033
Time               21.4
INSTRUM            spec
PROBHD   5 mm PABBO BE
PULPROG           zgpg3
TD                 6553
SOLVENT            CDCl
NS                   13
DS
SWH            24038.46
FIDRES          0.36679
AQ             1.363198
RG                195.7
DW                20.80
DE                  6.5
TE                 295.
D1           2.0000000
D11          0.0300000

======== CHANNEL f1 ==
NUC1                 13
P1                 10.0
PLW1        56.0000000
SFO1        100.622829

======== CHANNEL f2 ==
CPDPRG2          waltz1
NUC2                  1
PCPD2              80.0
PLW2        12.0000000
PLW12        0.4218800
PLW13        0.2700000
```

^{13}C NMR



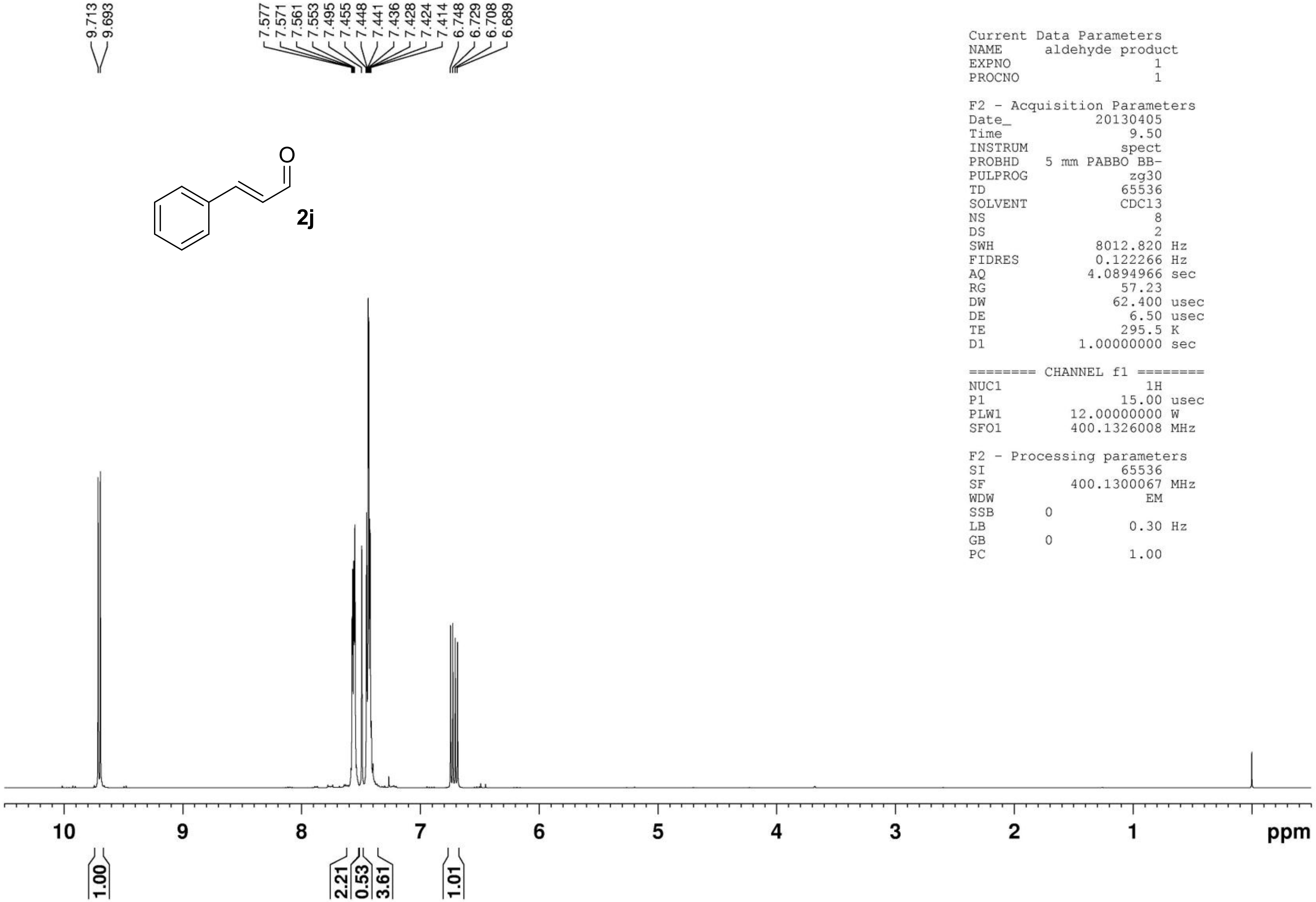
```
Current Data Parameters
NAME      20130403 aldehyde product
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20130404
Time                  17.35
INSTRUM               spect
PROBHD   5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH               8012.820 Hz
FIDRES            0.122266 Hz
AQ               4.0894966 sec
RG                    86.73
DW                   62.400 usec
DE                     6.50 usec
TE                    295.7 K
D1              1.00000000 sec

======== CHANNEL f1 ========
NUC1                     1H
P1                    15.00 usec
PLW1           12.00000000 W
SFO1           400.1326008 MHz

F2 - Processing parameters
SI                    65536
SF             400.1300067 MHz
WDW                      EM
SSB      0
LB                     0.30 Hz
GB       0
PC                     1.00
```

^{1}H NMR



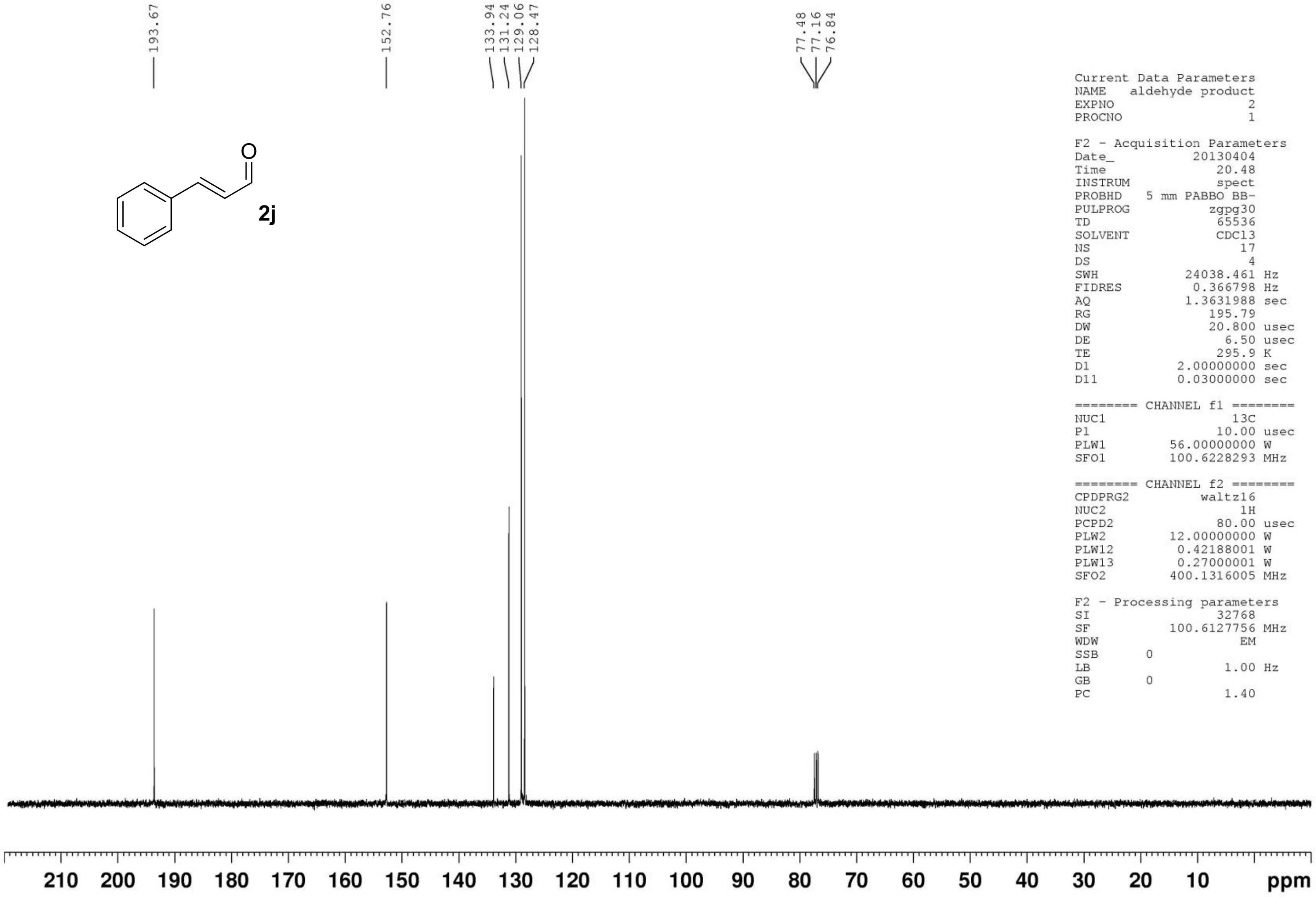
```
Current Data Parameters
NAME     20130403 aldehyde
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20130404
Time                17.40
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  1398
DS                     4
SWH            21739.131 Hz
FIDRES          0.331713 Hz
AQ             1.5073780 sec
RG                195.79
DW                23.000 use
DE                  6.50 use
TE                 295.7 K
D1            2.00000000 sec
D11           0.03000000 sec

======== CHANNEL f1 =======
NUC1                 13C
P1                 10.00 use
PLW1         56.00000000 W
SFO1         100.6242958 MHz

======== CHANNEL f2 =======
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 use
PLW2         12.00000000 W
PLW12         0.42188001 W
PLW13         0.27000001 W
SFO2         400.1316005 MHz
```

^{13}C NMR



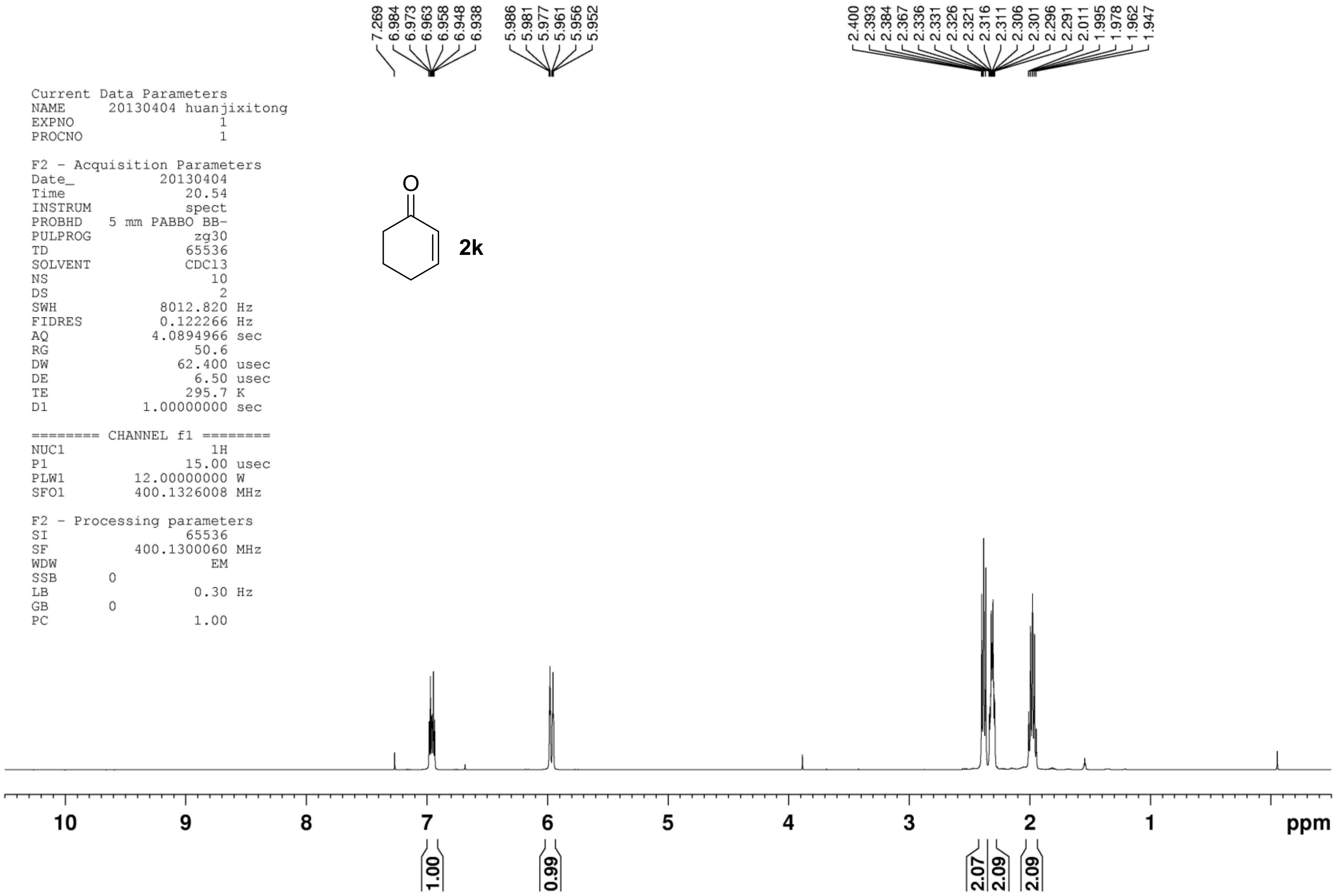
```
Current Data Parameters
NAME     aldehyde product
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20130405
Time                 9.50
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                      8
DS                      2
SWH              8012.820 Hz
FIDRES           0.122266 Hz
AQ              4.0894966 sec
RG                  57.23
DW                 62.400 usec
DE                   6.50 usec
TE                  295.5 K
D1             1.00000000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                  15.00 usec
PLW1          12.00000000 W
SFO1          400.1326008 MHz

F2 - Processing parameters
SI                  65536
SF            400.1300067 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00
```

^{1}H NMR



```
Current Data Parameters
NAME    aldehyde product
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20130404
Time               20.48
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   17
DS                    4
SWH          24038.461 Hz
FIDRES        0.366798 Hz
AQ           1.3631988 sec
RG              195.79
DW              20.800 usec
DE                6.50 usec
TE               295.9 K
D1          2.00000000 sec
D11         0.03000000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                 10.00 usec
PLW1         56.00000000 W
SFO1         100.6228293 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PLW2         12.00000000 W
PLW12         0.42188001 W
PLW13         0.27000001 W
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF           100.6127756 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  1.40
```

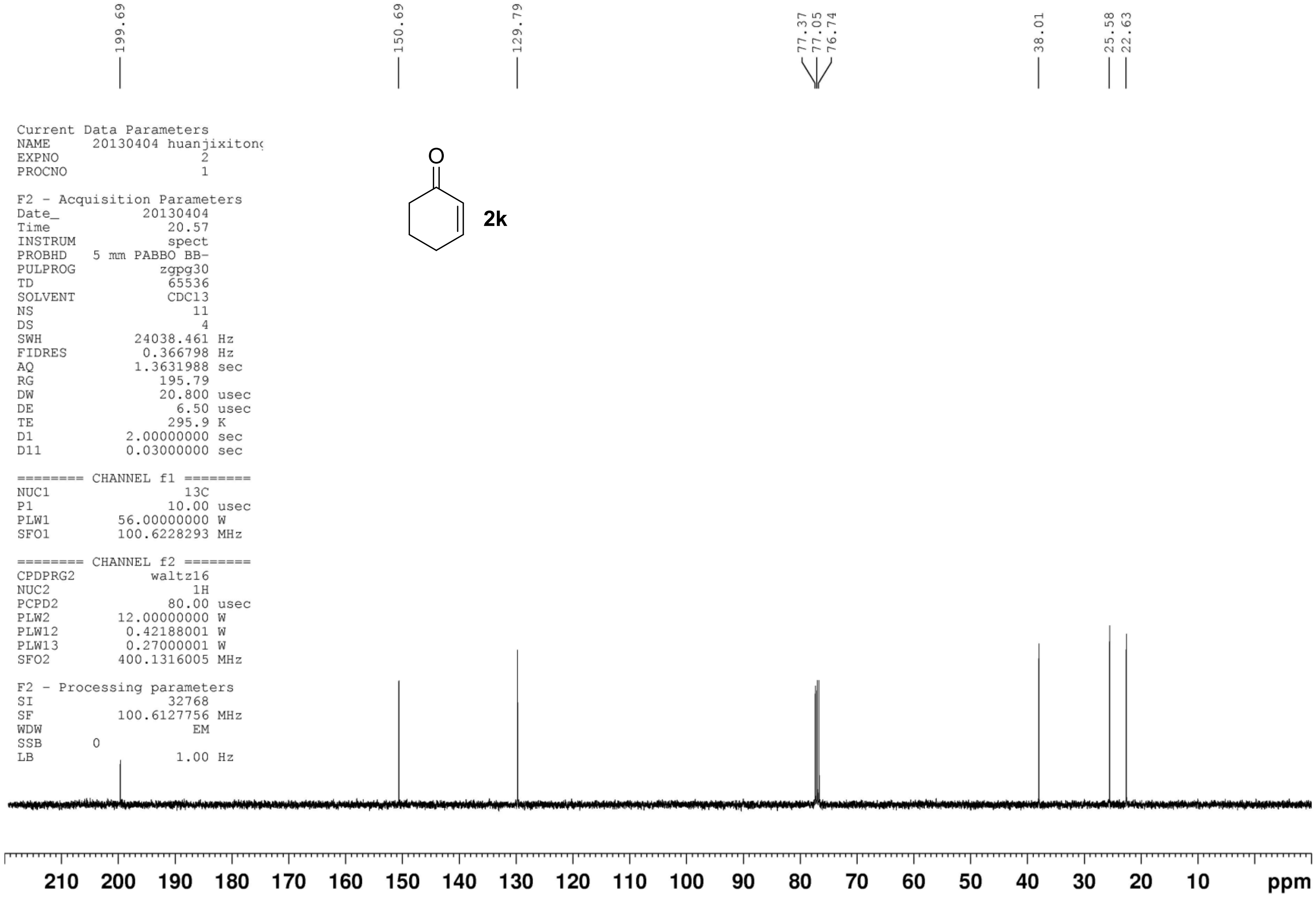
^{13}C NMR



```
Current Data Parameters
NAME     20130404 huanjixitong
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_           20130404
Time               20.54
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    10
DS                     2
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ             4.0894966 sec
RG                  50.6
DW                62.400 usec
DE                  6.50 usec
TE                 295.7 K
D1            1.00000000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 15.00 usec
PLW1         12.00000000 W
SFO1         400.1326008 MHz

F2 - Processing parameters
SI                 65536
SF           400.1300060 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```

2k

^{1}H NMR



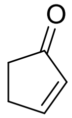
2k

```
Current Data Parameters
NAME     20130404 huanjixitong
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_             20130404
Time                 20.57
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                     11
DS                      4
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ              1.3631988 sec
RG                 195.79
DW                 20.800 usec
DE                   6.50 usec
TE                  295.9 K
D1             2.00000000 sec
D11            0.03000000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                  10.00 usec
PLW1          56.00000000 W
SFO1          100.6228293 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PLW2          12.00000000 W
PLW12          0.42188001 W
PLW13          0.27000001 W
SFO2          400.1316005 MHz

F2 - Processing parameters
SI                  32768
SF            100.6127756 MHz
WDW                    EM
SSB      0
LB                   1.00 Hz
```

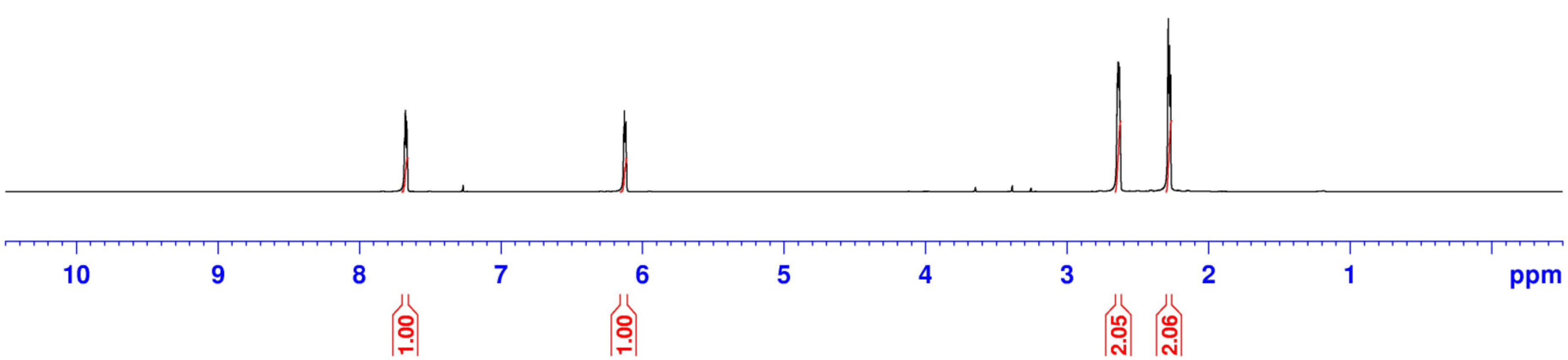
^{13}C NMR

^{13}C NMR

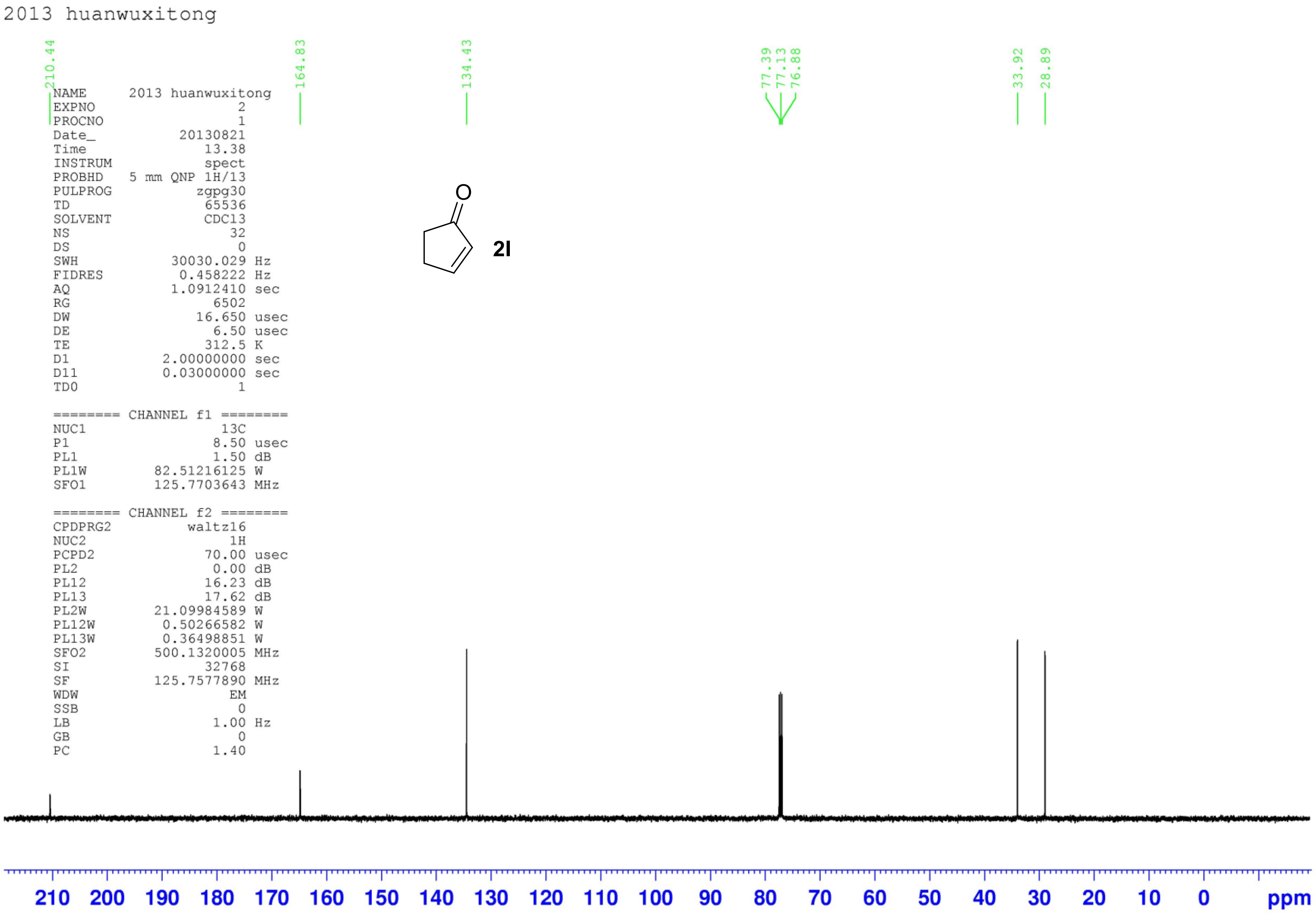
```
NAME     2013 huanwuxitong
EXPNO                    1
PROCNO                   1
Date_             20130821
Time                 13.36
INSTRUM              spect
PROBHD   5 mm QNP 1H/13
PULPROG               zg30
TD                   65536
SOLVENT              CDC13
NS                       8
DS                       0
SWH              10330.578 Hz
FIDRES            0.157632 Hz
AQ               3.1720407 sec
RG                    45.3
DW                  48.400 usec
DE                    6.50 usec
TE                   312.1 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   10.80 usec
PL1                   0.00 dB
PL1W           21.09984589 W
SFO1           500.1330885 MHz
SI                   32768
SF             500.1300077 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```



2l

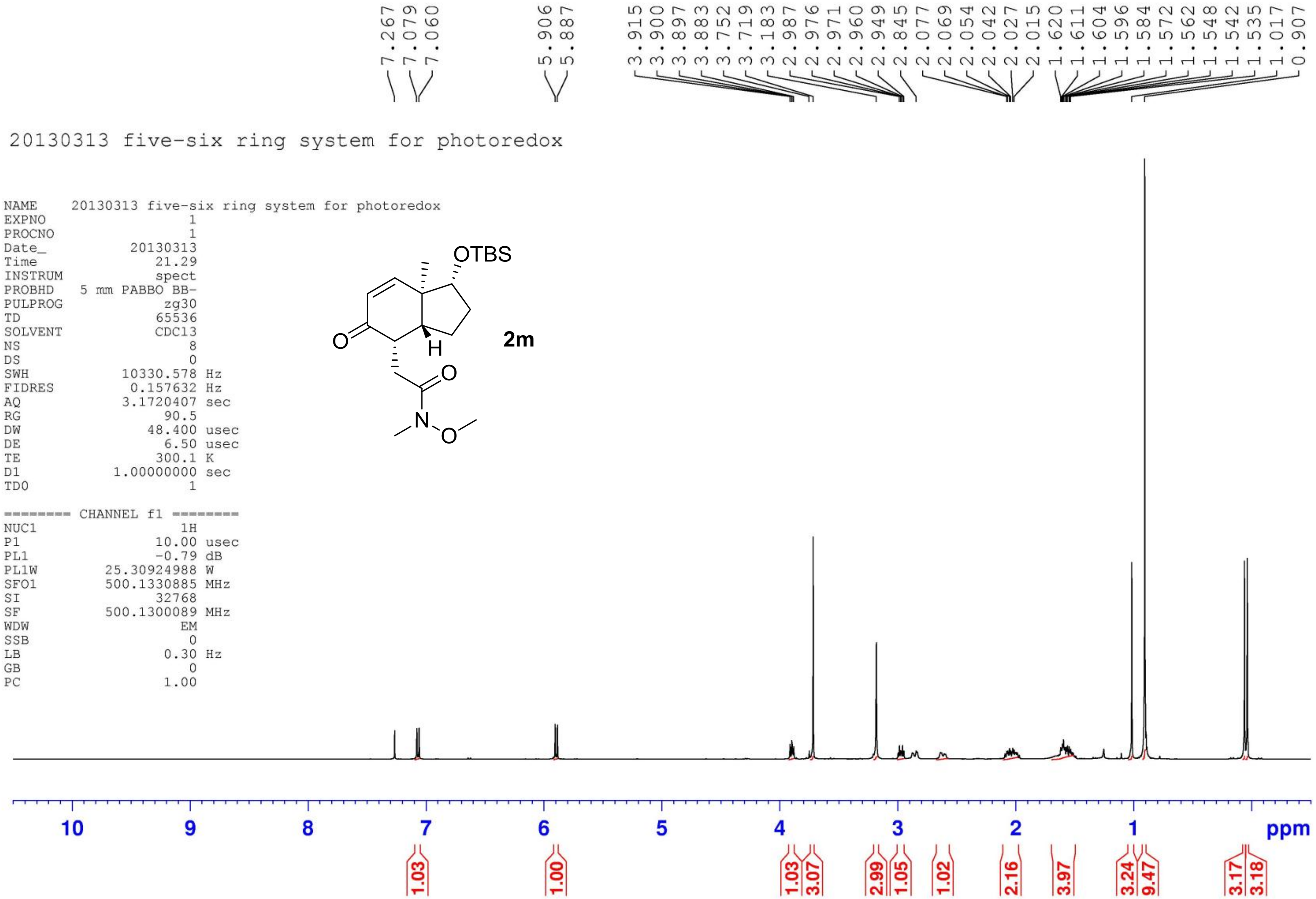


^{1}H NMR



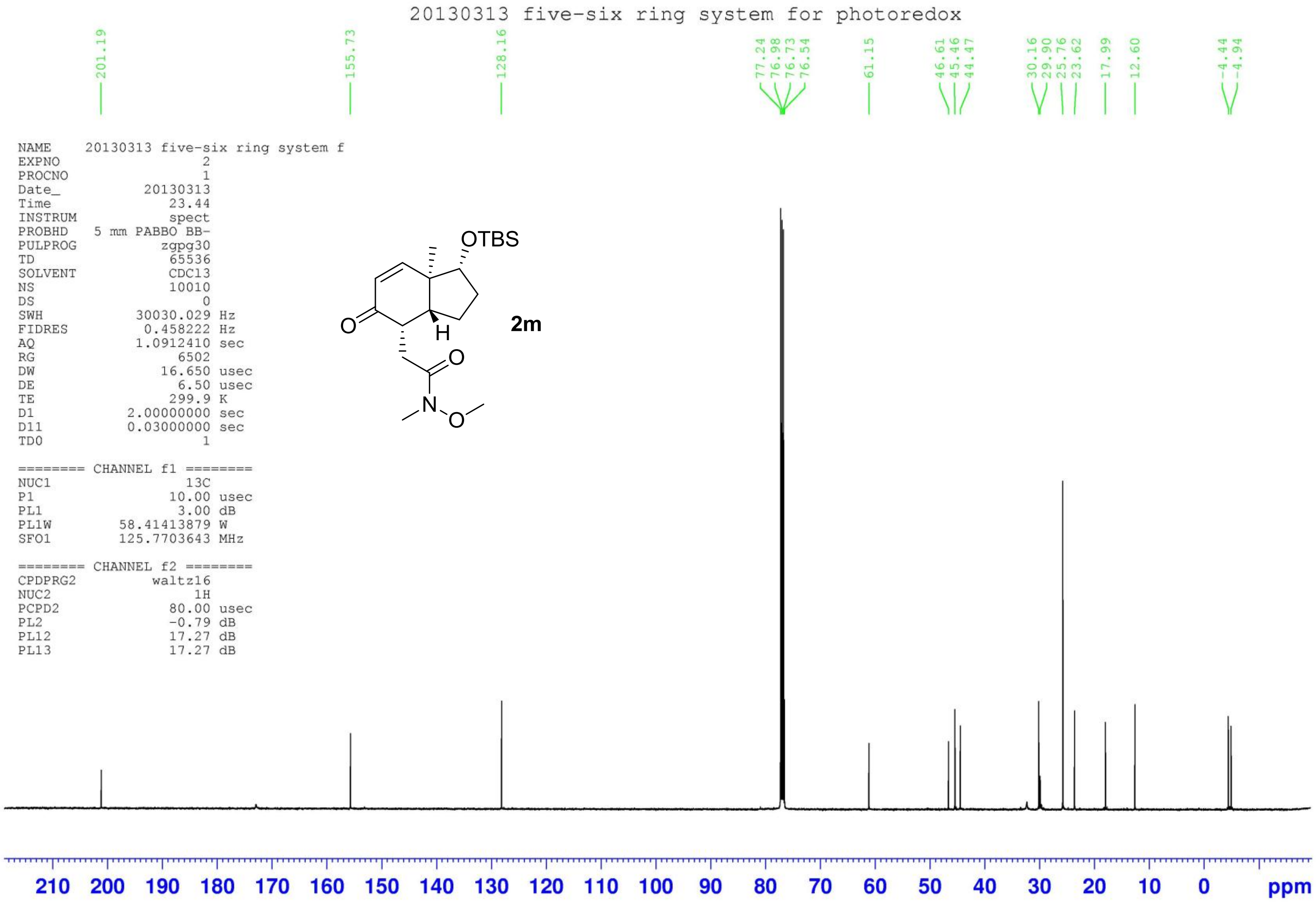
```
NAME      2013 huanwuxitong
EXPNO                   2
PROCNO                  1
Date_            20130821
Time                13.38
INSTRUM             spect
PROBHD   5 mm QNP 1H/13
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    32
DS                     0
SWH            30030.029 Hz
FIDRES          0.458222 Hz
AQ             1.0912410 sec
RG                  6502
DW                16.650 usec
DE                  6.50 usec
TE                 312.5 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  8.50 usec
PL1                 1.50 dB
PL1W         82.51216125 W
SFO1         125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              70.00 usec
PL2                 0.00 dB
PL12               16.23 dB
PL13               17.62 dB
PL2W         21.09984589 W
PL12W         0.50266582 W
PL13W         0.36498851 W
SFO2         500.1320005 MHz
SI                 32768
SF           125.7577890 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

^{13}C NMR



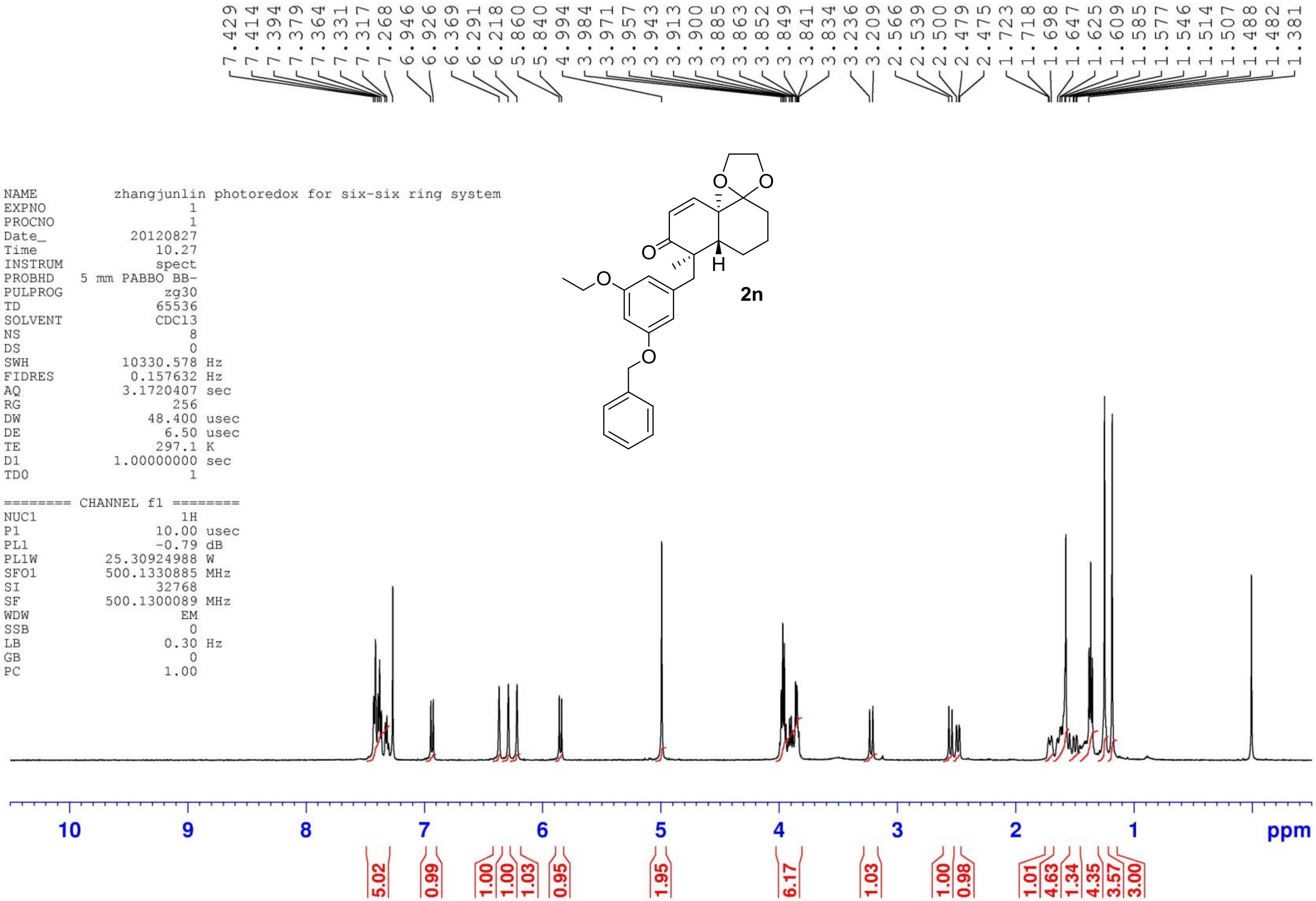
```
NAME     20130313 five-six ring system for photoredox
EXPNO                 1
PROCNO                1
Date_          20130313
Time              21.29
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    8
DS                    0
SWH           10330.578 Hz
FIDRES         0.157632 Hz
AQ            3.1720407 sec
RG                 90.5
DW               48.400 usec
DE                 6.50 usec
TE                300.1 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                10.00 usec
PL1               -0.79 dB
PL1W        25.30924988 W
SFO1        500.1330885 MHz
SI                32768
SF          500.1300089 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

^{1}H NMR



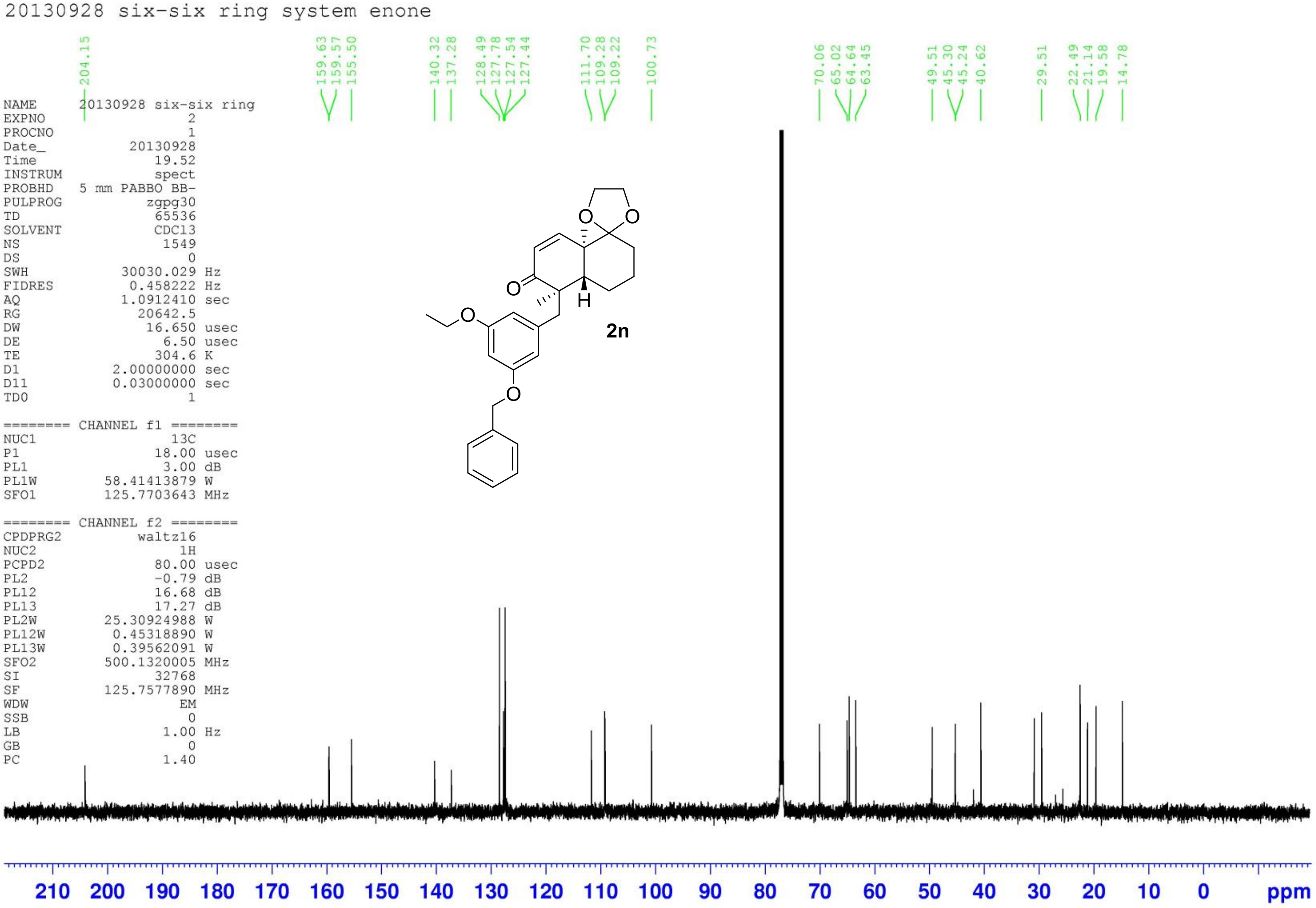
```
NAME     20130313 five-six ring system f
EXPNO                  2
PROCNO                 1
Date_           20130313
Time               23.44
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                 10010
DS                     0
SWH            30030.029 Hz
FIDRES          0.458222 Hz
AQ             1.0912410 sec
RG                  6502
DW                16.650 usec
DE                  6.50 usec
TE                 299.9 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 10.00 usec
PL1                 3.00 dB
PL1W         58.41413879 W
SFO1         125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -0.79 dB
PL12               17.27 dB
PL13               17.27 dB
```

^{13}C NMR



```
NAME          zhangjunlin photoredox for six-six ring system
EXPNO                  1
PROCNO                 1
Date_           20120827
Time               10.27
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     0
SWH           10330.578 Hz
FIDRES         0.157632 Hz
AQ            3.1720407 sec
RG                   256
DW                48.400 usec
DE                  6.50 usec
TE                 297.1 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 10.00 usec
PL1                -0.79 dB
PL1W         25.30924988 W
SFO1         500.1330885 MHz
SI                 32768
SF           500.1300089 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

^{1}H NMR

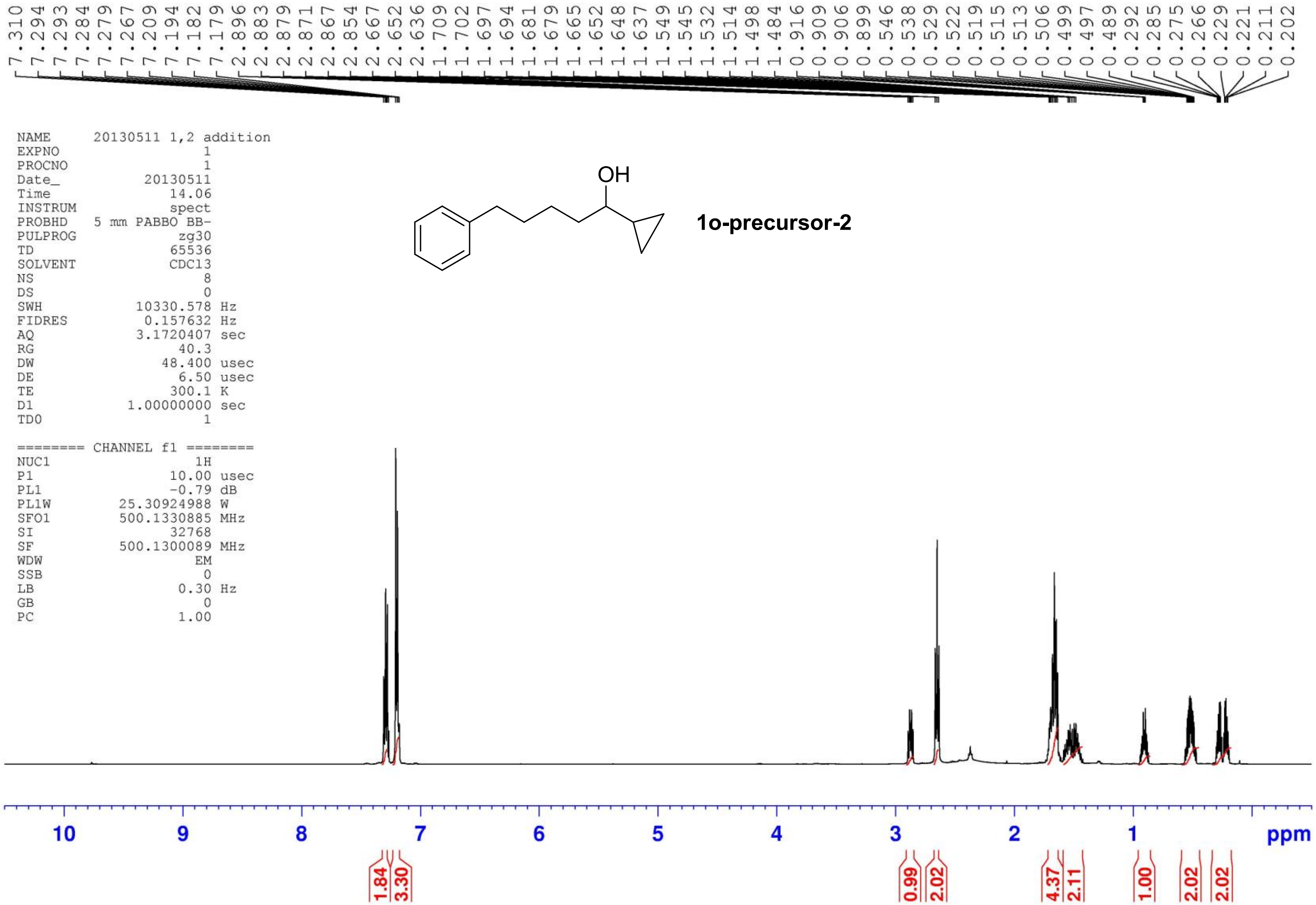


20130928 six-six ring system enone

```
NAME      20130928 six-six ring
EXPNO                         2
PROCNO                        1
Date_                  20130928
Time                      19.52
INSTRUM                   spect
PROBHD     5 mm PABBO BB-
PULPROG                 zgpg30
TD                        65536
SOLVENT                   CDCl3
NS                         1549
DS                            0
SWH                   30030.029 Hz
FIDRES                 0.458222 Hz
AQ                    1.0912410 sec
RG                      20642.5
DW                       16.650 usec
DE                         6.50 usec
TE                        304.6 K
D1                   2.00000000 sec
D11                  0.03000000 sec
TD0                           1

======== CHANNEL f1 ========
NUC1                        13C
P1                        18.00 usec
PL1                        3.00 dB
PL1W                58.41413879 W
SFO1                125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2                 waltz16
NUC2                         1H
PCPD2                     80.00 usec
PL2                       -0.79 dB
PL12                      16.68 dB
PL13                      17.27 dB
PL2W                25.30924988 W
PL12W                0.45318890 W
PL13W                0.39562091 W
SFO2                500.1320005 MHz
SI                        32768
SF                  125.7577890 MHz
WDW                          EM
SSB                           0
LB                         1.00 Hz
GB                            0
PC                         1.40
```

2n

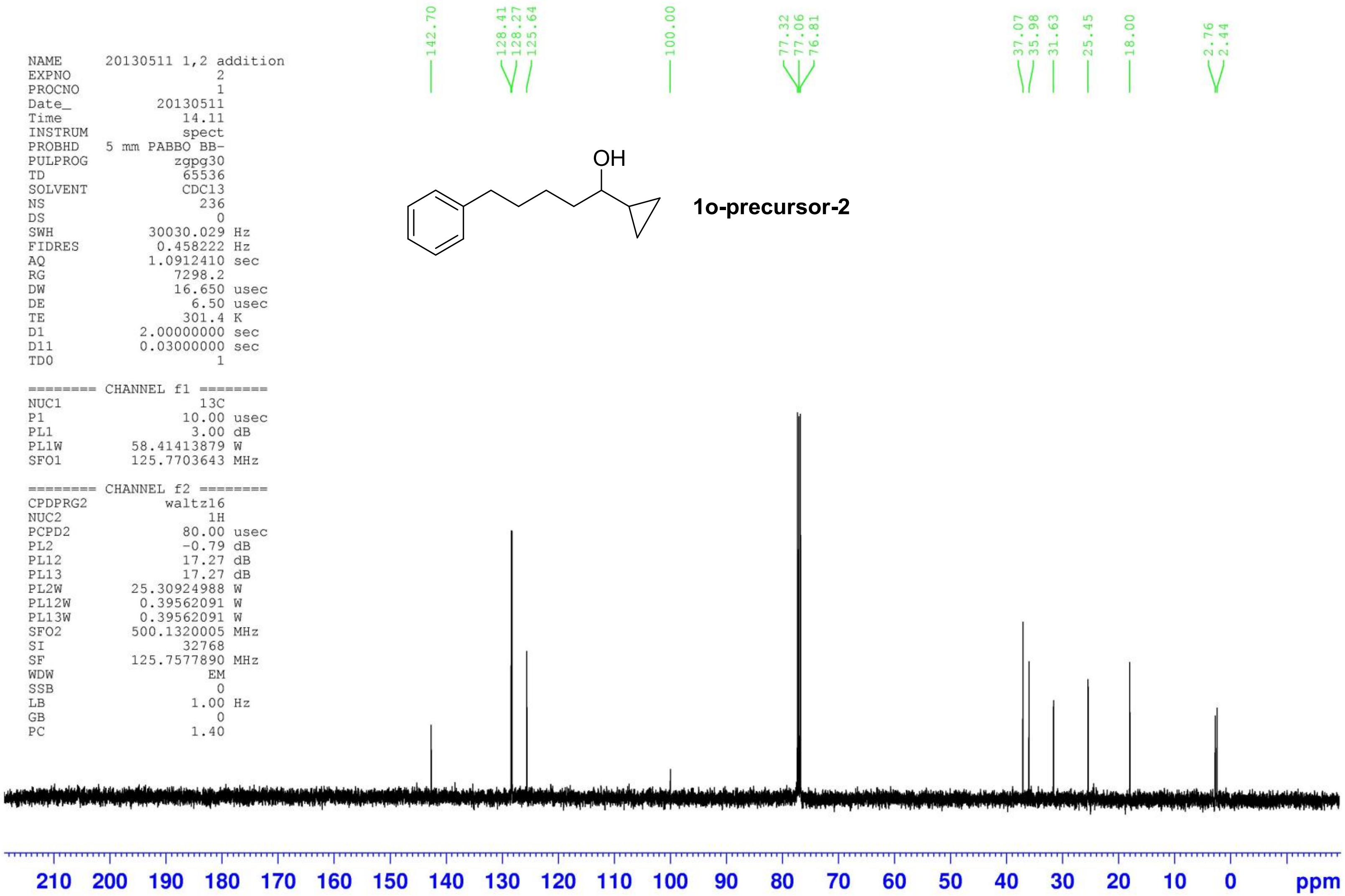
^{13}C NMR



```
NAME     20130511 1,2 addition
EXPNO                   1
PROCNO                  1
Date_            20130511
Time                14.06
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                      8
DS                      0
SWH             10330.578 Hz
FIDRES           0.157632 Hz
AQ              3.1720407 sec
RG                   40.3
DW                 48.400 usec
DE                   6.50 usec
TE                  300.1 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  10.00 usec
PL1                 -0.79 dB
PL1W          25.30924988 W
SFO1          500.1330885 MHz
SI                  32768
SF            500.1300089 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

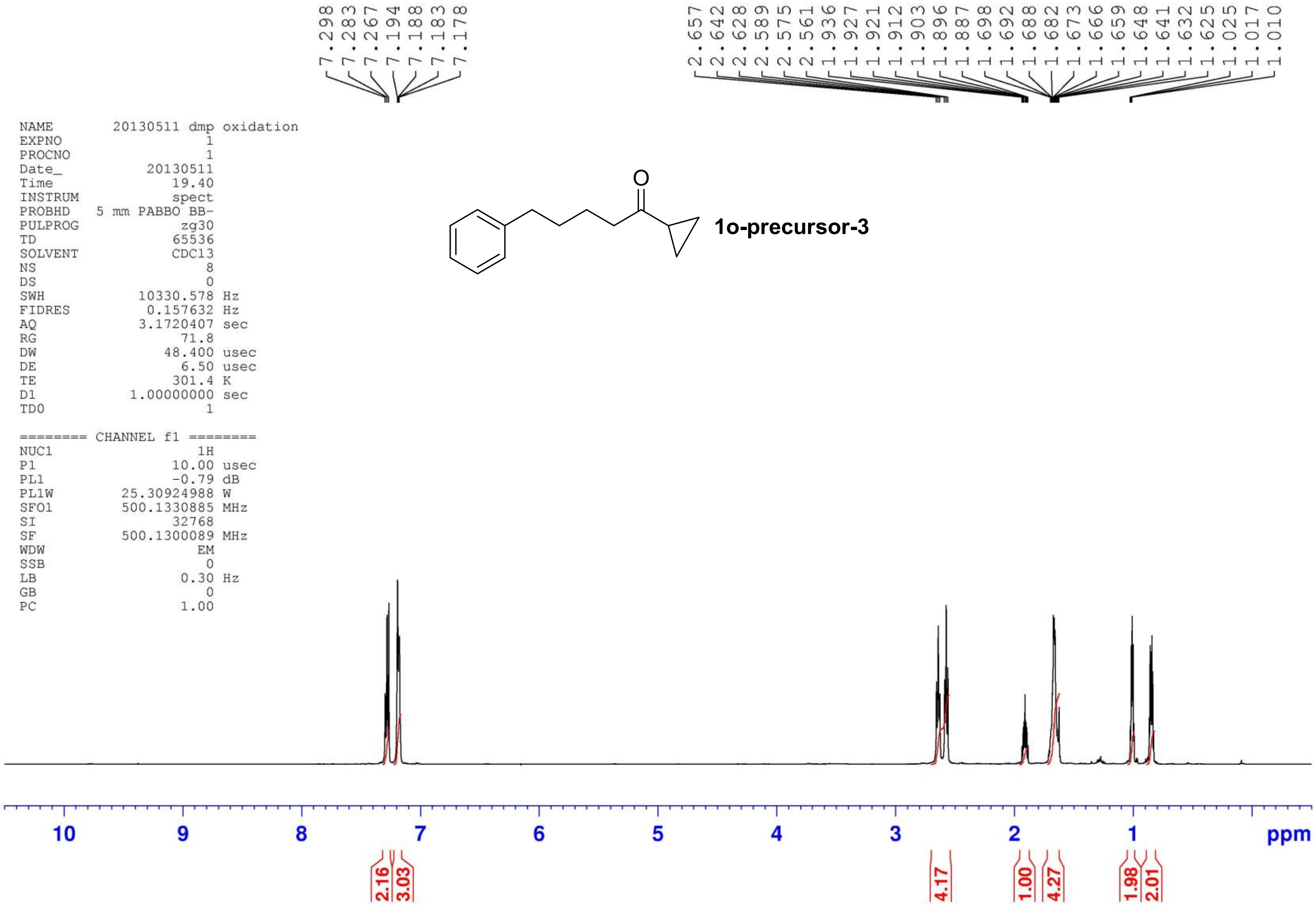
1o-precursor-2

^{1}H NMR



```
NAME      20130511 1,2 addition
EXPNO                 2
PROCNO                1
Date_          20130511
Time              14.11
INSTRUM           spect
PROBHD    5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  236
DS                    0
SWH           30030.029 Hz
FIDRES         0.458222 Hz
AQ            1.0912410 sec
RG               7298.2
DW               16.650 usec
DE                 6.50 usec
TE                301.4 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                10.00 usec
PL1                3.00 dB
PL1W        58.41413879 W
SFO1        125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2               -0.79 dB
PL12              17.27 dB
PL13              17.27 dB
PL2W        25.30924988 W
PL12W        0.39562091 W
PL13W        0.39562091 W
SFO2        500.1320005 MHz
SI                32768
SF          125.7577890 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

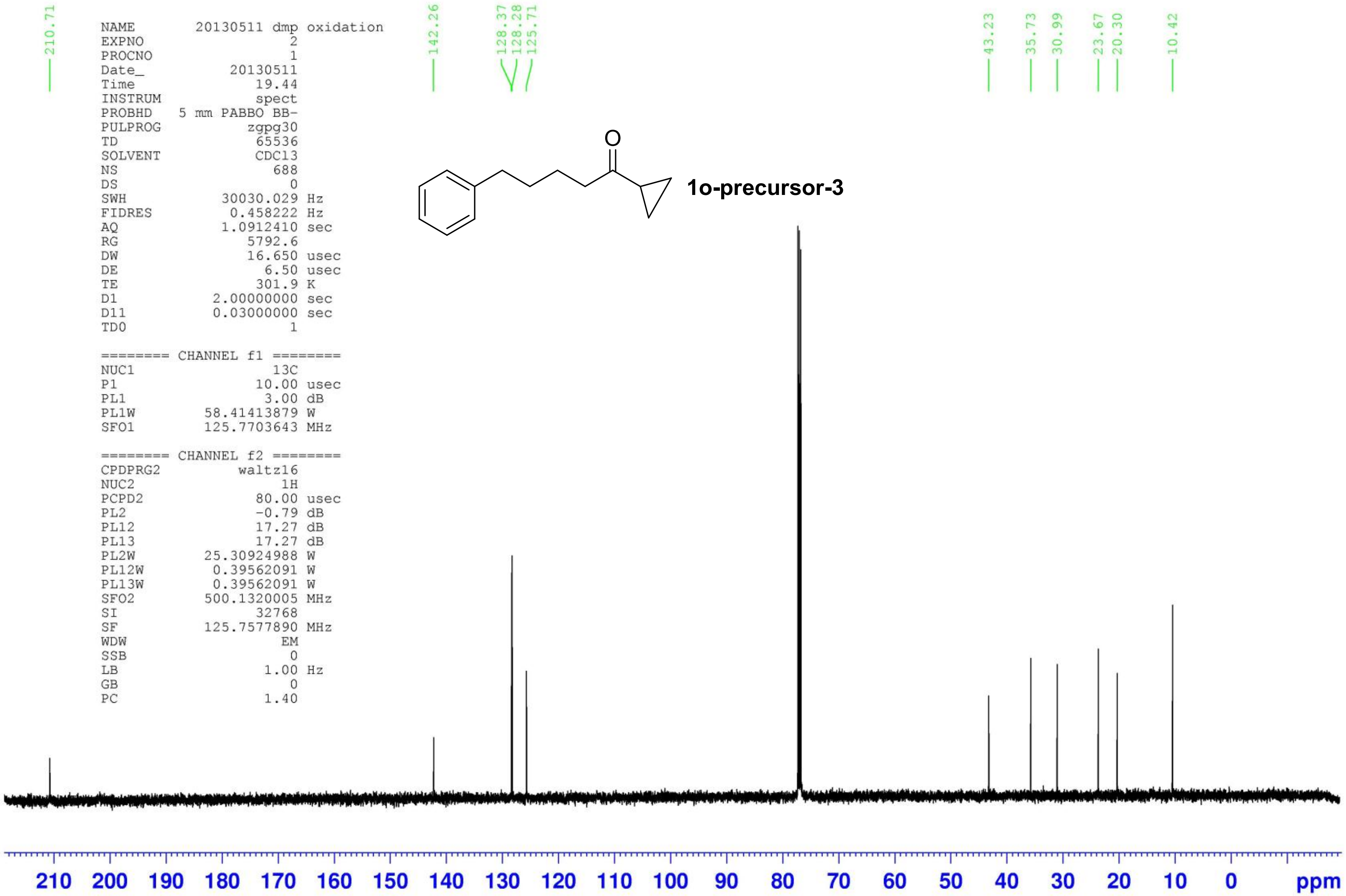
^{13}C NMR



1o-precursor-3

```
NAME       20130511 dmp oxidation
EXPNO                    1
PROCNO                   1
Date_             20130511
Time                 19.40
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                       8
DS                       0
SWH              10330.578 Hz
FIDRES            0.157632 Hz
AQ               3.1720407 sec
RG                    71.8
DW                  48.400 usec
DE                    6.50 usec
TE                   301.4 K
D1            1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   10.00 usec
PL1                  -0.79 dB
PL1W           25.30924988 W
SFO1         500.1330885 MHz
SI                   32768
SF           500.1300089 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

^{1}H NMR

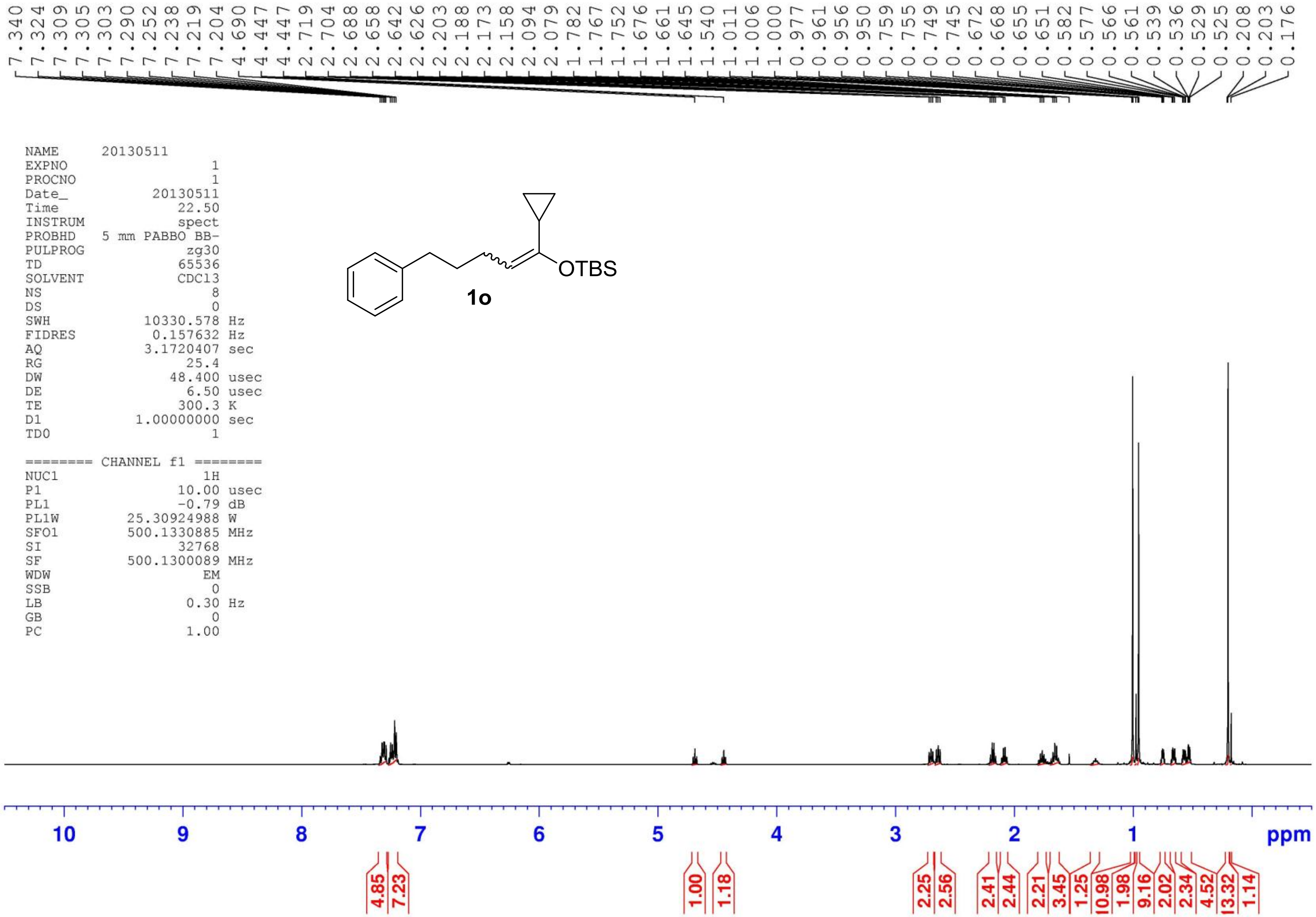


```
NAME       20130511 dmp oxidation
EXPNO                       2
PROCNO                      1
Date_                20130511
Time                    19.44
INSTRUM                 spect
PROBHD     5 mm PABBO BB-
PULPROG               zgpg30
TD                      65536
SOLVENT                 CDCl3
NS                        688
DS                          0
SWH                 30030.029 Hz
FIDRES               0.458222 Hz
AQ                  1.0912410 sec
RG                     5792.6
DW                     16.650 usec
DE                       6.50 usec
TE                      301.9 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                      13C
P1                      10.00 usec
PL1                      3.00 dB
PL1W              58.41413879 W
SFO1              125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2               waltz16
NUC2                       1H
PCPD2                   80.00 usec
PL2                     -0.79 dB
PL12                    17.27 dB
PL13                    17.27 dB
PL2W              25.30924988 W
PL12W              0.39562091 W
PL13W              0.39562091 W
SFO2              500.1320005 MHz
SI                      32768
SF                125.7577890 MHz
WDW                        EM
SSB                         0
LB                       1.00 Hz
GB                          0
PC                       1.40
```

^{13}C NMR

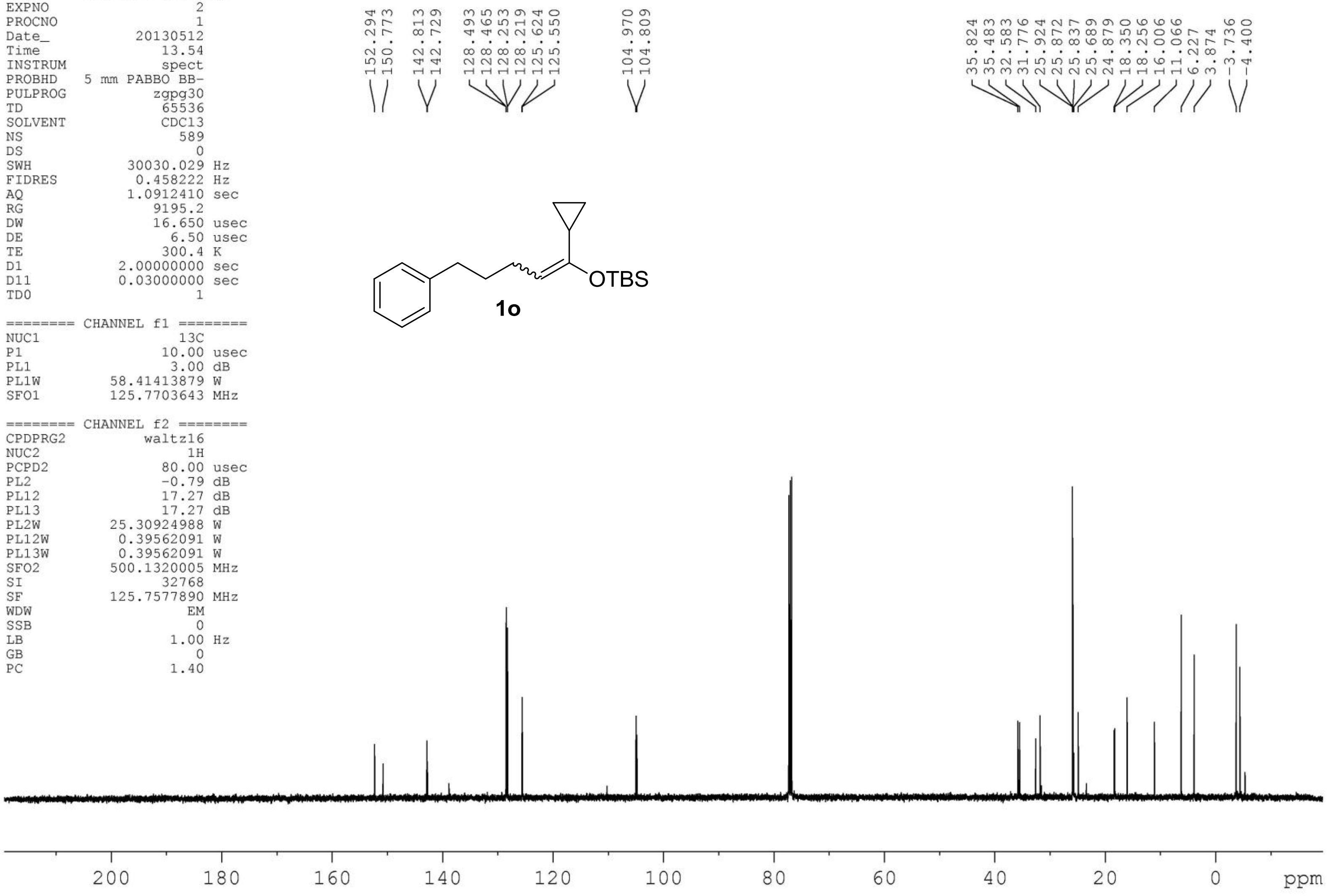
```
NAME       20130511
EXPNO             1
PROCNO            1
Date_      20130511
Time          22.50
INSTRUM       spect
PROBHD   5 mm PABBO BB-
PULPROG        zg30
TD            65536
SOLVENT       CDCl3
NS                8
DS                0
SWH       10330.578 Hz
FIDRES     0.157632 Hz
AQ        3.1720407 sec
RG             25.4
DW           48.400 usec
DE             6.50 usec
TE            300.3 K
D1       1.00000000 sec
TD0               1

======== CHANNEL f1 ========
NUC1             1H
P1            10.00 usec
PL1           -0.79 dB
PL1W    25.30924988 W
SFO1    500.1330885 MHz
SI            32768
SF      500.1300089 MHz
WDW              EM
SSB               0
LB             0.30 Hz
GB                0
PC             1.00
```

1o



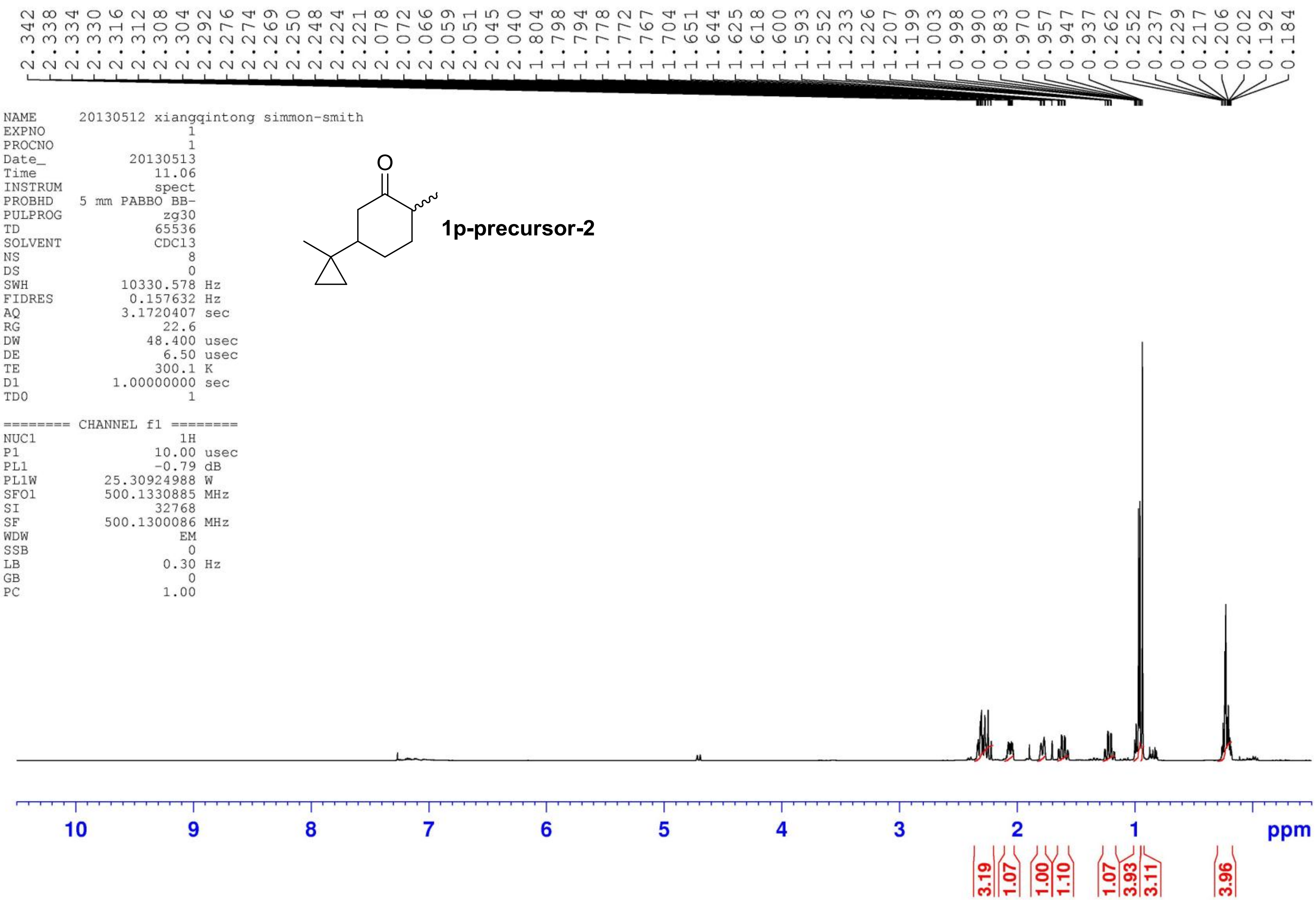
^{1}H NMR

```
NAME     20130511 jili one
EXPNO                   2
PROCNO                  1
Date_            20130512
Time                13.54
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   589
DS                     0
SWH            30030.029 Hz
FIDRES          0.458222 Hz
AQ             1.0912410 sec
RG                9195.2
DW                16.650 usec
DE                  6.50 usec
TE                 300.4 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 10.00 usec
PL1                 3.00 dB
PL1W         58.41413879 W
SFO1         125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -0.79 dB
PL12               17.27 dB
PL13               17.27 dB
PL2W         25.30924988 W
PL12W         0.39562091 W
PL13W         0.39562091 W
SFO2         500.1320005 MHz
SI                 32768
SF           125.7577890 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```



1o

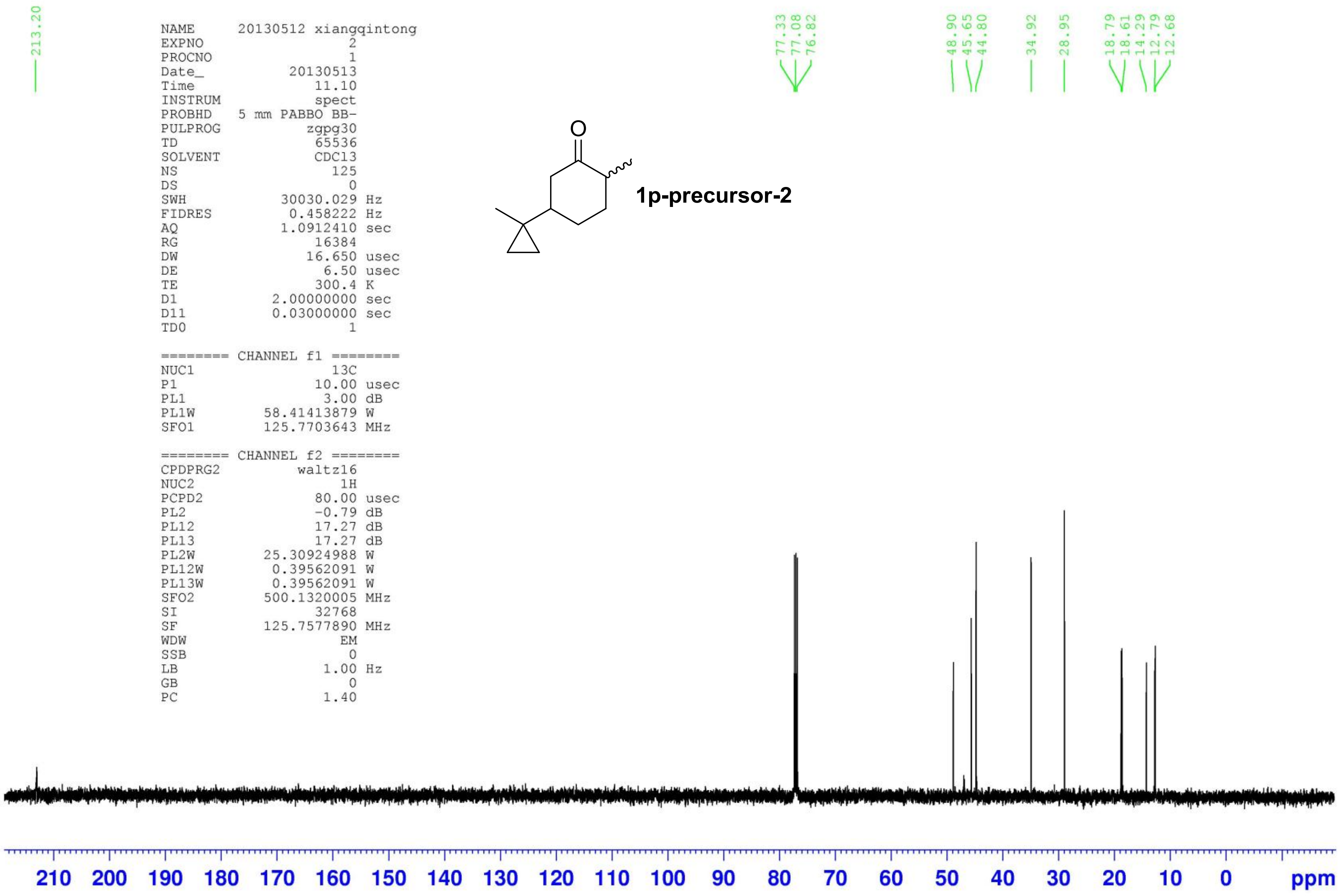
^{13}C NMR



```
NAME     20130512 xiangqintong simmon-smith
EXPNO                 1
PROCNO                1
Date_          20130513
Time              11.06
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    8
DS                    0
SWH           10330.578 Hz
FIDRES         0.157632 Hz
AQ            3.1720407 sec
RG                 22.6
DW               48.400 usec
DE                 6.50 usec
TE                300.1 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                10.00 usec
PL1               -0.79 dB
PL1W        25.30924988 W
SFO1        500.1330885 MHz
SI                32768
SF          500.1300086 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

1p-precursor-2

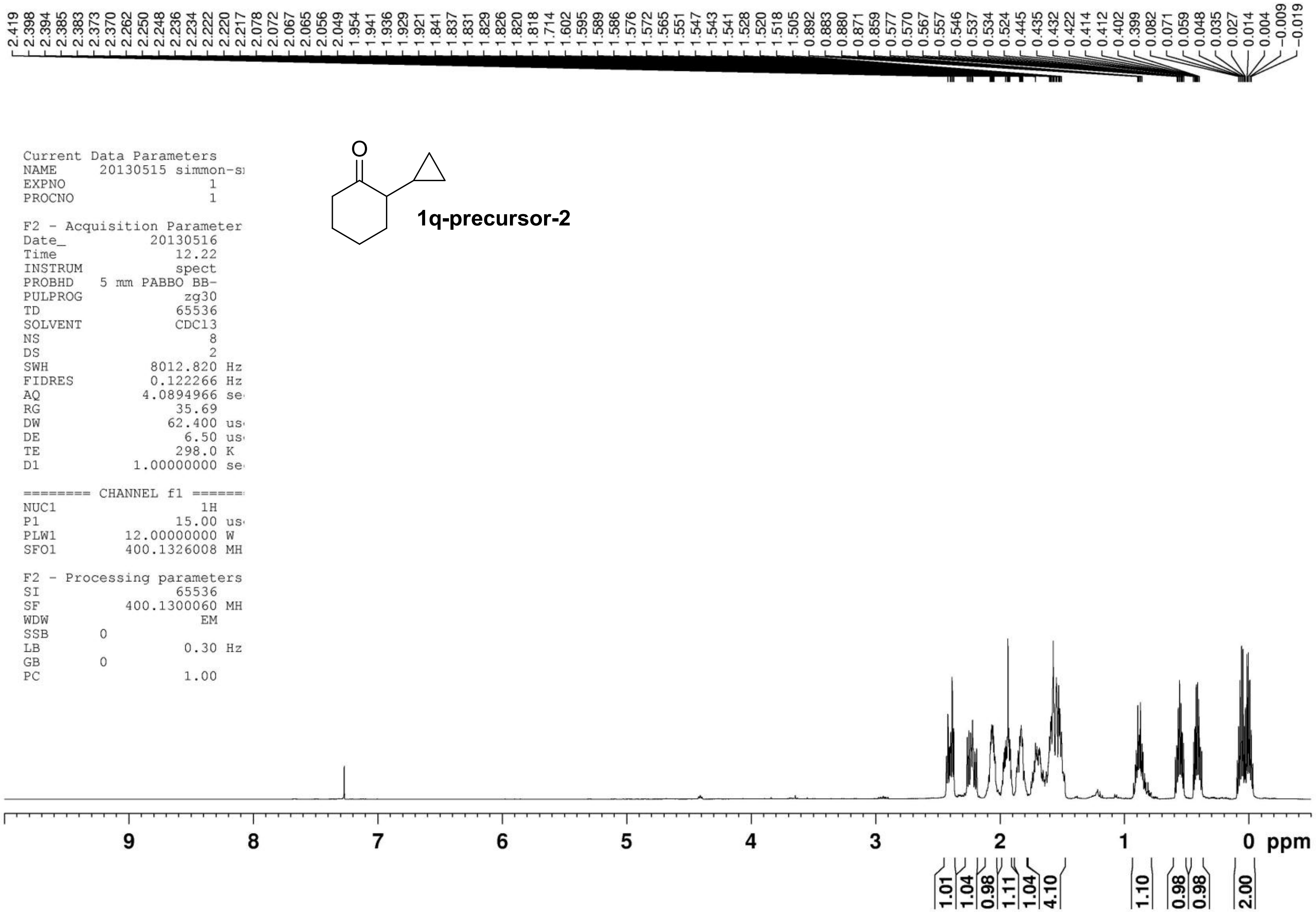
^{1}H NMR



1p-precursor-2

```
NAME     20130512 xiangqintong
EXPNO                 2
PROCNO                1
Date_          20130513
Time              11.10
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG         zgpg30
TD               65536
SOLVENT          CDCl3
NS                 125
DS                   0
SWH          30030.029 Hz
FIDRES        0.458222 Hz
AQ           1.0912410 sec
RG               16384
DW              16.650 usec
DE                6.50 usec
TE               300.4 K
D1          2.00000000 sec
D11         0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1               13C
P1               10.00 usec
PL1               3.00 dB
PL1W       58.41413879 W
SFO1       125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2        waltz16
NUC2                1H
PCPD2            80.00 usec
PL2              -0.79 dB
PL12             17.27 dB
PL13             17.27 dB
PL2W       25.30924988 W
PL12W       0.39562091 W
PL13W       0.39562091 W
SFO2       500.1320005 MHz
SI               32768
SF         125.7577890 MHz
WDW                 EM
SSB                  0
LB                1.00 Hz
GB                   0
PC                1.40
```

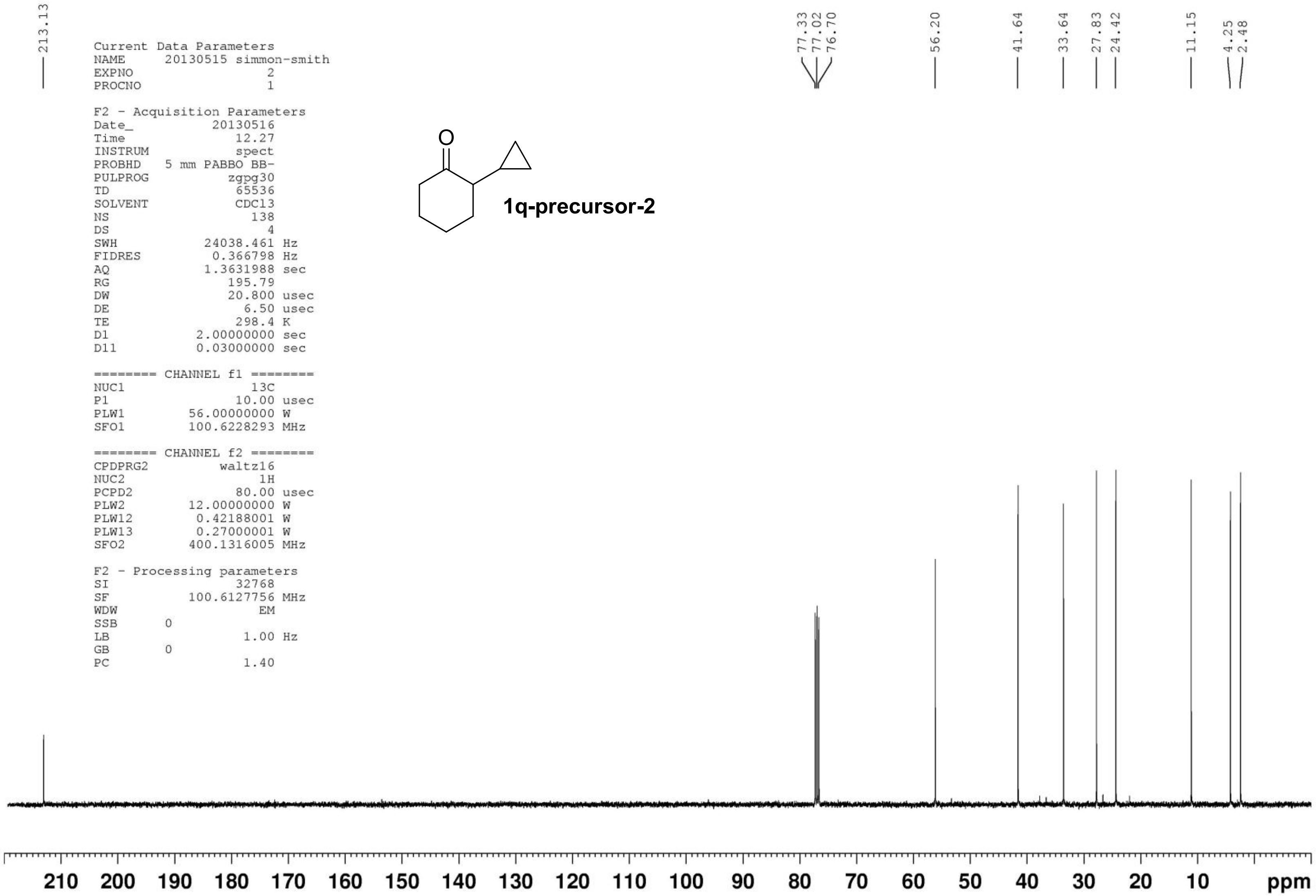
^{13}C NMR



1q-precursor-2

```
Current Data Parameters
NAME      20130515 simmon-s
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameter
Date_             20130516
Time                 12.22
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                       8
DS                       2
SWH               8012.820 Hz
FIDRES            0.122266 Hz
AQ               4.0894966 se
RG                   35.69
DW                  62.400 us
DE                    6.50 us
TE                   298.0 K
D1              1.00000000 se

======== CHANNEL f1 ======
NUC1                    1H
P1                   15.00 us
PLW1           12.00000000 W
SFO1           400.1326008 MH

F2 - Processing parameters
SI                   65536
SF             400.1300060 MH
WDW                     EM
SSB      0
LB                    0.30 Hz
GB       0
PC                    1.00
```

^{1}H NMR

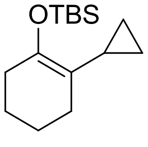


```
Current Data Parameters
NAME     20130515 simmon-smith
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20130516
Time               12.27
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   138
DS                     4
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                195.79
DW                20.800 usec
DE                  6.50 usec
TE                 298.4 K
D1            2.00000000 sec
D11           0.03000000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                 10.00 usec
PLW1         56.00000000 W
SFO1         100.6228293 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PLW2         12.00000000 W
PLW12         0.42188001 W
PLW13         0.27000001 W
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF           100.6127756 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  1.40
```

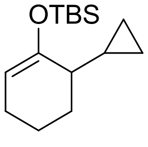
^{13}C NMR

NAME	20130503 TBS enol ether mixture	
EXPNO	1	
PROCNO	1	
Date_	20130504	
Time	6.22	
INSTRUM	spect	
PROBHD	5 mm PABBO BB-	
PULPROG	zg30	
TD	65536	
SOLVENT	CDCl3	
NS	8	
DS	0	
SWH	10330.578	Hz
FIDRES	0.157632	Hz
AQ	3.1720407	sec
RG	35.9	
DW	48.400	usec
DE	6.50	usec
TE	302.9	K
D1	1.00000000	sec
TD0	1	

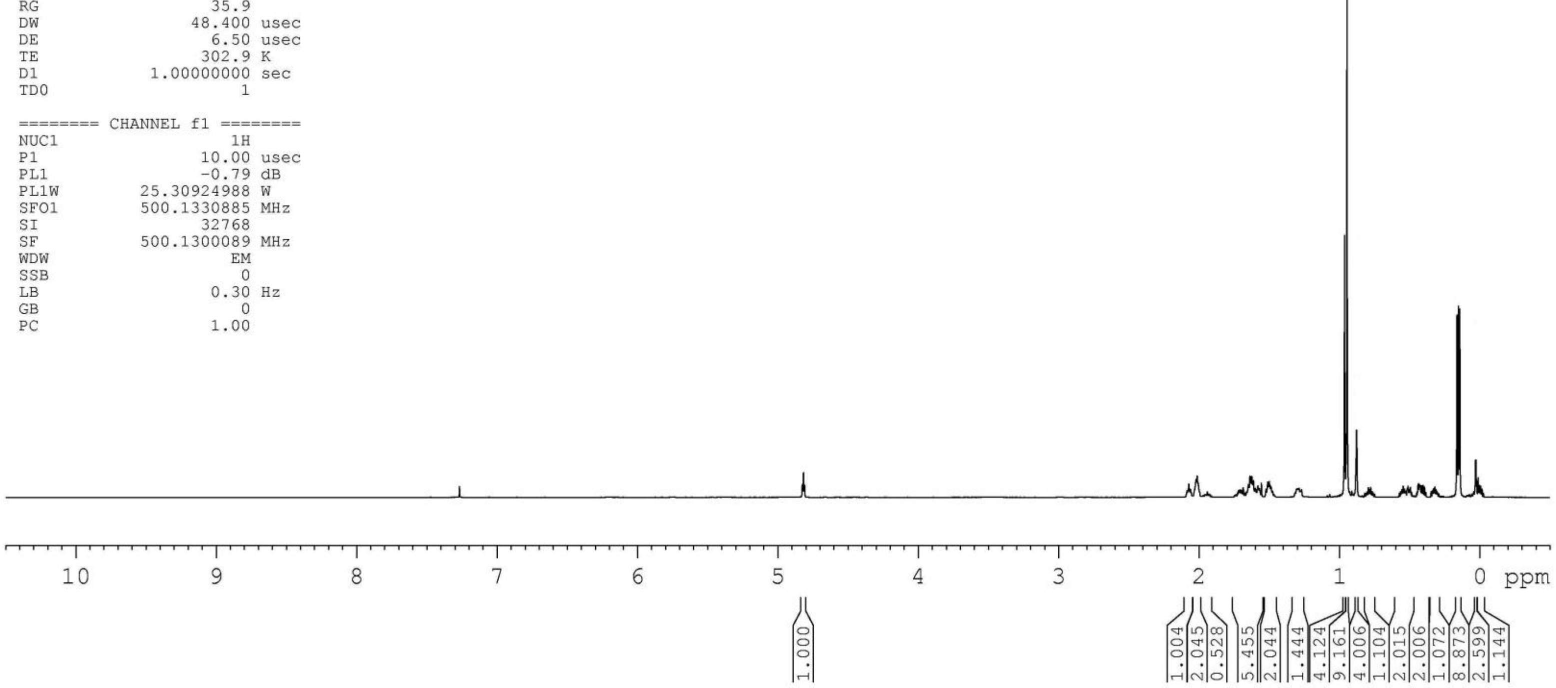
======== CHANNEL f1 ========		
NUC1	1H	
P1	10.00	usec
PL1	-0.79	dB
PL1W	25.30924988	W
SFO1	500.1330885	MHz
SI	32768	
SF	500.1300089	MHz
WDW	EM	
SSB	0	
LB	0.30	Hz
GB	0	
PC	1.00	



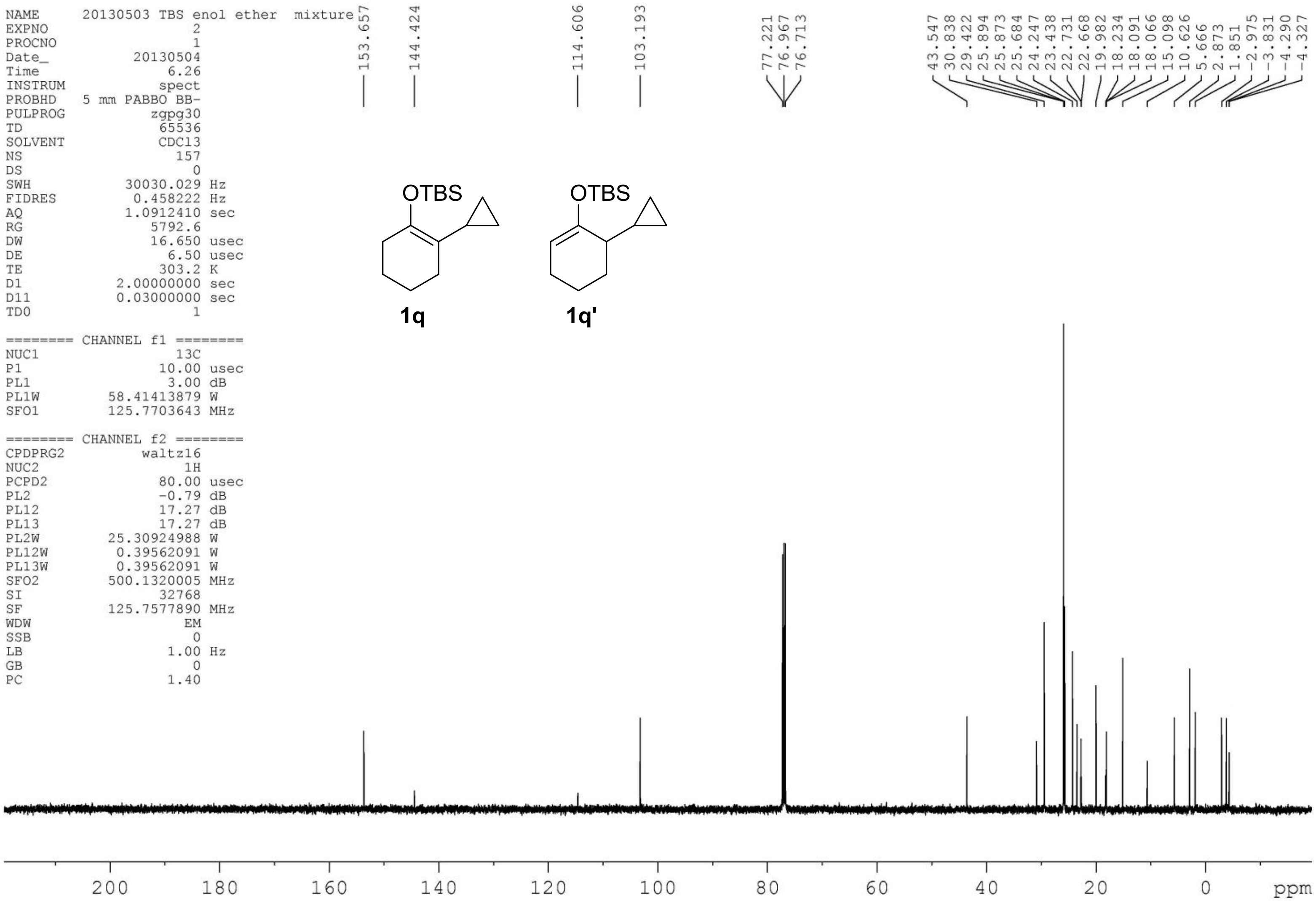
1q



1q'



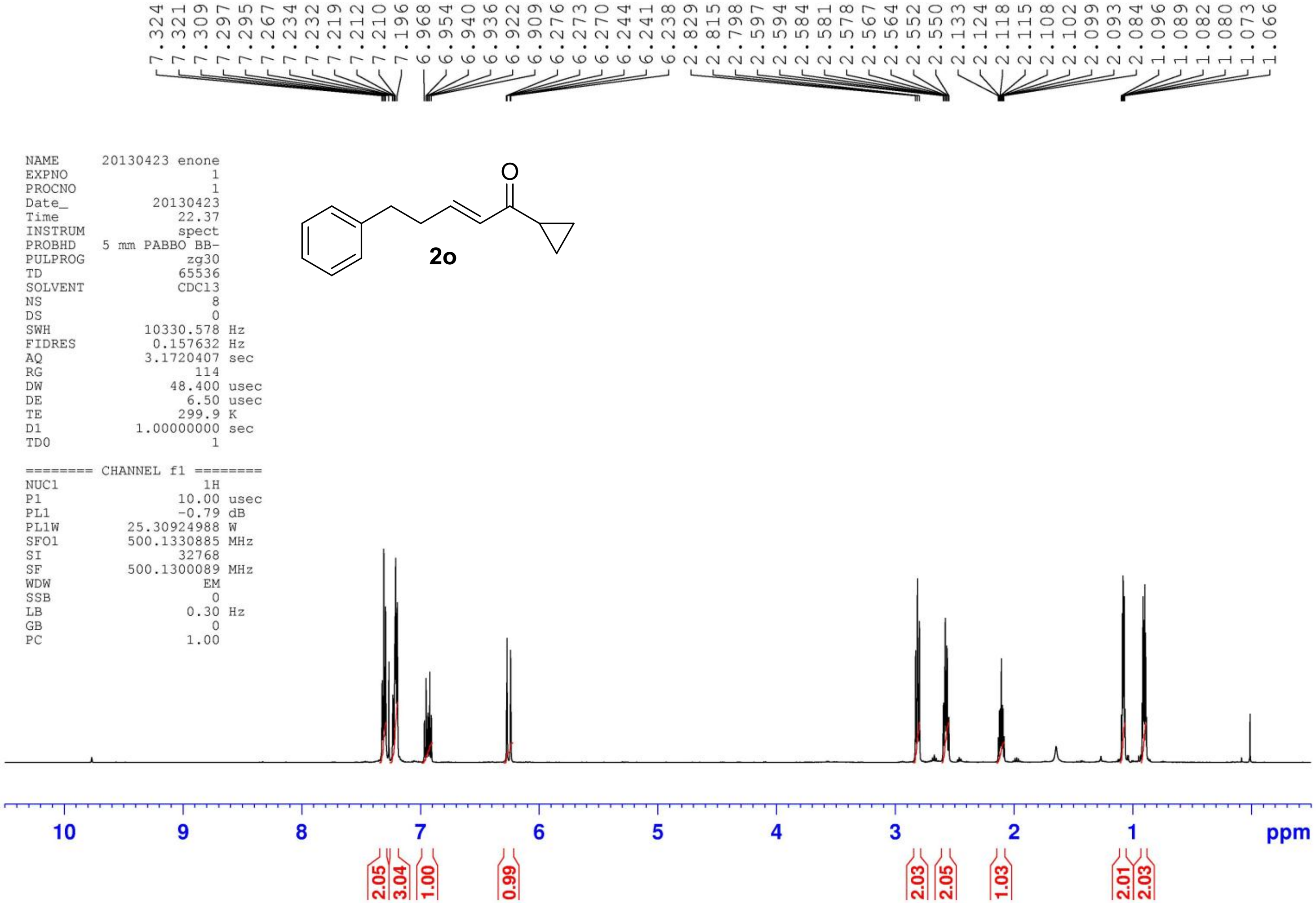
^{1}H NMR



```
NAME     20130503 TBS enol ether  mixture
EXPNO                 2
PROCNO                1
Date_          20130504
Time               6.26
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG         zgpg30
TD               65536
SOLVENT          CDCl3
NS                 157
DS                   0
SWH          30030.029 Hz
FIDRES        0.458222 Hz
AQ           1.0912410 sec
RG              5792.6
DW              16.650 usec
DE                6.50 usec
TE               303.2 K
D1          2.00000000 sec
D11         0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1               13C
P1               10.00 usec
PL1               3.00 dB
PL1W       58.41413879 W
SFO1       125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2        waltz16
NUC2                1H
PCPD2            80.00 usec
PL2              -0.79 dB
PL12             17.27 dB
PL13             17.27 dB
PL2W       25.30924988 W
PL12W       0.39562091 W
PL13W       0.39562091 W
SFO2       500.1320005 MHz
SI               32768
SF         125.7577890 MHz
WDW                 EM
SSB                  0
LB                1.00 Hz
GB                   0
PC                1.40
```

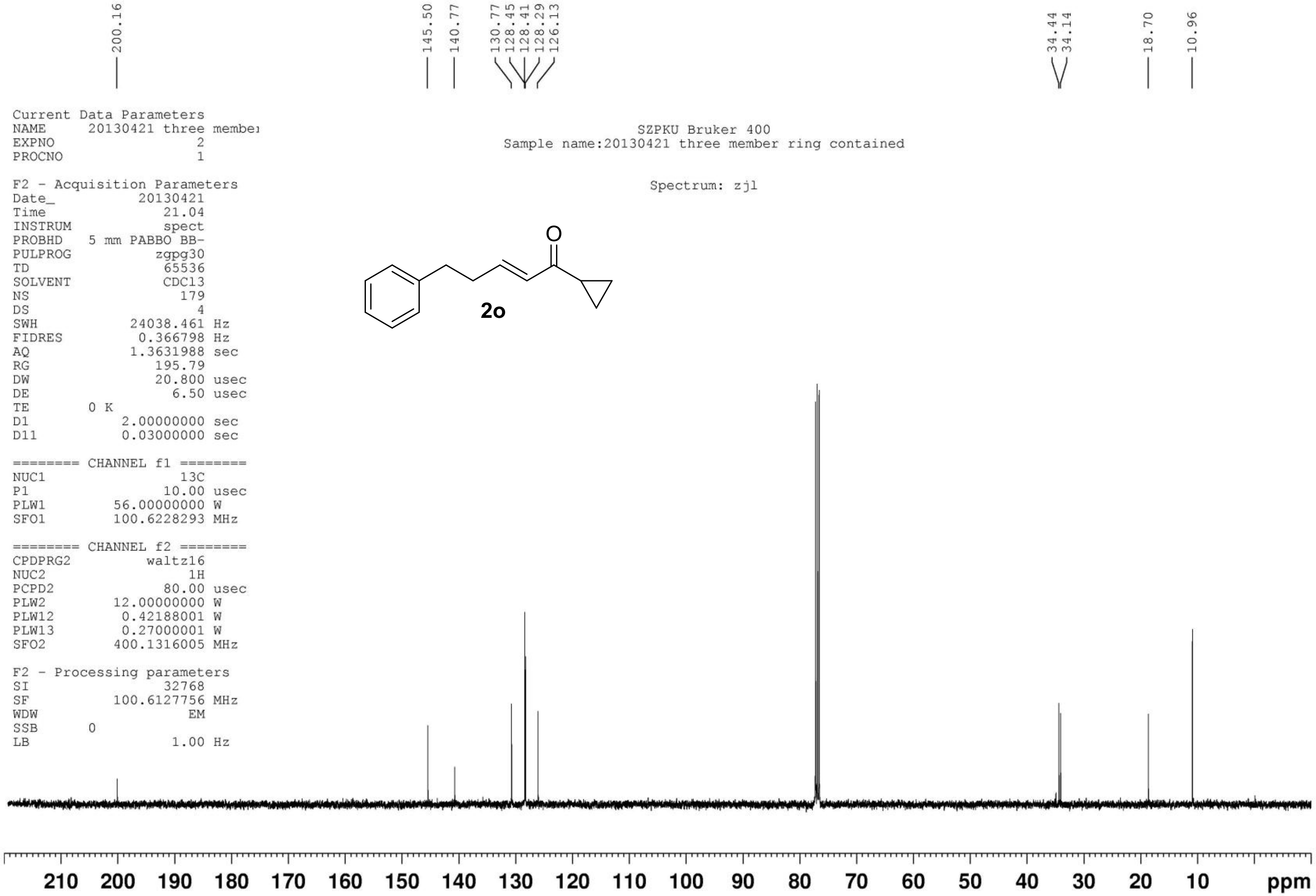
1q **1q'**

^{13}C NMR



```
NAME      20130423 enone
EXPNO                  1
PROCNO                 1
Date_           20130423
Time               22.37
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     0
SWH            10330.578 Hz
FIDRES          0.157632 Hz
AQ             3.1720407 sec
RG                   114
DW                48.400 usec
DE                  6.50 usec
TE                 299.9 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 10.00 usec
PL1                -0.79 dB
PL1W         25.30924988 W
SFO1         500.1330885 MHz
SI                 32768
SF           500.1300089 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

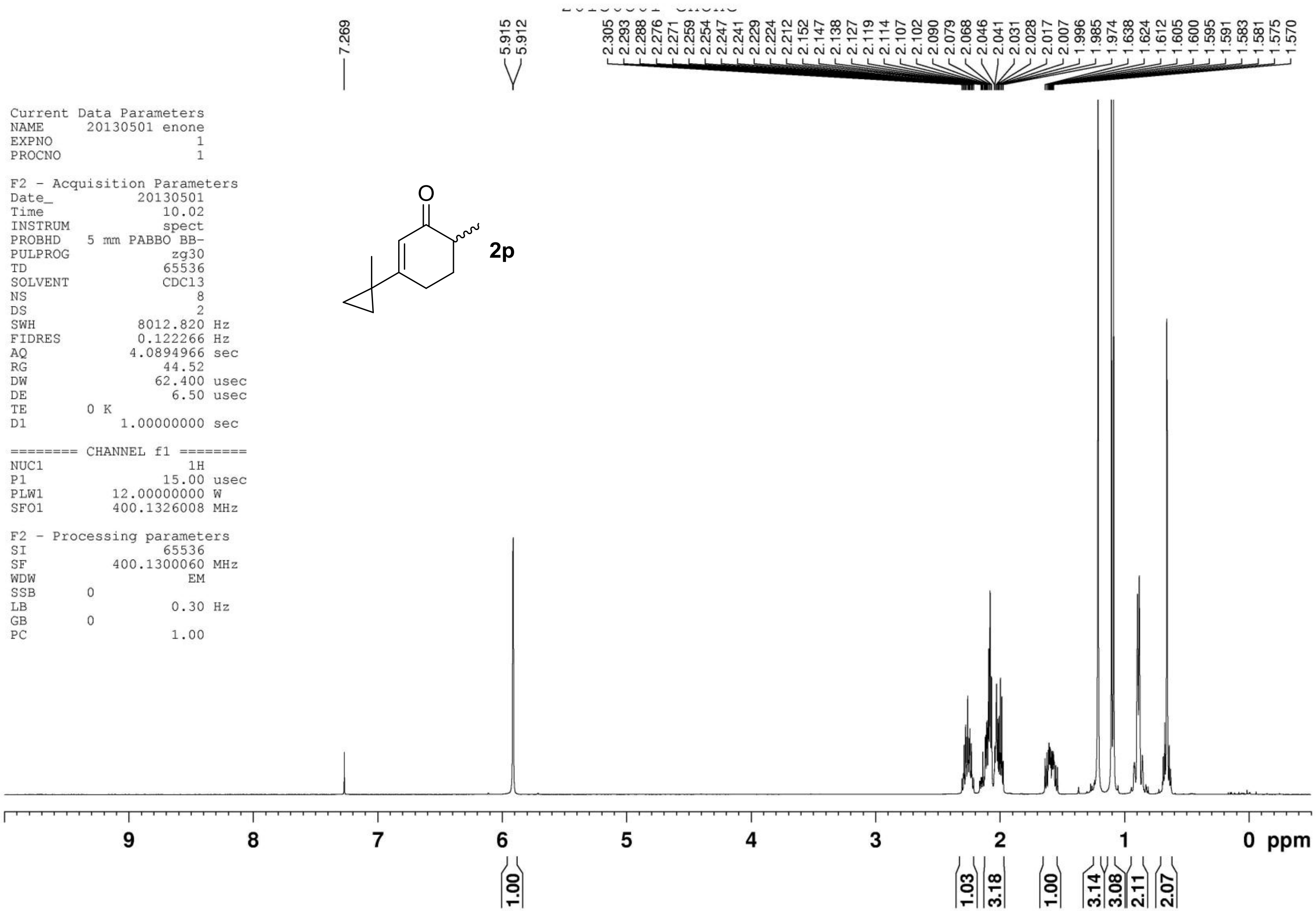
^{1}H NMR



```
Current Data Parameters
NAME     20130421 three membe
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20130421
Time                21.04
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   179
DS                     4
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                195.79
DW                20.800 usec
DE                  6.50 usec
TE          0 K
D1            2.00000000 sec
D11           0.03000000 sec

======== CHANNEL f1 ========
NUC1                 13C
P1                 10.00 usec
PLW1         56.00000000 W
SFO1         100.6228293 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PLW2         12.00000000 W
PLW12         0.42188001 W
PLW13         0.27000001 W
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF           100.6127756 MHz
WDW                   EM
SSB         0
LB                  1.00 Hz
```

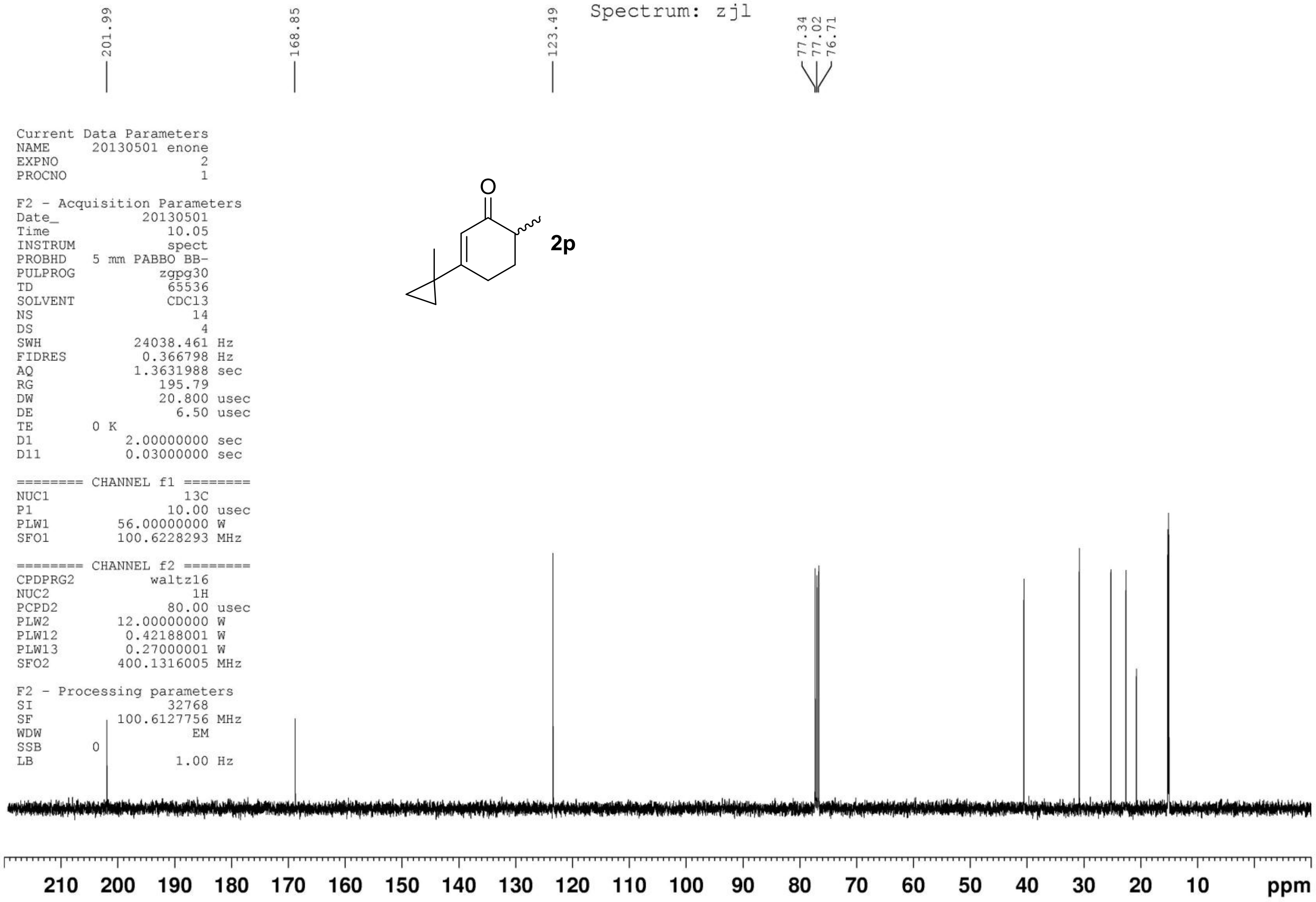
```
SZPKU Bruker 400
Sample name:20130421 three member ring contained

Spectrum: zjl
```

^{13}C NMR



```
Current Data Parameters
NAME     20130501 enone
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20130501
Time              10.02
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    8
DS                    2
SWH            8012.820 Hz
FIDRES         0.122266 Hz
AQ            4.0894966 sec
RG                44.52
DW               62.400 usec
DE                 6.50 usec
TE        0 K
D1           1.00000000 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                15.00 usec
PLW1        12.00000000 W
SFO1        400.1326008 MHz

F2 - Processing parameters
SI                65536
SF          400.1300060 MHz
WDW                  EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

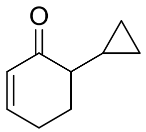
^{1}H NMR



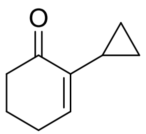
```
Current Data Parameters
NAME     20130501 enone
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20130501
Time              10.05
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG         zgpg30
TD                65536
SOLVENT           CDCl3
NS                   14
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG               195.79
DW               20.800 usec
DE                 6.50 usec
TE        0 K
D1           2.00000000 sec
D11          0.03000000 sec

======== CHANNEL f1 ========
NUC1                13C
P1                10.00 usec
PLW1        56.00000000 W
SFO1        100.6228293 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PLW2        12.00000000 W
PLW12        0.42188001 W
PLW13        0.27000001 W
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127756 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
```

^{13}C NMR

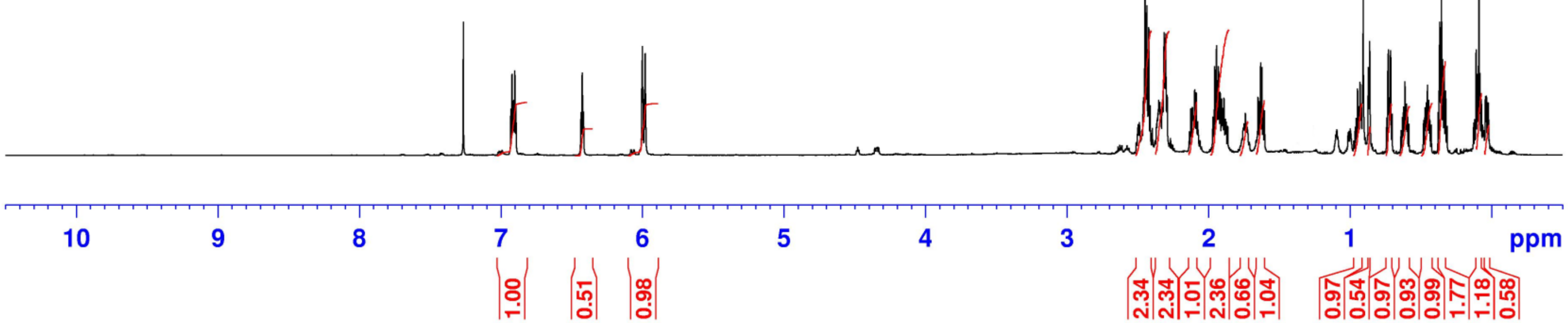
```
NAME            20130529
EXPNO                  1
PROCNO                 1
Date_           20130529
Time               10.08
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     0
SWH            10330.578 Hz
FIDRES          0.157632 Hz
AQ             3.1720407 sec
RG                  71.8
DW                48.400 usec
DE                  6.50 usec
TE                 302.4 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 10.00 usec
PL1                -0.79 dB
PL1W         25.30924988 W
SFO1         500.1330885 MHz
SI                 32768
SF           500.1300089 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



2q



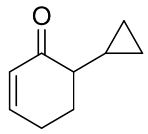
2q'



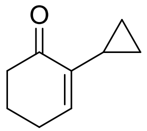
^{1}H NMR

Spectrum: zj1

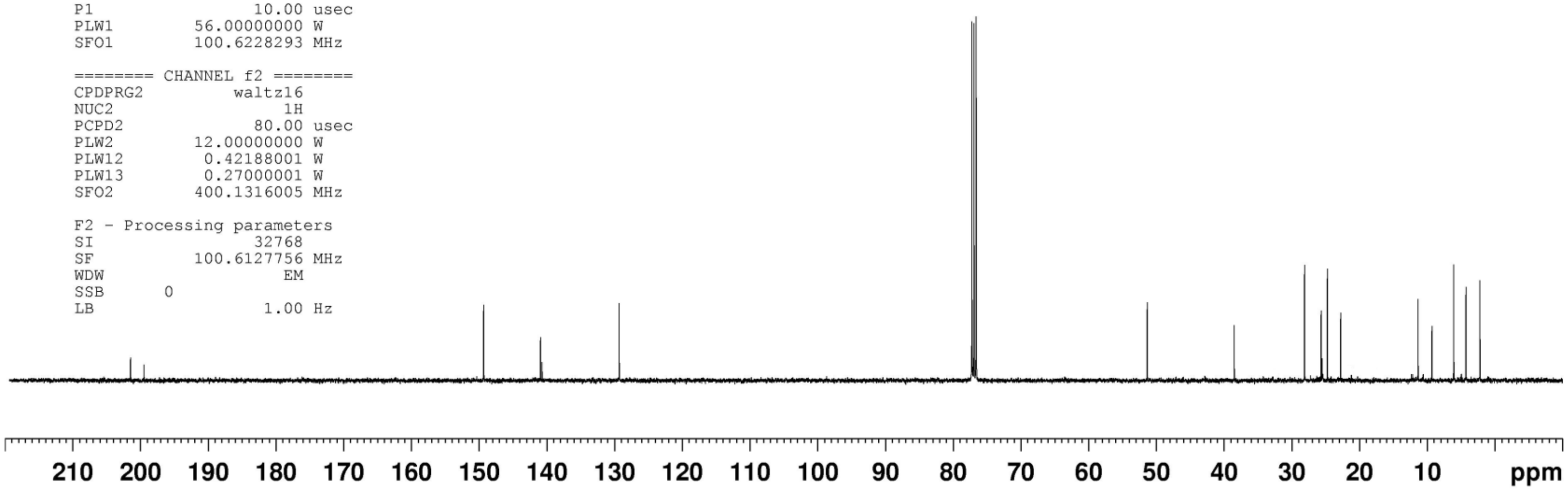
```
Current Data Parameters
NAME              20130529
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_             20130529
Time                 10.20
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    457
DS                      4
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ              1.3631988 sec
RG                 195.79
DW                 20.800 usec
DE                   6.50 usec
TE                  297.5 K
D1             2.00000000 sec
D11            0.03000000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                  10.00 usec
PLW1          56.00000000 W
SFO1         100.6228293 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PLW2          12.00000000 W
PLW12          0.42188001 W
PLW13          0.27000001 W
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                  32768
SF           100.6127756 MHz
WDW                    EM
SSB      0
LB                   1.00 Hz
```



2q



2q'



^{13}C NMR