Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

A selective C–H insertion/olefination protocol for the synthesis of α-methylene-γ-butyrolactone natural products

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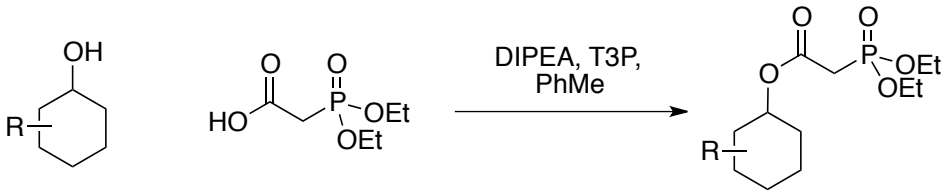
General Information

Except where stated, all reagents were purchased from commercial sources and used without further purification. Except where stated, all experimental procedures were carried out under an atmosphere of argon. Anhydrous CH_2Cl_2, toluene and DMF were obtained from an Innovative Technology Inc. PureSolv® solvent purification system. Anhydrous THF was obtained by distillation over sodium benzophenone ketyl immediately before use. ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra were recorded on a JEOL ECX400 or JEOL ECS400 spectrometer, operating at 400 MHz, 100 MHz and 162 MHz, respectively, or a Bruker DRX500 spectrometer, operating at 500 MHz, 125 MHz and 203 MHz, respectively. All spectral data was acquired at 295 K. Chemical shifts (δ) are quoted in parts per million (ppm). The residual solvent peak, δ_H 7.26 and δ_C 77.0 for $CDCl_3$, δ_H 2.50 and δ_C 39.5 for d6-DMSO and δ_H 7.16 and δ_C 128.06 for C_6D_6 was used as a reference. Coupling constants (*J*) are reported in Hertz (Hz) to the nearest 0.1 Hz. The multiplicity abbreviations used are: s singlet, d doublet, t triplet, q quartet, m multiplet. Signal assignment was achieved by analysis of DEPT, COSY, NOESY, HMBC and HSQC experiments where required. Infrared (IR) spectra were recorded on either a ThermoNicolet IR-100 spectrometer with NaCl plates as a thin film dispersed from either CH_2Cl_2 or $CDCl_3$, or a PerkinElmer UATR Two spectrometer. Mass-spectra (low and high-resolution) were obtained by the University of York Mass Spectrometry

Service, using electrospray ionisation (ESI) or atmosphereic pressure chemical ionisation (APCI) on a Bruker Daltonics, Micro-tof spectrometer. Melting points were determined using Gallenkamp apparatus and are uncorrected. Thin layer chromatography was carried out on Merck silica gel $60F_{254}$ pre-coated aluminium foil sheets and were visualised using UV light (254 nm) and stained with either basic aqueous potassium permanganate or ethanolic *p*-anisaldehyde as appropriate. Flash column chromatography was carried out using slurry packed Fluka silica gel (SiO_2), 35-70 µm, 60 Å, under a light positive pressure, eluting with the specified solvent system. Petrol refers to petroleum ether 40 – 60 °C. Ether refers to diethyl ether. Numbering schemes for compounds refer to NMR assignments not to compound naming.

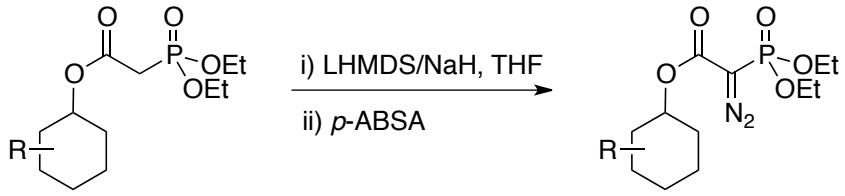
General Procedures

General Procedure A: T3P-mediated esterifications



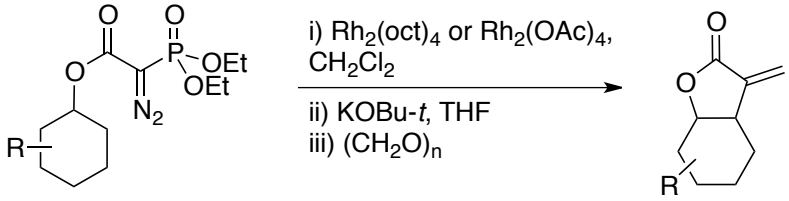
To a stirred solution of alcohol (8.00 mmol) in toluene (40 mL) under argon was added sequentially diethyl phosphonoacetic acid (1.35 mL, 8.40 mmol), DIPEA (3.62 mL, 20.8 mmol) and propyl phosphonic anhydride (6.62 g, 10.4 mmol, 50% w/w solution in ethyl acetate/THF). The solution was stirred at rt for 1 – 4 h, with progress monitored by TLC analysis, after which time it was diluted with water (50 mL) and extracted with ethyl acetate (3 × 25 mL) followed by sequential washing of the combined organic extracts with 10% aq. HCl (10 mL), sat. aq. $NaHCO_3$ (10 mL) and brine (10 mL). The organic extracts were dried over $MgSO_4$ and concentrated *in vacuo*, affording the α-(diethoxyphosphoryl)acetate product, which was used without further purification.

General Procedure B: Diazo transfer reactions



To a stirred solution of α-(diethoxyphosphoryl)acetate (10.0 mmol) in THF (50 mL), cooled to –78 °C under argon was added LHMDS (1.0 M solution in THF) or NaH (60% dispersion in mineral oil) (12.0 mmol). The solution was allowed to warm to rt and stirred for 10 min then *p*-ABSA or 4-DBSA (12.0 mmol) was added. After stirring for 1 h at rt the mixture was diluted with ether (50 mL) and water (50 mL) prior to extraction with ether (3 × 25 mL). The organic extracts were washed with sat. aq. $NaHCO_3$ (2 × 25 mL). The organic extracts were dried over $MgSO_4$, concentrated *in vacuo* and purified by column chromatography affording the α-diazo-α-(diethoxyphosphoryl)acetate product.

General Procedure C: One-pot Rh(II)-catalysed C–H insertion/HWE olefination

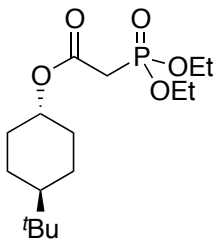


To an oven dried sealable tube flushed with argon containing a solution of α-diazo-α-(diethoxyphosphoryl)acetate (0.200 mmol) in CH_2Cl_2 (4.0 mL) was added $Rh_2(oct)_4$ or $Rh_2(OAc)_4$ (4.0 μmol, 2 mol%). The solution was stirred at 45 °C for 16–20 h and then concentrated *in vacuo*. The residue was diluted with THF (4.0 mL) and cooled to 0 °C prior to the addition of potassium *tert*-butoxide (27.6 mg, 0.246 mmol) which was stirred at 0 °C for 60 mins and then cooled to –78 °C. Paraformaldehyde (12.0 mg, 0.400 mmol) was added to the solution and stirred for 15 mins at –78 °C and a further 2 h at rt. The solution was quenched with sat. aq. NH_4Cl (10 mL). The organic layer was separated and the aqueous extracted with EtOAc (2 × 10 mL). The organic extracts were dried over $MgSO_4$, filtered, concentrated *in vacuo* and purified by column chromatography affording the α-methylene-γ-butyrolactone product.

Abbreviations

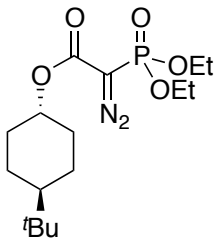
Ac	acetyl
acac	acetylacetonate
app.	apparent
aq.	aqueous
Bu	butyl
conc.	concentrated
COSY	correlation spectroscopy
δ	chemical shift
d	doublet
DCM	dichloromethane
DEPAA	diethylphosphonoacetic acid
DEPT	distortionless enhancement by polarisation transfer
DIPEA	*N*,*N*-diisopropylethylamine
DMF	*N*,*N*-dimethylformamide
DMP	Dess-Martin periodinane
DMSO	dimethylsulfoxide
DTBMP	2,6-di-*tert*-butylmethylpyridine
eq.	equivalent(s)
ESI	electrospray ionisation
ether/Et_2O	diethyl ether
Et	ethyl
EtOAc	ethyl acetate
h	hour(s)
hept.	heptet
HMBC	heteronuclear multiple bond correlation
HOMO	Highest Occupied Molecular Orbital
HRMS	high resolution mass spectrometry
HSQC	heteronuclear single quantum coherence
HWE	Horner–Wadsworth–Emmons
IR	infrared
J	coupling constant (Hz)
LHMDS	lithium bis(trimethylsilyl)amide
lit.	literature
m	*meta*
m	multiplet
Me	methyl
min(s)	minute(s)
m.p.	melting point
n	normal
NMP	*N*-methyl-2-pyrrolidone
NMR	nuclear magnetic resonance
o/n	overnight
o	*ortho*
OAc	acetate
oct	octanoate
OTf	trifluoromethanesulfonate (triflate)
p	*para*
p-ABSA	4-acetamidobenzenesulfonyl azide
PCC	pyridinium chlorochromate
petrol	petroleum ether 40–60 °C
Ph	phenyl
PMP	4-methoxyphenyl
ppm	parts per million
Pr	*n*-propyl
q	quartet
quin.	quintet
rbf	round-bottom flask
R_f	retention factor
rt	room temperature
s	singlet
sat.	saturated
sex.	sextet
t	triplet
T3P	propyl phosphonic anhydride
TBAF	tetra-*n*-butylammonium fluoride
TBS	*tert*-butyldimethylsilyl
TEA	*N,N,N*-triethylamine
Tf	trifluoromethanesulfonyl (triflyl)
tert	tertiary
THF	tetrahydrofuran
TIMO	telescoped intramolecular Michael/ olefination
tlc	thin layer chromatography
TMS	trimethylsilyl
UV	ultraviolet
vis	visible

***anti*-4-(*tert*-Butyl)cyclohexyl 2-(diethoxyphosphoryl)acetate (S1);** Synthesised using general procedure A with *anti*-4-(tert-butyl)cyclohexanol (1.56 g, 10.0 mmol), toluene (50 mL), DEPAA (2.06 g, 10.5 mmol), DIPEA (4.52 mL, 26.0 mmol) and T3P (8.27 g, 13.0 mmol, 50% w/w solution in ethyl acetate) affording the *title compound* as a yellow oil (3.23 g, 97%). No further purification was required; R_f 0.21 (1:1 hexane:ethyl acetate); ν_{max} (thin film)/cm^{-1} 2947, 2866, 1730, 1451, 1394, 1366, 1260, 1113, 1019, 966; δ_H (400 MHz, $CDCl_3$) 0.82 (9 H, s), 0.92–1.12 (3 H, m), 1.26–1.36 (8 H, m), 1.75–1.81 (2 H, m), 1.98–2.04 (2 H, m), 2.91 (2 H, d, *J* = 21.6), 4.10–4.17 (4 H, m), 4.65 (1 H, tt, *J* = 11.3, *J* = 4.5); δ_C (100 MHz, $CDCl_3$) 16.3 (d, *J* = 6.1), 25.3, 27.5, 31.8, 32.2, 34.7 (d, *J* = 133.6), 46.9, 62.5 (d, *J* = 6.1), 75.0, 165.3 (d, *J* = 5.8); δ_P (162 MHz, $CDCl_3$) 20.6; HRMS (ESI$^+$): Found: 357.1790; $C_{16}H_{31}NaO_5P$ (MNa^+) Requires 357.1801 (3.1 ppm error), Found: 335.1970; $C_{16}H_{32}O_5P$ (MH^+) Requires 335.1982 (3.5 ppm error).



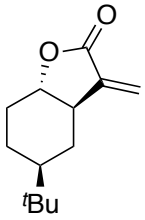
S1

***anti*-4-(*tert*-Butyl)cyclohexyl 2-diazo-2-(diethoxyphosphoryl)acetate (5A);** Synthesised using general procedure B with *anti*-4-(tert-butyl)cyclohexyl 2-(diethoxyphosphoryl)acetate **S1** (3.22 g, 9.63 mmol), THF (48 mL), LHMDS (11.6 mL, 11.6 mmol, 1.0 M solution in THF) and *p*-ABSA (2.78 g, 11.6 mmol). Purification by column chromatography (2:1 hexane:ethyl acetate) afforded the *title compound* as a yellow oil (2.99 g, 86%); R_f 0.51 (1:1 hexane:ethyl acetate); ν_{max} (thin film)/cm^{-1} 2949, 2866, 2126, 1698, 1453, 1363, 1279, 1020, 977; δ_H (400 MHz, $CDCl_3$) 0.83 (9 H, s), 0.94–1.14 (3 H, m), 1.27–1.37 (8 H, m), 1.76–1.84 (2 H, m), 2.00–2.06 (2 H, m), 4.07–4.25 (4 H, m), 4.72 (1 H, tt, *J* = 11.3, *J* = 4.5); δ_C (100 MHz, $CDCl_3$) 15.7 (d, *J* = 7.3), 24.9, 27.1, 31.7, 31.8, 46.5, 53.4 (d, *J* = 226.5), 63.1 (d, *J* = 6.3), 74.8, 162.5 (d, *J* = 12.3); δ_P (162 MHz, $CDCl_3$) 10.8; HRMS (ESI$^+$): Found: 383.1711; $C_{16}H_{29}N_2NaO_5P$ (MNa^+) Requires 383.1706 (–1.2 ppm error).

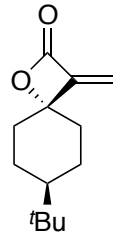


5a

(3a*RS*,5*SR*,7a*SR*)-5-(*tert*-Butyl)-3-Methylenehexahydrobenzofuran-2(3*H*)-one (6a) and *anti*-7-(*tert*-Butyl)-3-Methylene-1-oxaspiro[3.5]nonan-2-one (7a); Synthesised using general procedure C with *anti*-4-(*tert*-butyl)cyclohexyl 2-diazo-2-(diethoxyphosphoryl)acetate **5a** (73 mg, 0.203 mmol), DCM (4.0 mL), $Rh_2(oct)_4$ (3.2 mg, 4.1 μmol), THF (4.0 mL), potassium *tert*-butoxide (34.2 mg, 0.305 mmol) and paraformaldehyde (12.2 mg, 0.406 mmol). Purification by column chromatography (10:1 hexane:ethyl acetate) afforded the *title compounds* **7a** (5 mg, 12%) and **6a** (20 mg, 47%).



6a

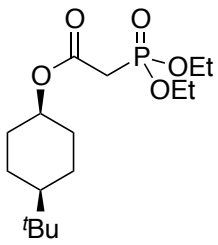


7a

Data for **6a**; colourless oil; R_f 0.36 (8:1 hexane:ethyl acetate); ν_{max} (thin film)/cm^{-1} 2954, 2870, 1772, 1395, 1366, 1251, 1132, 1079, 1034, 1019, 993; δ_H (400 MHz, $CDCl_3$) 0.91 (9 H, s), 1.06–1.34 (3 H, m), 1.62 (1 H, qd, *J* = 11.9, *J* = 3.7), 1.98–2.04 (1 H, m), 2.18 (1 H, dq, *J* = 12.5, *J* = 3.7), 2.29 (1 H, dq, *J* = 11.5, *J* = 3.7), 2.41 (1 H, tq, *J* = 11.1, *J* = 3.2), 3.65 (1 H, td, *J* = 11.1, *J* = 3.7), 5.39 (1 H, d, *J* = 3.1), 6.06 (1 H, d, *J* = 3.2); δ_C (100 MHz, $CDCl_3$) 25.0, 26.4, 27.7, 30.1, 32.6, 47.1, 48.7, 83.2, 116.9, 139.8, 171.0; HRMS (ESI$^+$): Found: 231.1362; $C_{13}H_{20}NaO_2$ (MNa^+) Requires 231.1356 (–2.7 ppm error), Found: 209.1532; $C_{13}H_{21}O_2$ (MH^+) Requires 209.1536 (1.8 ppm error).

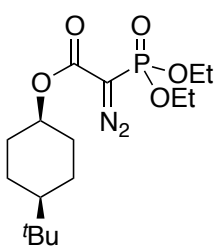
Data for **7a**; white needles; R_f 0.45 (8:1 hexane:ethyl acetate); m.p. 69–73 °C; ν_{max} (thin film)/cm^{-1} 2969, 2872, 1820, 1368, 1193, 1087, 1024, 959, 857, 808; δ_H (400 MHz, $CDCl_3$) 0.90 (9 H, s), 0.94–1.46 (3 H, m, H-3,4), 1.87–1.99 (4 H, m, H-2,3), 2.04–2.12 (2 H, m), 5.49 (1 H, d, *J* = 1.8, H-8b), 5.80 (1 H, d, *J* = 1.8, H-8a); δ_C (100 MHz, $CDCl_3$) 25.0, 27.5, 32.3, 35.0, 46.3, 87.1, 113.2, 150.1, 163.5; HRMS (ESI$^+$): Found: 231.1352; $C_{13}H_{20}NaO_2$ (MNa^+) Requires 231.1356 (1.5 ppm error).

***syn*-4-(*tert*-Butyl)cyclohexyl 2-(diethoxyphosphoryl)acetate (S2);** Synthesised using general procedure A with *syn*-4-(tert-butyl)cyclohexanol (285 mg, 1.82 mmol), toluene (9.3 mL), DEPAA (381 mg, 1.94 mmol), DIPEA (0.84 mL, 4.81 mmol) and T3P (1.53 g, 2.41 mmol, 50% w/w solution in ethyl acetate) affording the *title compound* as a yellow oil (575 mg, 94%). No further purification was required; R_f 0.21 (1:1 hexane:ethyl acetate); ν_{max} (thin film)/cm^{-1} 2945, 1731, 1446, 1393, 1363, 1267, 1108, 1051, 1022, 965; δ_H (400 MHz, $CDCl_3$) 0.84 (9 H, s), 1.00 (1 H, tt, *J* = 12.0, *J* = 3.0), 1.23–1.35 (8 H, m), 1.41–1.50 (2 H, m), 1.55–1.59 (2 H, m), 1.91–1.98 (2 H, m), 2.96 (2 H, d, *J* = 21.5), 4.12–4.20 (4 H, m), 5.05 (1 H, quin., *J* = 2.8); δ_C (100 MHz, $CDCl_3$) 16.3 (d, *J* = 6.5), 21.6, 27.4, 30.4, 32.4, 34.7 (d, *J* = 133.4), 47.5, 62.5 (d, *J* = 6.1), 70.9, 165.3 (d, *J* = 6.6); δ_P (162 MHz, $CDCl_3$) 20.9; HRMS (ESI$^+$): Found: 357.1814; $C_{16}H_{31}NaO_5P$ (MNa^+) Requires 357.1801 (–3.4 ppm error).



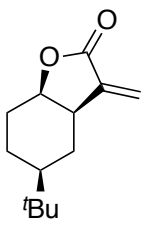
S2

***syn*-4-(*tert*-Butyl)cyclohexyl 2-diazo-2-(diethoxyphosphoryl)acetate (5b);** Synthesised using general procedure B with *syn*-4-(tert-butyl)cyclohexyl 2-(diethoxyphosphoryl)acetate **S2** (540 mg, 1.61 mmol), THF (8.0 mL), LHMDS (1.94 mL, 1.94 mmol, 1.0 M solution in THF) and *p*-ABSA (466 mg, 1.94 mmol). Purification by column chromatography (2:1 hexane:ethyl acetate) afforded the *title compound* as a yellow oil (505 mg, 87%); R_f 0.51 (1:1 hexane:ethyl acetate); ν_{max} (thin film)/cm^{-1} 2946, 2128, 1694, 1479, 1446, 1361, 1287, 1269, 1104, 1017, 975, 793, 747, 590, 560; δ_H (400 MHz, $CDCl_3$) 0.83 (9 H, s), 1.01 (1 H, tt, *J* = 12.0, *J* = 3.0), 1.21–1.35 (8 H, m), 1.42–1.52 (2 H, m), 1.55–1.59 (2 H, m), 1.89–1.96 (2 H, m), 4.08–4.24 (4 H, m), 5.12 (1 H, quin., *J* = 2.7); δ_C (100 MHz, $CDCl_3$) 16.1 (d, *J* = 7.0), 21.4, 27.3, 30.6, 32.4, 47.3, 54.1 (d, *J* = 228.0), 63.3 (d, *J* = 6.0), 71.2, 162.9 (d, *J* = 12.0); δ_P (162 MHz, $CDCl_3$) 11.3; HRMS (ESI$^+$): Found: 383.1714; $C_{16}H_{29}N_2NaO_5P$ (MNa^+) Requires 383.1706 (–1.9 ppm error).

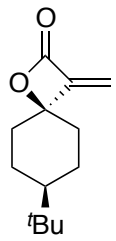


5b

(3a*RS*,5*SR*,7a*RS*)-5-(*tert*-Butyl)-3-Methylenehexahydrobenzofuran-2(3*H*)-one (6b) and *syn*-7-(*tert*-Butyl)-3-Methylene-1-oxaspiro[3.5]nonan-2-one (7b); Synthesised using general procedure C with *syn*-4-(*tert*-butyl)cyclohexyl 2-diazo-2-(diethoxyphosphoryl)acetate **5b** (72 mg, 0.200 mmol), DCM (4.0 mL), $Rh_2(oct)_4$ (3.1 mg, 4.0 μmol), THF (4.0 mL), potassium *tert*-butoxide (33.7 mg, 0.300 mmol) and paraformaldehyde (12.0 mg, 0.400 mmol). Purification by column chromatography (10:1 hexane:ethyl acetate) afforded the *title compounds* **7b**(8 mg, 19%) and **6b** (12 mg, 29%).



6b



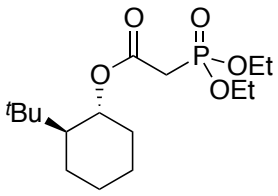
7b

Data for **6b**; white solid; R_f 0.24 (8:1 hexane:ethyl acetate); m.p. 48–51 °C; ν_{max} (thin film)/cm^{-1} 2952, 1763, 1359, 1259, 1181, 1124, 1100, 990, 964, 917; δ_H (400 MHz, $CDCl_3$) 0.84 (9 H, s), 0.94–1.42 (3 H, m), 1.61–1.70 (2 H, m), 1.77–1.82 (1 H, m), 2.26 (1 H, dq, *J* = 15.3, *J* = 3.4), 2.86–2.92 (1 H, m), 4.43 (1 H, q, *J* = 3.9),

5.53 (1 H, s), 6.08 (1 H, s); δ_C (100 MHz, $CDCl_3$) 20.6, 27.2, 27.9, 30.2, 32.4, 41.0, 44.9, 76.2, 119.6, 142.7, 171.1; HRMS (ESI^+): Found: 231.1363; $C_{13}H_{20}NaO_2$ (MNa^+) Requires 231.1356 (–3.3 ppm error), Found: 209.1538; $C_{13}H_{21}O_2$ (MH^+) Requires 209.1536 (–0.9 ppm error).

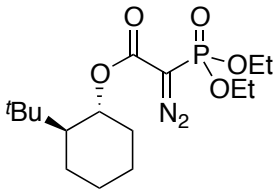
Data for **7b**; white solid; R_f 0.36 (8:1 hexane:ethyl acetate); m.p. 111–114 °C; ν_{max} (thin film)/cm^{-1} 2960, 1797, 1438, 1366, 1160, 1091, 952, 796; δ_H (400 MHz, $CDCl_3$) 0.88 (9 H, s), 1.08 (1 H, tt, *J* = 12.2, *J* = 2.9), 1.25–1.42 (2 H, m), 1.70–1.81 (4 H, m), 2.01–2.08 (2 H, m), 5.31 (1 H, d, *J* = 1.9), 5.81 (1 H, d, *J* = 1.9); δ_C (100 MHz, $CDCl_3$) 23.0, 27.4, 32.5, 34.5, 46.7, 87.3, 112.9, 149.8, 164.0; HRMS (ESI^+): Found: 231.1352; $C_{13}H_{20}NaO_2$ (MNa^+) Requires 231.1356 (1.4 ppm error).

(1*RS*,2*SR*)-2-(*tert*-Butyl)cyclohexyl 2-(diethoxyphosphoryl)acetate (S3); Synthesised using general procedure A with (1*RS*,2*SR*)-2-(*tert*-butyl)cyclohexanol (1.56 g, 10.0 mmol), toluene (50 mL), DEPAA (2.06 g, 10.5 mmol), DIPEA (4.52 mL, 26.0 mmol) and T3P (8.27 g, 13.0 mmol, 50% w/w solution in ethyl acetate) affording the *title compound* as a yellow oil (3.27 g, 98%). No further purification was required; R_f 0.31 (1:1 hexane:ethyl acetate); ν_{max} (thin film)/cm^{-1} 2937, 2865, 1727, 1479, 1449, 1396, 1368, 1263, 1164, 1113, 1051, 1022, 967, 835, 780; δ_H (400 MHz, $CDCl_3$) 0.86 (9 H, s), 0.90–1.41 (11 H, m), 1.60–1.67 (2 H, m), 1.80–1.86 (1 H, m), 1.94–1.99 (1 H, m), 2.81–2.95 (2 H, m), 4.09–4.16 (4 H, m), 4.72 (1 H, td, *J* = 10.2, *J* = 4.5); δ_C (100 MHz, $CDCl_3$) 16.2 (d, *J* = 6.4), 24.4, 25.7, 26.6, 28.9, 32.7, 32.8, 34.8 (d, *J* = 134.9), 50.1, 62.4 (d, *J* = 6.7), 62.5 (d, *J* = 6.7), 76.8, 165.0 (d, *J* = 6.0); δ_P (162 MHz, $CDCl_3$) 20.6; HRMS (ESI^+): Found: 357.1785; $C_{16}H_{31}NaO_5P$ (MNa^+) Requires 357.1801 (4.6 ppm error), Found: 335.1989; $C_{16}H_{32}O_5P$ (MH^+) Requires 335.1982 (–2.3 ppm error).



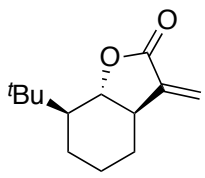
S3

(1*RS*,2*SR*)-2-(*tert*-Butyl)cyclohexyl 2-diazo-2-diethoxyphosphoryl)acetate (5c); Synthesised using general procedure B with (1*RS*,2*SR*)-2-(*tert*-butyl)cyclohexyl 2-(diethoxyphosphoryl)acetate **S3** (1.67 g, 5.00 mmol), THF (25 mL), LHMDS (6.00 mL, 6.00 mmol, 1.0 M solution in THF) and *p*-ABSA (1.44 g, 6.00 mmol). Purification by column chromatography (4:1 hexane:ethyl acetate) afforded the *title compound* as a yellow oil (1.37 g, 76%); R_f 0.60 (1:1 hexane:ethyl acetate); ν_{max} (thin film)/cm^{-1} 2936, 2865, 2122, 1698, 1478, 1449, 1395, 1367, 1319, 1272, 1220, 1164, 1130, 1108, 1018, 976, 951, 817, 795, 743; δ_H (400 MHz, $CDCl_3$) 0.82–1.40 (20 H, m), 1.61–1.67 (2 H, m), 1.81–1.87 (1 H, m), 1.92–1.96 (1 H, m), 4.04–4.23 (4 H, m), 4.84 (1 H, td, *J* = 10.1, *J* = 4.5); δ_C (100 MHz, $CDCl_3$) 16.0 (d, *J* = 7.4), 24.4, 25.5, 26.6, 28.8, 32.8, 33.4, 50.3, 53.8 (d, *J* = 227.2), 63.4 (d, *J* = 5.9), 63.5 (d, *J* = 5.9), 76.6, 162.4 (d, *J* = 13.0); δ_P (162 MHz, $CDCl_3$) 10.9; HRMS (ESI^+): Found: 383.1705; $C_{16}H_{29}N_2NaO_5P$ (MNa^+) Requires 383.1706 (0.4 ppm error).



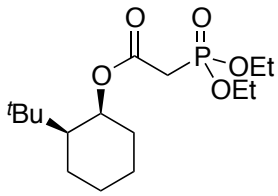
5c

(3a*RS*,7*SR*,7a*SR*)-7-(*tert*-Butyl)-3-methylenehexahydrobenzofuran-2(3*H*)-one (6c); Synthesised using general procedure C with (1*RS*,2*SR*)-2-(*tert*-butyl)cyclohexyl 2-diazo-2-diethoxyphosphoryl)acetate **5c** (75 mg, 0.208 mmol), DCM (4.2 mL), $Rh_2(oct)_4$ (3.2 mg, 4.2 μmol), THF (4.2 mL), potassium *tert*-butoxide (35.0 mg, 0.312 mmol) and paraformaldehyde (12.5 mg, 0.416 mmol). Purification by column chromatography (4:1 hexane:ethyl acetate) afforded the *title compound* as a yellow oil (33 mg, 76%); R_f 0.57 (4:1 hexane:ethyl acetate); ν_{max} (thin film)/cm^{-1} 2938, 2868, 1770, 1447, 1408, 1367, 1255, 1239, 1151, 1127, 1081, 1032, 1009, 995, 933; δ_H (400 MHz, $CDCl_3$) 0.97 (9 H, s), 1.05–1.16 (1 H, m), 1.22–1.32 (1 H, m), 1.41 (1 H, app. qt, *J* = 13.1, *J* = 4.0), 1.56–1.64 (1 H, m), 1.85–1.96 (2 H, m), 2.06–2.12 (1 H, m), 2.49 (1 H, app. tq, *J* = 10.8, *J* = 3.4), 3.63 (1 H, app. t, *J* = 10.6), 5.37 (1 H, d, *J* = 3.1), 6.06 (1 H, d, *J* = 3.3); δ_C (100 MHz, $CDCl_3$) 25.2, 26.0, 26.4, 28.1, 32.6, 49.0, 51.5, 85.4, 117.2, 139.3, 170.8; HRMS (ESI^+): Found: 231.1356; $C_{13}H_{20}NaO_2$ (MNa^+) Requires 231.1356 (0.0 ppm error).



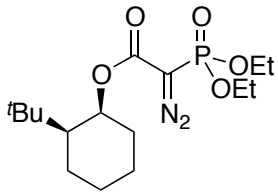
6c

(1*SR*,2*SR*)-2-(*tert*-Butyl)cyclohexyl 2-(diethoxyphosphoryl)acetate (S4); Synthesised using general procedure A with (1*SR*,2*SR*)-2-(*tert*-butyl)cyclohexanol (1.56 g, 10.0 mmol), toluene (50 mL), DEPAA (2.06 g, 10.5 mmol), DIPEA (4.52 mL, 26.0 mmol) and T3P (8.27 g, 13.0 mmol, 50% w/w solution in ethyl acetate) affording the *title compound* as a pink oil (3.28 g, 98%). No further purification was required; R_f 0.33 (1:1 hexane:ethyl acetate); ν_{max} (thin film)/cm^{-1} 2938, 2868, 1728, 1447, 1396, 1366, 1262, 1115, 1051, 1020, 966; δ_H (400 MHz, $CDCl_3$) 0.83 (9 H, s), 1.09 (1 H, ddd, *J* = 12.4, *J* = 3.5, *J* = 2.0), 1.14–1.34 (8 H, m), 1.40–1.62 (4 H, m), 1.73–1.80 (1 H, m), 1.90–1.97 (1 H, m), 2.83–2.98 (2 H, m), 4.08–4.16 (4 H, m), 5.24–5.27 (1 H, m); δ_C (100 MHz, $CDCl_3$) 16.1 (d, *J* = 6.7), 16.1 (d, *J* = 6.7), 20.2, 22.0, 26.3, 28.3, 31.1, 32.4, 34.6 (d, *J* = 134.4), 49.8, 62.3 (app. t, *J* = 6.5), 72.6, 165.0 (d, *J* = 6.3); δ_P (162 MHz, $CDCl_3$) 20.7; HRMS (ESI^+): Found: 357.1791; $C_{16}H_{31}NaO_5P$ (MNa^+) Requires 357.1801 (2.9 ppm error).



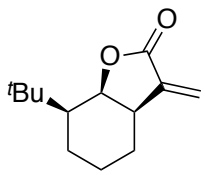
S4

(1*SR*,2*SR*)-2-(*tert*-Butyl)cyclohexyl 2-diazo-2-diethoxyphosphoryl)acetate (5d); Synthesised using general procedure B with (1*SR*,2*SR*)-2-(*tert*-butyl)cyclohexyl 2-(diethoxyphosphoryl)acetate **S4** (1.67 g, 5.00 mmol), THF (25 mL), LHMDS (6.00 mL, 6.00 mmol, 1.0 M solution in THF) and *p*-ABSA (1.44 g, 6.00 mmol). Purification by column chromatography (4:1 hexane:ethyl acetate) afforded the *title compound* as a yellow oil (1.47 g, 82%); R_f 0.63 (1:1 hexane:ethyl acetate); ν_{max} (thin film)/cm^{-1} 2939, 2868, 2125, 1693, 1480, 1447, 1368, 1277, 1269, 1222, 1018, 976; δ_H (400 MHz, $CDCl_3$) 0.84 (9 H, s), 1.10–1.49 (12 H, m), 1.57–1.64 (1 H, m), 1.74–1.82 (1 H, m), 1.86–1.93 (1 H, m), 4.05–4.23 (4 H, m), 5.40–5.43 (1 H, m); δ_C (100 MHz, $CDCl_3$) 16.0 (d, *J* = 7.2), 16.0 (d, *J* = 7.5), 20.3, 21.9, 26.4, 28.3, 31.7, 32.4, 50.2, 54.0 (d, *J* = 226.6), 63.3 (d, *J* = 5.9), 63.4 (d, *J* = 5.9), 72.6, 162.5 (d, *J* = 12.1); δ_P (162 MHz, $CDCl_3$) 11.2; HRMS (ESI^+): Found: 383.1690; $C_{16}H_{29}N_2NaO_5P$ (MNa^+) Requires 383.1706 (4.3 ppm error).



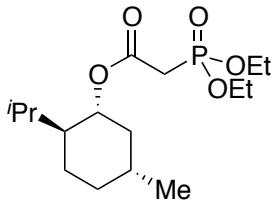
5d

(3a*RS*,7*SR*,7a*RS*)-7-(*tert*-Butyl)-3-methylenehexahydrobenzofuran-2(3*H*)-one (6d); Synthesised using general procedure C with (1*SR*,2*SR*)-2-(*tert*-butyl)cyclohexyl 2-diazo-2-diethoxyphosphoryl)acetate **5d** (75 mg, 0.208 mmol), DCM (4.2 mL), $Rh_2(oct)_4$ (3.2 mg, 4.2 μmol), THF (4.2 mL), potassium *tert*-butoxide (35.0 mg, 0.312 mmol) and paraformaldehyde (12.5 mg, 0.416 mmol). Purification by column chromatography (4:1 hexane:ethyl acetate) afforded the *title compound* as a white solid (39 mg, 90%); R_f 0.49 (4:1 hexane:ethyl acetate); m.p. 57–60 °C; ν_{max} (thin film)/cm^{-1} 2944, 2866, 1762, 1669, 1366, 1261, 1175, 1145, 1117, 1078, 962, 945, 896, 818; δ_H (400 MHz, $CDCl_3$) 1.00 (9 H, s), 1.15–1.34 (4 H, m), 1.65–1.79 (3 H, m), 2.81–2.86 (1 H, m), 4.58–4.60 (1 H, m), 5.49 (1 H, d, *J* = 0.8), 6.05 (1 H, d, *J* = 0.8); δ_C (100 MHz, $CDCl_3$) 20.2, 23.8, 28.3, 28.5, 32.9, 41.5, 48.1, 78.0, 119.1, 141.9, 171.4; HRMS (ESI^+): Found: 231.1361; $C_{13}H_{20}NaO_2$ (MNa^+) Requires 231.1356 (–2.5 ppm error), Found: 209.1538; $C_{13}H_{21}O_2$ (MH^+) Requires 209.1536 (–0.9 ppm error).



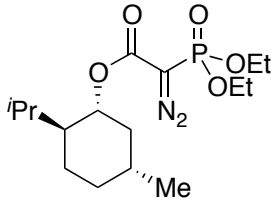
6d

(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl 2-(diethoxyphosphoryl)acetate (S5); Synthesised using general procedure A with L-menthol (781 mg, 5.00 mmol), toluene (25 mL), DEPAA (1.03 g, 5.25 mmol), DIPEA (2.26 mL, 13.0 mmol) and T3P (4.14 g, 6.50 mmol, 50% w/w solution in ethyl acetate) affording the *title compound* as a colourless oil (1.67 g, 100%). No further purification was required; R_f 0.44 (1:1 hexane:ethyl acetate); ν_{max} (thin film)/cm^{-1} 2955, 2931, 2870, 1728, 1456, 1390, 1369, 1264, 1114, 1052, 1023, 966; δ_H (400 MHz, $CDCl_3$) 0.73 (3 H, d, *J* = 6.9), 0.82–1.07 (9 H, m), 1.14–1.52 (8 H, m), 1.63–1.69 (2 H, m), 1.91–2.02 (2 H, m), 2.92 (2 H, d, *J* = 21.7), 4.10–4.18 (4 H, m), 4.70 (1 H, td, *J* = 10.9, *J* = 4.4); δ_C (100 MHz, $CDCl_3$) 16.0, 16.2 (d, *J* = 6.0), 20.7, 21.9, 23.1, 25.7, 31.3, 34.1, 34.5 (d, *J* = 133.3), 40.6, 46.8, 62.5 (app. t, *J* = 5.8), 75.6, 165.3 (d, *J* = 6.3); δ_P (162 MHz, $CDCl_3$) 20.7; HRMS (ESI^+): Found: 357.1801; $C_{16}H_{31}NaO_5P$ (MNa^+) Requires 357.1801 (0.2 ppm error).



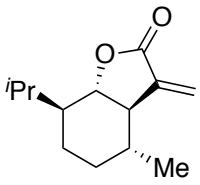
S5

(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl 2-diazo-2-(diethoxyphosphoryl)acetate (5e); Synthesised using general procedure B with (1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 2-(diethoxyphosphoryl)acetate **S5** (1.64 g, 4.90 mmol), THF (25.0 mL), LHMDS (5.90 mL, 5.90 mmol, 1.0 M solution in THF) and *p*-ABSA (1.41 g, 5.90 mmol). Purification by column chromatography (2:1 hexane:ethyl acetate) afforded the *title compound* as a yellow solid (1.59 g, 90%); R_f 0.67 (1:1 hexane:ethyl acetate); ν_{max} (thin film)/cm^{-1} 2956, 2127, 1697, 1457, 1369, 1275, 1119, 1021, 980, 957; δ_H (400 MHz, $CDCl_3$) 0.75 (3 H, d, *J* = 7.0), 0.80–1.08 (9 H, m), 1.32–1.52 (8 H, m), 1.64–1.70 (2 H, m), 1.81–1.92 (1 H, m), 1.99–2.04 (1 H, m), 4.07–4.25 (4 H, m), 4.77 (1 H, td, *J* = 10.9, *J* = 4.4); δ_C (100 MHz, $CDCl_3$) 16.0, 16.0 (d, *J* = 6.9), 16.1, 20.7, 21.9, 23.2, 26.1, 31.4, 34.0, 41.0, 47.1, 53.8 (d, *J* = 223.2), 63.4 (d, *J* = 5.7), 75.9, 163.1 (d, *J* = 11.4); δ_P (162 MHz, $CDCl_3$) 10.9; HRMS (ESI^+): Found: 383.1718; $C_{16}H_{29}N_2NaO_5P$ (MNa^+) Requires 383.1706 (–3.1 ppm error).



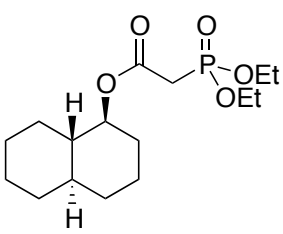
5e

(3a*R*,4*R*,7*S*,7a*S*)-7-Isopropyl-4-methyl-3-methylenehexahydrobenzofuran-2(3*H*)-one (6e); Synthesised using general procedure C with (1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 2-diazo-2-(diethoxyphosphoryl)acetate **5e** (71 mg, 0.197 mmol), DCM (4.0 mL), $Rh_2(oct)_4$ (3.1 mg, 3.9 μmol), THF (4.0 mL), potassium *tert*-butoxide (33.2 mg, 0.296 mmol) and paraformaldehyde (11.8 mg, 0.394 mmol). Purification by column chromatography (8:1 hexane:ethyl acetate) afforded the *title compound* as a colourless oil (30 mg, 73%); R_f 0.41 (8:1 hexane:ethyl acetate); ν_{max} (thin film)/cm^{-1} 2958, 1766, 1462, 1388, 1249, 1133, 1042, 980; δ_H (400 MHz, $CDCl_3$) 0.88 (3 H, d, *J* = 7.0), 0.94 (3 H, d, *J* = 7.0), 1.02–1.34 (5 H, m), 1.62–1.82 (4 H, m), 1.99 (1 H, hept. d, *J* = 7.0, *J* = 3.4), 2.19 (1 H, app. tt, *J* = 10.5, *J* = 3.1), 3.60 (1 H, app. t, *J* = 10.7), 5.63 (1 H, d, *J* = 3.0), 6.09 (1 H, d, *J* = 3.2); δ_C (100 MHz, $CDCl_3$) 17.6, 19.3, 19.9, 24.5, 28.1, 33.5, 35.4, 46.8, 53.9, 84.0, 118.3, 139.6, 171.0; HRMS (ESI^+): Found: 231.1354; $C_{13}H_{20}NaO_2$ (MNa^+) Requires 231.1356 (0.8 ppm error), Found: 209.1532; $C_{13}H_{21}O_2$ (MH^+) Requires 209.1536 (1.8 ppm error).



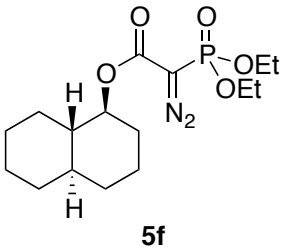
6e

(1*RS*,4a*SR*,8a*RS*)-Decahydronaphthalen-1-yl 2-(diethoxyphosphoryl)acetate (S6); Synthesised using general procedure A with (1*SR*,4a*RS*,8a*SR*)-decahydronaphthalen-1-ol (271 mg, 1.76 mmol), toluene (15 mL), DEPAA (0.30 mL, 1.85 mmol), DIPEA (0.82 mL, 4.60 mmol) and T3P (1.46 g, 2.30 mmol, 50% w/w solution in ethyl acetate) affording the *title compound* as a yellow oil (390 mg, 67%). No further purification was required; R_f 0.36 (3:7 petrol:ethyl acetate); ν_{max} (thin film)/cm^{-1} 2983, 2921, 2855, 1730, 1447, 1394, 1264, 1114, 1023, 963; δ_H (400 MHz, $CDCl_3$) 0.78–2.02 (22 H, m), 2.93 (2 H, d, *J* = 21.7), 4.11–4.18 (4 H, m), 4.50 (1 H, app. td, *J* = 10.3, *J* = 4.4); δ_C (100 MHz, $CDCl_3$) 16.3 (d, *J* = 6.6), 16.3 (d, *J* = 6.3), 23.7, 25.8, 26.1, 28.7, 31.9, 33.0, 33.8, 34.5 (d, *J* = 133.7), 41.2, 47.2, 62.5 (d, *J* = 6.2), 62.5 (d, *J* = 6.2), 78.6, 165.5 (d, *J* = 6.6); δ_P (162 MHz, $CDCl_3$) 20.8; HRMS (ESI^+): Found: 355.1648; $C_{16}H_{29}NaO_5P$ (MNa^+) Requires 355.1645 (–0.8 ppm error), Found: 333.1830; $C_{16}H_{30}O_5P$ (MH^+) Requires 333.1825 (–1.3 ppm error).



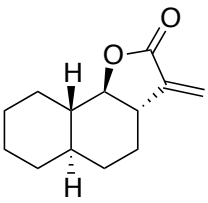
S6

(1*RS*,4a*SR*,8a*RS*)-Decahydronaphthalen-1-yl 2-diazo-2-(diethoxyphosphoryl)acetate (5f); Synthesised using general procedure B with (1*SR*,4a*RS*,8a*SR*)-decahydronaphthalen-1-yl 2-(diethoxyphosphoryl)acetate **S6** (390 mg, 1.17 mmol), THF (7.0 mL), NaH (56.2 mg, 1.40 mmol, 60% dispersion in mineral oil) and *p*-ABSA (337 mg, 1.40 mmol). Purification by column chromatography (2:1 petrol:ethyl acetate) afforded the *title compound* as a yellow oil (330 mg, 78%); R_f 0.67 (3:7 petrol:ethyl acetate); ν_{max} (thin film)/cm^{-1} 2983, 2925, 2853, 2132, 1697, 1448, 1344, 1275, 1120, 1019, 978; δ_H (400 MHz, $CDCl_3$) 0.84–2.05 (22 H, m), 4.10–4.27 (4 H, m), 4.58 (1 H, app. td, *J* = 10.2, *J* = 4.2); δ_C (100 MHz, $CDCl_3$) 16.0 (d, *J* = 7.1), 16.0 (d, *J* = 7.1), 23.6, 25.7, 26.0, 28.7, 32.2, 32.9, 33.4, 41.2, 47.4, 53.8 (d, *J* = 226.6), 63.4 (d, *J* = 5.7), 79.1, 163.3 (d, *J* = 12.0); δ_P (162 MHz, $CDCl_3$) 11.0; HRMS (ESI^+): Found: 381.1532; $C_{16}H_{27}N_2NaO_5P$ (MNa^+) Requires 381.1550 (4.7 ppm error), Found: 359.1718; $C_{16}H_{30}N_2O_5P$ (MH^+) Requires 359.1730 (3.4 ppm error).



5f

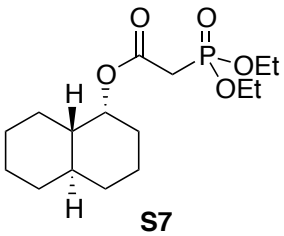
(3a*RS*,5a*SR*,9a*RS*,9b*SR*)-3-Methylenedecahydronaphtho[1,2-*b*]furan-2(9b*H*)-one (6f); Synthesised using general procedure C with (1*SR*,4a*RS*,8a*SR*)-decahydronaphthalen-1-yl 2-diazo-2-(diethoxyphosphoryl)acetate **5f** (79 mg, 0.221 mmol), DCM (4.4 mL), $Rh_2(oct)_4$ (3.4 mg, 4.4 μmol), THF (4.4 mL), potassium *tert*-butoxide (37.2 mg, 0.332 mmol) and paraformaldehyde (13.3 mg, 0.442 mmol). Purification by column chromatography (4:1 hexane:ethyl acetate) afforded the *title compound* as a white solid (29 mg, 64%); R_f 0.72 (4:1 hexane:ethyl acetate); m.p. 80–83 °C (literature 75–77 °C)[1]; ν_{max} (thin film)/cm^{-1} 2924, 2852, 1766, 1672, 1449, 1256, 1241, 1125, 990, 967; δ_H (400 MHz, $CDCl_3$) 0.98–1.46 (8 H, m), 1.65–1.77 (4 H, m), 2.08–2.13 (2 H, m), 2.43–2.51 (1 H, m), 3.44 (1 H, app. t, *J* = 10.6), 5.36 (1 H, d, *J* = 3.1), 6.04 (1 H, d, *J* = 3.3); δ_C (100 MHz, $CDCl_3$) 25.1, 25.2, 26.1, 29.0, 32.6, 32.8, 41.6, 47.0, 48.6, 86.7, 117.0, 139.9, 171.0; HRMS (ESI^+): Found: 229.1203; $C_{13}H_{18}NaO_2$ (MNa^+) Requires 229.1199 (–1.6 ppm error), Found: 207.1380; $C_{13}H_{19}O_2$ (MH^+) Requires 207.1380 (0.0 ppm error).



6f

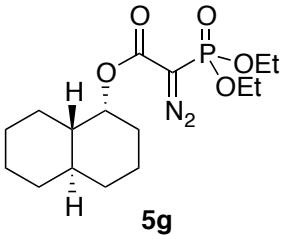
Obtained data in accord with reported literature.[1]

(1*SR*,4a*SR*,8a*RS*)-Decahydronaphthalen-1-yl 2-(diethoxyphosphoryl)acetate (S7); Synthesised using general procedure A with (1*RS*,4a*RS*,8a*SR*)-decahydronaphthalen-1-ol (201 mg, 1.30 mmol), toluene (10 mL), DEPAA (0.22 mL, 1.37 mmol), DIPEA (0.60 mL, 3.38 mmol) and T3P (1.08 g, 1.70 mmol, 50% w/w solution in ethyl acetate) affording the *title compound* as a yellow oil (425 mg, 98%). No further purification was required; R_f 0.54 (3:7 petrol:ethyl acetate); ν_{max} (thin film)/cm^{-1} 2982, 2924, 2853, 1731, 1448, 1394, 1263, 1114, 1021, 960; δ_H (400 MHz, $CDCl_3$) 0.79–1.95 (22 H, m), 2.94–3.00 (2 H, m), 4.13–4.20 (4 H, m), 4.93–4.96 (1 H, m); δ_C (100 MHz, $CDCl_3$) 16.3 (d, *J* = 6.3), 16.3 (d, *J* = 6.3), 20.4, 26.2, 26.4, 29.1, 30.6, 33.4, 34.2, 34.6 (d, *J* = 134.0), 36.3, 45.7, 62.5 (d, *J* = 6.3), 75.0, 165.4 (d, *J* = 6.8); δ_P (162 MHz, $CDCl_3$) 20.9; HRMS (ESI^+): Found: 355.1638; $C_{16}H_{29}NaO_5P$ (MNa^+) Requires 355.1645 (1.9 ppm error), Found: 333.1818; $C_{16}H_{30}O_5P$ (MH^+) Requires 333.1825 (2.2 ppm error).



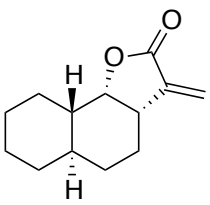
S7

(1*SR*,4a*SR*,8a*RS*)-Decahydronaphthalen-1-yl 2-diazo-2-(diethoxyphosphoryl)acetate (5g); Synthesised using general procedure B with (1*RS*,4a*RS*,8a*SR*)-decahydronaphthalen-1-yl 2-(diethoxyphosphoryl)acetate **S7** (475 mg, 1.43 mmol), THF (9.0 mL), NaH (68.6 mg, 1.72 mmol, 60% dispersion in mineral oil) and *p*-ABSA (412 mg, 1.72 mmol). Purification by column chromatography (2:1 petrol:ethyl acetate) afforded the *title compound* as a yellow oil (350 mg, 68%); R_f 0.80 (3:7 petrol:ethyl acetate); ν_{max} (thin film)/cm^{-1} 2927, 2857, 2126, 1698, 1448, 1290, 1277, 1118, 1023, 981; δ_H (400 MHz, $CDCl_3$) 0.87–1.97 (22 H, m), 4.11–4.29 (4 H, m), 5.02–5.04 (1 H, m); δ_C (100 MHz, $CDCl_3$) 16.0 (d, *J* = 6.9), 16.1 (d, *J* = 6.9), 20.3, 26.1, 26.3, 29.2, 30.8, 33.3, 34.0, 36.3, 45.7, 54.0 (d, *J* = 227.6), 63.2 (d, *J* = 5.5), 63.2 (d, *J* = 5.4), 75.3, 163.3 (d, *J* = 11.1); δ_P (162 MHz, $CDCl_3$) 11.6; HRMS (ESI^+): Found: 381.1556; $C_{16}H_{27}N_2NaO_5P$ (MNa^+) Requires 381.1550 (–1.7 ppm error), Found: 359.1731; $C_{16}H_{30}N_2O_5P$ (MH^+) Requires 359.1730 (–0.2 ppm error).



5g

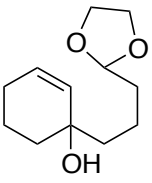
(3a*RS*,5a*SR*,9a*RS*,9b*RS*)-3-Methylenedecahydronaphtho[1,2-*b*]furan-2(9b*H*)-one (6g); Synthesised using general procedure C with (1*RS*,4a*RS*,8a*SR*)-decahydronaphthalen-1-yl 2-diazo-2-(diethoxyphosphoryl)acetate **5g** (82 mg, 0.229 mmol), DCM (4.6 mL), $Rh_2(oct)_4$ (3.6 mg, 4.6 μmol), THF (4.6 mL), potassium *tert*-butoxide (38.5 mg, 0.344 mmol) and paraformaldehyde (13.8 mg, 0.458 mmol). Purification by column chromatography (4:1 hexane:ethyl acetate) afforded the *title compound* as a colourless oil (32 mg, 68%); R_f 0.56 (4:1 hexane:ethyl acetate); ν_{max} (thin film)/cm^{-1} 2923, 2854, 1761, 1447, 1260, 1144, 1117, 1081, 949; δ_H (400 MHz, $CDCl_3$) 0.89–1.06 (2 H, m), 1.18–1.35 (5 H, m), 1.46–1.85 (7 H, m), 2.84–2.90 (1 H, m), 4.25 (1 H, dd, *J* = 4.6, *J* = 2.6), 5.49 (1 H, d, *J* = 1.0), 6.04 (1 H, d, *J* = 1.1); δ_C (100 MHz, $CDCl_3$) 26.0, 26.7, 28.7, 28.8, 31.0, 33.7, 34.9, 40.8, 43.8, 80.6, 119.1, 142.5, 171.0; HRMS (ESI^+): Found: 229.1207; $C_{13}H_{18}NaO_2$ (MNa^+) Requires 229.1199 (–3.4 ppm error), Found: 207.1384; $C_{13}H_{19}O_2$ (MH^+) Requires 207.1380 (–2.0 ppm error).



6g

Obtained data in accord with reported literature.[1]

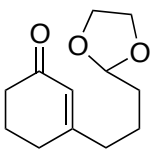
1-(3-(1,3-Dioxolan-2-yl)propyl)cyclohex-2-enol (15); Procedure developed based on literature precedent.[2] Freshly chopped lithium wire (1.33 g, 192 mmol) and naphthalene (410 mg, 3.20 mmol) in dry THF (132 mL) was stirred under argon was stirred until the mixture turned dark green and then continued for 1 h. The mixture was then cooled to –78 °C and neat 2-(3-chloropropyl)-1,3-dioxolane **14** (13.3 g, 88.0 mmol) was added over 5 mins during which time the mixture turned light green then colourless. The mixture was stirred at –78 °C for 1 h. To the now yellow solution was added freshly distilled neat 2-cyclohexen-1-one (7.69 g, 80.0 mmol) dropwise over 5 mins and stirred for 16 h with warming to rt. The mixture was diluted with sat. aq. NH_4Cl (800 mL) and extracted with EtOAc (2 × 1000 mL). The combined organic extracts were washed with brine (800 mL), dried over Na_2SO_4 and concentrated *in vacuo* to afford the title compound as a colourless oil (17.00 g, 100%), which was used without further purification; R_f 0.30 (2:1 hexane:ethyl acetate); ν_{max} (thin film)/cm^{-1} 3447, 2933, 2872, 1704, 1408, 1140, 1031, 941, 733; δ_H (400 MHz, $CDCl_3$) 1.40–2.09 (12 H, m), 3.83–3.98 (4 H, m), 4.86 (1 H, t, *J* = 4.8), 5.62 (1 H, d, *J* = 10.0), 5.80 (1 H, ddd, *J* = 10.0, *J* = 4.5, *J* = 2.9); δ_C (100 MHz, $CDCl_3$) 18.2, 19.0, 25.2, 34.3, 35.3, 42.1, 64.8, 69.6, 104.5, 130.0, 132.6; HRMS (ESI^+): Found: 235.1311; $C_{12}H_{20}NaO_3$ (MNa^+) Requires 235.1305 (–2.5 ppm error).



15

Obtained data in accord with those reported in the literature.[3]

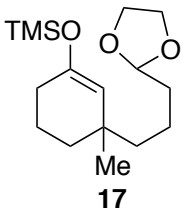
3-(3-(1,3-Dioxolan-2-yl)propyl)cyclohex-2-enone (16); Prepared according to the literature procedure.[3] To a suspension of PCC (4.31 g, 20.0 mmol) and Al_2O_3 (4.08 g, 40.0 mmol) in DCM (50 mL) cooled to 0 °C was added 1-(3-(1,3-dioxolan-2-yl)propyl)cyclohex-2-enol **15** (2.12 g, 10.0 mmol) and stirred at rt for 1 h. The mixture was filtered through a pad of Celite and silica. The filtrate was concentrated *in vacuo* and purified by column chromatography (1:1 hexane:ethyl acetate) to afford the title compound as a pale yellow oil (1.11 g, 52%); R_f 0.40 (1:1 hexane:ethyl acetate); ν_{max} (thin film)/cm^{-1} 2948, 2874, 1665, 1623, 1130, 1041; δ_H (400 MHz, $CDCl_3$) 1.59–1.70 (4 H, m), 1.98 (2 H, app. quin., *J* = 6.5), 2.24–2.29 (4 H, m), 2.35 (2 H, t, *J* = 6.7), 3.83–3.97 (4 H, m), 4.86 (1 H, t, *J* = 3.9), 5.88 (1 H, s); δ_C (100 MHz, $CDCl_3$) 21.2, 22.7, 29.5, 33.2, 37.3, 37.7, 64.9, 104.0, 125.8, 165.9, 199.8; HRMS (ESI^+): Found: 233.1153; $C_{12}H_{18}NaO_3$ (MNa^+) Requires 233.1148 (–2.2 ppm error), Found: 211.1336; $C_{12}H_{19}O_3$ (MH^+) Requires 211.1329 (–3.6 ppm error).



16

Obtained data in accord with reported literature.[3]

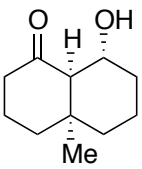
((3-(3-(1,3-Dioxolan-2-yl)propyl)-3-methylcyclohex-1-en-1-yl)oxy)trimethylsilane (17); Procedure developed based on literature precedent.[4] LiCl (90.0 mg, 2.12 mmol) and CuI (202 mg, 1.06 mmol) were thoroughly heat-dried under vacuum then dissolved in dry THF (106 mL) under argon at rt. The solution was cooled to –40 °C at which time 3-(3-(1,3-dioxolan-2-yl)propyl)cyclohex-2-enone **16** (4.46 g, 21.2 mmol) and freshly distilled TMSCl (2.96 mL, 23.3 mmol) were added and the solution stirred for 10 mins. MeMgCl (10.6 mL, 31.8 mmol, 3.0 M solution in THF) was added dropwise over 5 mins and stirred at –40 °C for 45 mins. The reaction mixture was then poured onto sat. aq. NH_4Cl (300 mL) and extracted with EtOAc (3 × 300 mL). The combined organic extracts were dried over $MgSO_4$ and concentrated *in vacuo* to afford the *title compound* as a yellow oil (6.18 g, 98%), which was used without further purification; R_f 0.81 (2:1 hexane:ethyl acetate); ν_{max} (thin film)/cm^{-1} 2951, 2871, 1662, 1363, 1251, 1204, 1192, 1132, 964, 884, 839; δ_H (400 MHz, $CDCl_3$) 0.17 (9 H, s), 0.94 (3 H, s), 1.22–1.43 (6 H, m), 1.58–1.72 (4 H, m), 1.82–2.02 (2 H, m), 3.80–4.00 (4 H, m), 4.65 (1 H, s), 4.84 (1 H, t, *J* = 4.8); δ_C (100 MHz, $CDCl_3$) 0.3, 18.9, 19.6, 27.9, 29.9, 34.5, 34.6, 34.7, 43.4, 64.8, 104.7, 114.6, 149.2; HRMS (ESI^+): Found: 321.1846; $C_{16}H_{30}NaO_3Si$ (MNa^+) Requires 321.1856 (3.2 ppm error), Found: 299.2031; $C_{16}H_{31}O_3Si$ (MH^+) Requires 299.2037 (1.9 ppm error).



17

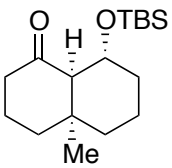
(4a*SR*,8*RS*,8a*RS*)-8-Hydroxy-4a-methyloctahydronaphthalen-1(2*H*)-one (18); Procedure developed based on literature precedent.[3] To a solution of ((3-(3-(1,3-dioxolan-2-yl)propyl)-3-methylcyclohex-1-en-1-yl)oxy)trimethylsilane **17** (298 mg, 1.00 mmol), in MeOH (3.0 mL) was added 10% aq. HCl (1.6 mL) and refluxed at 80 °C for 1 h. The reaction mixture was neutralised by sat. aq. $NaHCO_3$ and concentrated *in vacuo*. The aqueous layer was extracted with EtOAc (3 × 50 mL) and the combined organic extracts dried over $MgSO_4$ and concentrated *in vacuo*. Purification by column chromatography afforded the title compound as a brown solid (119 mg, 65%); R_f 0.32 (1:1 hexane:ethyl acetate); m.p. 52–55 °C; ν_{max} (thin film)/cm^{-1} 3406, 2931, 2870, 1702, 1048; δ_H (400 MHz, $CDCl_3$) 0.93 (3 H, s), 1.10–1.25 (3 H, m), 1.50 (1 H, dtd, *J* = 13.8, *J* = 3.3, *J* = 1.1), 1.60–1.67 (2 H, m), 1.71–2.10 (6 H, m), 2.26 (1 H, ddq, *J* = 14.5, *J* = 4.8, *J* = 1.7), 2.53 (1 H, ddd, *J* = 14.5, *J* = 13.3, *J* = 7.3), 4.00 (1 H, app. tt, *J* = 10.5, *J* = 5.1); δ_C (100 MHz, $CDCl_3$) 19.8, 22.1, 27.7, 29.8, 35.0, 37.1, 38.5, 39.4, 67.4, 69.6, 215.0 (CO); HRMS (ESI^+): Found: 205.1204; $C_{11}H_{18}NaO_2$ (MNa^+) Requires 205.1199 (–2.2 ppm error), Found: 183.1382; $C_{11}H_{19}O_2$ (MH^+) Requires 183.1380 (–1.6 ppm error).

Obtained data in accord with reported literature.[3]



18

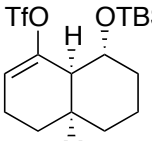
(4a*SR*,8*RS*,8a*RS*)-8-((*tert*-Butyldimethylsilyl)oxy)-4a-methyloctahydronaphthalen-1(2*H*)-one (19); To a solution of (4a*SR*,8*RS*,8a*RS*)-8-hydroxy-4a-methyloctahydronaphthalen-1(2*H*)-one **18** (273 mg, 1.50 mmol) in DCM (15 mL) at 0 °C was added 2,6-lutidine (0.44 mL, 3.75 mmol) then TBSOTf (0.38 mL, 1.65 mmol). The solution was stirred at 0 °C for 1 h then quenched with NH_4Cl (50 mL) and the organic fraction separated. The aqueous layer was extracted with DCM (2 × 50 mL) and the combined organic fractions dried over $MgSO_4$ and concentrated *in vacuo*. Purification by column chromatography (4:1 hexane:ethyl acetate) afforded the *title compound* as a white crystalline solid (440 mg, 99%); R_f 0.67 (4:1 hexane:ethyl acetate); m.p. 55–58 °C; ν_{max} (thin film)/cm^{-1} 2929, 2857, 1713, 1472, 1462, 1252, 1089, 832, 774; δ_H (400 MHz, $CDCl_3$) –0.01 (3 H, s), 0.03 (3 H, s), 0.82 (9 H, s), 0.94 (3 H, s), 1.10–1.29 (3 H, m), 1.45 (1 H, dtd, *J* = 13.7, *J* = 3.8, *J* = 0.7), 1.53–1.67 (2 H, m), 1.80–2.04



19

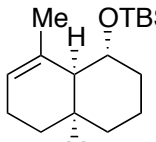
(5 H, m), 2.18 (1 H, dddd, *J* = 13.7, *J* = 4.6, *J* = 3.1, *J* = 1.5), 2.46 (1 H, ddd, *J* = 13.5, *J* = 12.7, *J* = 6.7), 4.12 (1 H, app. td, *J* = 9.9, *J* = 4.2); δ_C (100 MHz, $CDCl_3$) –4.9, –3.8, 17.9, 19.7, 22.6, 25.6, 27.9, 31.2, 35.1, 37.9, 38.3, 39.6, 67.0, 70.5, 212.7; HRMS (ESI^+): Found: 319.2055; $C_{17}H_{32}NaO_2Si$ (MNa^+) Requires 319.2064 (2.8 ppm error), Found: 297.2232; $C_{17}H_{33}O_2Si$ (MH^+) Requires 297.2244 (4.1 ppm error).

(4a*SR*,8*RS*,8a*RS*)-8-((*tert*-Butyldimethylsilyl)oxy)-4a-methyl-3,4,4a,5,6,7,8,8a-octahydronaphthalen-1-yl trifluoromethanesulfonate (20); To a solution of (4a*SR*,8*RS*,8a*RS*)-8-((*tert*-butyldimethylsilyl)oxy)-4a-methyloctahydronaphthalen-1(2*H*)-one **19** (720 mg, 2.43 mmol) in THF (12.2 mL) cooled to –40 °C under argon was added LHMDS (7.28 mL, 7.28 mmol, 1.0 M solution in THF) dropwise. The solution was stirred at –40 °C for 1 h then trifluoromethanesulfonic anhydride (1.23 mL, 7.28 mmol) was added dropwise. The solution was stirred at –40 °C for 20 mins then quenched by addition of water (25 mL). The mixture was extracted with diethyl ether (3 × 50 mL) and the combined organic extracts dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification by column chromatography (40:1 hexane:diethyl ether) afforded the *title compound* as a colourless oil (835 mg, 80%); R_f 0.77 (8:1 hexane:ethyl acetate); ν_{max} (thin film)/cm^{-1} 2931, 2858, 1416, 1246, 1205, 1144, 1116, 1082, 1028, 934, 874, 836, 775, 628, 601; δ_H (400 MHz, $CDCl_3$) 0.02 (3 H, s), 0.03 (3 H, s), 0.88 (9 H, s), 1.02–1.08 (4 H, m), 1.25–1.49 (4 H, m), 1.57–1.64 (1 H, m), 1.68–1.81 (2 H, m), 1.97 (1 H, d, *J* = 8.5), 2.24–2.29 (2 H, m), 3.69 (1 H, td, *J* = 9.3, *J* = 3.7), 5.68 (1 H, t, *J* = 3.9); δ_C (100 MHz, $CDCl_3$) –4.8, –4.9, 17.9, 19.3, 21.5, 25.8, 26.9, 28.0, 35.4, 35.7, 38.1, 52.9, 74.3, 117.7, 118.5 (q, *J* = 319.9), 151.9; HRMS (ESI^+): Found: 451.1546; $C_{18}H_{31}F_3NaO_4SSi$ (MNa^+) Requires 451.1557 (2.4 ppm error), Found: 429.1737; $C_{18}H_{32}F_3O_4SSi$ (MH^+) Requires 429.1737 (0.1 ppm error).



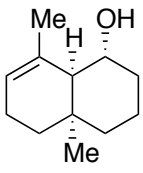
20

***tert*-Butyl(((1*RS*,4a*SR*,8a*SR*)-4a,8-dimethyl-1,2,3,4,4a,5,6,8a-octahydronaphthalen-1-yl)oxy)dimethylsilane (21);** Prepared according to a modified literature procedure.[5] To a solution of (4a*SR*,8*RS*,8a*RS*)-8-((*tert*-butyldimethylsilyl)oxy)-4a-methyl-3,4,4a,5,6,7,8,8a-octahydronaphthalen-1-yl trifluoromethanesulfonate **20** (355 mg, 0.828 mmol) in THF (1.24 mL) and NMP (3.31 mL) under argon was added $Fe(acac)_3$ (322 mg, 0.911 mmol). The solution was cooled to –25 °C and MeMgCl (2.76 mL, 8.28 mmol, 3.0 M solution in THF) was added dropwise. The orange solution was stirred at –25 °C for 1 h then quenched by careful addition of sat. aq. NH_4Cl (25 mL). The mixture was extracted with diethyl ether (3 × 25 mL) and the combined organic extracts dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification by column chromatography (hexane) afforded the *title compound* as a colourless oil (201 mg, 82%); R_f 0.45 (hexane); ν_{max} (thin film)/cm^{-1} 2928, 2858, 1462, 1373, 1251, 1095, 1071, 1041, 921, 860, 834, 773; δ_H (400 MHz, $CDCl_3$) 0.01 (3 H, s), 0.03 (3 H, s), 0.87–0.95 (12 H, m), 1.19–1.55 (7 H, m), 1.69–1.79 (5 H, m), 1.98–2.15 (2 H, m), 3.61 (1 H, app. td, *J* = 9.6, *J* = 3.8), 5.24–5.30 (1 H, m); δ_C (100 MHz, $CDCl_3$) –4.6, –4.5, 18.1, 19.9, 23.0, 26.0, 26.4, 27.4, 28.0, 34.0, 36.4, 39.0, 54.1, 75.8, 120.1, 136.6; HRMS (ESI^+): Found: 317.2265; $C_{18}H_{34}NaOSi$ (MNa^+) Requires 317.2271 (2.0 ppm error).



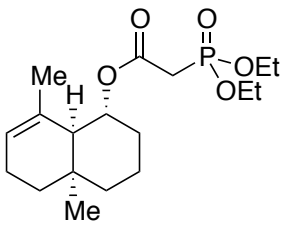
21

(1*RS*,4a*SR*,8a*SR*)-4a,8-Dimethyl-1,2,3,4,4a,5,6,8a-octahydronaphthalen-1-ol (22); To a solution of *tert*-butyl(((1*RS*,4a*SR*,8a*SR*)-4a,8-dimethyl-1,2,3,4,4a,5,6,8a-octahydronaphthalen-1-yl)oxy)dimethylsilane **21** (321 mg, 1.09 mmol) in THF (5.5 mL) under argon at rt was added TBAF (5.45 mL, 5.00 mmol, 1.0 M in THF). The solution was refluxed for 1 h, allowed to cool to rt, then quenched by addition of water (25 mL). The aqueous layer was extracted with diethyl ether (3 × 25 mL) and the combined organic extracts dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification by column chromatography (8:1 hexane:ethyl acetate) afforded the *title compound* as a white solid (172 mg, 88%); R_f 0.39 (8:1 hexane:ethyl acetate); m.p. 65–67 °C; ν_{max} (thin film)/cm^{-1} 3337, 2924, 2863, 2842, 1450, 1373, 1353, 1180, 1133, 1080, 1061, 1027, 1008, 854, 804; δ_H (400 MHz, $CDCl_3$) 0.86–0.91 (4 H, m), 1.21–1.31 (2 H, m), 1.37–1.56 (5 H, m), 1.69–1.77 (1 H, m), 1.85–1.91 (4 H, m), 2.04–2.08 (2 H, m), 3.56 (1 H, ddd, *J* = 11.2, *J* = 9.7, *J* = 4.3), 5.34–5.37 (1 H, m); δ_C (100 MHz, $CDCl_3$) 20.1, 23.1, 26.5, 27.0, 27.1, 34.0, 36.6, 39.7, 54.6, 75.6, 120.9, 135.9; HRMS (ESI$^+$): Found: 203.1405; $C_{12}H_{20}NaO$ (MNa^+) Requires 203.1406 (0.5 ppm error).



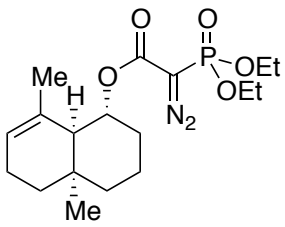
22

(1*RS*,4a*SR*,8a*SR*)-4a,8-Dimethyl-1,2,3,4,4a,5,6,8a-octahydronaphthalen-1-yl 2-(diethoxyphosphoryl)acetate (23); Synthesised using general procedure A with (1*RS*,4a*SR*,8a*SR*)-4a,8-dimethyl-1,2,3,4,4a,5,6,8a-octahydronaphthalen-1-ol **22** (145 mg, 0.804 mmol), toluene (4.0 mL), DEPAA (166 mg, 0.844 mmol), DIPEA (0.36 mL, 2.09 mmol) and T3P (665 mg, 1.05 mmol, 50% w/w solution in THF) affording the *title compound* as a yellow oil (288 mg, 100%). No further purification was required; R_f 0.33 (1:1 hexane:ethyl acetate); ν_{max} (thin film)/cm^{-1} 2978, 2931, 2869, 1731, 1450, 1393, 1375, 1261, 1111, 1051, 1020, 967; δ_H (400 MHz, $CDCl_3$) 0.89–0.97 (4 H, m), 1.23–1.36 (8 H, m), 1.41–1.58 (3 H, m), 1.68 (1 H, d, *J* = 9.9), 1.72–1.80 (4 H, m), 1.96–2.13 (3 H, m), 2.86–3.01 (2 H, m), 4.13–4.21 (4 H, m), 4.82 (1 H, app. td, *J* = 10.4, *J* = 4.2), 5.32–5.37 (1 H, m); δ_C (100 MHz, $CDCl_3$) 16.2 (d, *J* = 5.7), 16.3 (d, *J* = 5.7), 19.4, 22.8, 25.4, 26.9, 27.4, 31.9, 34.0, 34.6 (d, *J* = 135.1), 38.9, 50.5, 62.5 (app. t, *J* = 5.3), 79.2, 122.0, 134.0, 165.2 (d, *J* = 5.8); δ_P (162 MHz, $CDCl_3$) 20.5; HRMS (ESI$^+$): Found: 381.1802; $C_{18}H_{31}NaO_5P$ (MNa^+) Requires 381.1801 (–0.1 ppm error), Found: 359.1981; $C_{18}H_{32}O_5P$ (MH^+) Requires 359.1982 (0.1 ppm error).



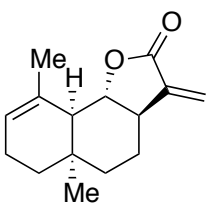
23

(1*RS*,4a*SR*,8a*SR*)-4a,8-Dimethyl-1,2,3,4,4a,5,6,8a-octahydronaphthalen-1-yl 2-diazo-2-diethoxyphosphoryl)acetate (24); Synthesised using general procedure B with (1*RS*,4a*SR*,8a*SR*)-4a,8-dimethyl-1,2,3,4,4a,5,6,8a-octahydronaphthalen-1-yl 2-diethoxyphosphoryl)acetate **23** (279 mg, 0.778 mmol), THF (3.9 mL), LHMDS (0.93 mL, 0.934 mmol, 1.0 M solution in THF) and *p*-ABSA (224 mg, 0.934 mmol). Purification by column chromatography (4:1 hexane:ethyl acetate) afforded the *title compound* as a pale yellow oil (265 mg, 89%); R_f 0.63 (1:1 hexane:ethyl acetate); ν_{max} (thin film)/cm^{-1} 2932, 2870, 2124, 1705, 1451, 1376, 1286, 1273, 1022, 980; δ_H (400 MHz, $CDCl_3$) 0.91–0.99 (4 H, m), 1.24–1.38 (8 H, m), 1.43–1.60 (3 H, m), 1.68–1.79 (5 H, m), 1.92–2.15 (3 H, m), 4.10–4.28 (4 H, m), 4.95 (1 H, app. td, *J* = 10.2, *J* = 4.2), 5.35–5.39 (1 H, m); δ_C (100 MHz, $CDCl_3$) 16.0 (d, *J* = 7.2), 19.3, 22.8, 25.1, 26.9, 27.6, 32.3, 34.1, 38.7, 50.6, 53.7 (d, *J* = 227.8), 63.4 (d, *J* = 5.8), 63.5 (d, *J* = 5.8), 79.1, 122.4, 133.6, 162.7 (d, *J* = 12.5); δ_P (162 MHz, $CDCl_3$) 11.0; HRMS (ESI$^+$): Found: 407.1704; $C_{18}H_{29}N_2NaO_5P$ (MNa^+) Requires 407.1706 (0.5 ppm error).

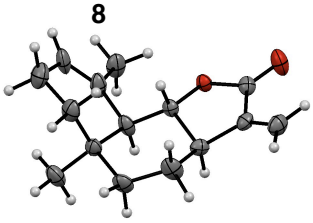


24

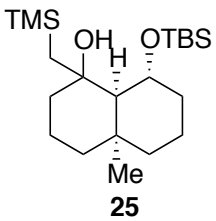
(3a*RS*,5a*RS*,9a*SR*,9b*RS*)-5a,9-Dimethyl-3-methylene-3a,4,5,5a,6,7,9a,9b-octahydronaphtho[1,2-*b*]furan-2(3*H*)-one (8); Synthesised using general procedure C with (1*RS*,4a*SR*,8a*SR*)-4a,8-dimethyl-1,2,3,4,4a,5,6,8a-octahydronaphthalen-1-yl 2-diazo-2-diethoxyphosphoryl)acetate **24** (72 mg, 0.187 mmol), DCM (3.7 mL), $Rh_2(oct)_4$ (2.9 mg, 3.7 μmol), THF (3.7 mL), potassium *tert*-butoxide (31.5 mg, 0.281 mmol) and paraformaldehyde (11.2 mg, 0.374 mmol). Purification by column chromatography (8:1 hexane:ethyl acetate) afforded the *title compound* as a white crystalline solid (28 mg, 64%); R_f 0.33 (8:1 hexane:ethyl acetate); m.p. 63–66 °C; ν_{max} (thin film)/cm^{-1} 2931, 2871, 1771, 1451, 1378, 1278, 1244, 1081, 1127, 1014, 980; δ_H (400 MHz, $CDCl_3$) 0.98–1.04 (4 H, m), 1.42–1.77 (4 H, m), 1.83–1.86 (4 H, m), 1.93–1.97 (1 H, m), 2.06–2.12 (2 H, m), 2.45–2.53 (1 H, m), 3.73 (1 H, app. t, *J* = 10.9), 5.39 (1 H, d, *J* = 3.1), 5.39–5.43 (1 H, m), 6.06 (1 H, d, *J* = 3.3); δ_C (100 MHz, $CDCl_3$) 21.8, 22.8, 24.7, 26.7, 27.9, 34.9, 40.2, 49.2, 50.5, 87.4, 117.3, 121.1, 133.4, 139.3, 170.9; HRMS (ESI$^+$): Found: 255.1355; $C_{15}H_{20}NaO_2$ (MNa^+) Requires 255.1356 (0.2 ppm error), Found: 233.1545; $C_{15}H_{21}O_2$ (MH^+) Requires 233.1536 (–4.0 ppm error).



8

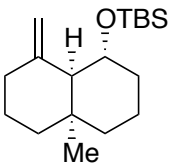


4a*SR*,8*RS*,8a*RS*)-8-((*tert*-Butyldimethylsilyl)oxy)-4a-methyl-1-((trimethylsilyl)methyl)decahydronaphthalen-1-ol (25); To a solution of (trimethylsilyl)methyllithium (4.63 mL, 4.63 mmol, 1.0 M in pentane) in THF (2.5 mL) cooled to –78 °C under argon was added dropwise via cannula a solution of (4a*SR*,8*RS*,8a*RS*)-8-((*tert*-butyldimethylsilyl)oxy)-4a-methyloctahydronaphthalen-1(2*H*)-one **19** (458 mg, 1.54 mmol) in THF (2.5 mL) pre-cooled to –78 °C. The solution was stirred at –78 °C for 30 mins then rt for 1 h. The solution was quenched by careful addition of water (10 mL) and stirred for 10 mins. The aqueous layer was extracted with diethyl ether (3 × 25 mL) and the combined organic extracts dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification by column chromatography (20:1 hexane:ethyl acetate) afforded the *title compound* as a colourless oil (497 mg, 84%); R_f 0.58 (8:1 hexane:ethyl acetate); ν_{max} (thin film)/cm^{-1} 2928, 2857, 1462, 1361, 1249, 1056, 1027, 1005, 862, 836, 772; δ_H (400 MHz, $CDCl_3$) 0.05 (3 H, s), 0.06 (3 H, s), 0.07 (9 H, s), 0.89 (9 H, s), 0.92–1.00 (2 H, m), 1.12 (3 H, s), 1.16–1.97 (14 H, m), 4.33–4.36 (1 H, m); δ_C (100 MHz, $CDCl_3$) –4.6, –4.2, 0.6, 16.9, 17.6, 17.9, 25.8, 32.0, 32.3, 33.1, 33.8, 34.2, 42.0, 42.7, 56.4, 69.1, 74.7; HRMS (ESI$^+$): Found: 407.2754; $C_{21}H_{44}NaO_2Si_2$ (MNa^+) Requires 407.2772 (4.3 ppm error).



25

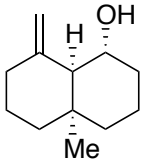
***tert*-Butyldimethyl(((1*RS*,4a*RS*,8a*RS*)-4a-methyl-8-methylenedecahydronaphthalen-1-yl)oxy)silane (26);** Sodium hydride (60% dispersion in mineral oil) was purified by washing with hexane and drying *in vacuo* immediately prior to the reaction. To a suspension of sodium hydride (827 mg, 20.7 mmol) in THF (6.5 mL) under argon was added via cannula a solution of (4a*SR*,8*RS*,8a*RS*)-8-((*tert*-butyldimethylsilyl)oxy)-4a-methyl-1-((trimethylsilyl)methyl)decahydronaphthalen-1-ol **25** (497 mg, 1.29 mmol) in THF (3 mL). The mixture was heated to reflux and stirred for 4 h then cooled to rt. The mixture was carefully poured into sat. aq. NH_4Cl (100 mL) and extracted with diethyl ether (3 × 100 mL). The combined organic extracts were dried over $MgSO_4$, filtered and concentrated *in vacuo* affording the *title compound* as a yellow oil (385 mg, 100%). No further purification was required; R_f 0.88 (8:1 hexane:ethyl acetate); ν_{max} (thin film)/cm^{-1} 2929, 2856, 1650, 1461, 1362, 1248, 1096, 1082, 1055, 919, 888, 833, 772; δ_H (400 MHz, $CDCl_3$) –0.03 (3 H,



26

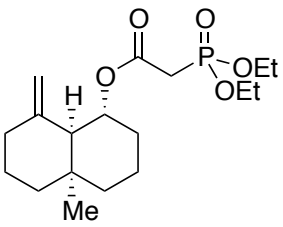
s), 0.01 (3 H, s), 0.84 (9 H, s), 0.89 (3 H, s), 0.91–0.97 (1 H, m), 1.16–1.28 (2 H, m), 1.37 (1 H, app. dtd, *J* = 13.5, *J* = 3.2, *J* = 1.6), 1.44–1.67 (4 H, m), 1.70–1.78 (2 H, m), 1.92 (1 H, app. ddtd, *J* = 12.5, *J* = 4.7, *J* = 3.2, *J* = 1.6), 2.00–2.13 (2 H, m), 3.76 (1 H, ddd, *J* = 10.8, *J* = 10.0, *J* = 4.6), 4.66 (1 H, app. dd, *J* = 2.8, *J* = 1.2), 4.76 (1 H, app. t, *J* = 2.1); δ_C (100 MHz, $CDCl_3$) –4.8, –4.1, 18.1, 20.0, 23.3, 25.9, 28.4, 31.0, 31.3, 36.0, 36.4, 40.1, 60.0, 68.9, 112.0, 146.4; HRMS (ESI^+): Found: 317.2267; $C_{18}H_{34}NaOSi$ (MNa^+) Requires 317.2271 (1.4 ppm error).

(1*RS*,4a*RS*,8a*RS*)-4a-Methyl-8-methylenedecahydronaphthalen-1-ol (27); To a solution of *tert*-butyldimethyl(((1*RS*,4a*RS*,8a*RS*)-4a-methyl-8-methylenedecahydronaphthalen-1-yl)oxy)silane **26** (85 mg, 0.289 mmol) in THF (1.5 mL) under argon at rt was added TBAF (1.44 mL, 1.44 mmol, 1.0 M in THF). The solution was refluxed for 1 h, allowed to cool to rt, then quenched by addition of water (10 mL). The aqueous layer was extracted with diethyl ether (3 × 25 mL) and the combined organic extracts dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification by column chromatography (8:1 hexane:ethyl acetate) afforded the *title compound* as a pale yellow oil (42 mg, 81%); R_f 0.31 (8:1 hexane:ethyl acetate); ν_{max} (thin film)/cm^{-1} 3431, 3068, 2933, 2867, 1646, 1450, 1264, 1159, 1064, 1049, 1022, 1011, 896; δ_H (400 MHz, $CDCl_3$) 0.89 (3 H, s), 0.97 (1 H, app. dddt, *J* = 13.3, *J* = 3.9, *J* = 2.6, *J* = 1.3), 1.11–1.27 (2 H, m), 1.39–1.80 (8 H, m), 2.03–2.18 (3 H, m), 3.70 (1 H, ddd, *J* = 11.0, *J* = 10.2, *J* = 4.4), 4.78 (1 H, app. t, *J* = 2.2), 4.91 (1 H, app. t, *J* = 2.1); δ_C (100 MHz, $CDCl_3$) 19.7, 22.7, 28.3, 30.2, 30.8, 33.6, 35.7, 39.9, 60.2, 67.1, 112.8, 146.9; HRMS (ESI^+): Found: 203.1400; $C_{12}H_{20}NaO$ (MNa^+) Requires 203.1406 (3.3 ppm error).



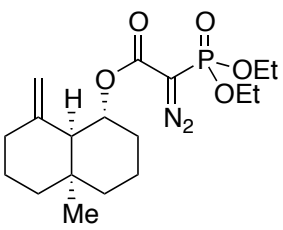
27

(1*RS*,4a*RS*,8a*RS*)-4a-Methyl-8-methylenedecahydronaphthalen-1-yl 2-(diethoxyphosphoryl)acetate (28); Synthesised using general procedure A with (1*RS*,4a*RS*,8a*RS*)-4a-methyl-8-methylenedecahydronaphthalen-1-ol **27** (108 mg, 0.600 mmol), toluene (3.0 mL), DEPAA (124 mg, 0.630 mmol), DIPEA (0.27 mL, 1.56 mmol) and T3P (496 mg, 0.780 mmol, 50% w/w solution in THF) affording the *title compound* as a yellow oil (176 mg, 82%). No further purification was required; R_f 0.14 (2:1 hexane:ethyl acetate); ν_{max} (thin film)/cm^{-1} 2978, 2932, 2869, 1731, 1648, 1445, 1393, 1267, 1113, 1051, 1024, 965; δ_H (400 MHz, $CDCl_3$) 0.89 (3 H, s), 0.94–1.00 (1 H, m), 1.16–1.66 (13 H, m), 1.78 (1 H, td, *J* = 13.5, *J* = 4.6), 1.85 (1 H, d, *J* = 10.8), 1.96–2.07 (2 H, m), 2.13–2.22 (1 H, m), 2.83 (1 H, dd, *J* = 21.4, *J* = 14.5), 2.90 (1 H, dd, *J* = 21.4, *J* = 14.5), 4.09–4.17 (4 H, m), 4.62 (1 H, app. t, *J* = 2.0), 4.73 (1 H, app. t, *J* = 2.3), 5.15 (1 H, app. td, *J* = 11.2, *J* = 4.5); δ_C (100 MHz, $CDCl_3$) 16.3 (d, *J* = 6.5), 19.7, 22.7, 28.0, 30.3, 30.7, 31.8, 34.2 (d, *J* = 134.6), 36.3, 39.6, 56.8, 62.5 (app. t, *J* = 5.7), 72.0, 112.0, 145.8, 165.1 (d, *J* = 5.9); δ_P (162 MHz, $CDCl_3$) 20.7; HRMS (ESI^+): Found: 381.1783; $C_{18}H_{31}NaO_5P$ (MNa^+) Requires 381.1801 (4.7 ppm error).



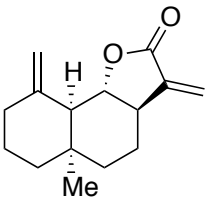
28

(1*RS*,4a*RS*,8a*RS*)-4a-Methyl-8-methylenedecahydronaphthalen-1-yl 2-diazo-2-diethoxyphosphoryl)acetate (29); Synthesised using general procedure B with (1*RS*,4a*RS*,8a*RS*)-4a-methyl-8-methylenedecahydronaphthalen-1-yl 2-diethoxyphosphoryl)acetate **28** (175 mg, 0.488 mmol), THF (2.5 mL), LHMDS (0.59 mL, 0.585 mmol, 1.0 M solution in THF) and *p*-ABSA (141 mg, 0.585 mmol). Purification by column chromatography (2:1 hexane:ethyl acetate) afforded the *title compound* as a colourless oil (146 mg, 78%); R_f 0.28 (2:1 hexane:ethyl acetate); ν_{max} (thin film)/cm^{-1} 2982, 2934, 2870, 2124, 1703, 1445, 1361, 1289, 1273, 1218, 1161, 1120, 1021, 978; δ_H (400 MHz, $CDCl_3$) 0.91 (3 H, s), 0.96–1.02 (1 H, m), 1.17–1.67 (13 H, m), 1.78 (1 H, td, *J* = 13.5, *J* = 4.6), 1.86 (1 H, d, *J* = 10.8), 1.98–2.09 (2 H, m), 2.16–2.25 (1 H, m), 4.03–4.24 (4 H, m), 4.64 (1 H, app. t, *J* = 2.1), 4.74 (1 H, app. t, *J* = 2.3), 5.22 (1 H, app. td, *J* = 11.2, *J* = 4.5); δ_C (100 MHz, $CDCl_3$) 16.1 (app. t, *J* = 7.6), 19.8, 22.7, 28.0, 30.3, 30.7, 32.1, 36.4, 39.5, 53.0 (d, *J* = 225.1), 57.2, 63.4 (d, *J* = 5.5), 63.5 (d, *J* = 5.7), 72.2, 111.9, 146.1, 162.6 (d, *J* = 12.4); δ_P (162 MHz, $CDCl_3$) 11.0; HRMS (ESI$^+$): Found: 385.1884; $C_{18}H_{30}N_2O_5P$ (MH^+) Requires 385.1887 (0.7 ppm error).

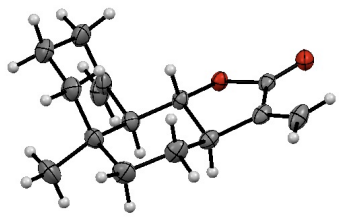


29

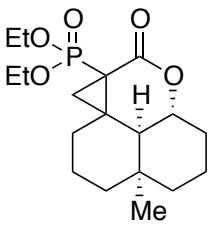
(3a*RS*,5*aRS*,9a*RS*,9b*RS*)-5a-Methyl-3,9-dimethylenedecahydronaphtho[1,2-b]furan-2(9b*H*)-one (9) and Diethyl ((3a*RS*,3a^1*SR*,6a*RS*)-6a-methyl-2-oxododecahydrobenzo[*de*]cyclopropa[*c*]chromen-1a-yl)phosphonate (30); Synthesised using general procedure C with (1*RS*,4a*RS*,8a*RS*)-4a-methyl-8-methylenedecahydronaphthalen-1-yl 2-diazo-2-(diethoxyphosphoryl)acetate **29** (77 mg, 0.200 mmol), DCM (4.0 mL), $Rh_2(OAc)_4$ (1.8 mg, 4.0 μmol), THF (4.0 mL), potassium *tert*-butoxide (33.7 mg, 0.300 mmol) and paraformaldehyde (12.0 mg, 0.400 mmol). Purification by column chromatography (8:1 hexane:ethyl acetate → 1:4 hexane:ethyl acetate) afforded the *title compounds* **9** as a white crystalline solid (21 mg, 45%) and **30** as a pale yellow oil (8 mg, 11%).



9



Data for **9**: R_f 0.39 (4:1 hexane:ethyl acetate); m.p. 66–68 °C; ν_{max} (thin film)/cm^{-1} 2932, 2869, 1770, 1650, 1456, 1378, 1247, 1171, 1131, 1024, 991, 964, 936, 892; δ_H (400 MHz, $CDCl_3$) 1.00 (3 H, s), 1.07 (1 H, dddt, *J* = 13.6, *J* = 3.9, *J* = 2.6, *J* = 1.3), 1.42–1.71 (5 H, m), 1.77 (1 H, td, *J* = 13.6, *J* = 4.6), 1.96–2.02 (1 H, m), 2.09–2.23 (3 H, m), 2.45 (1 H, app. tq, *J* = 11.1, *J* = 3.2), 4. 1 (1 H, app. t, *J* = 11.1), 4.80 (1 H, app. t, *J* = 1.8), 4.88 (1 H, app. t, *J* = 2.0), 5.40 (1 H, d, *J* = 3.0), 6.07 (1 H, d, *J* = 3.2); δ_C (100 MHz, $CDCl_3$) 21.9, 22.9, 27.6, 30.0, 31.7, 37.3, 40.0, 48.8, 55.9, 80.6, 112.7, 117.3, 139.8, 144.0, 170.6; HRMS (ESI$^+$): Found: 255.1362; $C_{15}H_{20}NaO_2$ (MNa^+) Requires 255.1356 (–2.5 ppm error), Found: 233.1541; $C_{15}H_{21}O_2$ (MH^+) Requires 233.1536 (–2.2 ppm error).

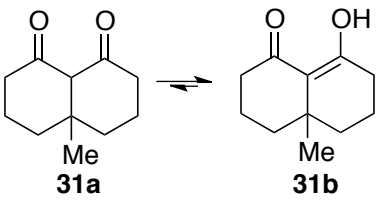


30

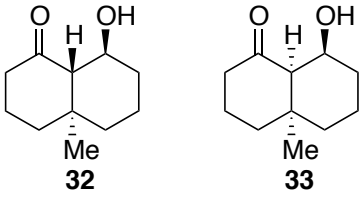
Data for **30**: R_f 0.33 (1:1 hexane:ethyl acetate); ν_{max} (thin film)/cm^{-1} 2980, 2934, 2868, 1735, 1452, 1392, 1375, 1317, 1296, 1249, 1208, 1051, 1031, 971; δ_H (400 MHz, $CDCl_3$) 0.58 (1 H, d, *J* = 9.8), 1.07–1.14 (4 H, m), 1.20–1.68 (15 H, m), 1.80 (1 H, dd, *J* = 17.5, *J* = 4.8), 1.85–1.93 (1 H, m), 2.05–2.08 (1 H, m), 2.13–2.22 (1 H, m), 4.09–4.34 (4 H, m), 4.47 (1 H, ddd, *J* = 10.9, *J* = 9.9, *J* = 5.7); δ_C (100 MHz, $CDCl_3$) 16.2 (d, *J* = 6.8), 16.3 (d, *J* = 6.6), 18.4 (C-2/8), 19.6, 24.5 (d, *J* = 182.9), 26.4 (d, *J* = 4.8), 26.7 (d, *J* = 3.9), 29.1, 29.6 (d, *J* = 3.2), 31.6, 32.1, 34.3, 40.2, 55.4 (d, *J* = 2.0), 62.4 (d, *J* = 7.4), 63.2 (d, *J* = 5.7), 78.4, 168.3

(d, *J* = 6.0); δ_P (162 MHz, $CDCl_3$) 21.6; HRMS (ESI^+): Found: 379.1635; $C_{18}H_{29}NaO_5P$ (MNa^+) Requires 379.1645 (2.7 ppm error), Found: 357.1817; $C_{18}H_{30}O_5P$ (MH^+) Requires 357.1825 (2.2 ppm error).

4a-Methylhexahydronaphthalene-1,8(2*H*,8a*H*)-dione (31); To a solution of (4a*SR*,8*RS*,8a*RS*)-8-hydroxy-4a-methyloctahydronaphthalen-1(2*H*)-one **18** (2.59 g, 14.2 mmol) in DCM (140 mL), cooled to 0 °C was added DMP (9.04 g, 21.3 mmol). The solution was stirred for 15 mins at 0 °C then 30 mins at rt after which a mixture of 1:1 sat. aq. $NaHCO_3$: sat. aq. $Na_2S_2O_3$ (500 mL) and DCM (500 mL) was added and stirred vigourously for 1 h. The organic phase was separated and the aqueous phase extracted with DCM (2 × 500 mL). The combined organic extracts were dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification by column chromatography (2:1 hexane:ethyl acetate) afforded the *title compound* as a pale yellow solid (2.04 g, 80%); N.B. The product appears as two spots by TLC, a major (less polar) and minor (more polar); R_f 0.94 (major), 0.71 (minor) (2:1 hexane:ethyl acetate); m.p. 50–53 °C; ν_{max} (thin film)/cm^{-1} 2940, 1593, 1457, 1407, 1336, 1248, 1168, 1081, 1038, 962, 829; δ_H (400 MHz, $CDCl_3$) 1.03 (3 H, s), 1.37 (2 H, td, *J* = 13.4, *J* = 4.0), 1.54 (2 H, dt, *J* = 13.0, *J* = 3.4), 1.69–1.77 (2 H, m), 1.87–1.99 (2 H, m), 2.28–2.43 (4 H, m), 16.02 (1 H, s); δ_C (100 MHz, $CDCl_3$) 17.1, 26.7, 32.1, 32.8, 37.4, 114.4, 189.9; HRMS (ESI^+): Found: 203.1036; $C_{11}H_{16}NaO_2$ (MNa^+) Requires 203.1043 (3.1 ppm error), Found: 181.1215; $C_{11}H_{17}O_2$ (MH^+) Requires 181.1223 (4.7 ppm error).



(4a*SR*,8*SR*,8a*SR*)-8-Hydroxy-4a-methyloctahydronaphthalen-1(2*H*)-one (32) and (4a*SR*,8*SR*,8a*RS*)-8-Hydroxy-4a-methyloctahydronaphthalen-1(2*H*)-one (33); To a solution of 4a-methylhexahydronaphthalene-1,8(2*H*,8a*H*)-dione **31** (2.04 g, 11.3 mmol) in MeOH (57 mL) cooled to 0 °C under argon was added $NaBH_4$ (470 mg, 12.4 mmol) in small portions over 1 h. The solution was stirred at 0 °C for 1 h then quenched with sat. aq. $NaHCO_3$ (25 mL) and concentrated *in vacuo*. To the resulting white residue was added DCM (50 mL) and water (50 mL). The organic layer was separated and the aqueous layer extracted with DCM (2 × 50 mL). The combined organic extracts were dried over $MgSO_4$ and concentrated *in vacuo*. The crude material was purified by column chromatography (1:1 hexane:diethyl ether → ethyl acetate) affording the *title compounds* **32** (216 mg, 10%) and **33** (333 mg, 16%) in addition to mixed fractions of **32** and **33** (202 mg, 10%).

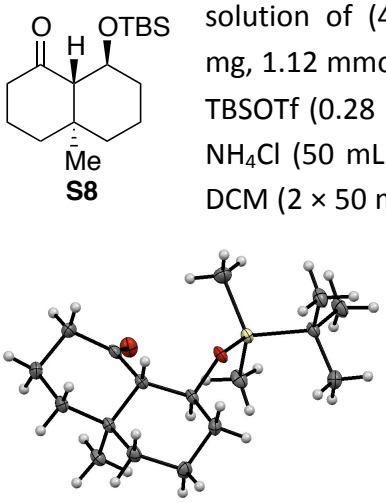


Data for **32**: Colourless oil, R_f 0.61 (1:1 hexane:ethyl acetate); ν_{max} (thin film)/cm^{-1} 3554, 2931, 1699, 1458, 1384, 1275, 1178, 1087, 1056, 1038, 936; δ_H (400 MHz, $CDCl_3$) 0.80 (3 H, s), 1.17–1.36 (2 H, m), 1.41–1.47 (1 H, m), 1.49–1.67 (4 H, m), 1.82–2.02 (3 H, m), 2.12 (1 H, d, *J* 9.8), 2.25–2.36 (2 H, m), 3.17 (1 H, s), 3.94 (1 H, app. td, *J* 10.6, *J* 4.5); δ_C (100 MHz, $CDCl_3$) 17.9, 19.8, 22.2, 32.9, 39.7, 40.2, 40.8, 41.4, 64.5, 65.5, 214.7; HRMS (ESI^+): Found: 205.1206; $C_{11}H_{18}NaO_2$ (MNa^+) Requires 205.1199 (–3.4 ppm error).

Data for **33**: Colourless oil, R_f 0.68 (4:1 hexane:ethyl acetate); ν_{max} (thin film)/cm^{-1} 3420, 2937, 1692, 1458, 1421, 1380, 1321, 1267, 1233, 1189, 1141, 1057; δ_H (400 MHz, $CDCl_3$) 0.97–1.02 (1 H, m), 1.07 (3 H, s), 1.34 (1 H, td, *J* 13.0, 4.2), 1.46–1.71 (5 H, m), 1.80–1.93 (3 H, m), 2.19–2.33 (2 H, m), 2.45–2.46 (1 H, m), 3.70–3.81 (2 H, m); δ_C (100 MHz, $CDCl_3$) 20.3, 21.2, 26.5, 31.1, 31.8, 39.2, 40.8, 42.3, 59.2, 68.4, 216.0; HRMS (ESI^+): Found: 205.1192; $C_{11}H_{18}NaO_2$ (MNa^+) Requires 205.1199 (3.5 ppm error).

Note: The structure of **32** was assigned retrospectively from the X-ray crystal structure of compound **S8**.

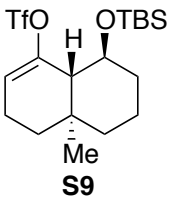
(4a*SR*,8*SR*,8a*SR*)-8-((*tert*-Butyldimethylsilyl)oxy)-4a-methyloctahydronaphthalen-1(2*H*)-one (S8); To a solution of (4a*SR*,8*SR*,8a*SR*)-8-hydroxy-4a-methyloctahydronaphthalen-1(2*H*)-one **32** (205 mg, 1.12 mmol) in DCM (11.2 mL) at 0 °C was added 2,6-lutidine (0.33 mL, 2.80 mmol) then TBSOTf (0.28 mL, 1.24 mmol). The solution was stirred at 0 °C for 1 h then quenched with NH_4Cl (50 mL) and the organic fraction separated. The aqueous layer was extracted with DCM (2 × 50 mL) and the combined organic fractions dried over $MgSO_4$ and concentrated *in vacuo*. Purification by column chromatography (4:1 hexane:ethyl acetate) afforded the *title compound* as a white crystalline solid (1.12 g, 100%); R_f 0.24 (20:1 hexane:ethyl acetate); m.p. 36–39 °C; ν_{max} (thin film)/cm^{-1} 2925, 2853, 1714, 1470, 1381, 1358, 1242, 1142, 1094, 1077, 1031, 1004, 940, 901, 830, 779, 666; δ_H (400 MHz, benzene-d_6) 0.28 (3 H, s), 0.38 (3 H, s), 0.57 (3 H, s), 0.90–1.44 (17 H, m), 1.48–1.61 (1 H, m), 1.87–1.95 (2 H, m), 2.09–2.15 (2 H, m), 4.01–4.07 (1 H, m); δ_C (100 MHz, benzene-d_6) –4.3, –4.1, 17.7, 18.4, 20.2, 23.6, 26.4, 36.3, 40.2, 40.9, 41.8, 42.5, 64.8, 65.7, 208.6; HRMS (ESI^+): Found: 319.2062; $C_{17}H_{32}NaO_2Si$ (MNa^+) Requires 319.2064 (0.5 ppm error), Found: 297.2244; $C_{17}H_{33}O_2Si$ (MH^+) Requires 297.2244 (0.0 ppm error).



S8

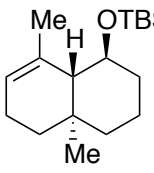
(4a*SR*,8*SR*,8a*SR*)-8-((*tert*-Butyldimethylsilyl)oxy)-4a-methyl-3,4,4a,5,6,7,8,8a-octahydronaphthalen-1-yl trifluoromethanesulfonate (S9); To a solution of (4a*SR*,8*SR*,8a*SR*)-8-((*tert*-butyldimethylsilyl)oxy)-4a-methyloctahydronaphthalen-1(2*H*)-one **S8** (95 mg, 0.320 mmol) and trifluoromethanesulfonic anhydride (64.0 μL, 0.384 mmol) in DCM (1.6 mL) at rt under argon was added DTBMP (99 mg, 0.480 mmol) in one portion. The suspension was stirred for 2 h at rt then concentrated *in vacuo*. The residue was taken up in hexane (25 mL), filtered and washed with hexane (3 × 25 mL). The solution was concentrated *in vacuo*. Purification by column chromatography (20:1 hexane:ethyl acetate) afforded the *title compound* as a yellow oil (92 mg, 67%); R_f 0.55 (20:1 hexane:ethyl acetate); ν_{max} (thin film)/cm^{-1} 2930, 2856, 1669, 1416, 1245, 1198, 1142, 1079, 1032, 1005, 974, 940, 894, 857, 833, 776, 602; δ_H (400 MHz, $CDCl_3$) 0.09 (3 H, s), 0.10 (3 H, s), 0.89–0.93 (12 H, m), 1.19–1.46 (5 H, m), 1.55–1.73 (2 H, m), 2.00–2.06 (1 H, m), 2.11–2.38 (3 H, m), 3.94 (1 H, app. td, *J* = 10.3, *J* = 4.3), 5.70–5.73 (1 H, m); δ_C (100 MHz, $CDCl_3$) –4.2, –3.2, 16.9, 18.4, 20.2, 21.1, 26.4, 36.8, 36.9, 38.3, 38.7, 52.9, 69.2, 118.8 (q, *J* = 321.6), 119.1 (q, *J* = 1.7), 151.0; HRMS (ESI^+): Found: 451.1545; $C_{18}H_{31}F_3NaO_4SSi$ (MNa^+) Requires 451.1557 (2.5 ppm error), Found: 429.1732; $C_{18}H_{32}F_3O_4SSi$ (MH^+) Requires 429.1737 (1.2 ppm error).

Procedure developed from literature precedent.[6-9]



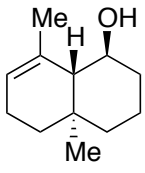
S9

***tert*-Butyl(((1*SR*,4a*SR*,8a*RS*)-4a,8-dimethyl-1,2,3,4,4a,5,6,6,8a-octahydronaphthalen-1-yl)oxy)dimethylsilane (S10);** Prepared according to a modified literature procedure.[5] To a solution of (4a*SR*,8*SR*,8a*SR*)-8-((*tert*-butyldimethylsilyl)oxy)-4a-methyl-3,4,4a,5,6,7,8,8a-octahydronaphthalen-1-yl trifluoromethanesulfonate **S9** (154 mg, 0.359 mmol) in THF (0.54 mL) and NMP (1.44 mL) under argon was added $Fe(acac)_3$ (139 mg, 0.395 mmol). The solution was cooled to –25 °C and MeMgCl (1.20 mL, 3.59 mmol, 3.0 M solution in THF) was added dropwise. The orange solution was stirred at –25 °C for 1 h then quenched by careful addition of sat. aq. NH_4Cl (25 mL). The mixture was extracted with diethyl ether (3 × 25 mL) and the combined organic extracts dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification by column chromatography (hexane) afforded the *title compound* as a colourless oil (97 mg, 92%); R_f 0.50 (hexane); ν_{max} (thin film)/cm^{-1} 2927, 2855, 1461, 1378, 1362, 1255, 1119, 1069, 1006, 946, 884, 832, 772, 666; δ_H (400 MHz, $CDCl_3$) 0.06 (3 H, s), 0.09 (3 H, s), 0.80 (3 H, s), 0.90 (9 H, s), 1.11–1.66 (7 H, m), 1.82–1.84 (3 H, m), 1.89–2.12 (4 H, m), 3.79 (1 H, app. td, *J* = 10.3, *J* = 4.7), 5.28–5.32 (1 H, m); δ_C (100 MHz, $CDCl_3$) –3.5, –2.8, 16.8, 18.3, 20.3, 22.9, 25.5, 26.7, 34.9, 38.6, 38.7, 40.1, 53.5, 70.7, 122.5, 135.9; HRMS (ESI^+): Found: 317.2261; $C_{18}H_{34}NaOSi$ (MNa^+) Requires 317.2271 (3.3 ppm error).



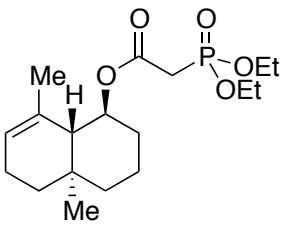
S10

(1*SR*,4a*SR*,8a*RS*)-4a,8-Dimethyl-1,2,3,4,4a,5,6,6,8a-octahydronaphthalen-1-ol (S11); To a solution of *tert*-butyl(((1*SR*,4a*SR*,8a*RS*)-4a,8-dimethyl-1,2,3,4,4a,5,6,6,8a-octahydronaphthalen-1-yl)oxy)dimethylsilane **S10** (90 mg, 0.306 mmol) in THF (1.5 mL) under argon at rt was added TBAF (1.53 mL, 1.53 mmol, 1.0 M in THF). The solution was refluxed for 1 h, allowed to cool to rt, then quenched by addition of water (25 mL). The aqueous layer was extracted with diethyl ether (3 × 25 mL) and the combined organic extracts dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification by column chromatography (8:1 hexane:ethyl acetate) afforded the *title compound* as a white solid (51 mg, 92%); R_f 0.27 (8:1 hexane:ethyl acetate); m.p. 59–61 °C; ν_{max} (thin film)/cm^{-1} 3350, 2910, 2848, 1446, 1375, 1352, 1267, 1163, 1079, 1058, 1018, 933, 8966, 843; δ_H (400 MHz, $CDCl_3$) 0.79 (3 H, s), 1.10–1.44 (6 H, m), 1.54–1.70 (2 H, m), 1.77–1.82 (1 H, m), 1.88 (3 H, s), 1.95–2.12 (3 H, m), 3.95 (1 H, app. td, *J* = 10.4, *J* = 4.4), 5.31–5.35 (1 H, m); δ_C (100 MHz, $CDCl_3$) 16.6, 20.2, 23.0, 24.6, 34.8, 38.2, 38.2, 40.0, 53.5, 69.3, 123.3, 134.8; HRMS (ESI^+): Found: 203.1403; $C_{12}H_{20}NaO$ (MNa^+) Requires 203.1406 (1.7 ppm error).



S11

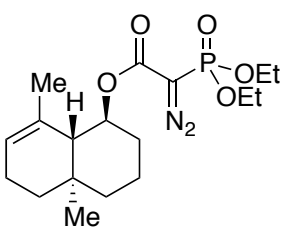
(1*SR*,4a*SR*,8a*RS*)-4a,8-Dimethyl-1,2,3,4,4a,5,6,6,8a-octahydronaphthalen-1-yl 2-(diethoxyphosphoryl)acetate (S12); Synthesised using general procedure A with (1*SR*,4a*SR*,8a*RS*)-4a,8-dimethyl-1,2,3,4,4a,5,6,6,8a-octahydronaphthalen-1-ol **S11** (49 mg, 0.272 mmol), toluene (1.4 mL), DEPAA (56 mg, 0.285 mmol), DIPEA (0.12 mL, 0.707 mmol) and T3P (225 mg, 0.354 mmol, 50% w/w solution in THF) affording the *title compound* as a yellow oil (97 mg, 99%). No further purification was required; R_f 0.39 (1:1 hexane:ethyl acetate); ν_{max} (thin film)/cm^{-1} 2928, 1729, 1444, 1393, 1261, 1208, 1163, 1114, 1051, 1021, 967, 823, 783; δ_H (400 MHz, $CDCl_3$) 0.81 (3 H, s), 1.11–1.71 (16 H, m), 1.93–2.14 (4 H, m), 2.82–2.97 (2 H, m), 4.10–4.18 (4 H, m), 4.90 (1 H, app. td, *J* = 11.0, *J* = 4.9), 5.29–5.33 (1 H, m); δ_C (100 MHz, $CDCl_3$) 16.2–16.3 (3 C, m), 19.7, 22.7, 23.4, 33.2, 34.8 (d, *J* = 135.1), 34.9, 38.0, 39.5, 49.3, 62.5 (d, *J* = 6.4), 62.5 (d, *J* = 6.4), 74.1, 123.7, 133.2, 165.3 (d, *J* = 5.8); δ_P (162 MHz,



S12

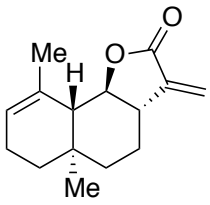
$CDCl_3$) 20.5; HRMS (ESI^+): Found: 381.1806; $C_{18}H_{31}NaO_5P$ (MNa^+) Requires 381.1801 (–1.1 ppm error), Found: 359.1977; $C_{18}H_{32}O_5P$ (MH^+) Requires 359.1982 (1.3 ppm error).

(1*SR*,4a*SR*,8a*RS*)-4a,8-Dimethyl-1,2,3,4,4a,5,6,8a-octahydronaphthalen-1-yl 2-diazo-2-diethoxyphosphoryl)acetate (34); Synthesised using general procedure B with (1*SR*,4a*SR*,8a*RS*)-4a,8-dimethyl-1,2,3,4,4a,5,6,8a-octahydronaphthalen-1-yl 2-diethoxyphosphoryl)acetate **S12** (96 mg, 0.268 mmol), THF (1.34 mL), LHMDS (0.32 mL, 0.321 mmol, 1.0 M solution in THF) and *p*-ABSA (77 mg, 0.321 mmol). Purification by column chromatography (4:1 hexane:ethyl acetate) afforded the *title compound* as a pale yellow oil (91 mg, 88%); R_f 0.74 (1:1 hexane:ethyl acetate); ν_{max} (thin film)/cm^{-1} 2929, 2122, 1697, 1445, 1368, 1318, 1297, 1270, 1163, 1017, 977, 957, 804, 743, 590, 553; δ_H (400 MHz, $CDCl_3$) 0.80 (3 H, s), 1.10–1.71 (16 H, m), 1.92–2.12 (4 H, m), 4.04–4.24 (4 H, m), 4.98 (1 H, app. td, *J* = 11.0, *J* = 5.0), 5.30–5.33 (1 H, m); δ_C (100 MHz, $CDCl_3$) 16.0, 16.1, 16.3, 19.7, 22.7, 23.0, 33.8, 35.0, 37.9, 39.4, 49.4, 54.0 (d, *J* = 229.1), 63.4 (d, *J* = 5.7), 63.6 (d, *J* = 5.9), 74.2, 123.8, 132.9, 162.7 (d, *J* = 12.2); δ_P (162 MHz, $CDCl_3$) 10.8; HRMS (ESI^+): Found: 407.1716; $C_{18}H_{29}N_2NaO_5P$ (MNa^+) Requires 407.1706 (–2.3 ppm error).



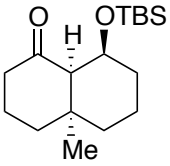
34

α-cyclocostunolide ((3a*SR*,5a*RS*,9a*RS*,9b*SR*)-5a,9-Dimethyl-3-methylene-3a,4,5,5a,6,7,9a,9b-octahydronaphtho[1,2-*b*]furan-2(3*H*)-one) (12); Synthesised using general procedure C with (1*SR*,4a*SR*,8a*RS*)-4a,8-dimethyl-1,2,3,4,4a,5,6,8a-octahydronaphthalen-1-yl 2-diazo-2-diethoxyphosphoryl)acetate **34** (90 mg, 0.234 mmol), DCM (4.7 mL), $Rh_2(oct)_4$ (3.6 mg, 4.7 μmol), THF (4.7 mL), potassium *tert*-butoxide (39.4 mg, 0.351 mmol) and paraformaldehyde (14.1 mg, 0.468 mmol). Purification by column chromatography (8:1 hexane:ethyl acetate) afforded the *title compound* as a white crystalline solid (28 mg, 52%); R_f 0.38 (8:1 hexane:ethyl acetate); m.p. 80–82 °C (lit. 83–84 °C)[10]; ν_{max} (thin film)/cm^{-1} 2920, 2851, 1771, 1445, 1377, 1344, 1286, 1249, 1220, 1132, 1118, 1076, 1046, 1014, 982; δ_H (400 MHz, $CDCl_3$) 0.90 (3 H, s), 1.21–1.74 (6 H, m), 1.83 (3 H, s), 1.97–2.18 (2 H, m), 2.34 (1 H, d, *J* = 11.2), 2.52 (1H, app. tq, *J* = 11.2, *J* = 3.5), 3.86 (1 H, app. t, *J* = 11.0), 5.35–5.38 (2 H, m), 6.05 (1 H, d, *J* = 3.2); δ_C (100 MHz, $CDCl_3$) 17.4, 21.5, 22.8, 23.7, 35.9, 37.7, 39.2, 51.2, 51.5, 82.2, 116.4, 122.4, 133.0, 139.4, 171.0; HRMS (ESI^+): Found: 255.1360; $C_{15}H_{20}NaO_2$ (MNa^+) Requires 255.1356 (–1.7 ppm error).
Obtained data in accord with reported literature.[10-12]



12

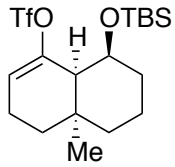
(4a*SR*,8*SR*,8a*RS*)-8-((*tert*-Butyldimethylsilyl)oxy)-4a-methyloctahydronaphthalen-1(2*H*)-one (S13); To a solution of (4a*SR*,8*SR*,8a*RS*)-8-hydroxy-4a-methyloctahydronaphthalen-1(2*H*)-one **33** (316 mg, 1.73 mmol) in DCM (17.3 mL) at 0 °C was added 2,6-lutidine (0.50 mL, 4.33 mmol) then TBSOTf (0.44 mL, 1.91 mmol). The solution was stirred at 0 °C for 1 h then quenched with NH_4Cl (50 mL) and the organic fraction separated. The aqueous layer was extracted with DCM (2 × 50 mL) and the combined organic fractions dried over $MgSO_4$ and concentrated *in vacuo*. Purification by column chromatography (4:1 hexane:ethyl acetate) afforded the *title compound* as a pale yellow oil (491 mg, 96%); R_f 0.20 (20:1 hexane:ethyl acetate); ν_{max} (thin film)/cm^{-1} 2951, 2930, 2856, 1699, 1471, 1462, 1383, 1255, 1226, 1172, 1150, 1060, 1033, 973, 961, 900, 836, 775, 688; δ_H (400 MHz, benzene-d_6) –0.09 (3 H, s), –0.04 (3 H, s), 0.73 (3 H, s), 0.81–1.41 (14 H, m), 1.57–1.68 (3 H, m), 1.84 (1 H, qt,



S13

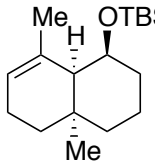
J = 13.1, *J* = 3.3), 1.94–1.96 (1 H, m), 2.33–2.56 (3 H, m), 4.02 (1 H, app. q, *J* = 3.2); δ_C (100 MHz, benzene-d_6) –5.0, –4.9, 16.3, 18.1, 20.7, 26.1, 29.5, 31.7, 33.8, 35.4, 39.6, 40.6, 61.7, 69.9, 212.3; HRMS (ESI^+): Found: 319.2068; $C_{17}H_{32}NaO_2Si$ (MNa^+) Requires 319.2064 (–1.4 ppm error), Found: 297.2249; $C_{17}H_{33}O_2Si$ (MH^+) Requires 297.2244 (–1.5 ppm error).

(4a*SR*,8*SR*,8a*RS*)-8-((*tert*-Butyldimethylsilyl)oxy)-4a-methyl-3,4,4a,5,6,7,8,8a-octahydronaphthalen-1-yl trifluoromethanesulfonate (S14); To a solution of (4a*SR*,8*SR*,8a*RS*)-8-((*tert*-butyldimethylsilyl)oxy)-4a-methyloctahydronaphthalen-1(2*H*)-one **S13** (325 mg, 1.10 mmol) in THF (5.5 mL) cooled to –40 °C under argon was added LHMDS (3.29 mL, 3.29 mmol, 1.0 M solution in THF) dropwise. The solution was stirred at –40 °C for 1 h then trifluoromethanesulfonic anhydride (0.55 mL, 3.29 mmol) was added dropwise. The solution was stirred at –40 °C for 20 mins then quenched by addition of water (25 mL). The mixture was extracted with diethyl ether (3 × 50 mL) and the combined organic extracts dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification by column chromatography (hexane) afforded the *title compound* as a colourless oil (291 mg, 62%); R_f 0.74 (20:1 hexane:ethyl acetate); ν_{max} (thin film)/cm^{-1} 2931, 2857, 1416, 1246, 1205, 1143, 1074, 1042, 990, 977, 939, 908, 878, 837, 802, 776, 604; δ_H (400 MHz, $CDCl_3$) –0.02 (3 H, s), 0.02 (3 H, s), 0.84–0.94 (13 H, m), 1.26–1.40 (3 H, m), 1.51–1.59 (1 H, m), 1.74–1.86 (2 H, m), 1.94 (1 H, d, *J* = 3.1), 2.12–2.32 (3 H, m), 4.11 (1 H, app. q, *J* = 2.8), 5.75–5.77 (1 H, m); δ_C (100 MHz, $CDCl_3$) –5.5, –4.9, 15.4, 17.8, 21.6, 25.7, 28.0, 28.2, 33.2, 33.7, 39.9, 50.2, 65.9, 118.5 (q, *J* = 320.2), 119.2, 149.0; HRMS (ESI^+): Found: 451.1541; $C_{18}H_{31}F_3NaO_4SSi$ (MNa^+) Requires 451.1557 (3.4 ppm error).



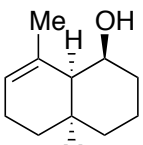
S14

***tert*-Butyl(((1*SR*,4a*SR*,8a*SR*)-4a,8-dimethyl-1,2,3,4,4a,5,6,8a-octahydronaphthalen-1-yl)oxy)dimethylsilane (S15);** Prepared according to a modified literature procedure.[5] To a solution of (4a*SR*,8*SR*,8a*RS*)-8-((*tert*-butyldimethylsilyl)oxy)-4a-methyl-3,4,4a,5,6,7,8,8a-octahydronaphthalen-1-yl trifluoromethanesulfonate **S14** (270 mg, 0.630 mmol) in THF (0.95 mL) and NMP (2.52 mL) under argon was added $Fe(acac)_3$ (245 mg, 0.693 mmol). The solution was cooled to –25 °C and MeMgCl (2.10 mL, 6.30 mmol, 3.0 M solution in THF) was added dropwise. The orange solution was stirred at –25 °C for 1 h then quenched by careful addition of sat. aq. NH_4Cl (25 mL). The mixture was extracted with diethyl ether (3 × 25 mL) and the combined organic extracts dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification by column chromatography (hexane) afforded the *title compound* as a colourless oil (110 mg, 59%); R_f 0.93 (hexane); ν_{max} (thin film)/cm^{-1} 2928, 2855, 1446, 1378, 1251, 1153, 1079, 1060, 1040, 977, 907, 834, 798, 772, 679; δ_H (400 MHz, $CDCl_3$) –0.04 (3 H, s), 0.00 (3 H, s), 0.77–0.89 (13 H, m), 1.23–1.49 (5 H, m), 1.63–1.65 (3 H, m), 1.74–1.88 (2 H, m), 1.98–2.04 (2 H, m), 2.28–2.35 (1 H, m), 4.06 (1 H, app. q, *J* = 2.7), 5.37–5.39 (1 H, m); δ_C (100 MHz, $CDCl_3$) –5.2, –4.7, 16.1, 18.0, 22.5, 23.3, 25.7, 28.6, 28.8, 31.9, 34.4, 40.8, 51.5, 67.2, 122.6, 131.9; HRMS ($APCI^+$): Found: 295.2443; $C_{18}H_{35}OSi$ (MH^+) Requires 295.2452 (2.9 ppm error).



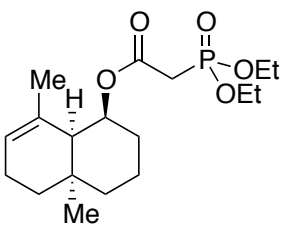
S15

(1*SR*,4a*SR*,8a*SR*)-4a,8-Dimethyl-1,2,3,4,4a,5,6,8a-octahydronaphthalen-1-ol (S16); To a solution of *tert*-butyl(((1*SR*,4a*SR*,8a*SR*)-4a,8-dimethyl-1,2,3,4,4a,5,6,8a-octahydronaphthalen-1-yl)oxy)dimethylsilane **S15** (99 mg, 0.336 mmol) in THF (1.68 mL) under argon at rt was added TBAF (1.68 mL, 1.68 mmol, 1.0 M in THF). The solution was refluxed for 24 h, allowed to cool to rt, then quenched by addition of water (25 mL). The aqueous layer was extracted with diethyl ether (3 × 25 mL) and the combined organic extracts dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification by column chromatography (8:1 hexane:ethyl acetate) afforded the *title compound* as a colourless oil (43 mg, 71%); R_f 0.45 (8:1 hexane:ethyl acetate); ν_{max} (thin film)/cm^{-1} 3354, 2929, 2871, 2842, 1448, 1389, 1377, 1342, 1255, 1199, 1162, 1072, 1012, 963, 949, 831; δ_H (400 MHz, $CDCl_3$) 0.80 (3 H, s), 0.87–0.92 (1 H, m), 1.22–1.86 (10 H, m), 1.97–2.17 (4 H, m), 3.98 (1 H, app. q, *J* = 3.0), 5.65–5.68 (1 H, m); δ_C (100 MHz, $CDCl_3$) 15.8, 21.9, 22.8, 28.4, 28.5, 31.3, 31.6, 40.4, 51.2, 65.3, 125.1, 132.3; HRMS (ESI^+): Found: 203.1406; $C_{12}H_{20}NaO$ (MNa^+) Requires 203.1406 (0.0 ppm error).



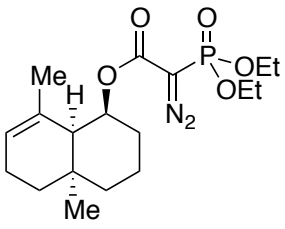
S16

(1*SR*,4a*SR*,8a*SR*)-4a,8-Dimethyl-1,2,3,4,4a,5,6,8a-octahydronaphthalen-1-yl 2-(diethoxyphosphoryl)acetate (S17); Synthesised using general procedure A with (1*SR*,4a*SR*,8a*SR*)-4a,8-dimethyl-1,2,3,4,4a,5,6,8a-octahydronaphthalen-1-ol **S16** (21 mg, 0.116 mmol), toluene (0.58 mL), DEPAA (24 mg, 0.122 mmol), DIPEA (0.05 mL, 0.302 mmol) and T3P (96 mg, 0.151 mmol, 50% w/w solution in THF). Purification by column chromatography (1:1 hexane:ethyl acetate) afforded the *title compound* as a pale yellow oil (26 mg, 63%); R_f 0.38 (1:1 hexane:ethyl acetate); ν_{max} (thin film)/cm^{-1} 2929, 1732, 1448, 1393, 1261, 1113, 1021, 968, 813; δ_H (400 MHz, $CDCl_3$) 0.83–0.91 (4 H, m), 1.24–1.54 (9 H, m), 1.58 (1 H, d, *J* = 2.6), 1.62–1.64 (3 H, m), 1.67–1.92 (2 H, m), 1.98–2.16 (3 H, m), 2.79–2.94 (2 H, m), 4.10–4.18 (4 H, m), 5.32 (1 H, app. q, *J* = 3.1), 5.38–5.41 (1 H, m); δ_C (100 MHz, $CDCl_3$) 16.2–16.3 (2 C, m), 16.4, 22.3, 22.8, 28.0, 28.3, 30.4, 31.6, 34.5 (d, *J* = 134.5), 40.0, 49.4, 62.4 (d, *J* = 6.5), 62.5 (d, *J* = 6.5), 70.4, 122.9, 131.1, 164.8 (d, *J* = 6.1); δ_P (162 MHz, $CDCl_3$) 20.9; HRMS (ESI^+): Found: 381.1802; $C_{18}H_{31}NaO_5P$ (MNa^+) Requires 381.1801 (–0.3 ppm error), Found: 359.1975; $C_{18}H_{32}O_5P$ (MH^+) Requires 359.1982 (2.0 ppm error).



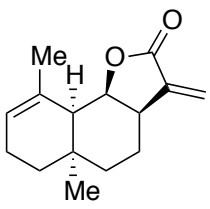
S17

(1*SR*,4a*SR*,8a*SR*)-4a,8-Dimethyl-1,2,3,4,4a,5,6,8a-octahydronaphthalen-1-yl 2-diazo-2-diethoxyphosphoryl)acetate (35); Synthesised using general procedure B with (1*SR*,4a*SR*,8a*SR*)-4a,8-dimethyl-1,2,3,4,4a,5,6,8a-octahydronaphthalen-1-yl 2-diethoxyphosphoryl)acetate **S17** (26 mg, 72.5 μmol), THF (0.36 mL), LHMDS (0.09 mL, 87.1 μmol, 1.0 M solution in THF) and *p*-ABSA (20.9 mg, 87.1 μmol). Purification by column chromatography (2:1 hexane:ethyl acetate) afforded the *title compound* as a pale yellow solid (21 mg, 75%); R_f 0.67 (1:1 hexane:ethyl acetate); m.p. 65–68 °C; ν_{max} (thin film)/cm^{-1} 2932, 2123, 1706, 1448, 1368, 1271, 1217, 1021, 977; δ_H (400 MHz, $CDCl_3$) 0.86 (3 H, s), 0.89–0.93 (1 H, m), 1.17–1.55 (9 H, m), 1.61–1.72 (5 H, m), 1.89–2.12 (3 H, m), 4.06–4.25 (4 H, m), 5.39–5.43 (2 H, m); δ_C (100 MHz, $CDCl_3$) 16.0 (d, *J* = 7.4), 16.1 (d, *J* = 6.7), 16.3, 22.3, 22.8, 28.0, 28.3, 30.7, 31.6, 40.0, 49.5, 52.9 (d, *J* = 226.5), 63.4 (d, *J* = 5.7), 63.6 (d, *J* = 5.7), 70.5, 122.9, 131.2, 162.6 (d, *J* = 13.1); δ_P (162 MHz, $CDCl_3$) 11.3; HRMS (ESI^+): Found: 407.1707; $C_{18}H_{29}N_2NaO_5P$ (MNa^+) Requires 407.1706 (–0.2 ppm error).



35

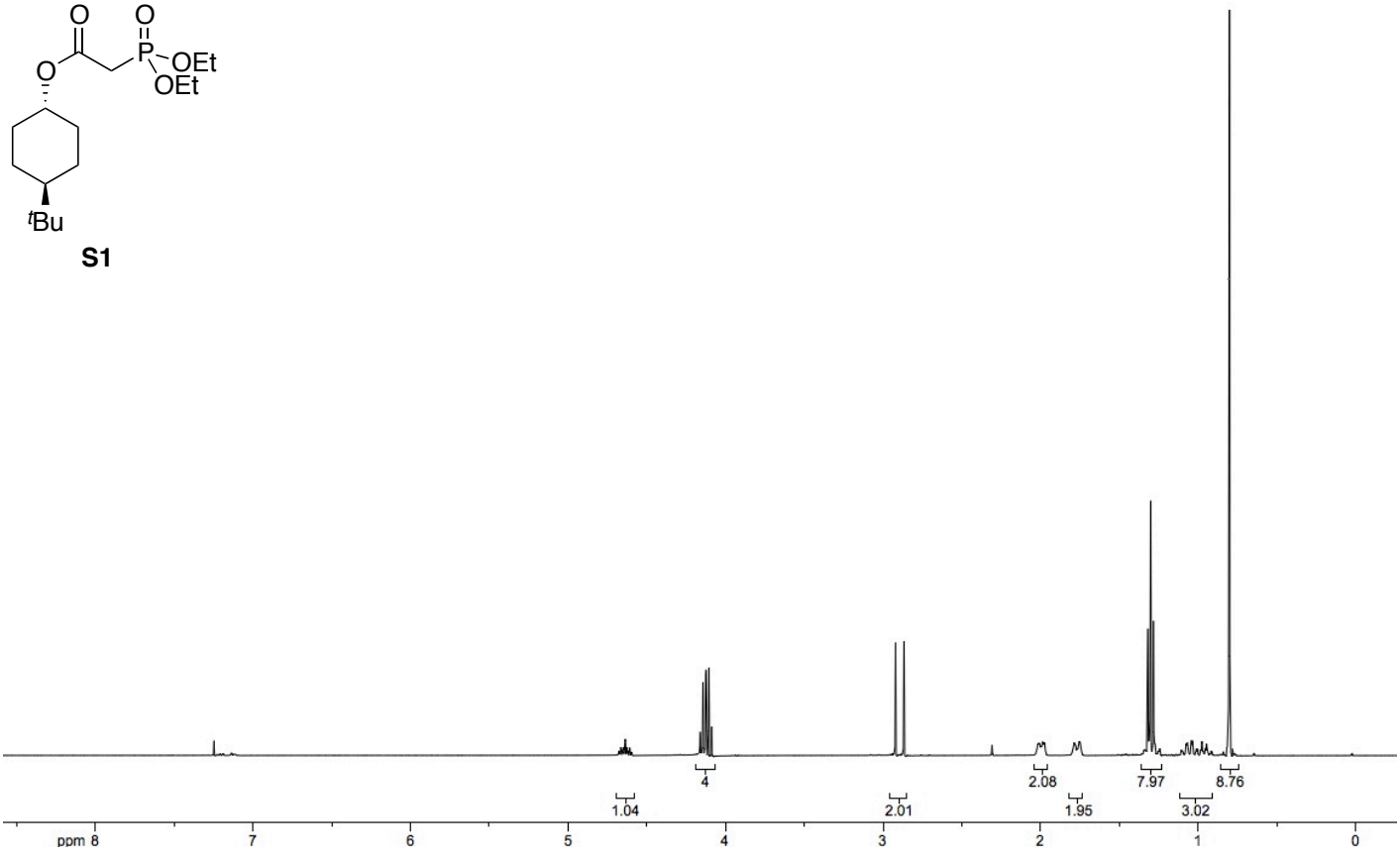
(3a*RS*,5a*RS*,9a*SR*,9b*SR*)-5a,9-Dimethyl-3-methylene-3a,4,5,5a,6,7,9a,9b-octahydronaphtho[1,2-*b*]furan-2(3*H*)-one (36); Synthesised using general procedure C with (1*SR*,4a*SR*,8a*SR*)-4a,8-dimethyl-1,2,3,4,4a,5,6,8a-octahydronaphthalen-1-yl 2-diazo-2-diethoxyphosphoryl)acetate **35** (20 mg, 52.0 μmol), DCM (1.04 mL), $Rh_2(oct)_4$ (0.8 mg, 1.04 μmol), THF (1.04 mL), potassium *tert*-butoxide (8.8 mg, 78.0 μmol) and paraformaldehyde (3.1 mg, 104 μmol). Purification by column chromatography (8:1 hexane:ethyl acetate) afforded the *title compound* as a pale yellow oil (8 mg, 66%); R_f 0.36 (4:1 hexane:ethyl acetate); ν_{max} (thin film)/cm^{-1} 2928, 2865, 1759, 1452, 1402, 1380, 1346, 1263, 1156, 1143, 1130, 1080, 957; δ_H (400 MHz, $CDCl_3$) 0.91 (3 H, s), 1.05–1.09 (1 H, m), 1.21-1.81 (9 H, m), 2.00–2.09 (2 H, m), 3.00–3.06 (1 H, m), 4.74 (1 H, dd, *J* = 6.1, *J* = 3.8), 5.57–5.59 (2 H, m), 6.19 (1 H, d, *J* = 1.6); δ_C (100 MHz, $CDCl_3$) 22.1, 22.5, 24.9, 27.1, 30.4, 30.7, 35.8, 39.7, 46.5, 76.9, 121.0, 124.3, 129.5, 142.0, 170.6; HRMS (ESI^+): Found: 255.1359; $C_{15}H_{20}NaO_2$ (MNa^+) Requires 255.1356 (–1.3 ppm error), Found: 233.1536; $C_{15}H_{21}O_2$ (MH^+) Requires 233.1536 (–0.1 ppm error).



36

n4530mgl
M LLOYD MGL/06/63-P

S1



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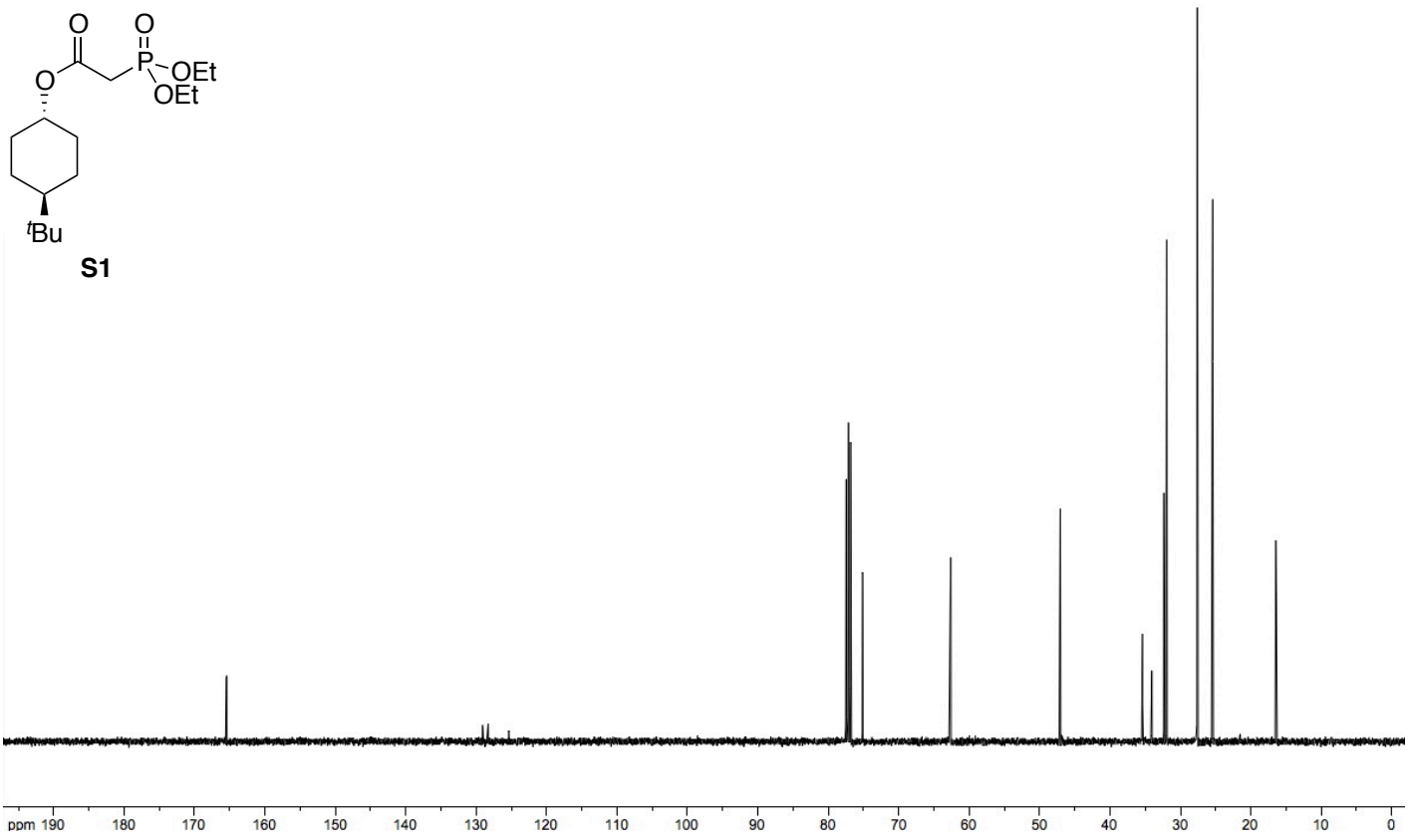
S1



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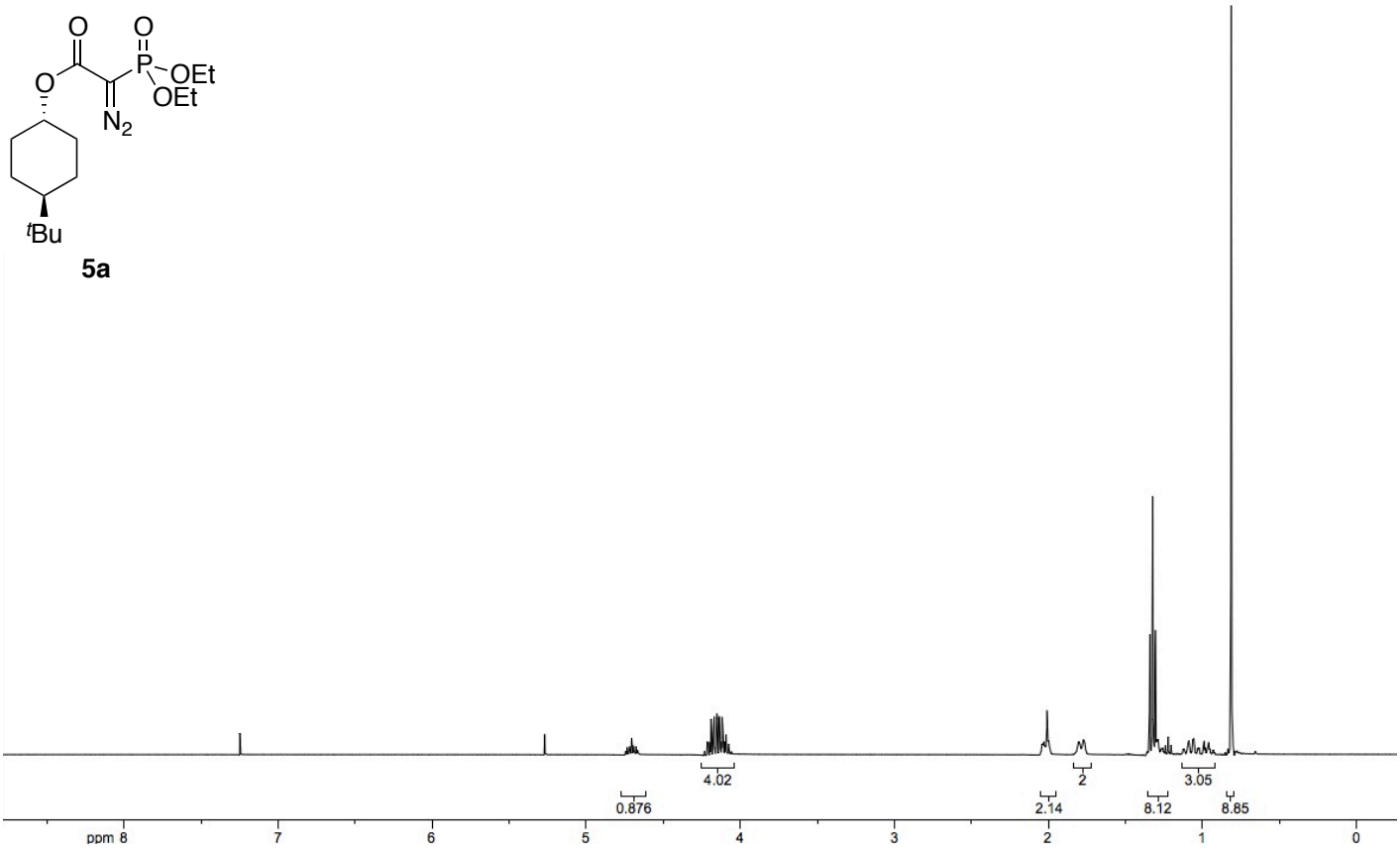
5a



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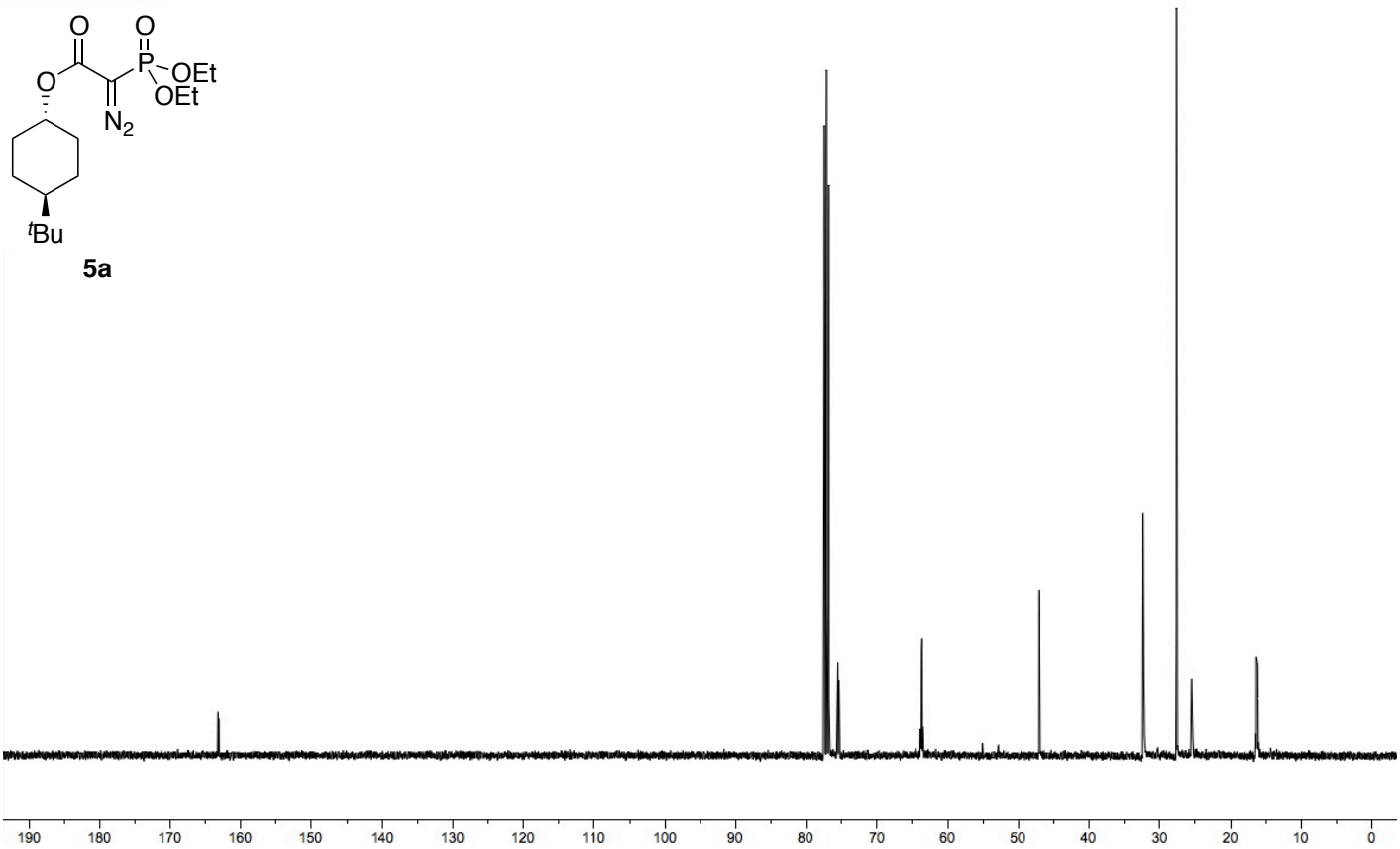
5a



n4847mgl
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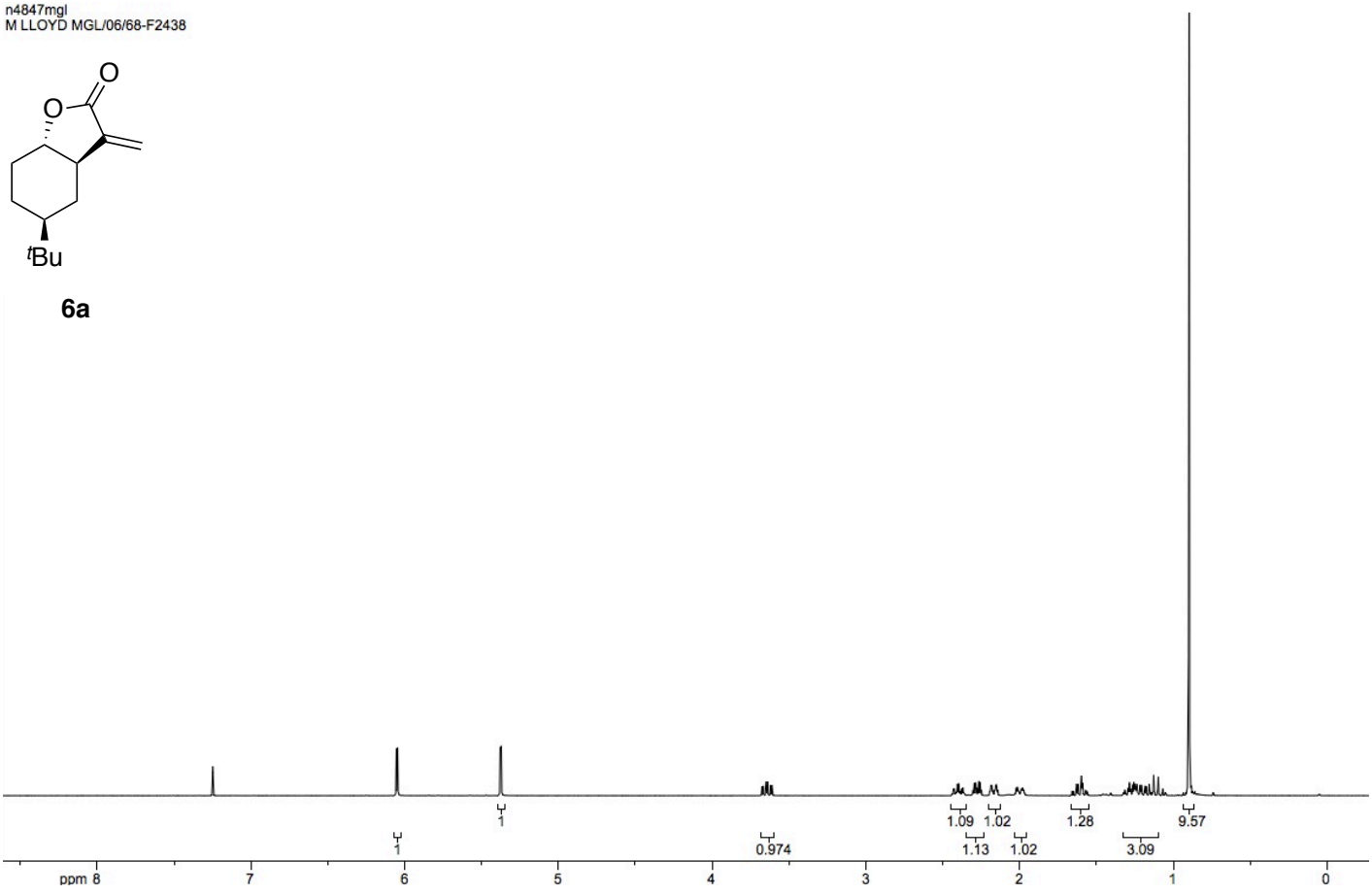
6a



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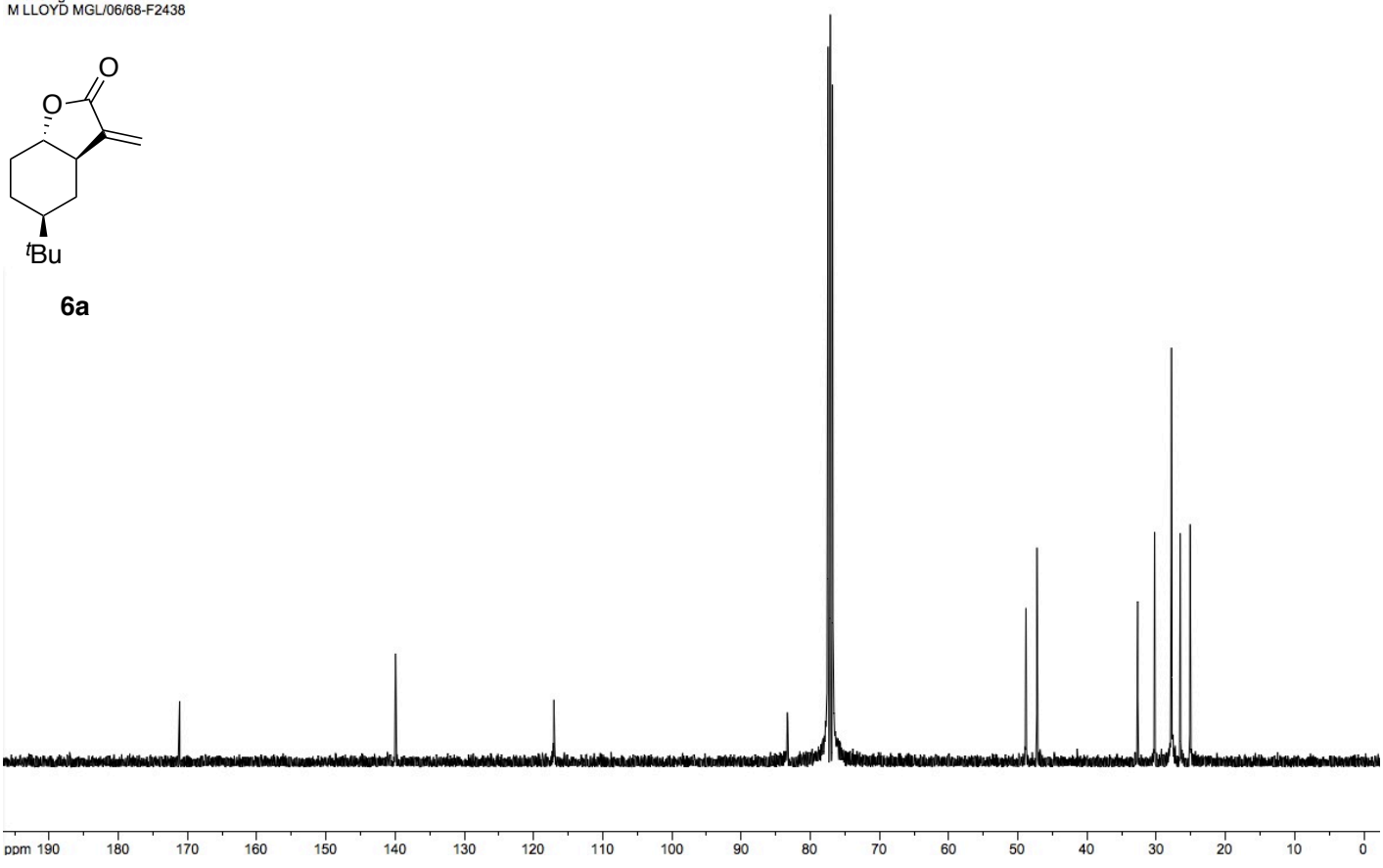

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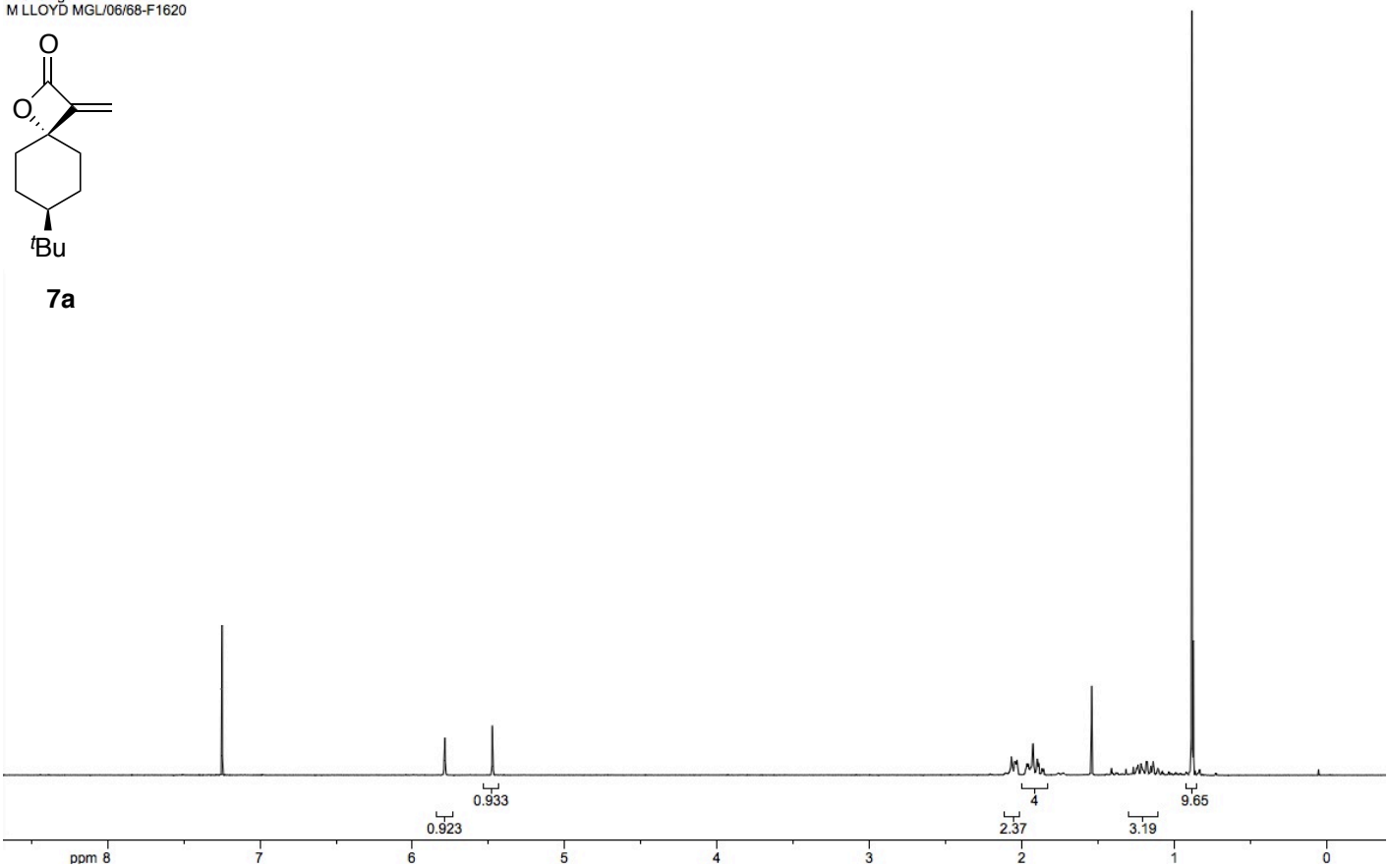
7a



n4922mgl
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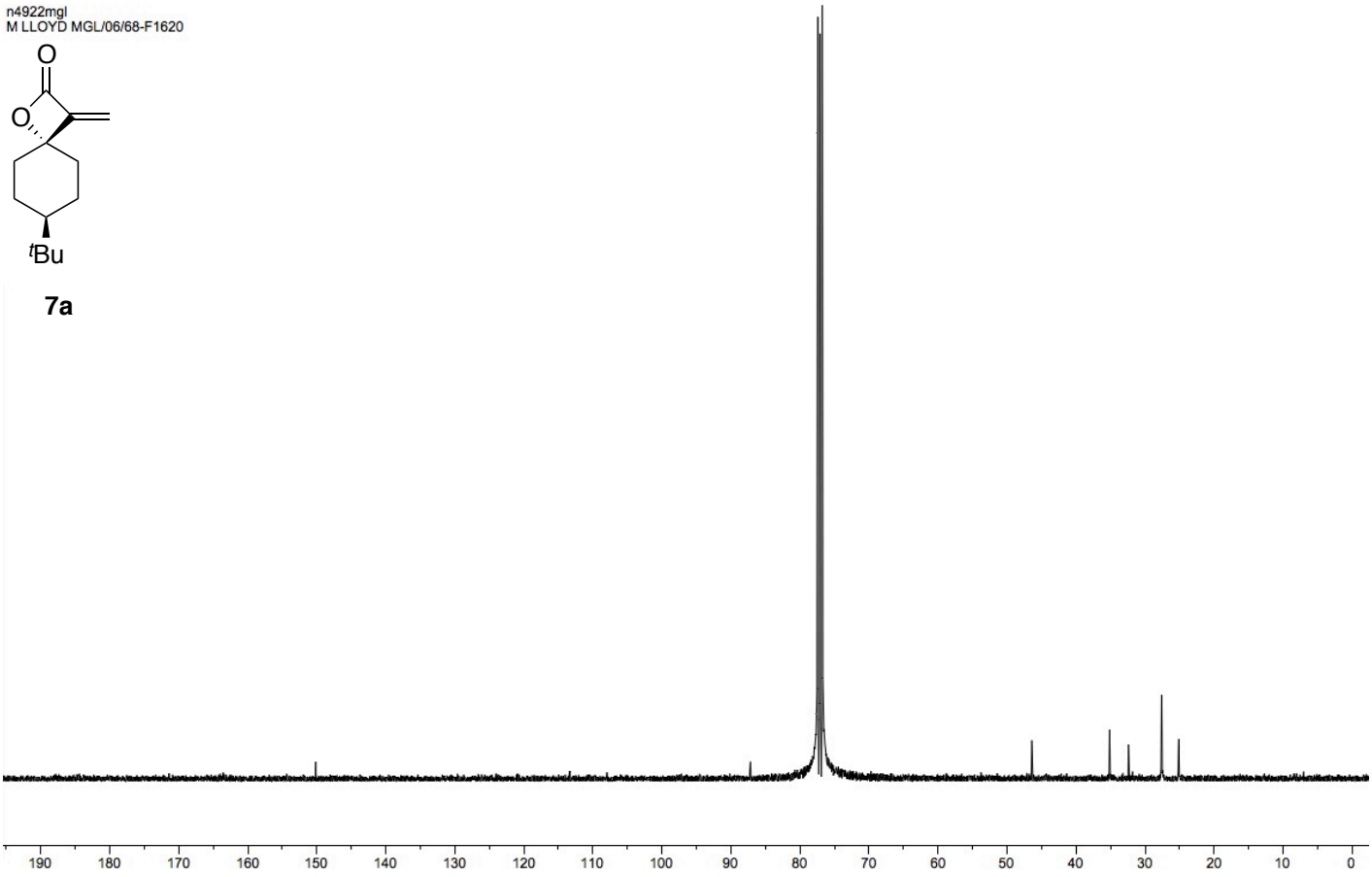
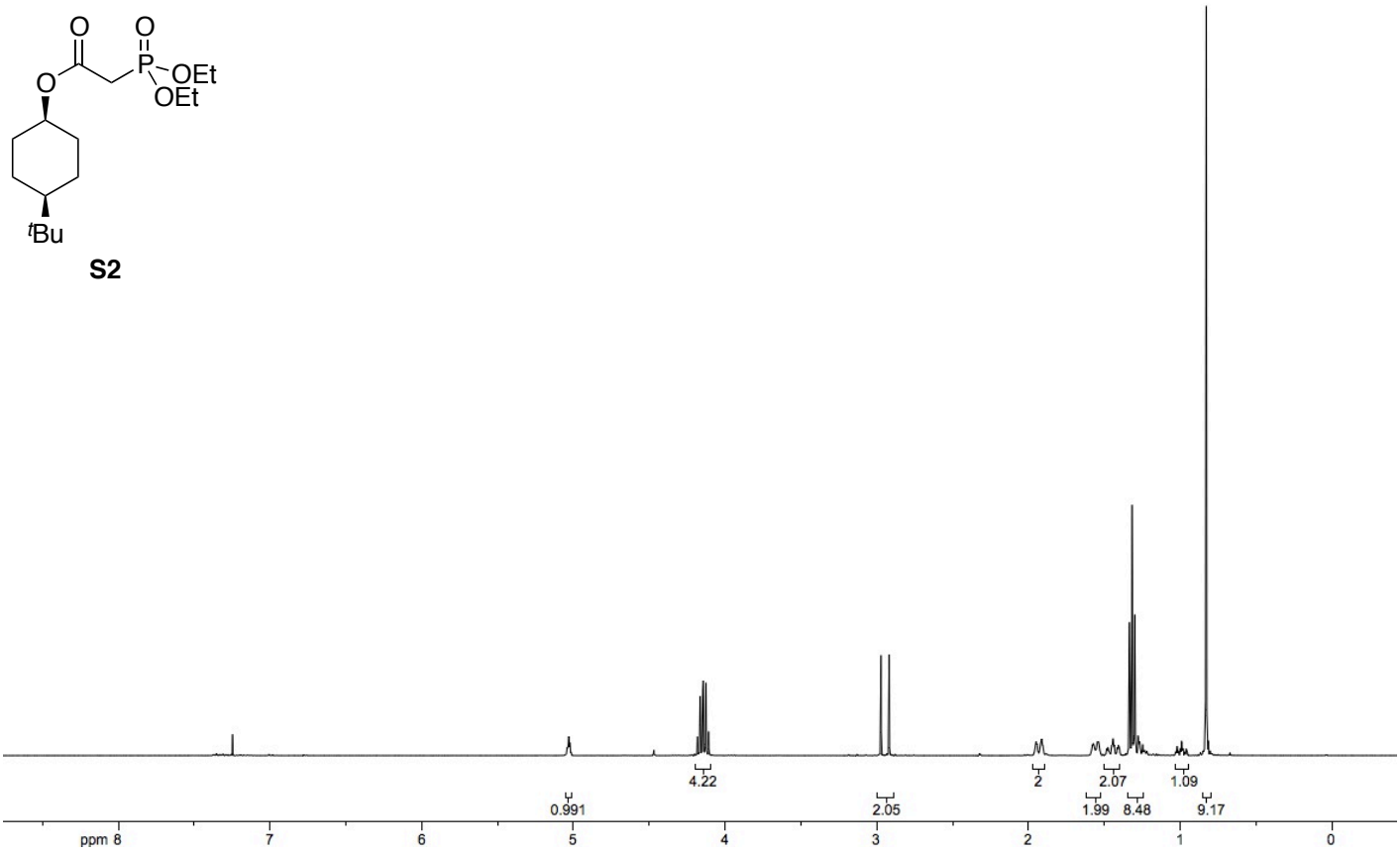
7a



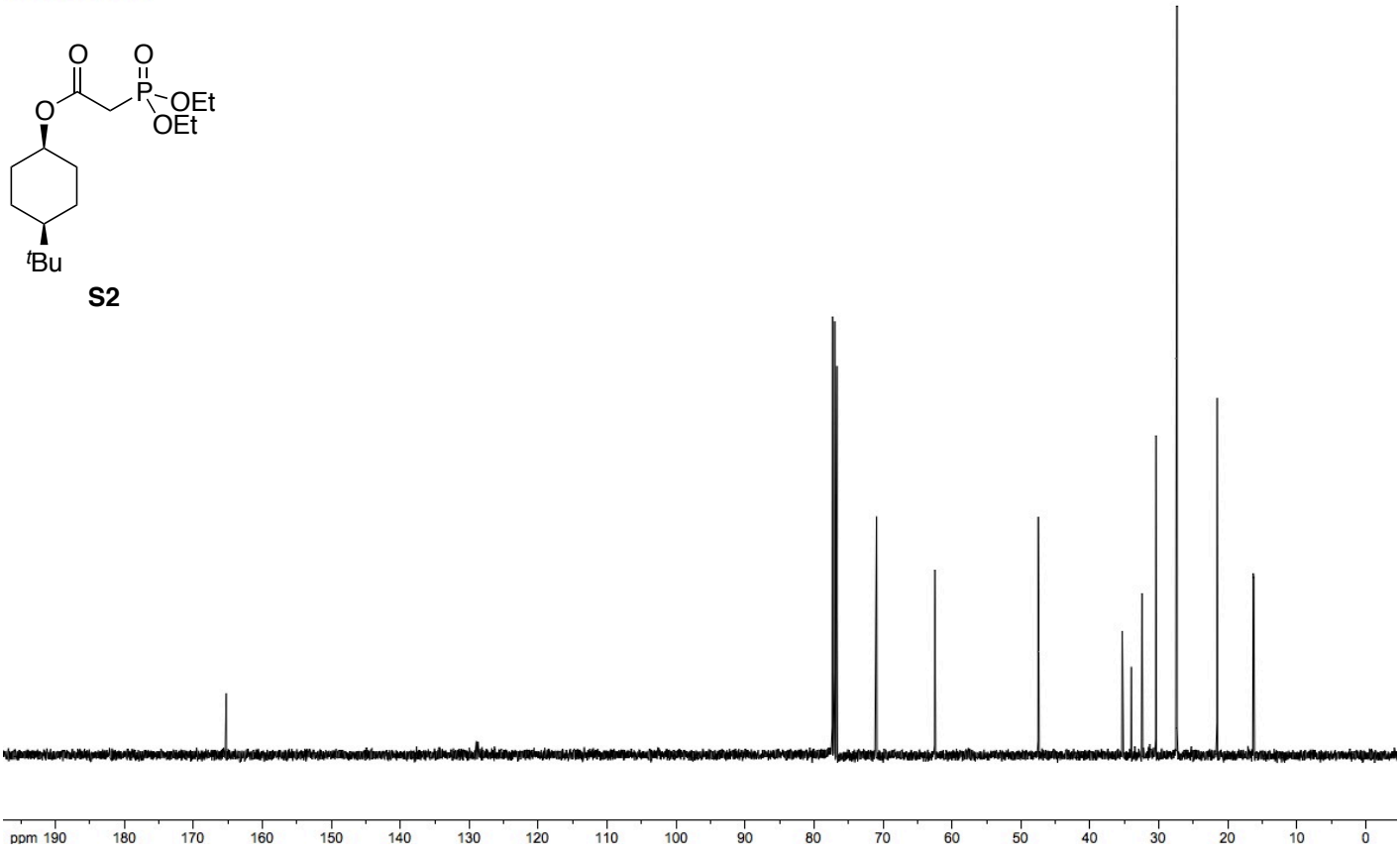
n4529mgl
M LLOYD MGL/06/62-P

S2



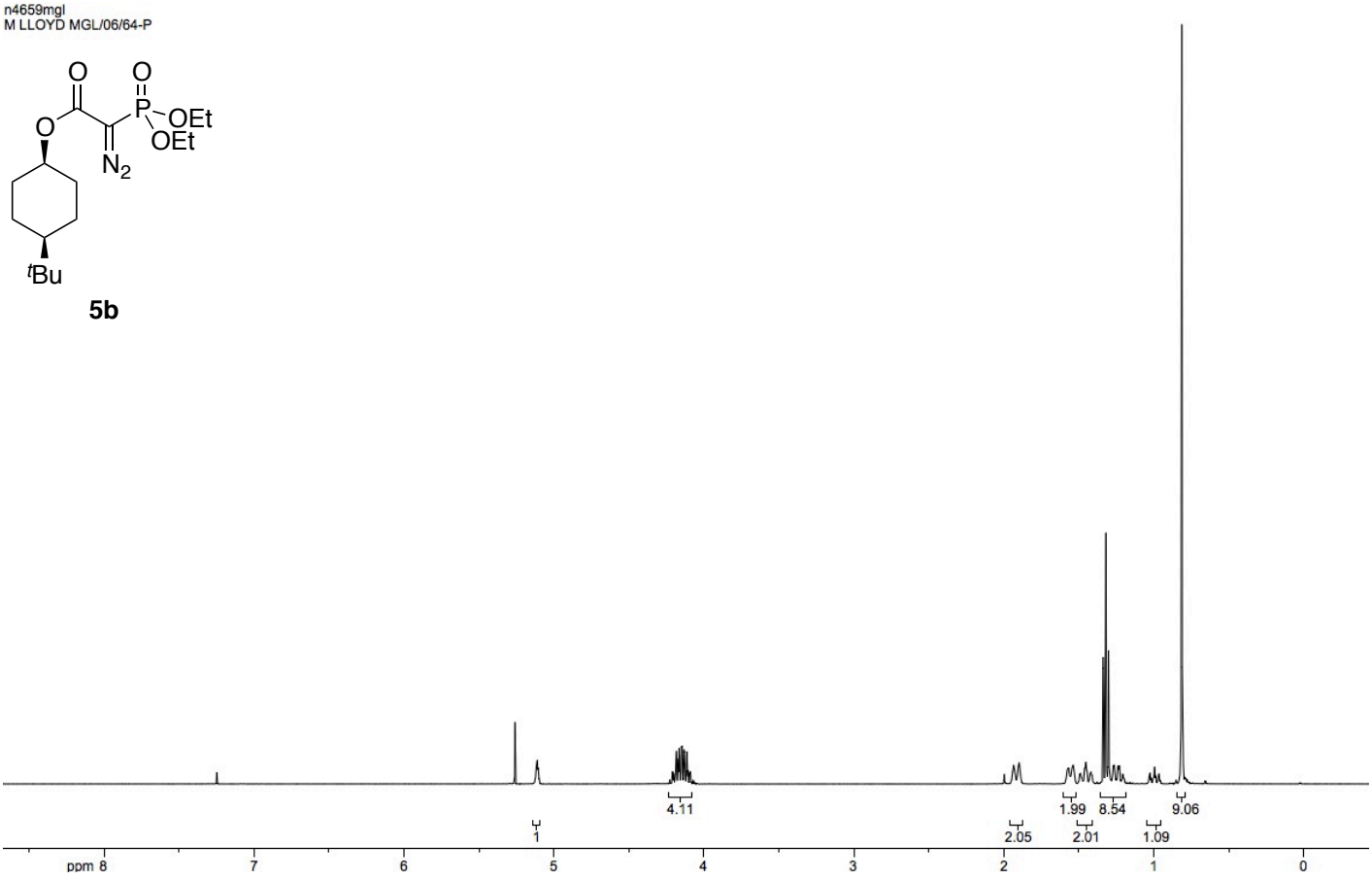
n4554mgl
M LLOYD MGL/06/62-P

S2



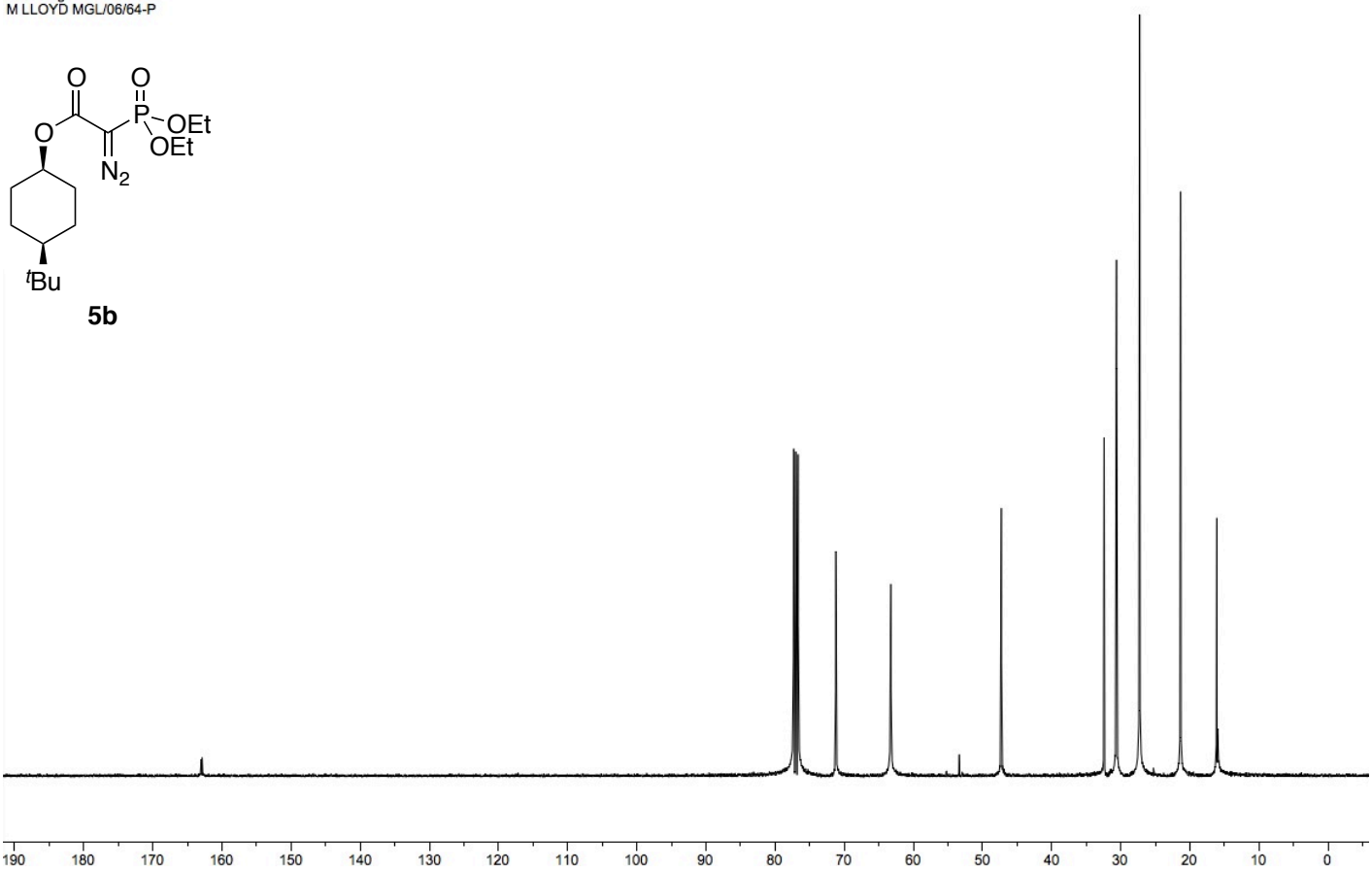
n4659mgl
M LLOYD MGL/06/64-P

5b



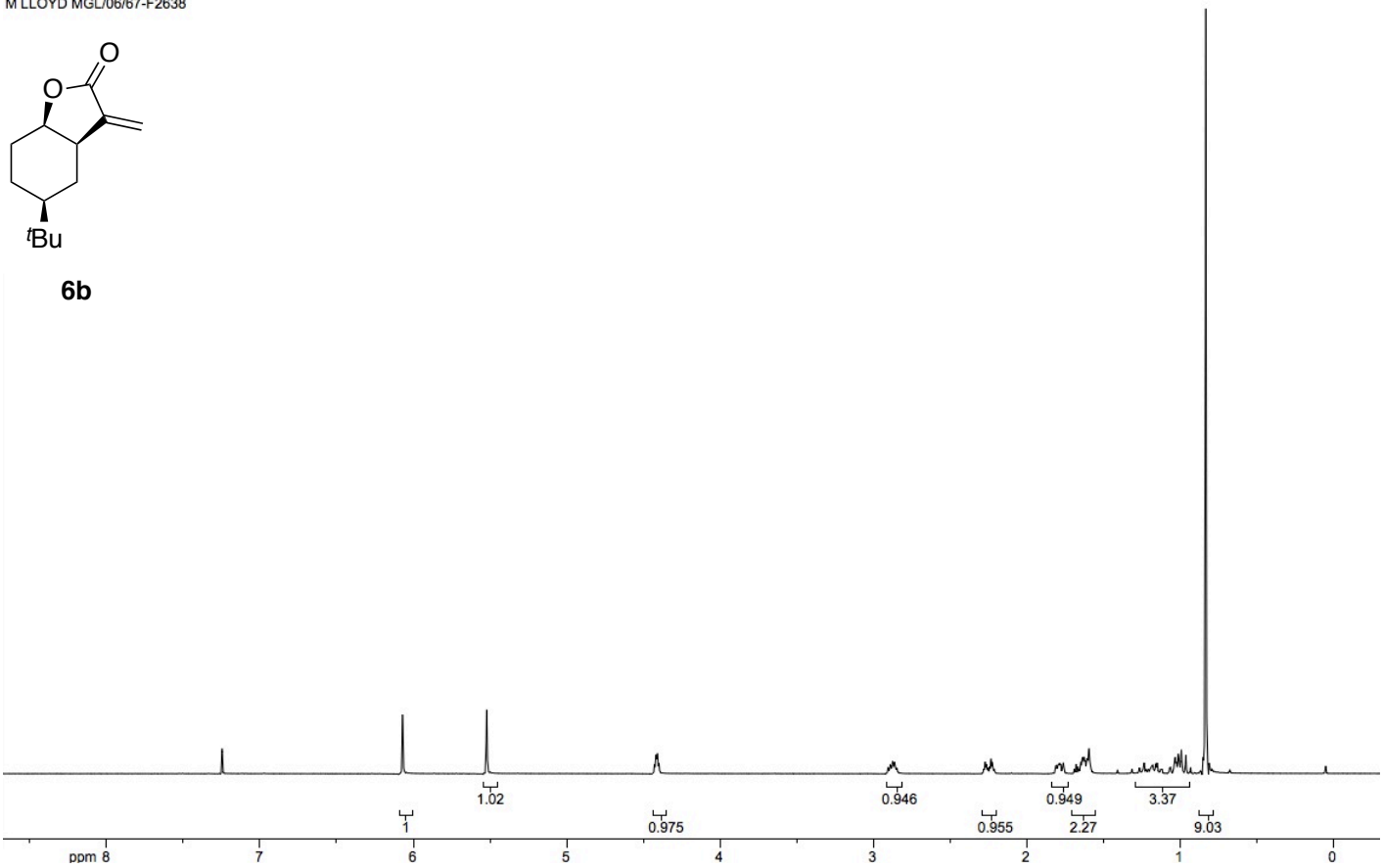
n4695mgl
M LLOYD MGL/06/64-P

5b



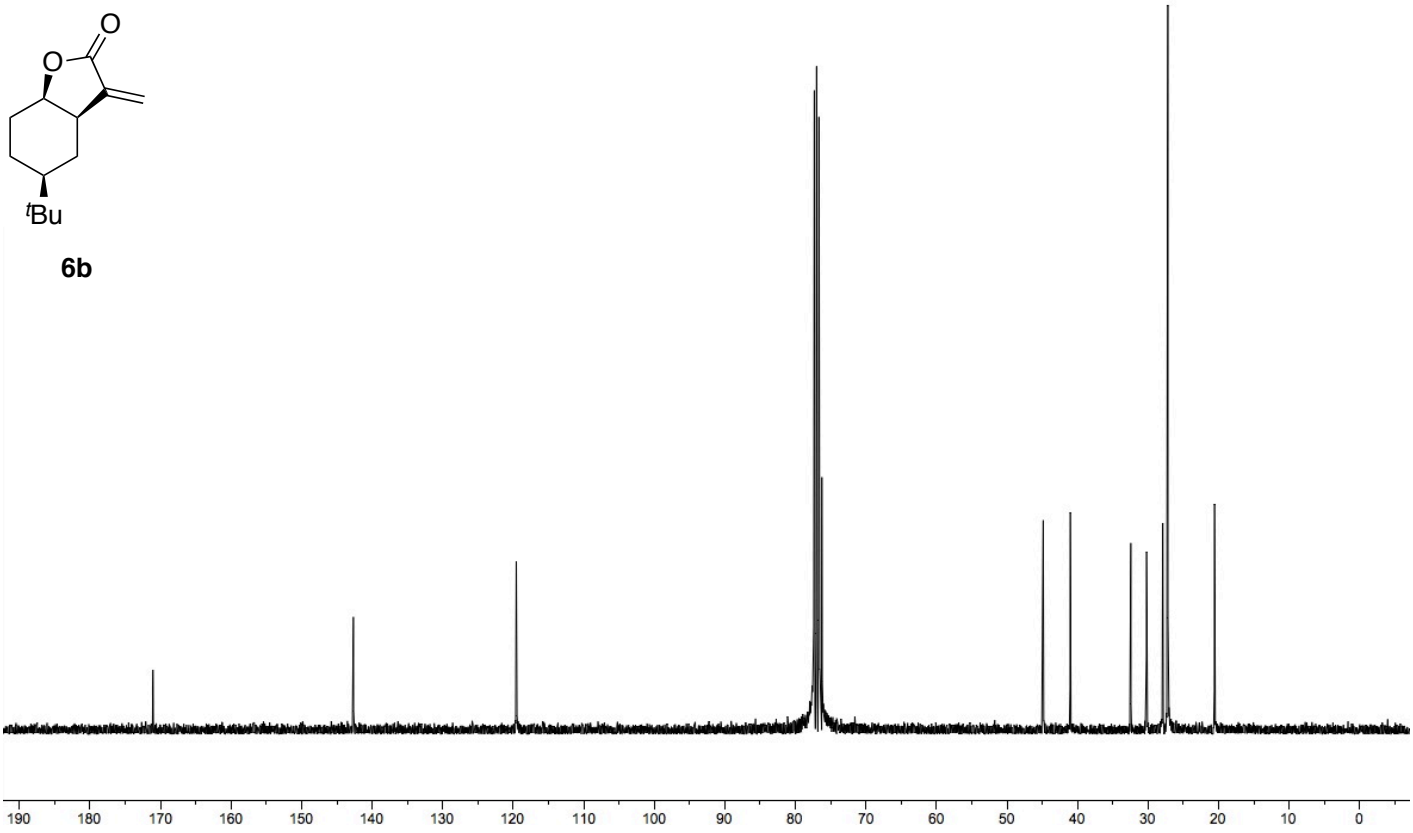
n4817mgl
M LLOYD MGL/06/67-F2638

6b



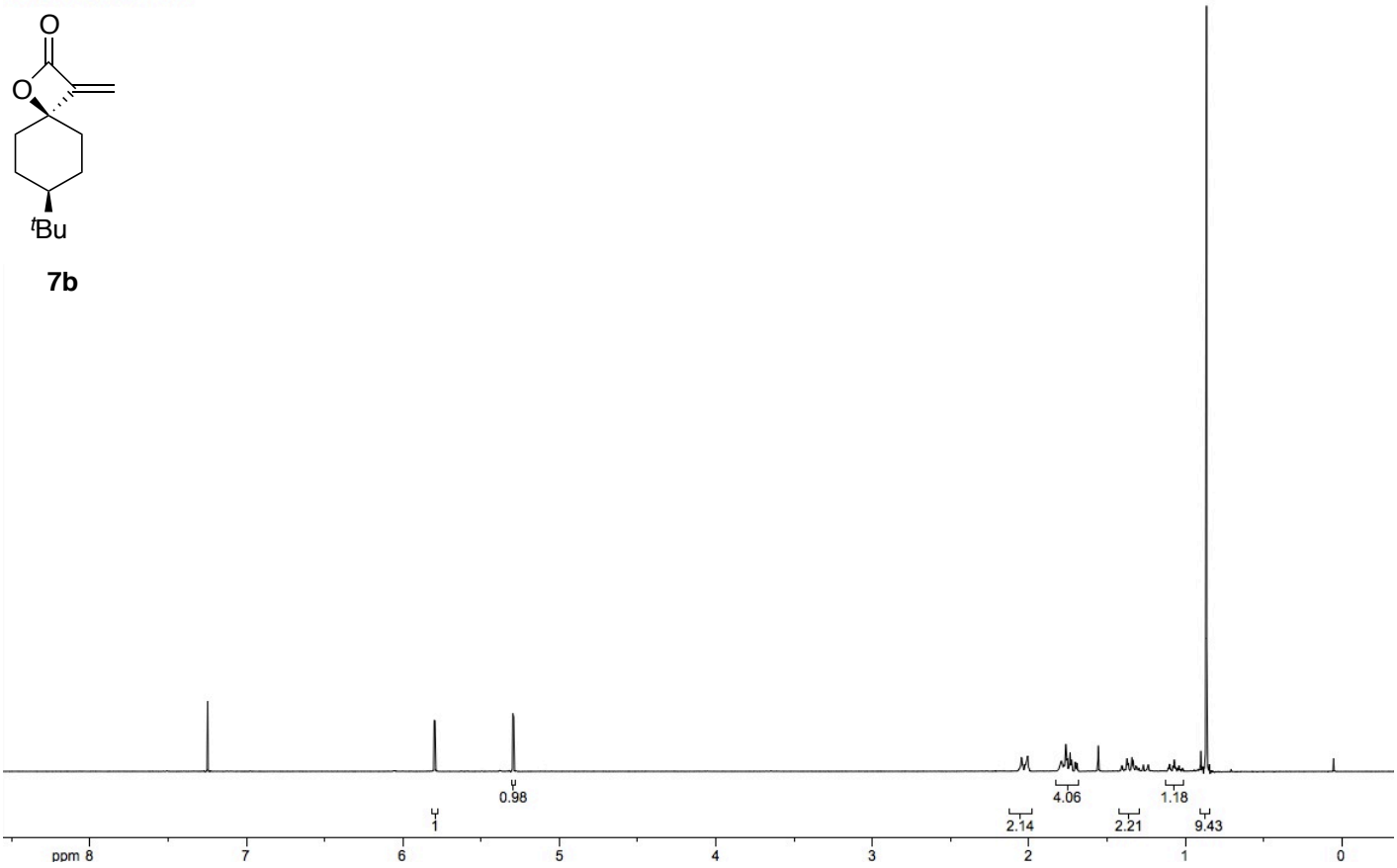
n4921mgl
M LLOYD MGL/06/67-F2638

6b

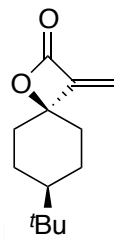


n4816mgl
M LLOYD MGL/06/67-F1522

7b



n4920mgl
M LLOYD MGL/06/67-F1522



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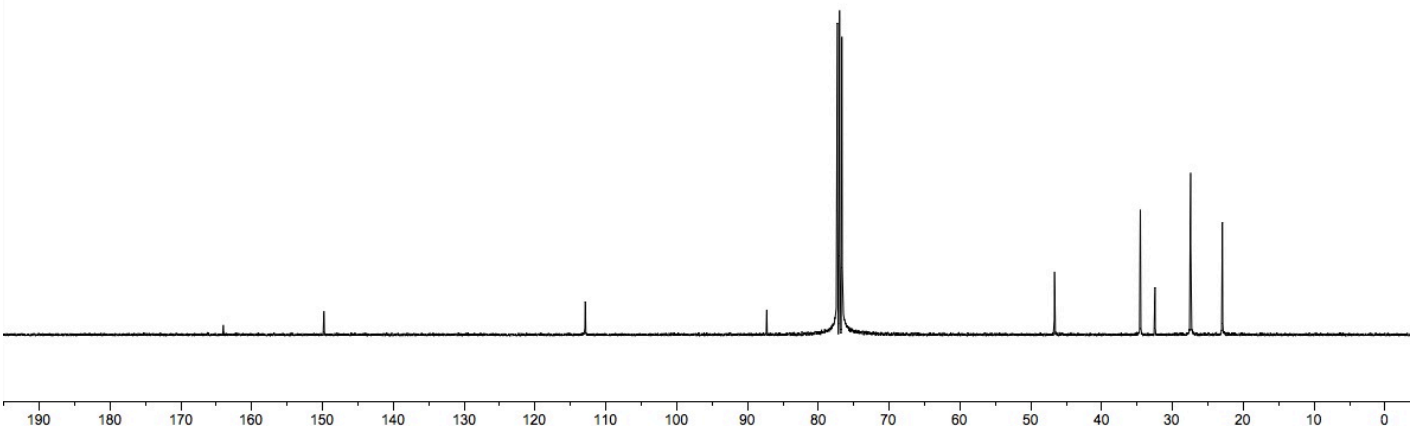
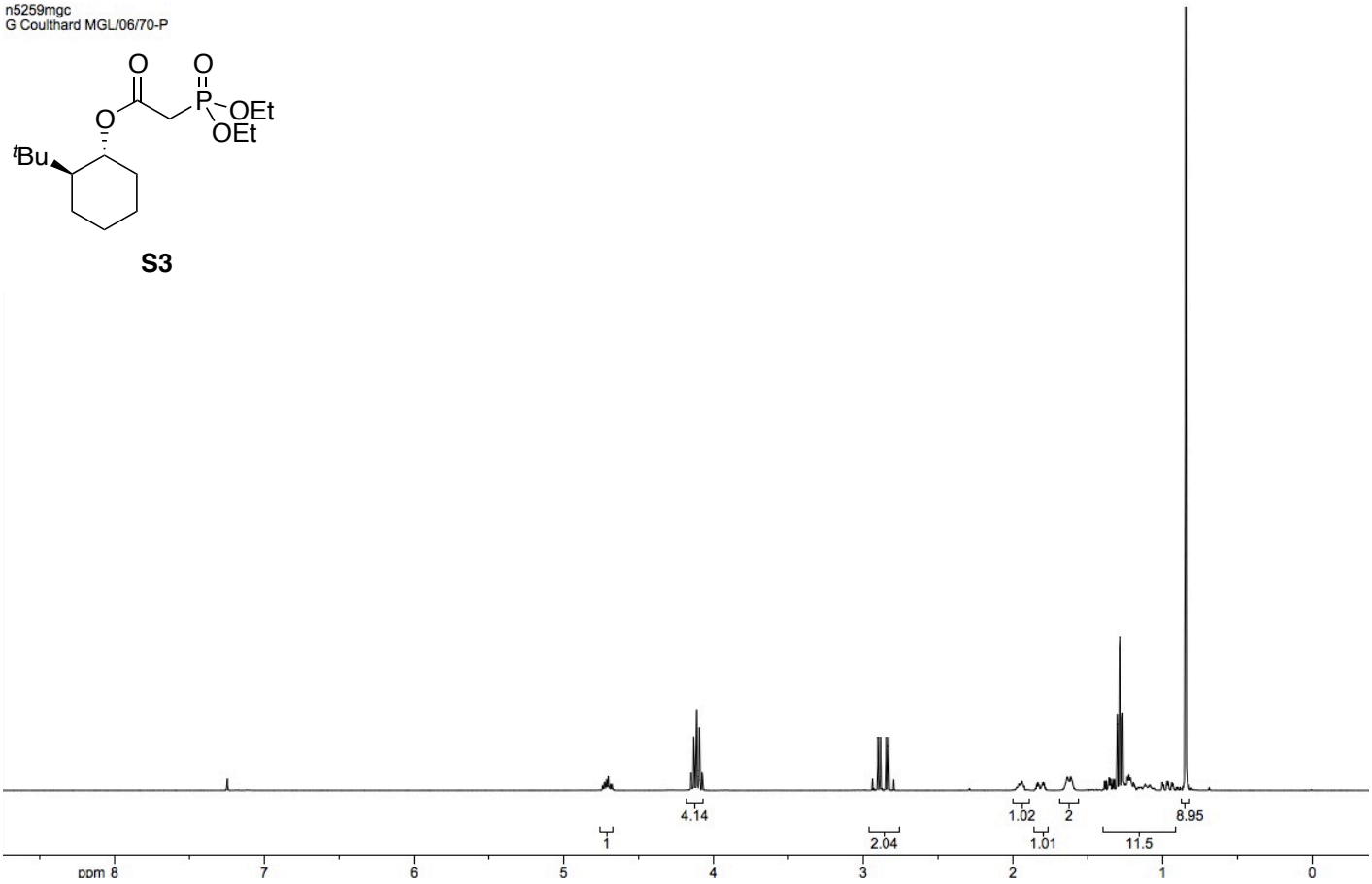


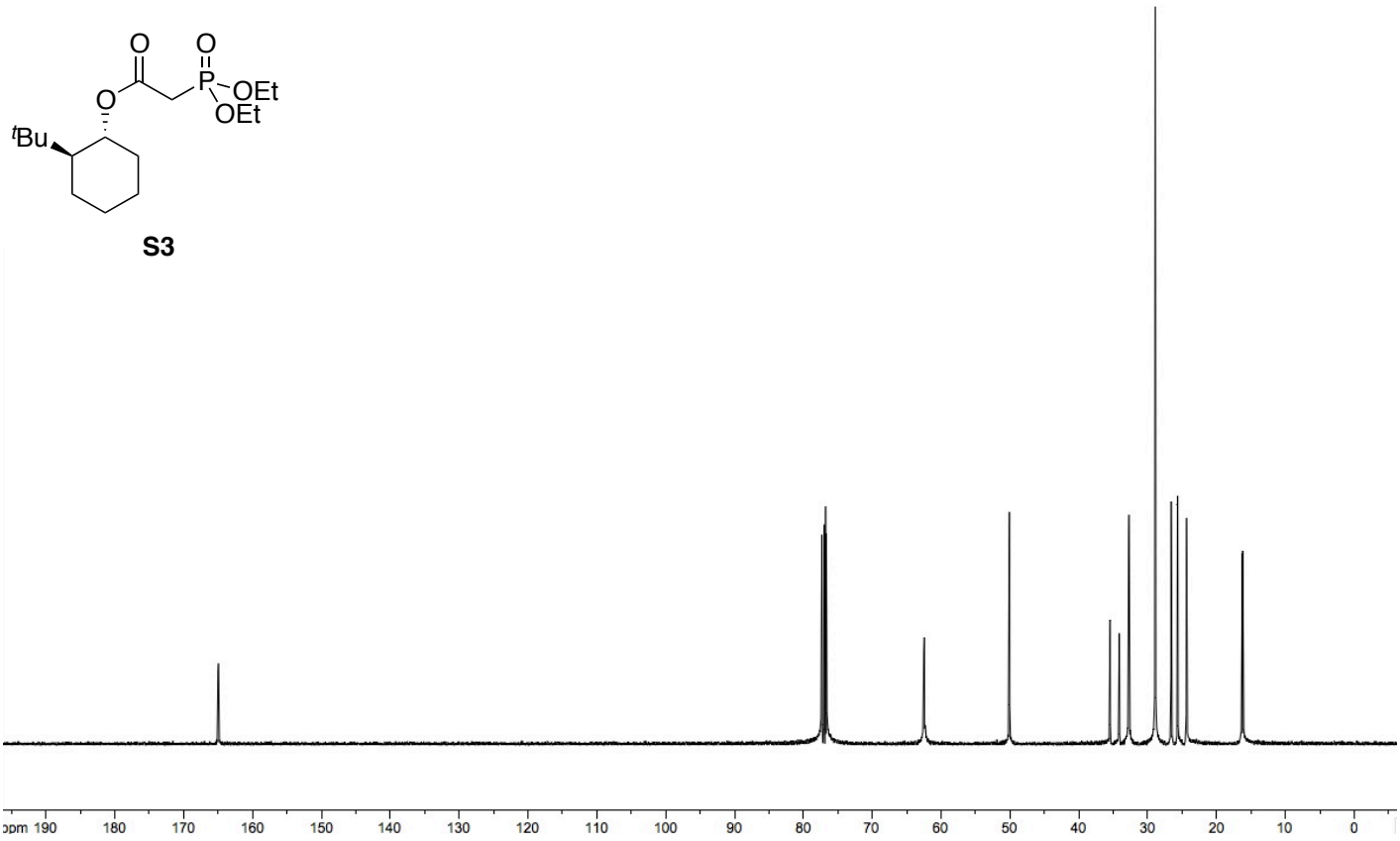
n5259mgc
G Coulthard MGL/06/70-P

S3



n7272mgl
M LLOYD MGL/06/70-P

S3



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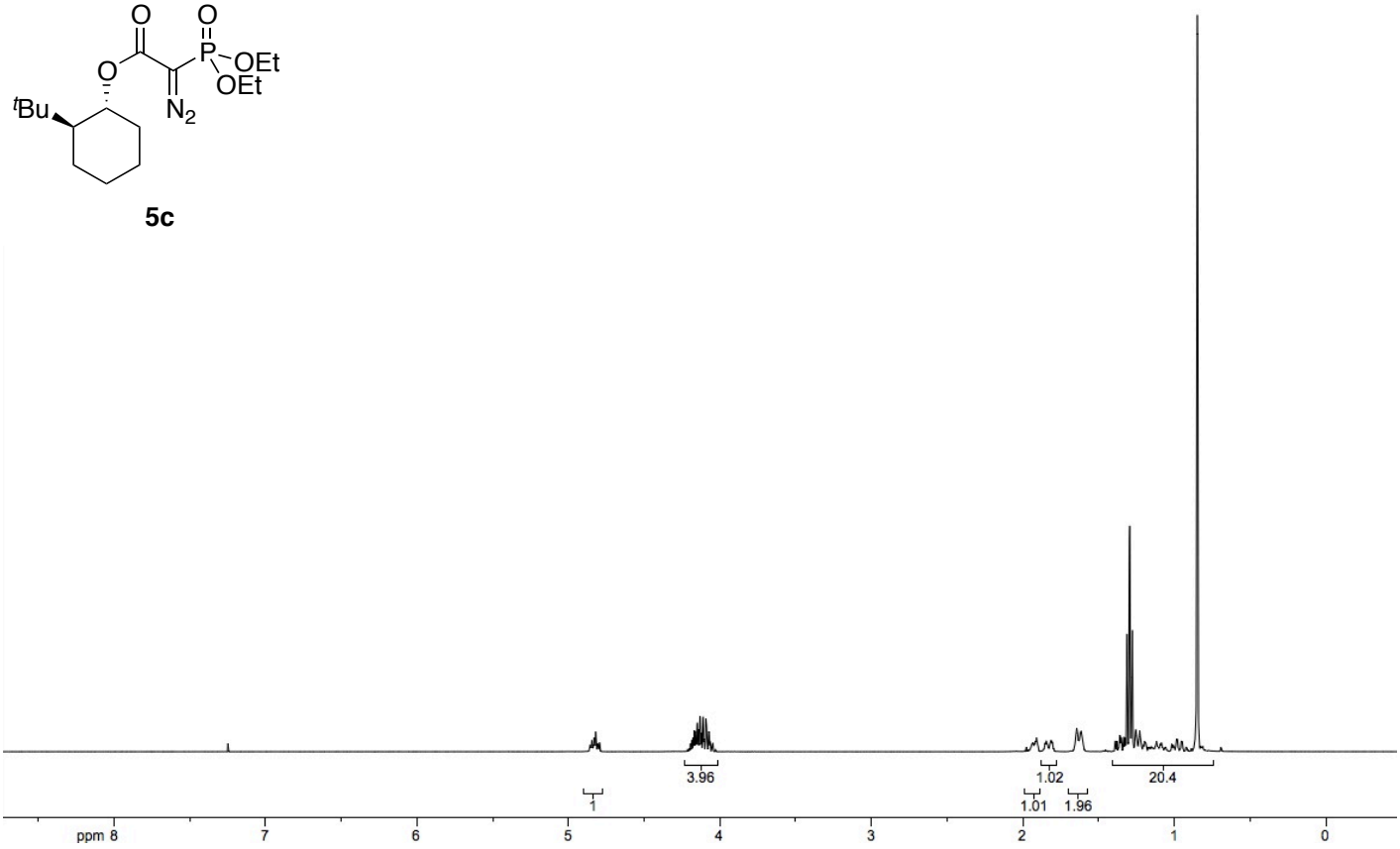
M LLOYD MGL/06/73-P

5c



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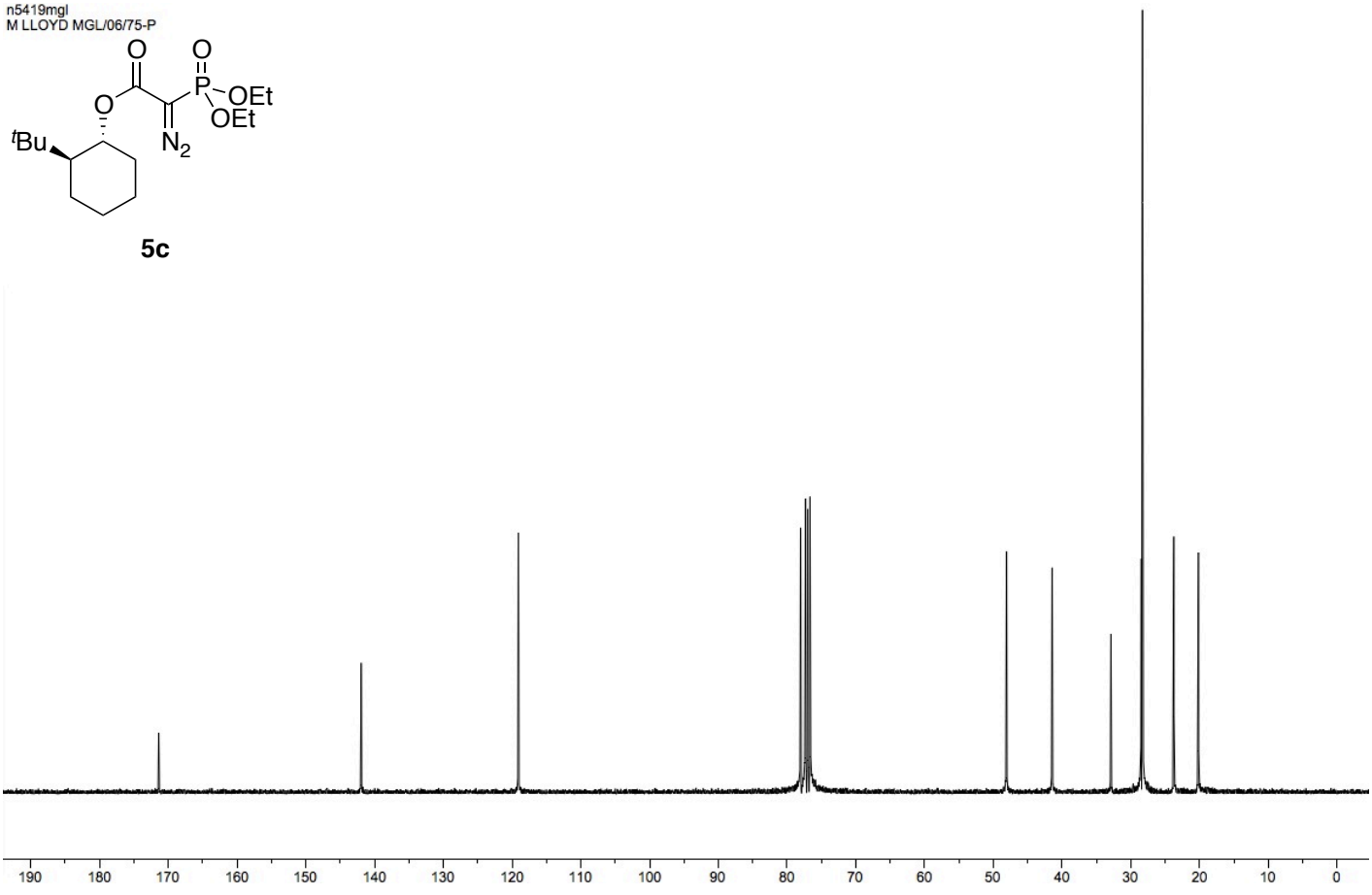
M LLOYD MGL/06/75-P

5c



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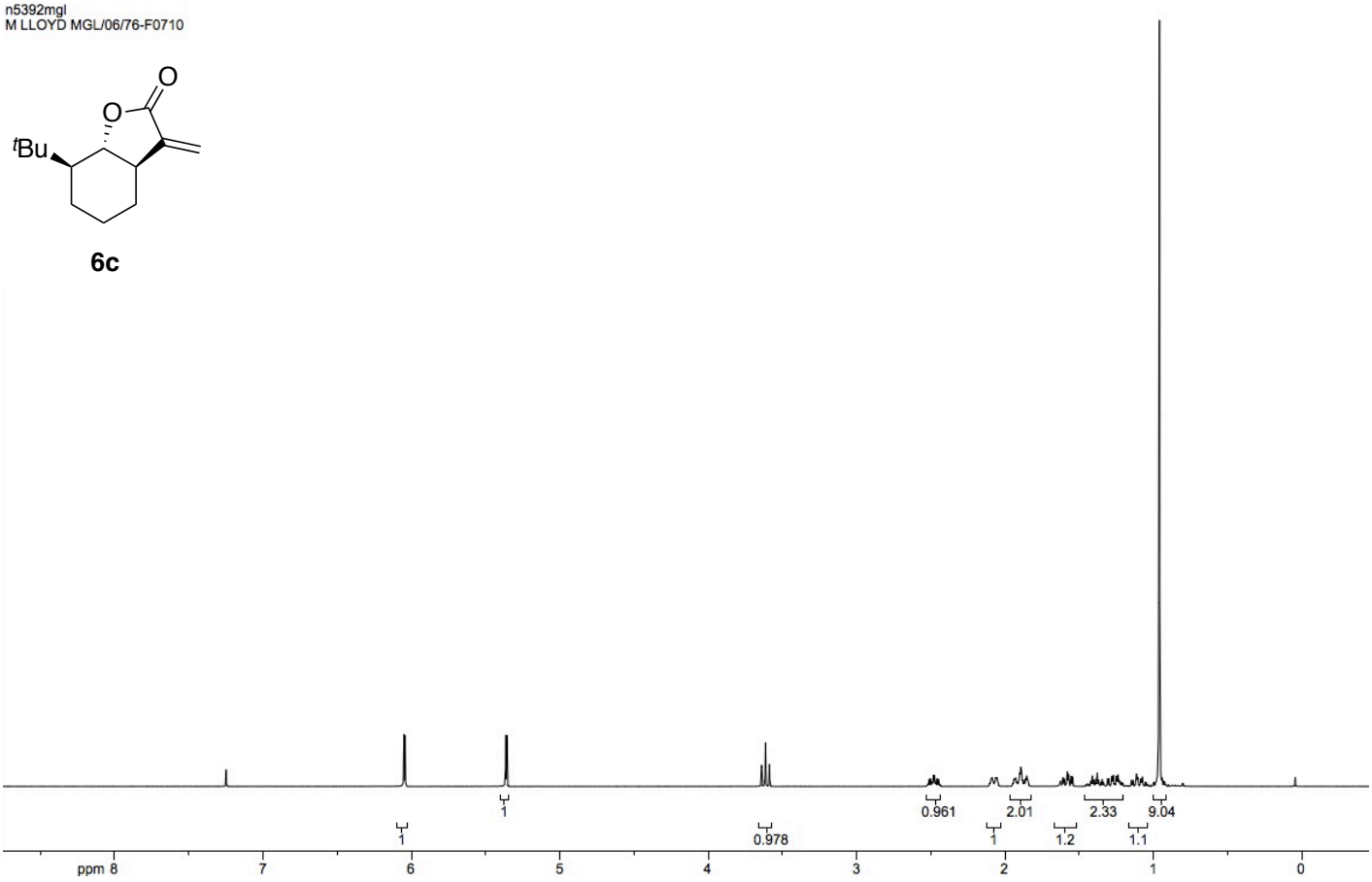
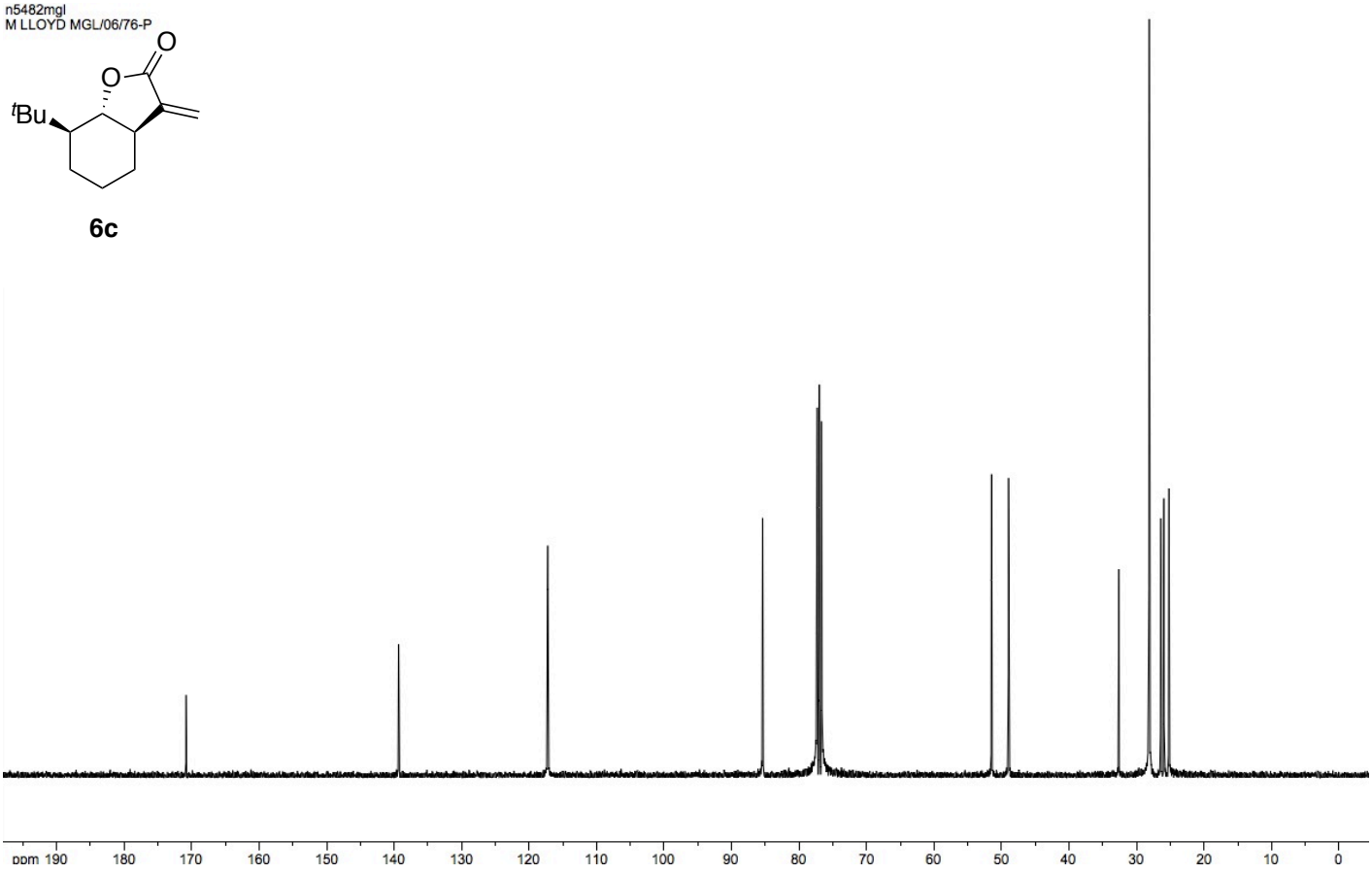
6c



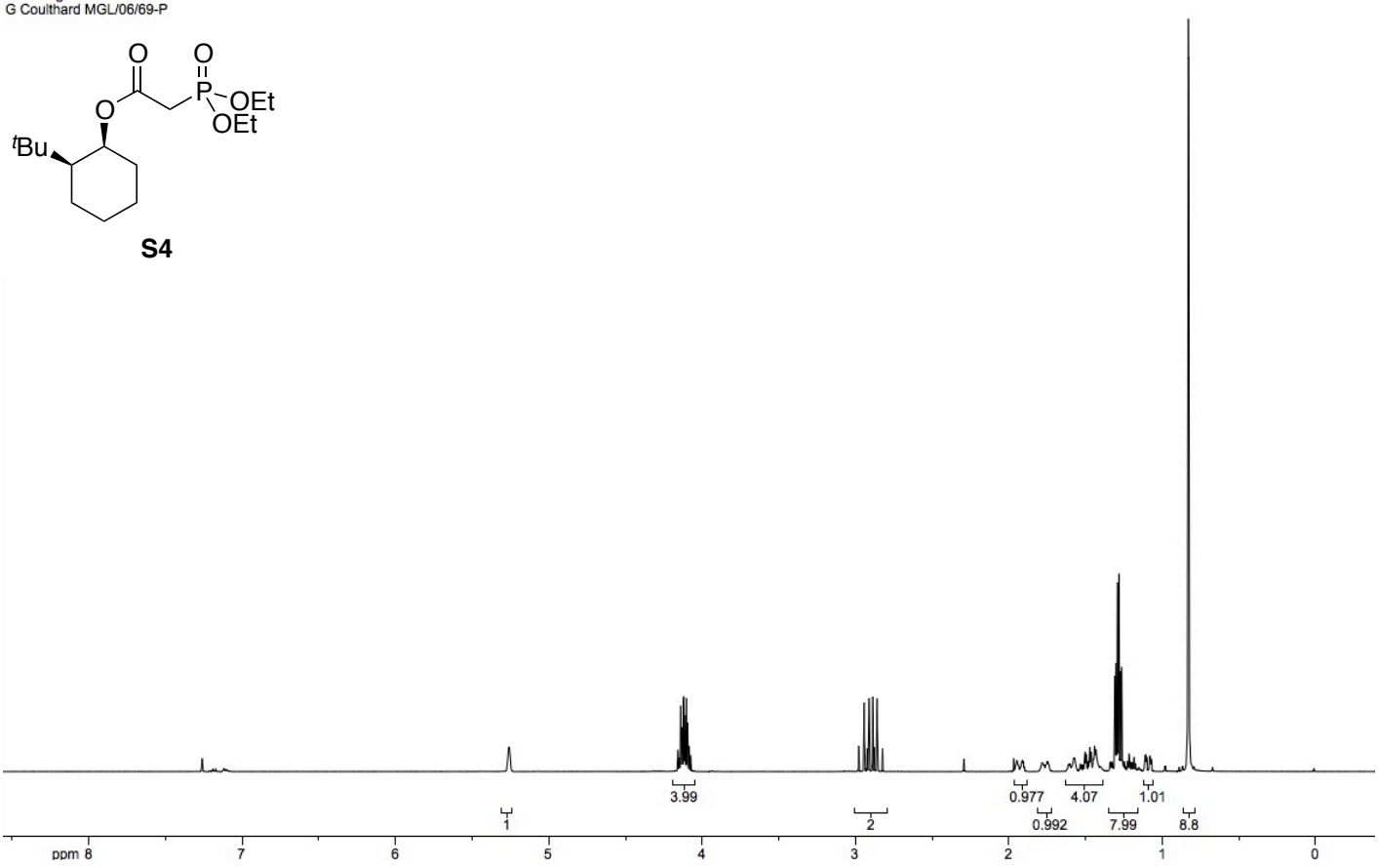
n5482mgl
M LLOYD MGL/06/76-P

6c



n5258mgc
G Coulthard MGL/06/69-P

S4



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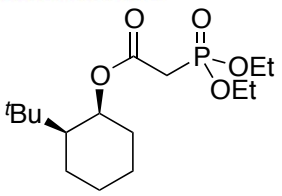
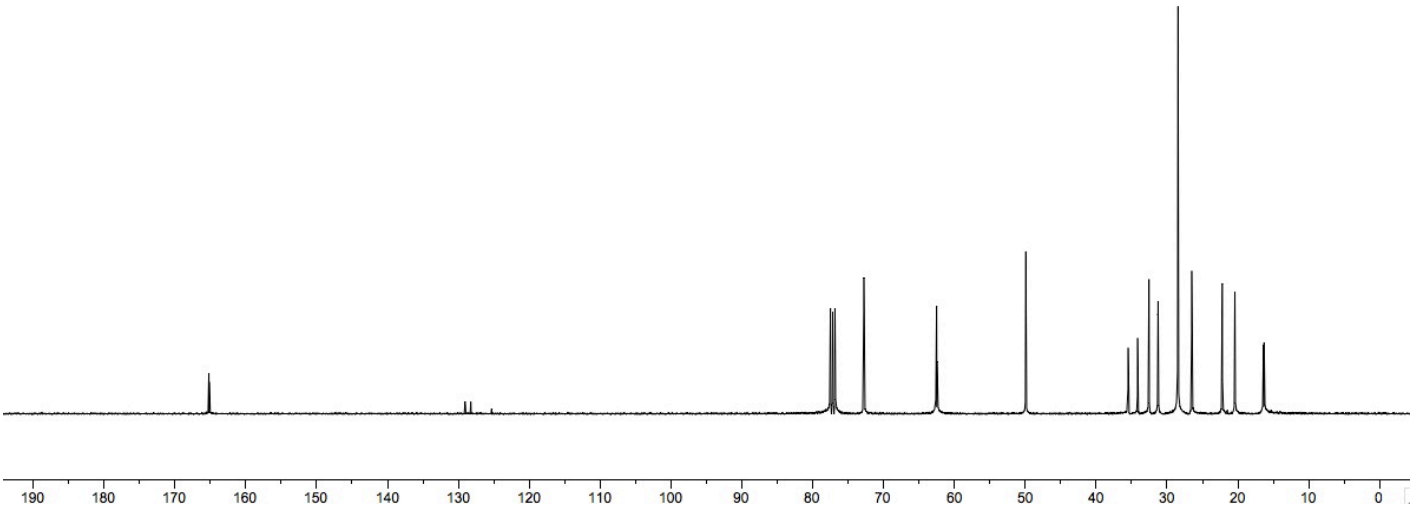
G Coulthard MGL/06/69-P

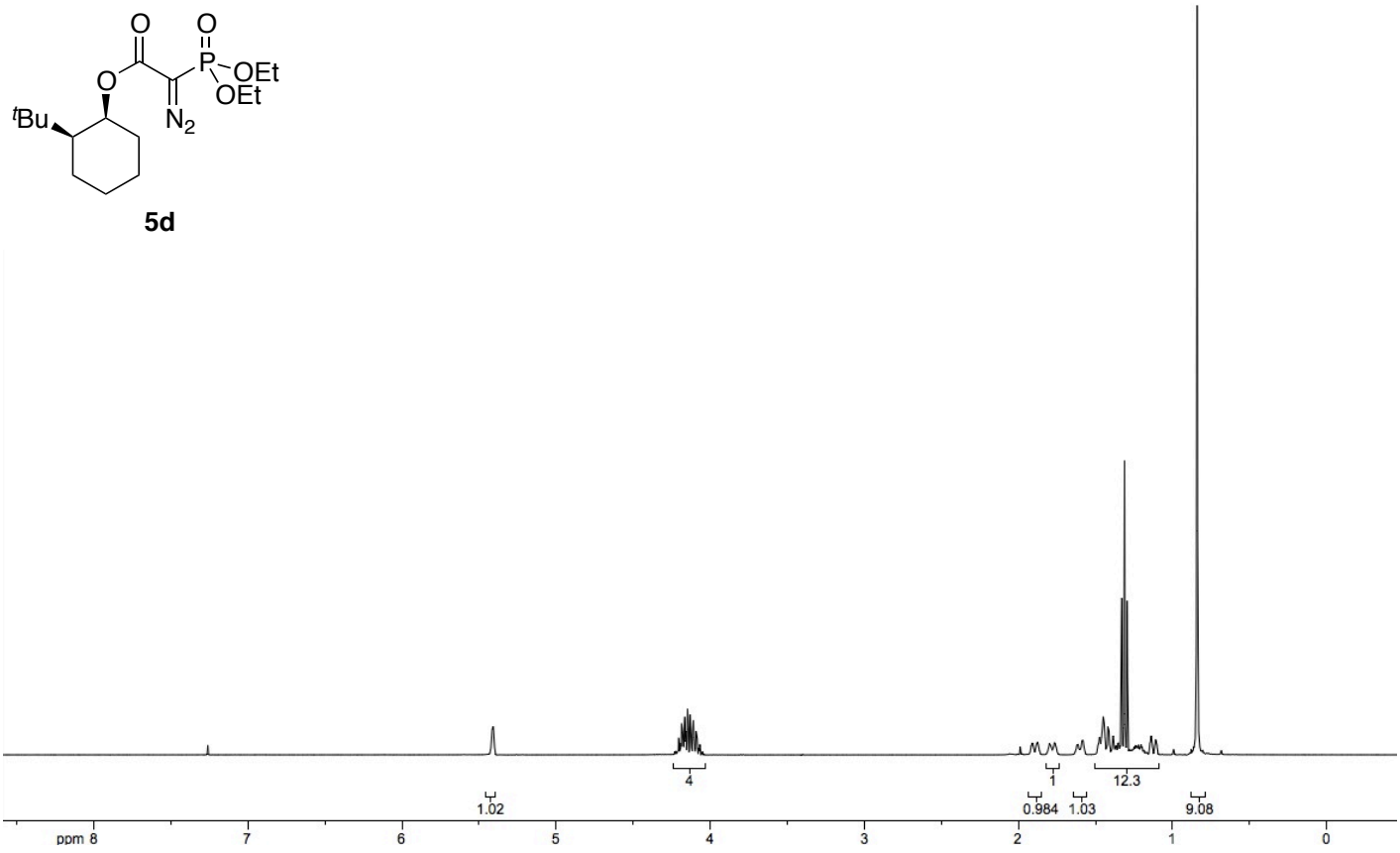


S4



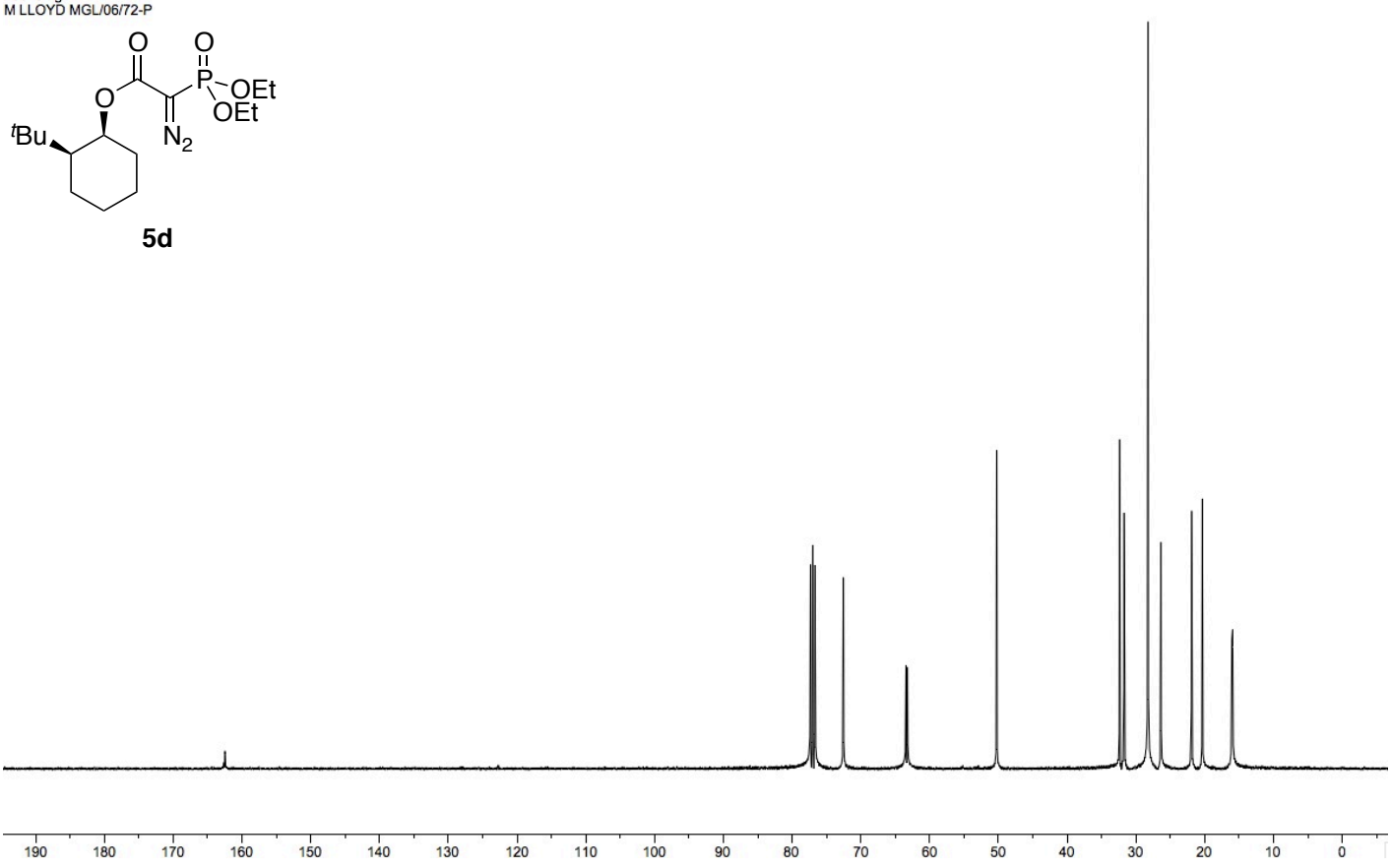
n5340mgl
M LLOYD MGL/06/72-P

5d



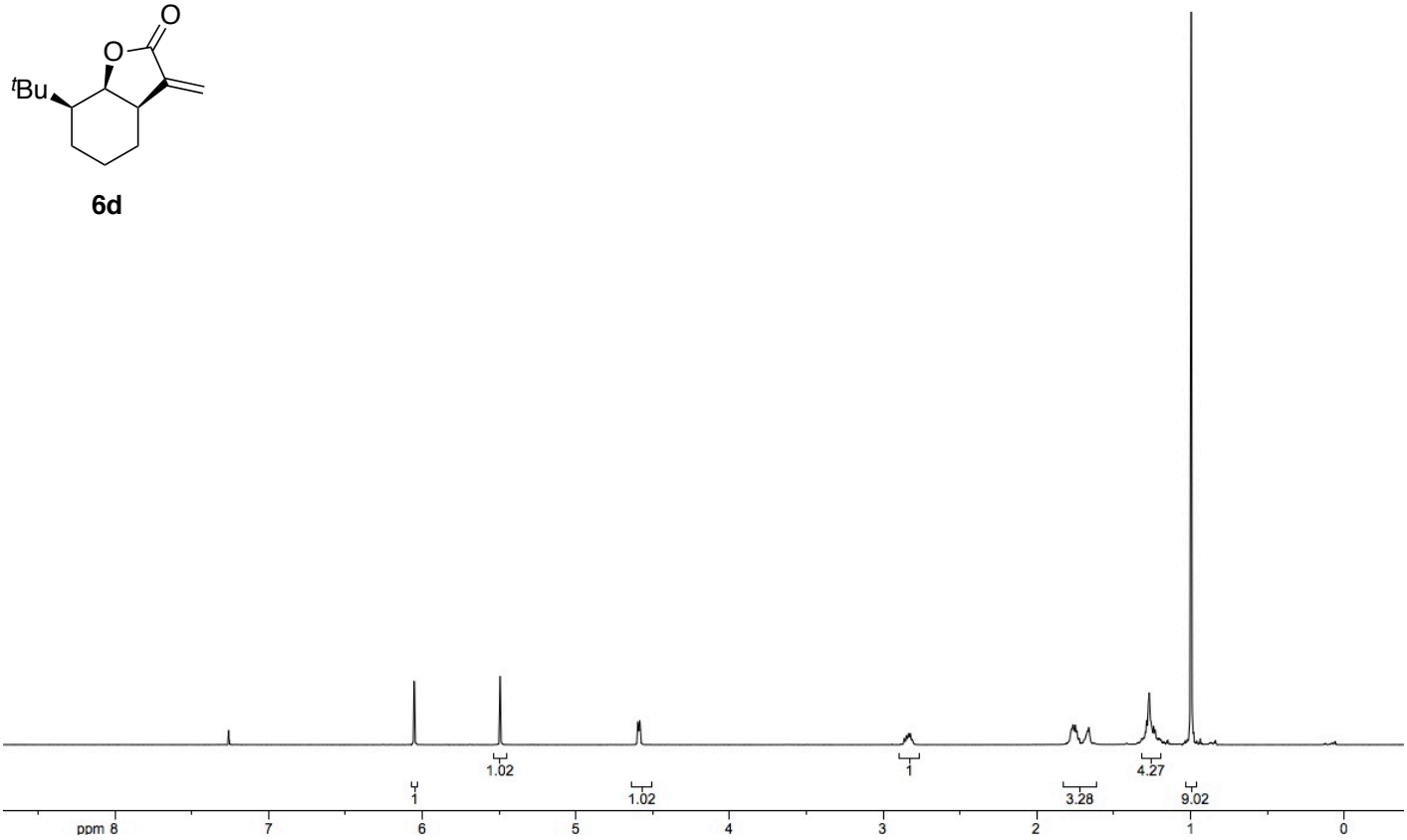
n5340mgl
M LLOYD MGL/06/72-P

5d



n5391mgl
M LLOYD MGL/06/75-P

6d



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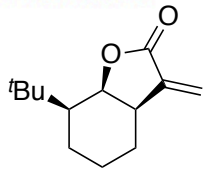
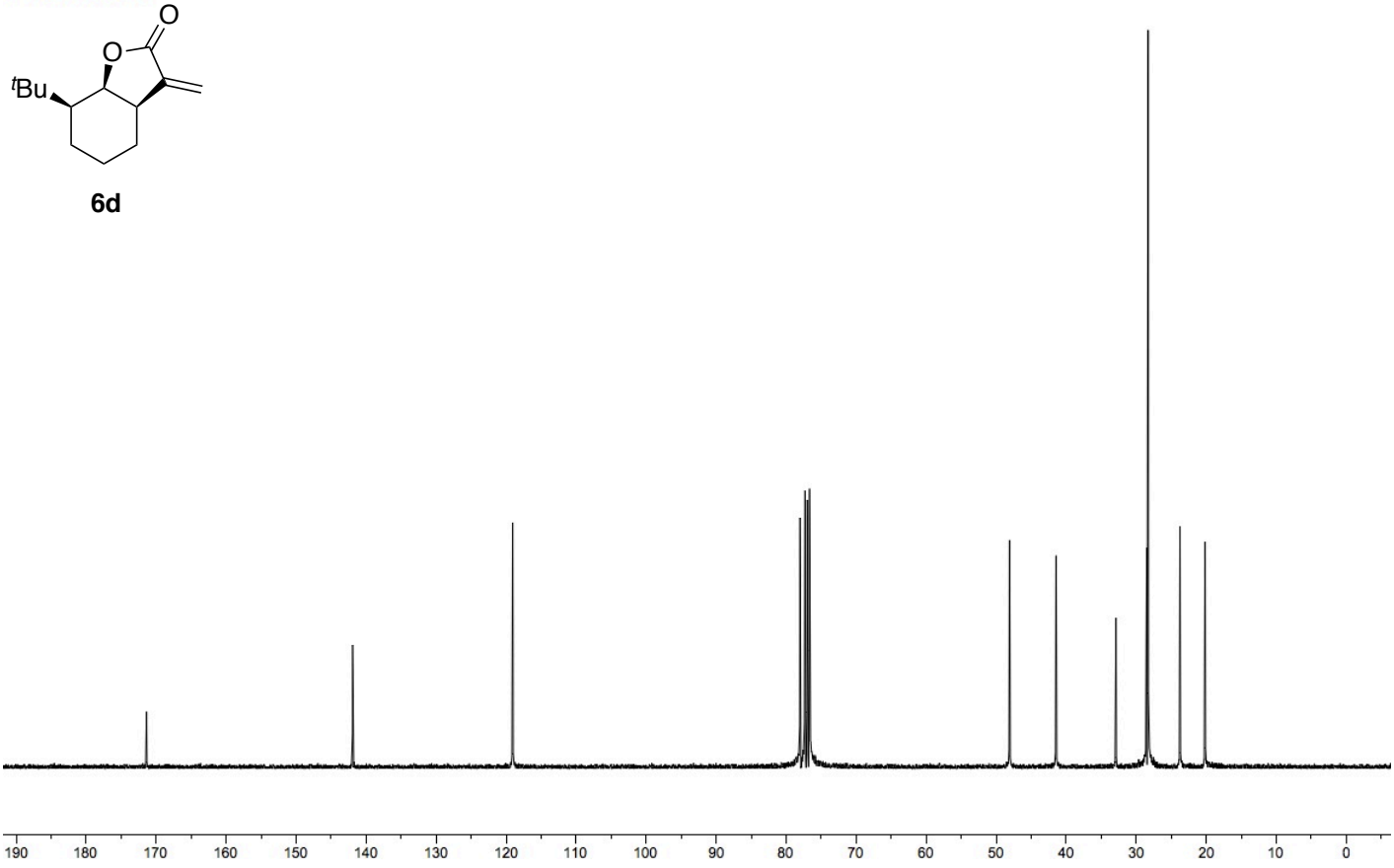
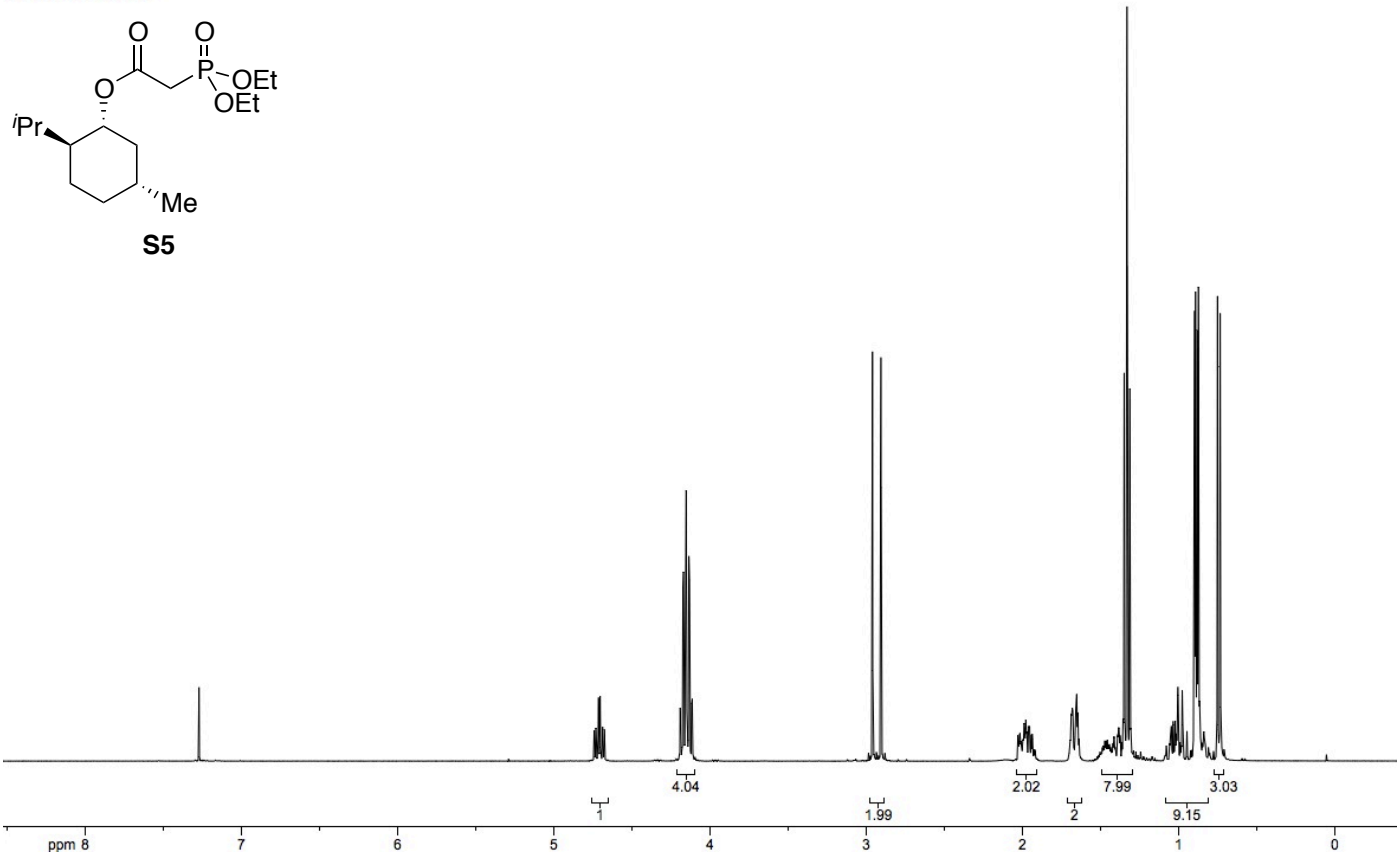


6d

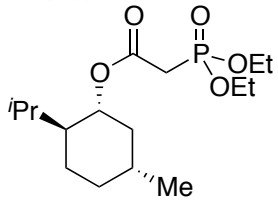


d4003mgl
M LLOYD MGL/06/54-P

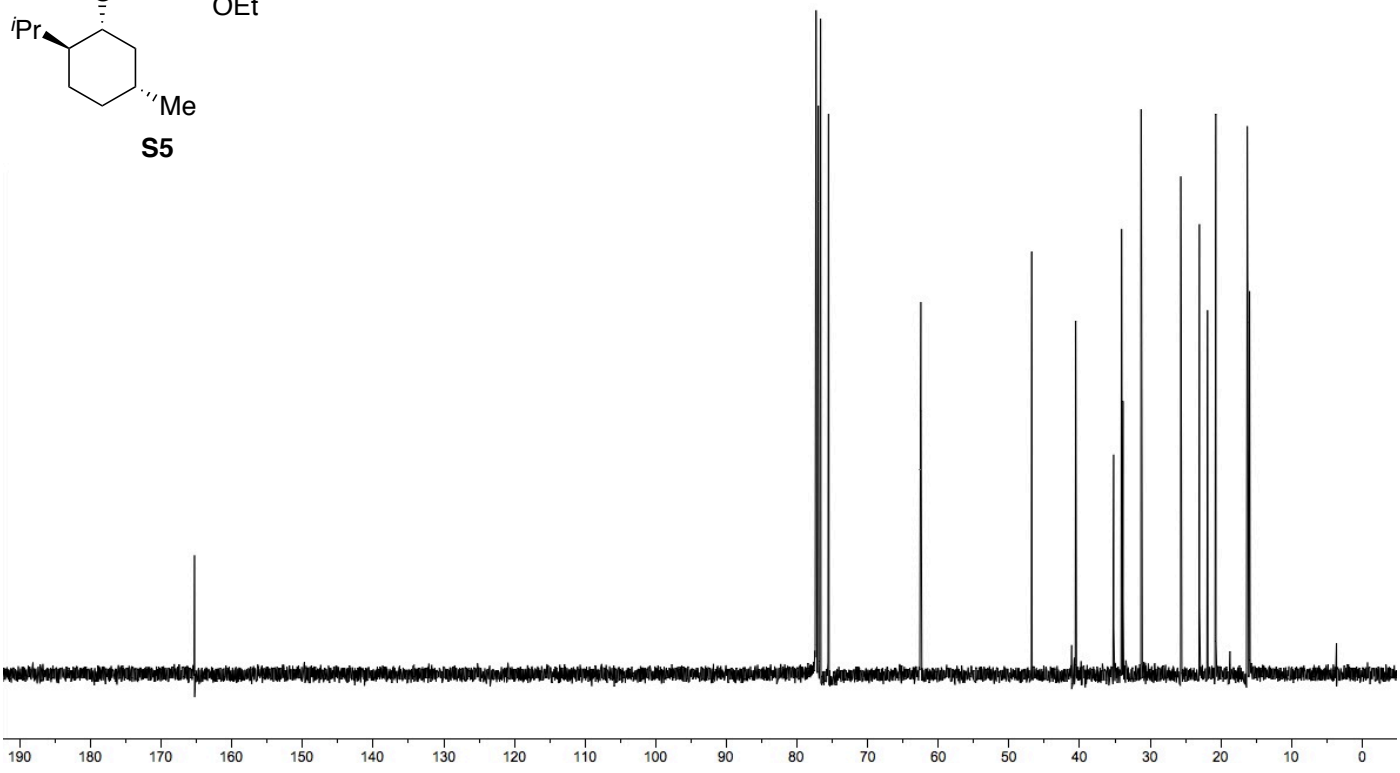
S5



d4277mgl
M LLOYD MGL/06/54-P



S5



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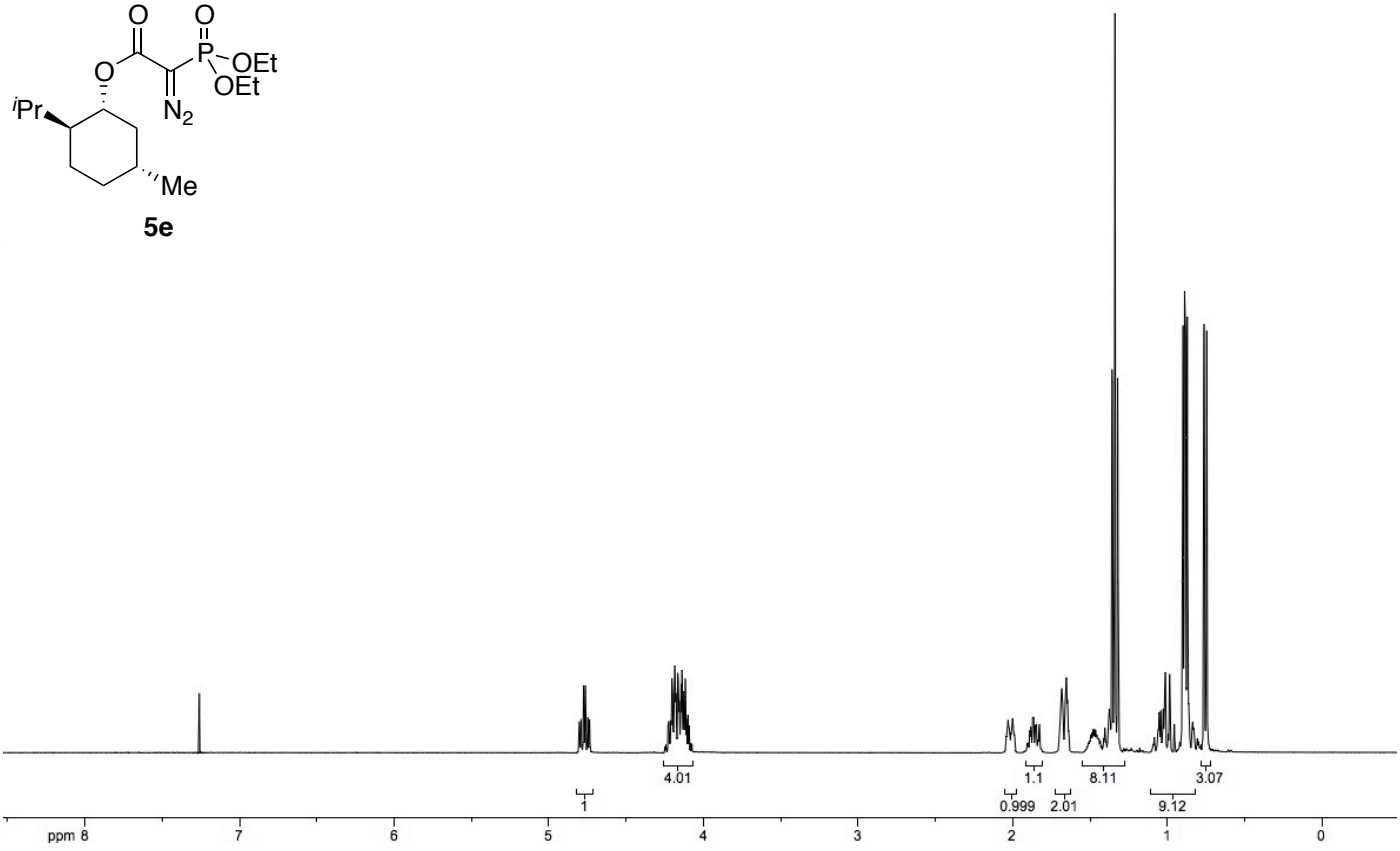
5e



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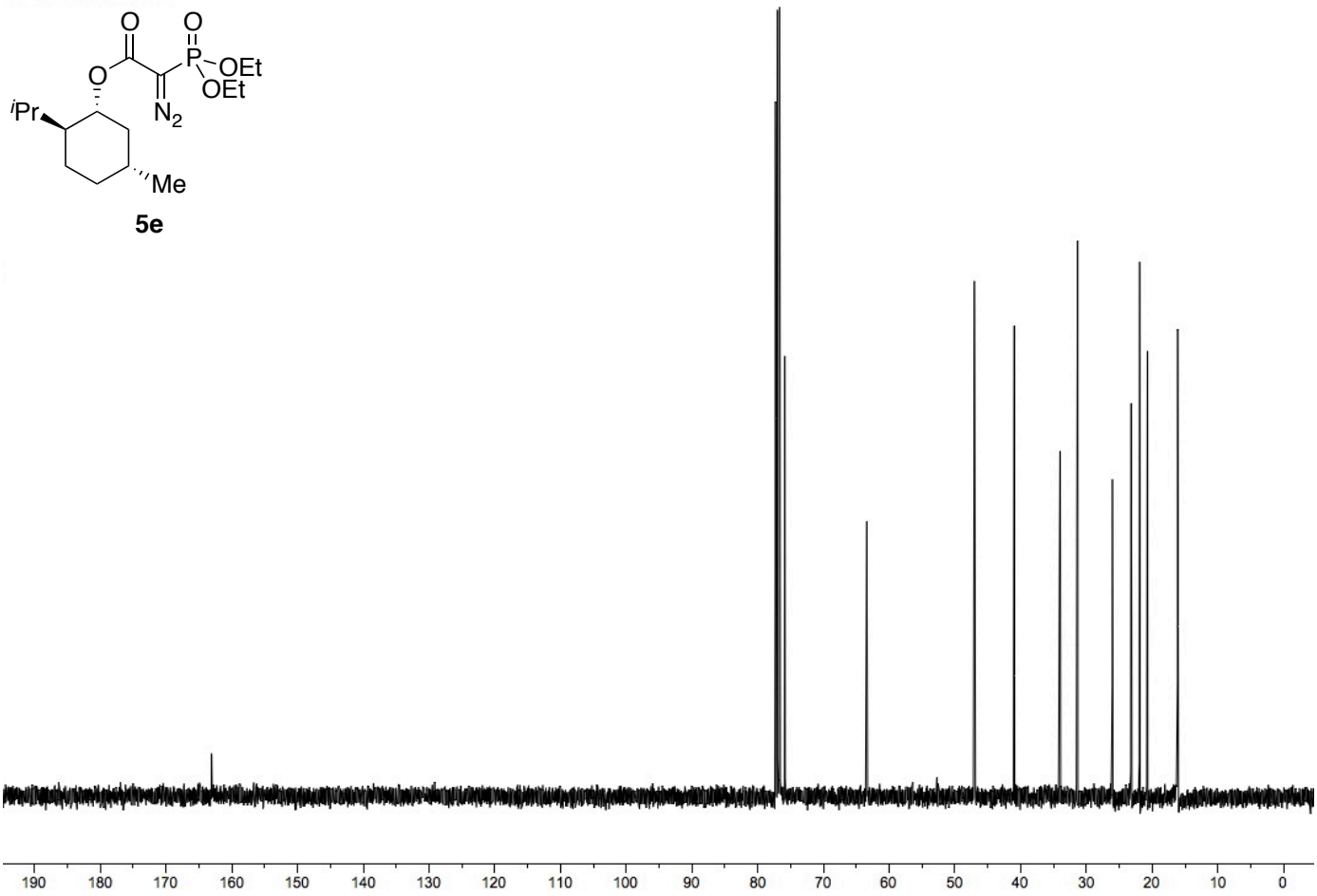
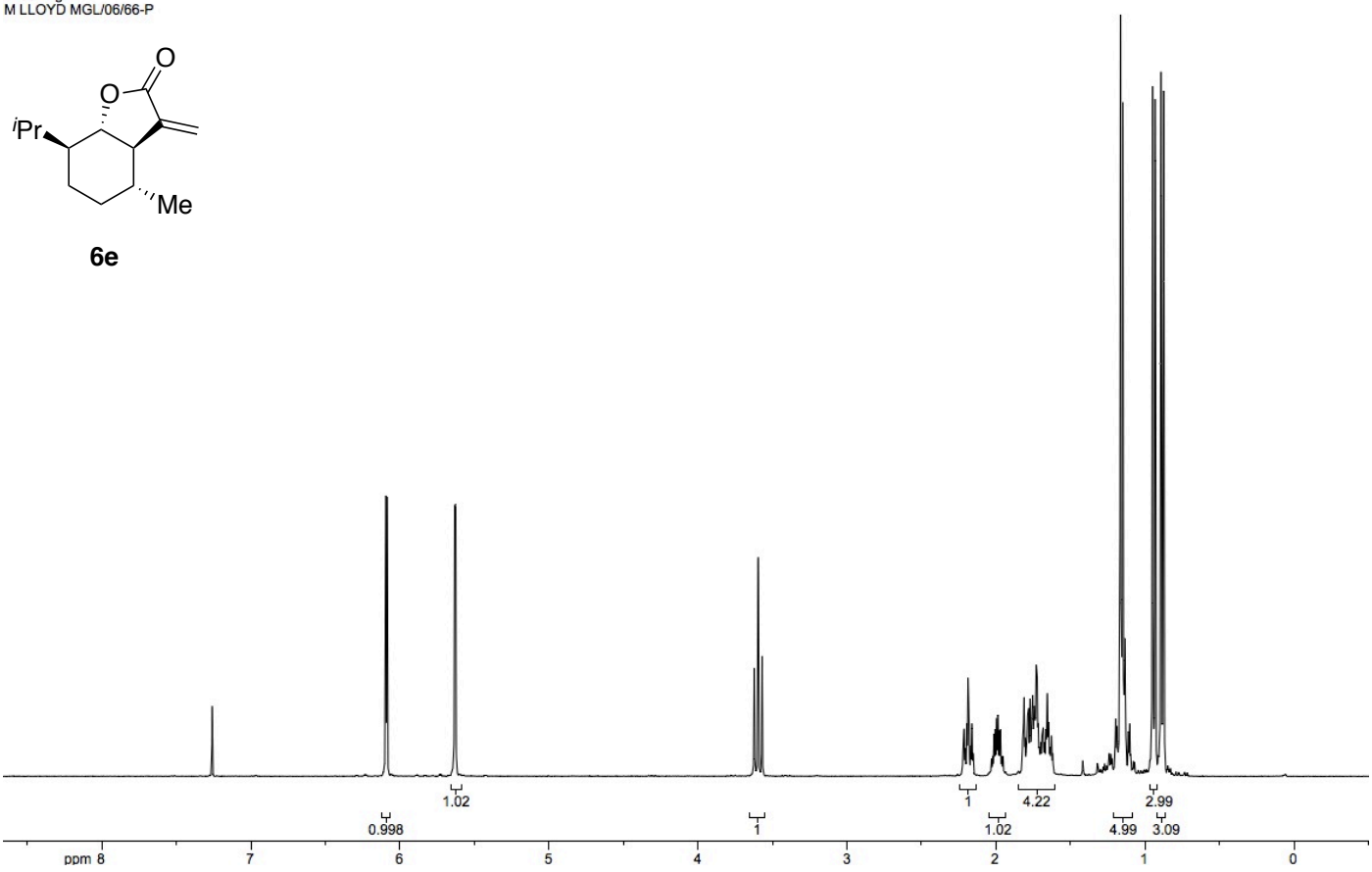
5e

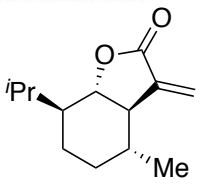


n4807mgl
M LLOYD MGL/06/66-P

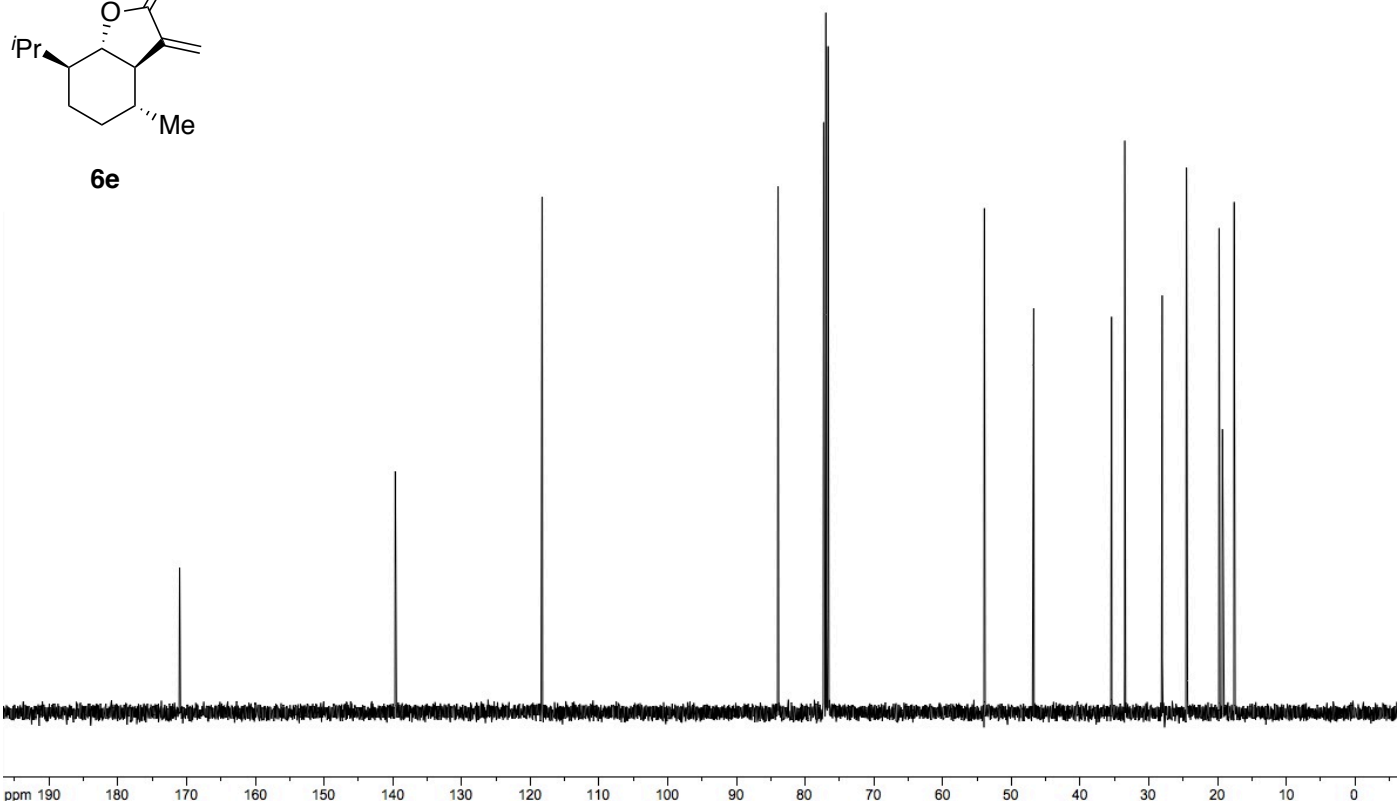
6e



n4848mgl
M LLOYD MGL/06/66-P

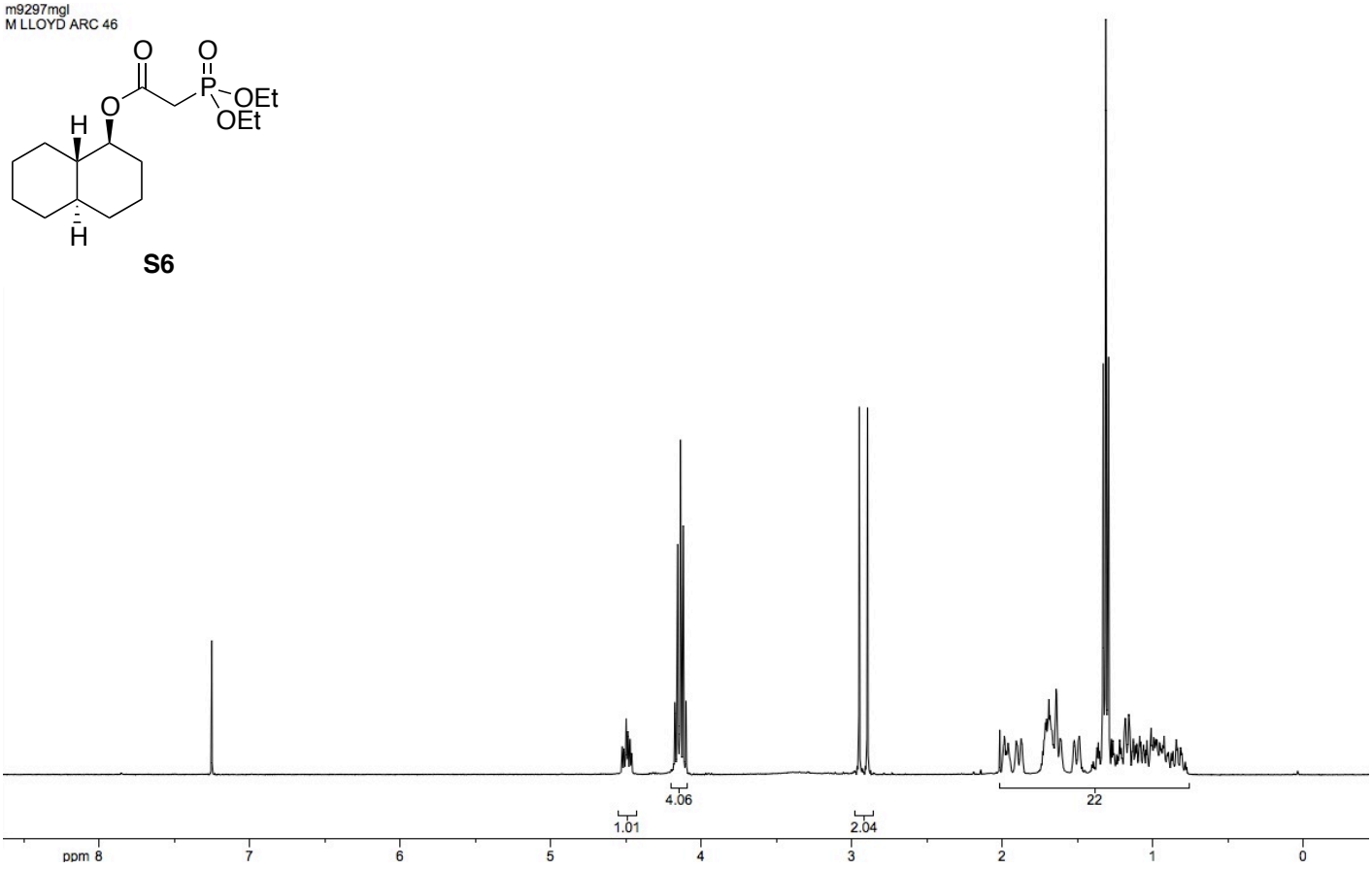


6e



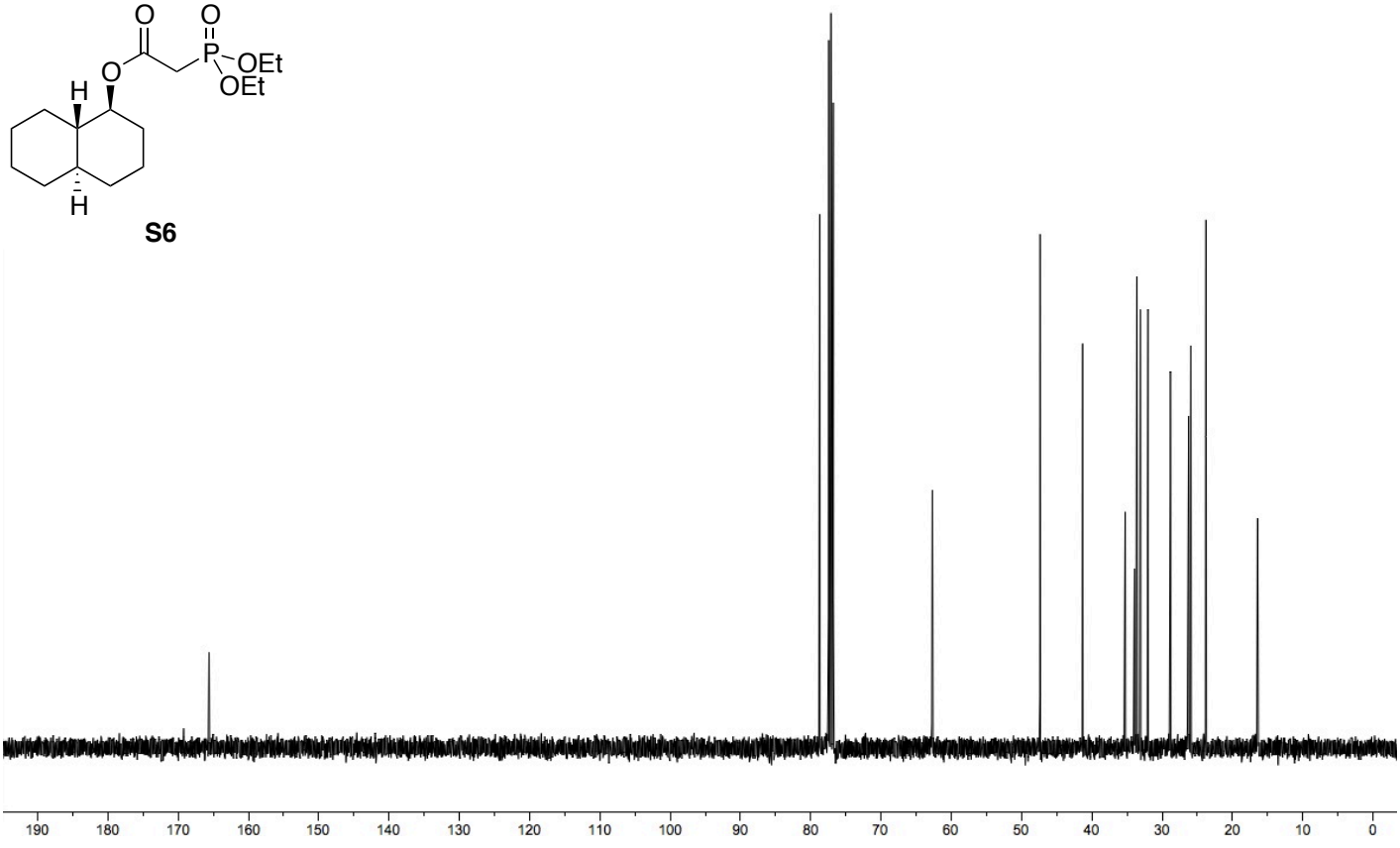
m9297mgl
M LLOYD ARC 46

S6



m9297mgl
M LLOYD ARC 46

S6



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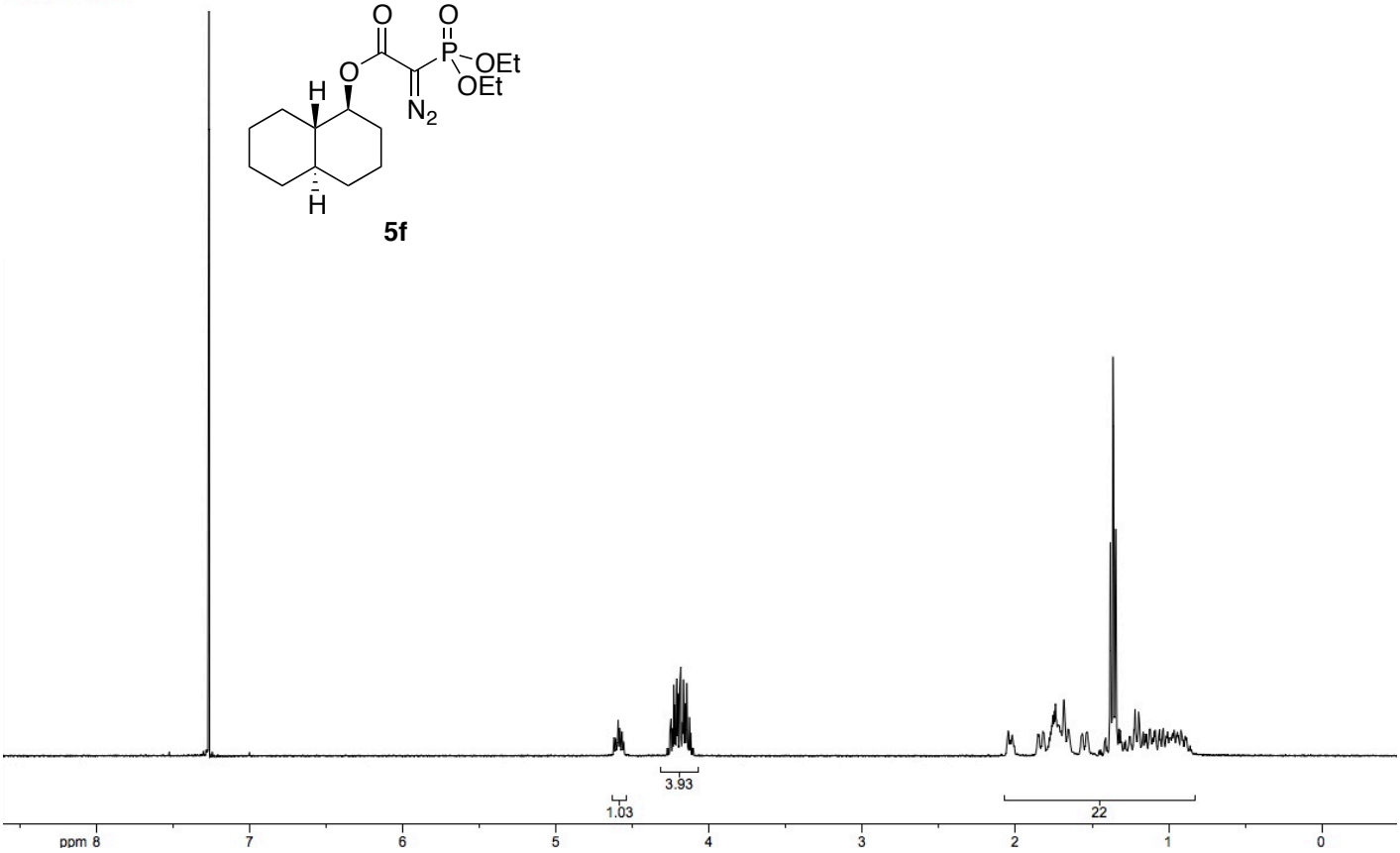
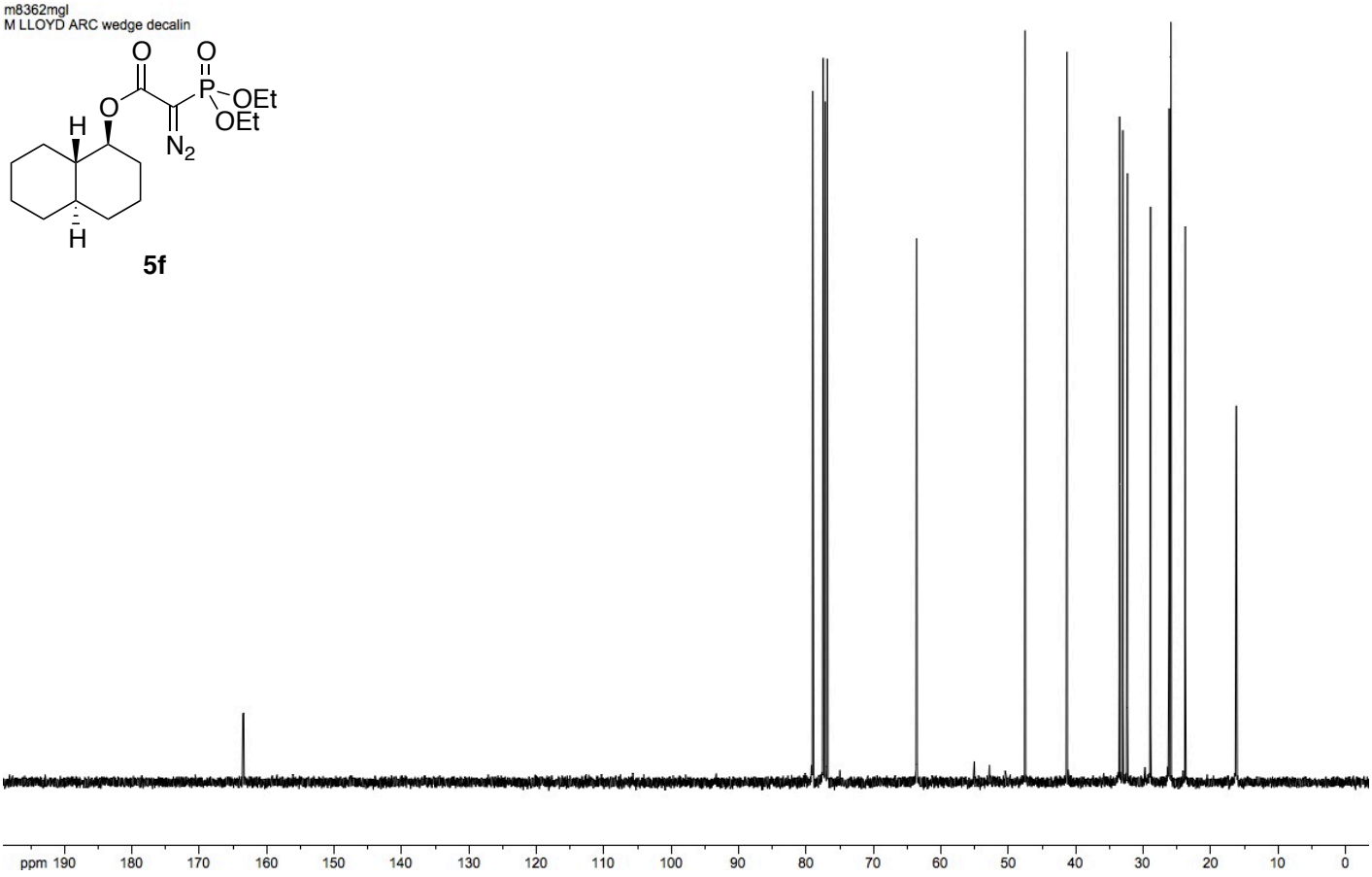


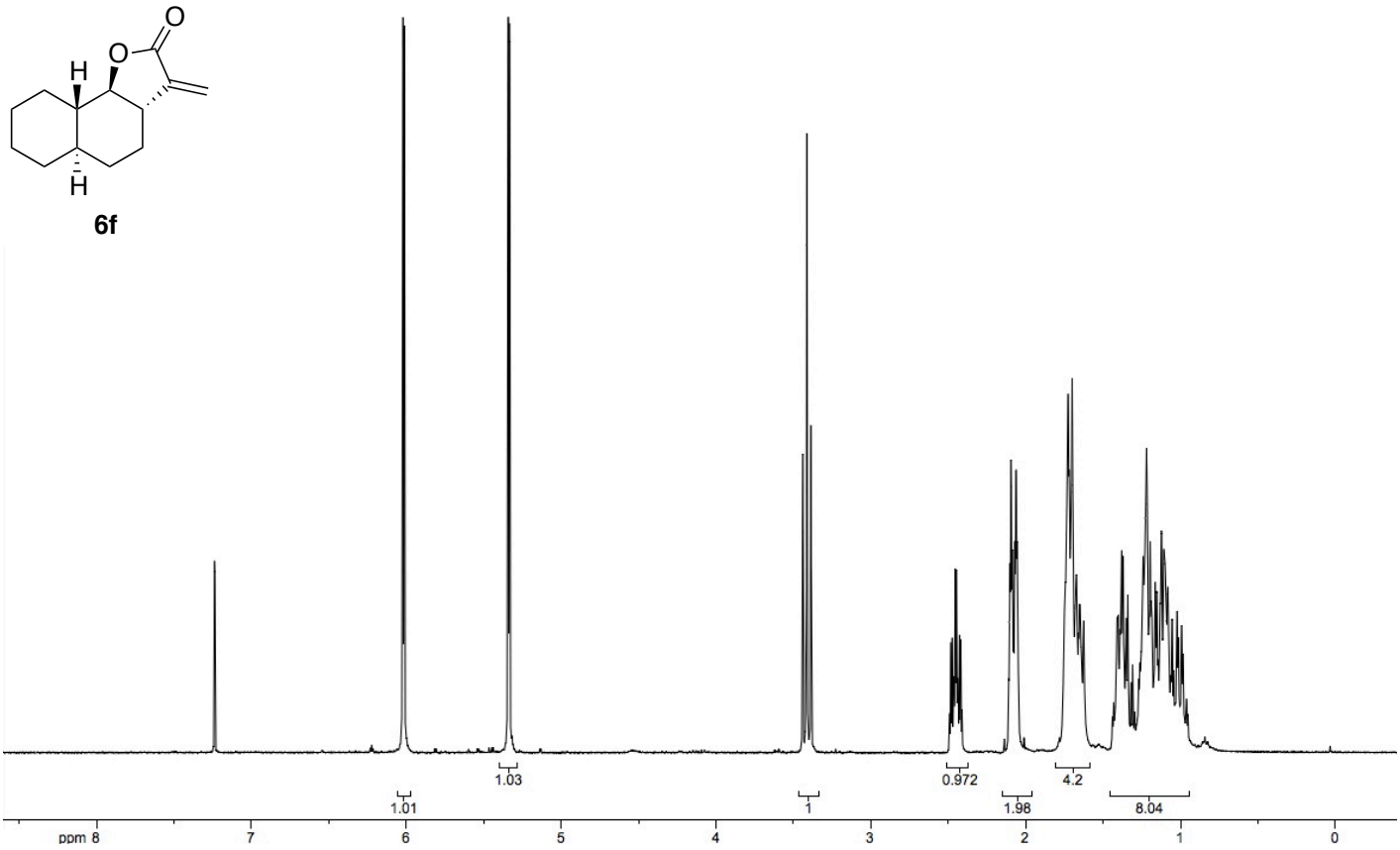
m8362mgl
M LLOYD ARC wedge decalin

5f



m8304mgl
M LLOYD MGL/05/34-P

6f



m8304mgl
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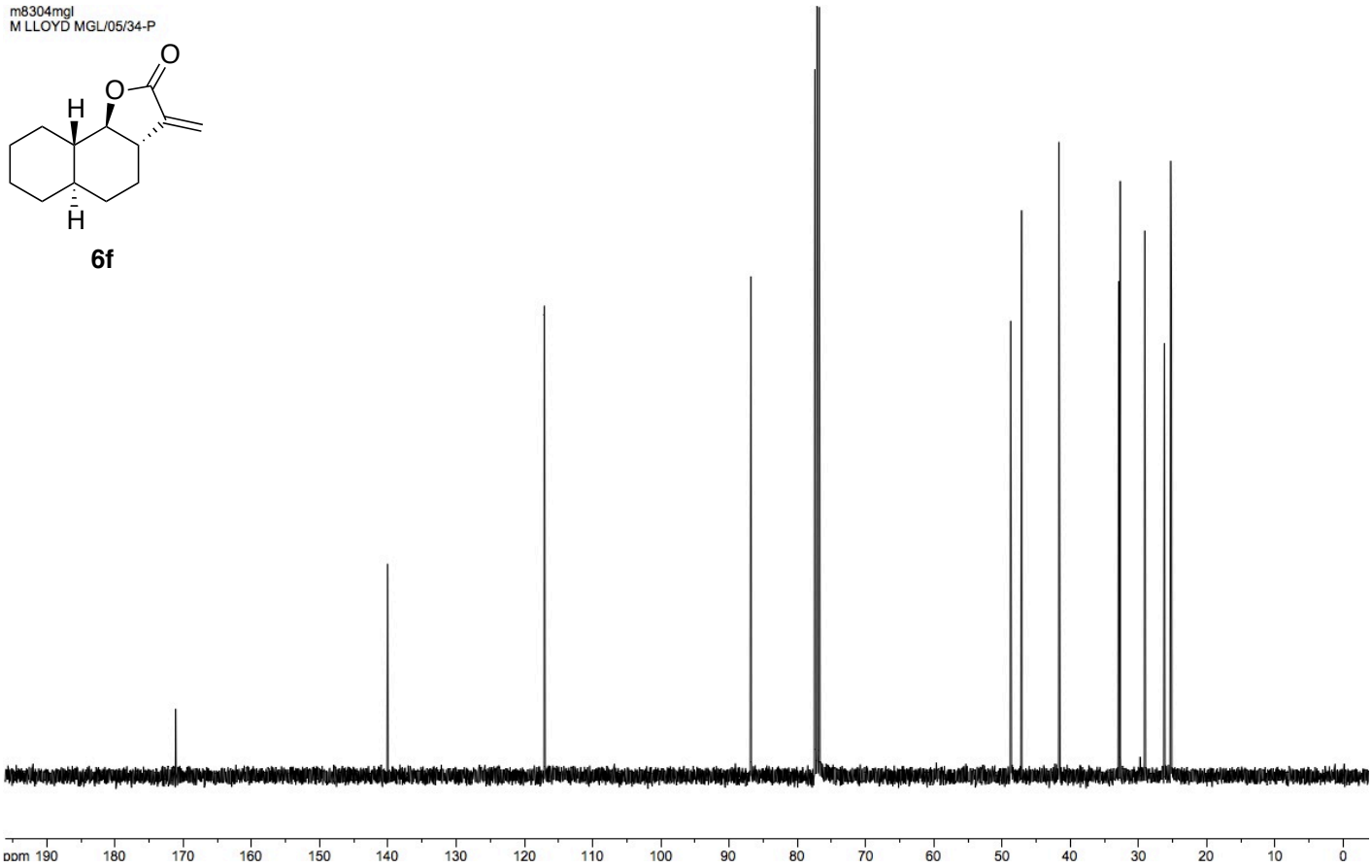
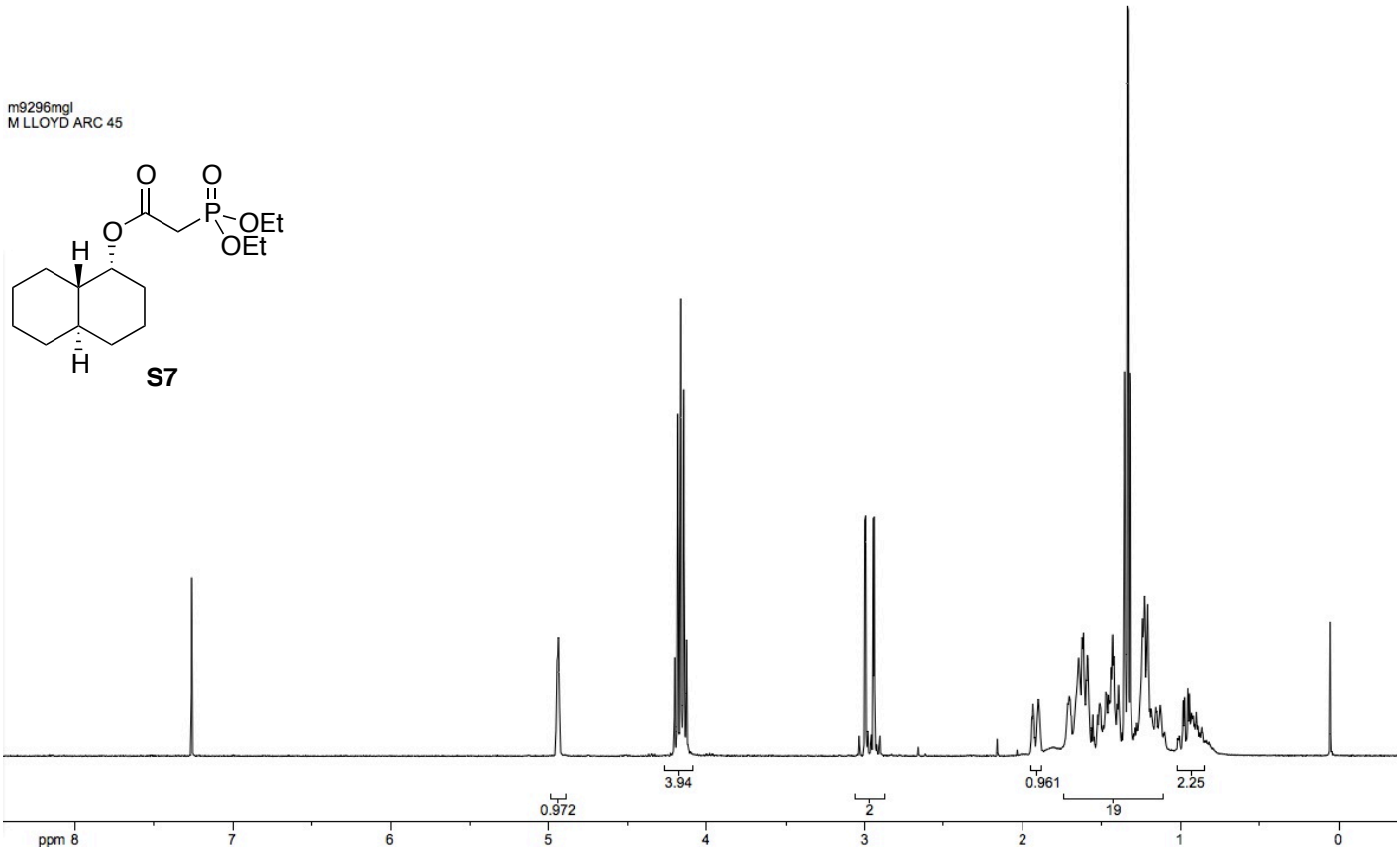
6f




m9296mgl
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O
O
P
OEt
OEt
H
H
S7
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2
0.961
19
2.25
ppm 8
7
6
5
4
3
2
1
0
m9296mgl
M LLOYD ARC 45
O
O
O
P
OEt
OEt
H
H
S7
ppm 190
180
170
160
150
140
130
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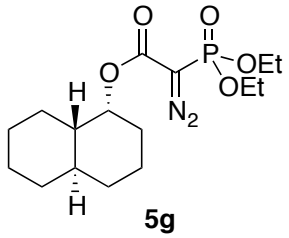
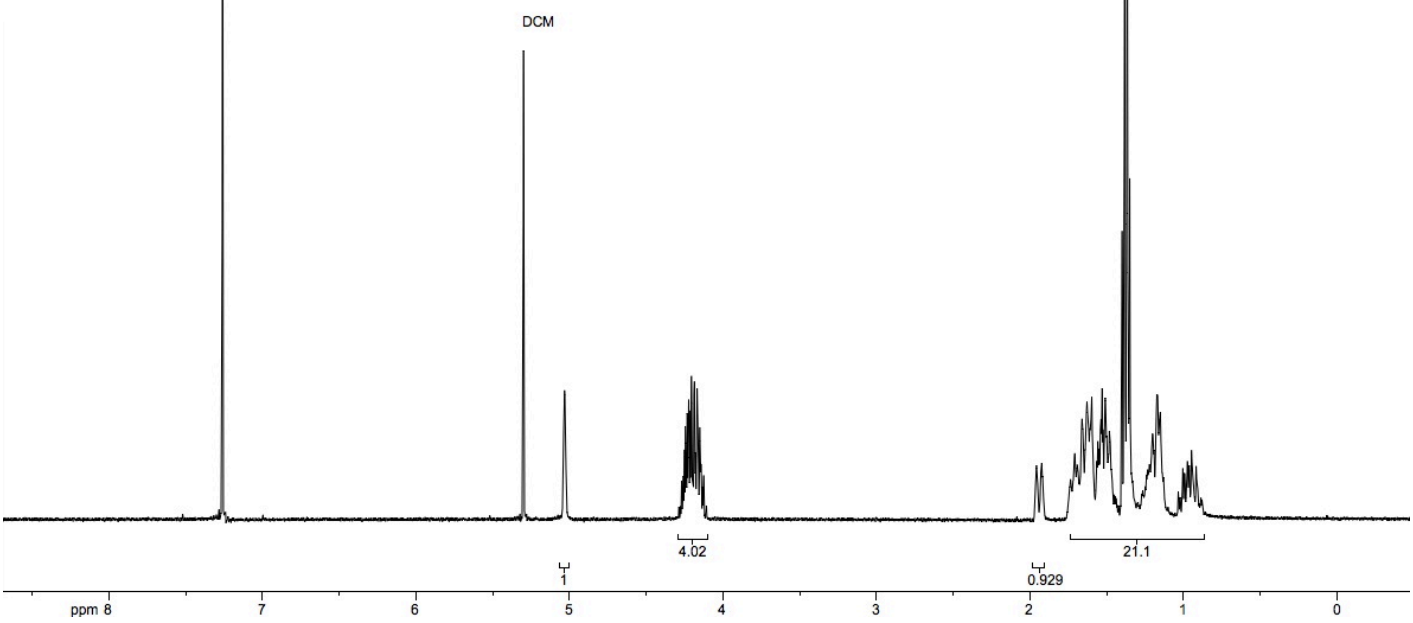
40
30
20
10
0

m8195mgl
M LLOYD ARC57

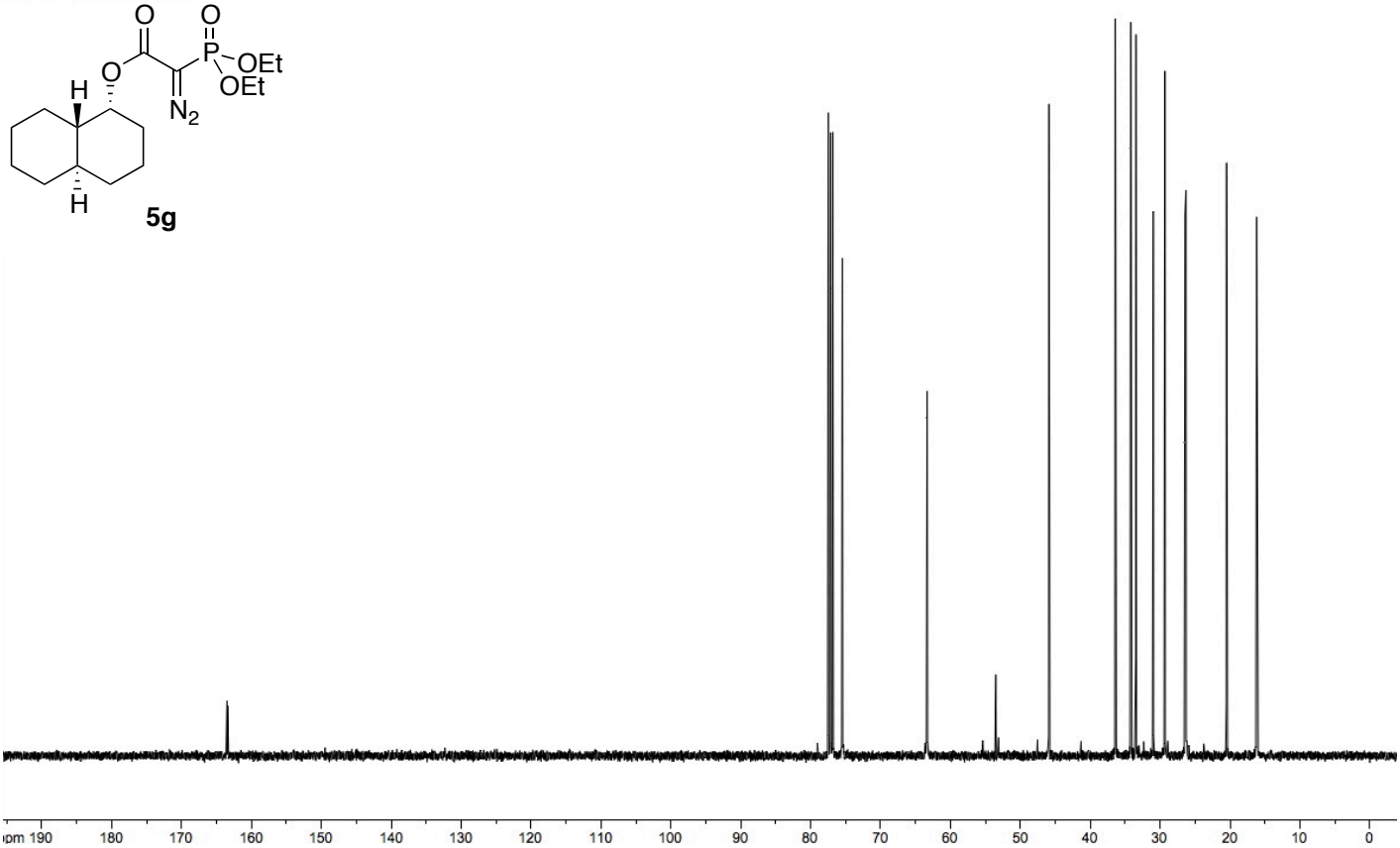


5g



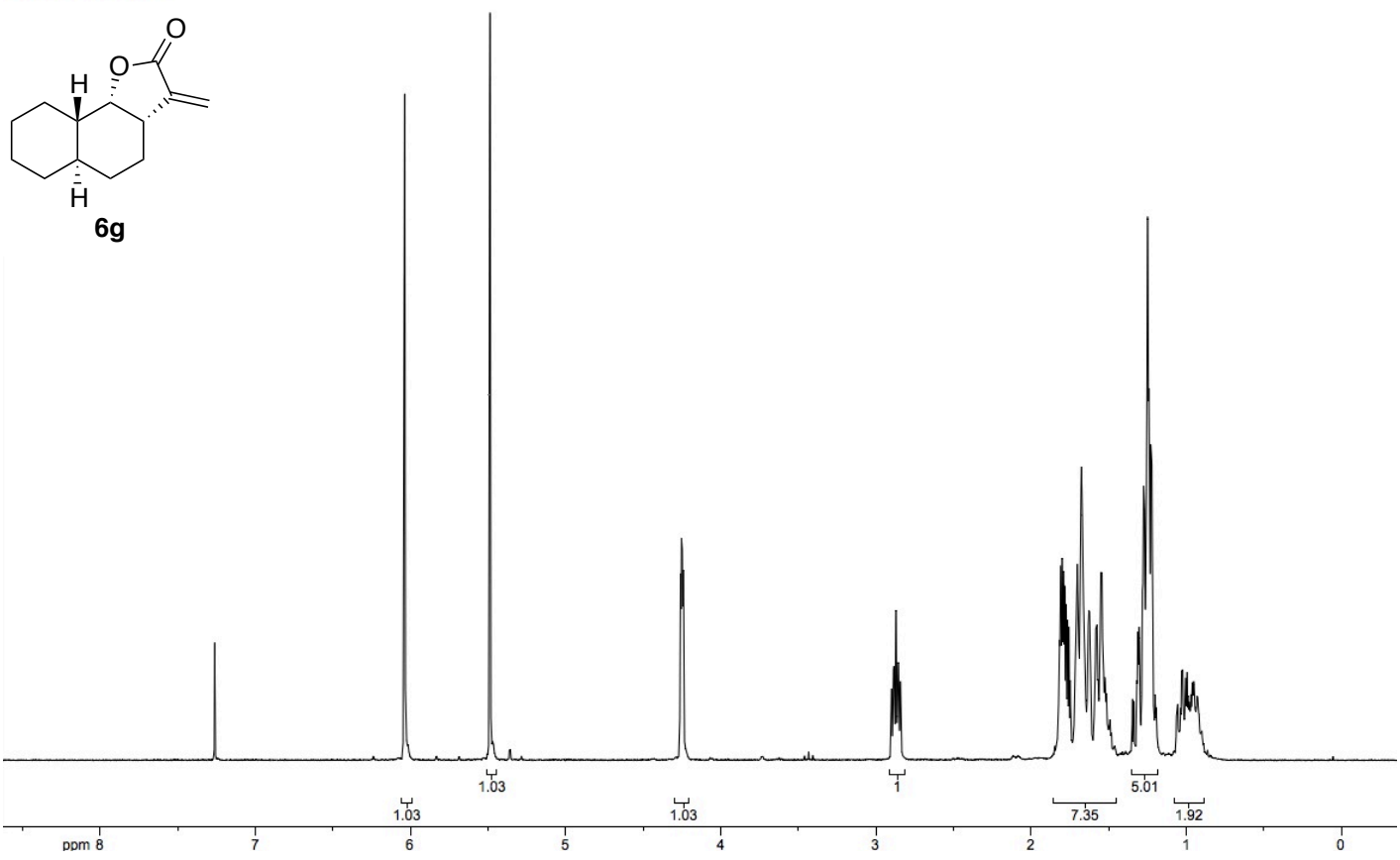
m8363mgl
M LLOYD ARC dash decalin

5g



m8305mgl
M LLOYD MGL/05/35-P

6g



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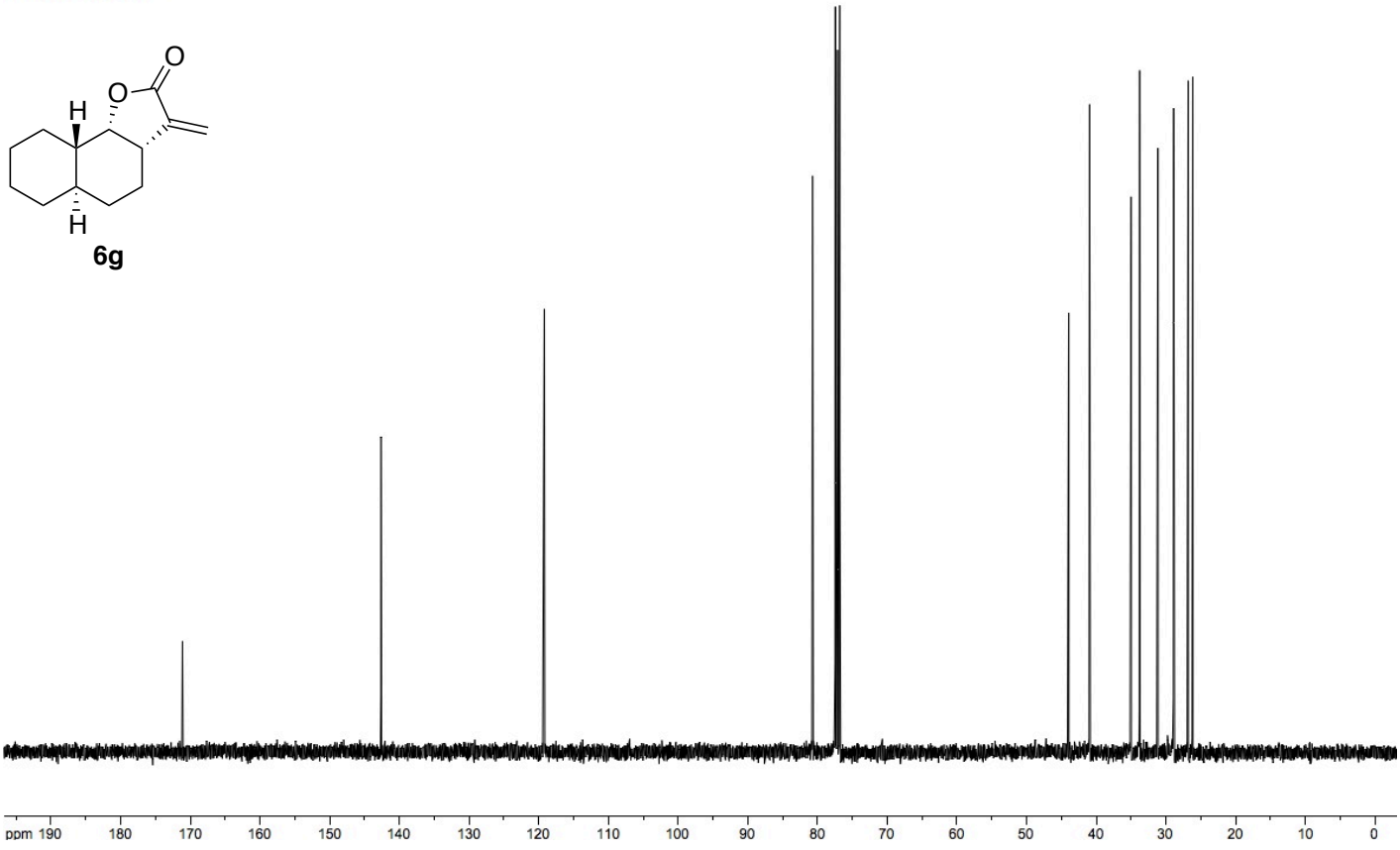
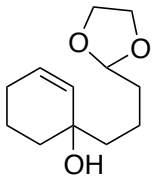
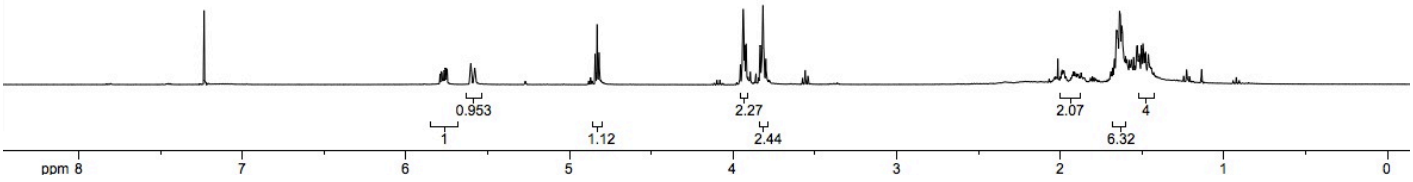
6g



c7986mgl
M LLOYD MGL/05/90-P

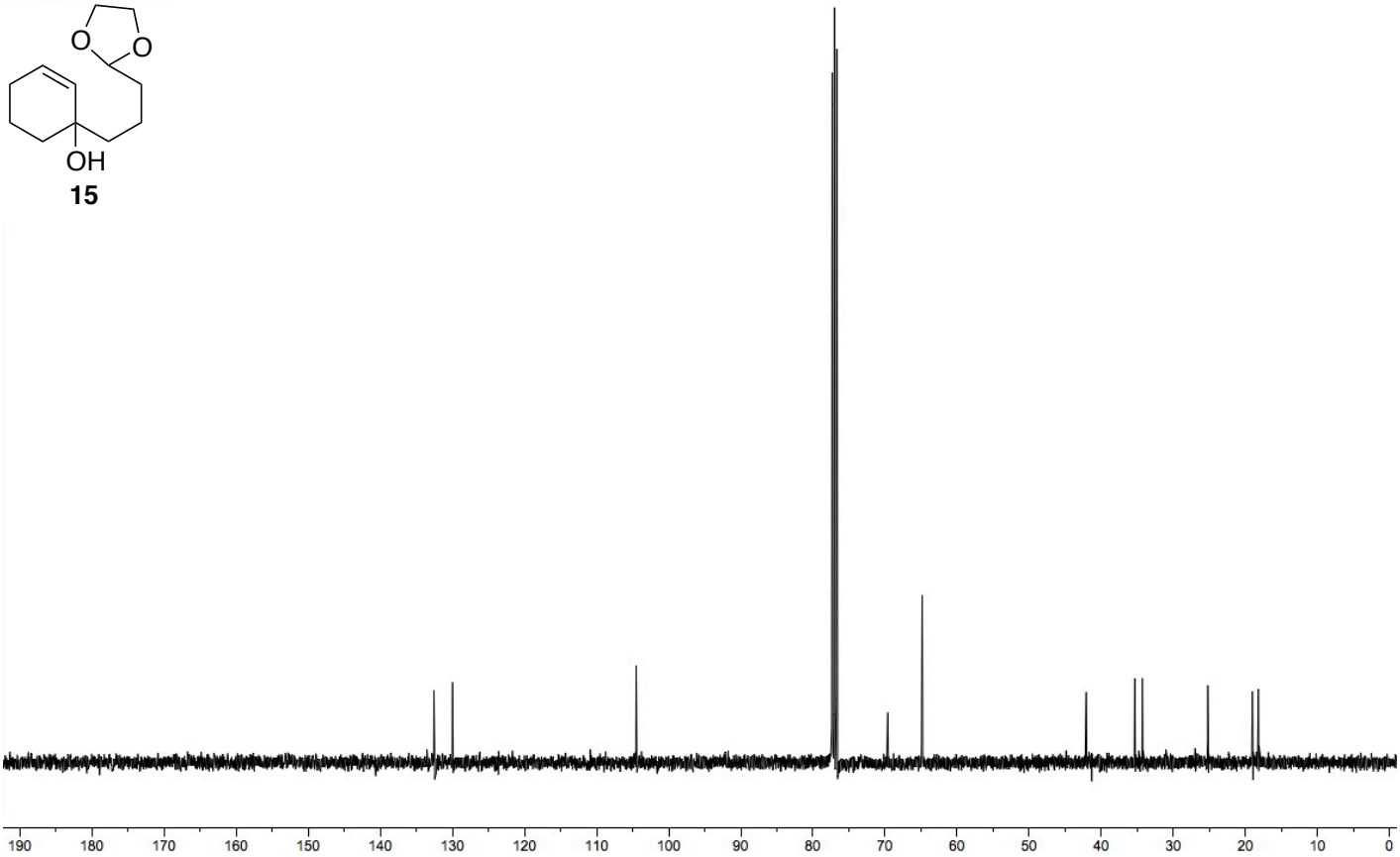


15

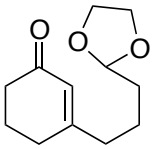


c7986mgl
M LLOYD MGL/05/90-P

15



c8018mgl
M LLOYD MGL/05/92-P



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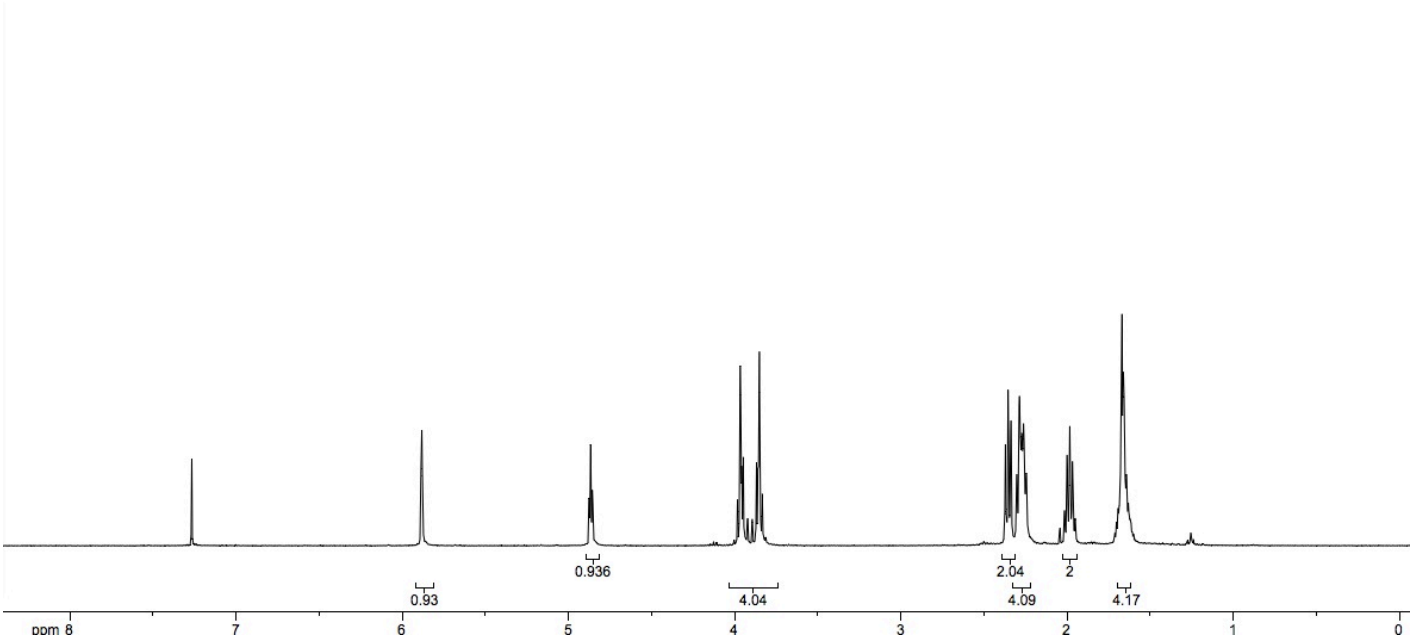

c7987mgl
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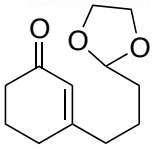

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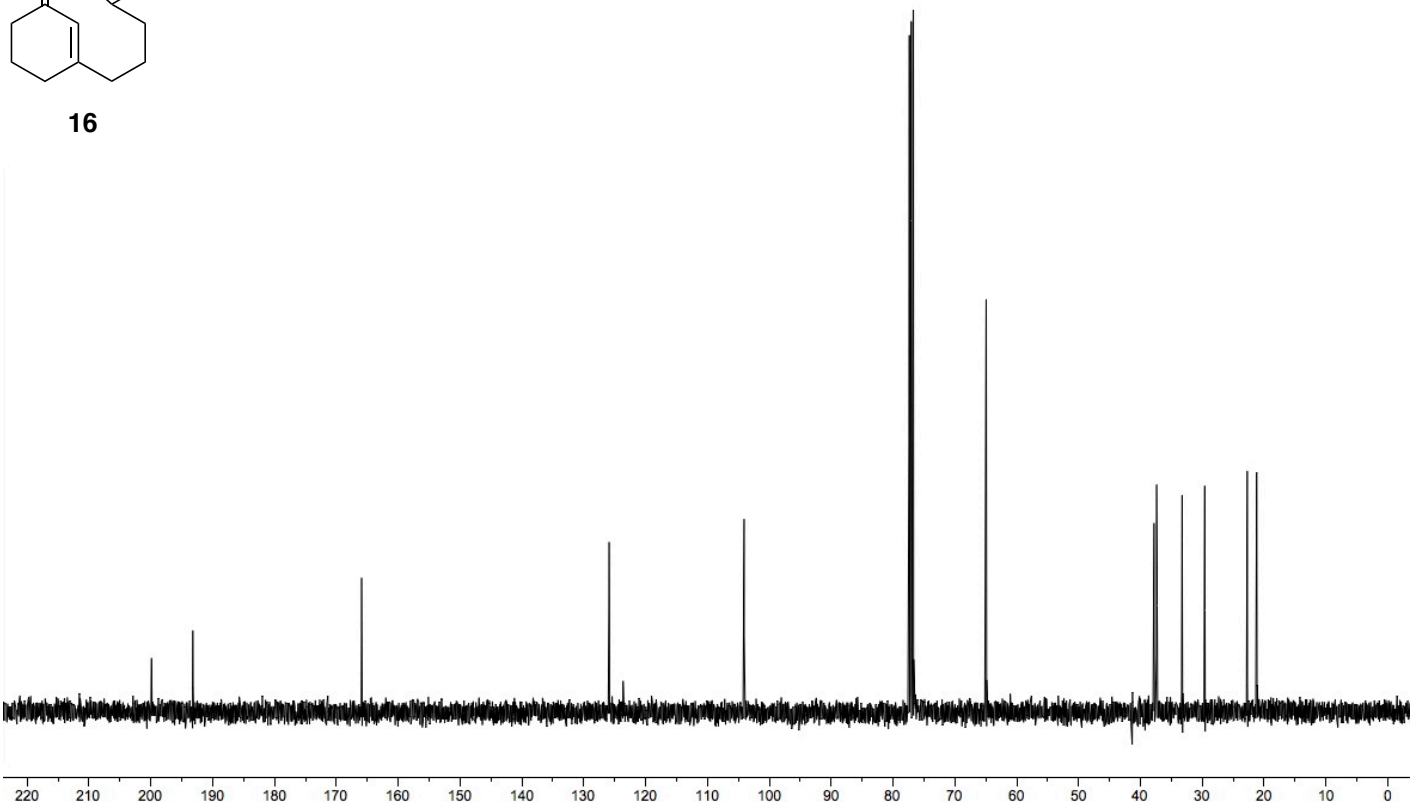
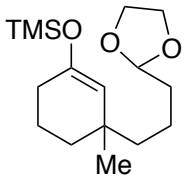


c8078mgl
M LLOYD MGL/05/93-C



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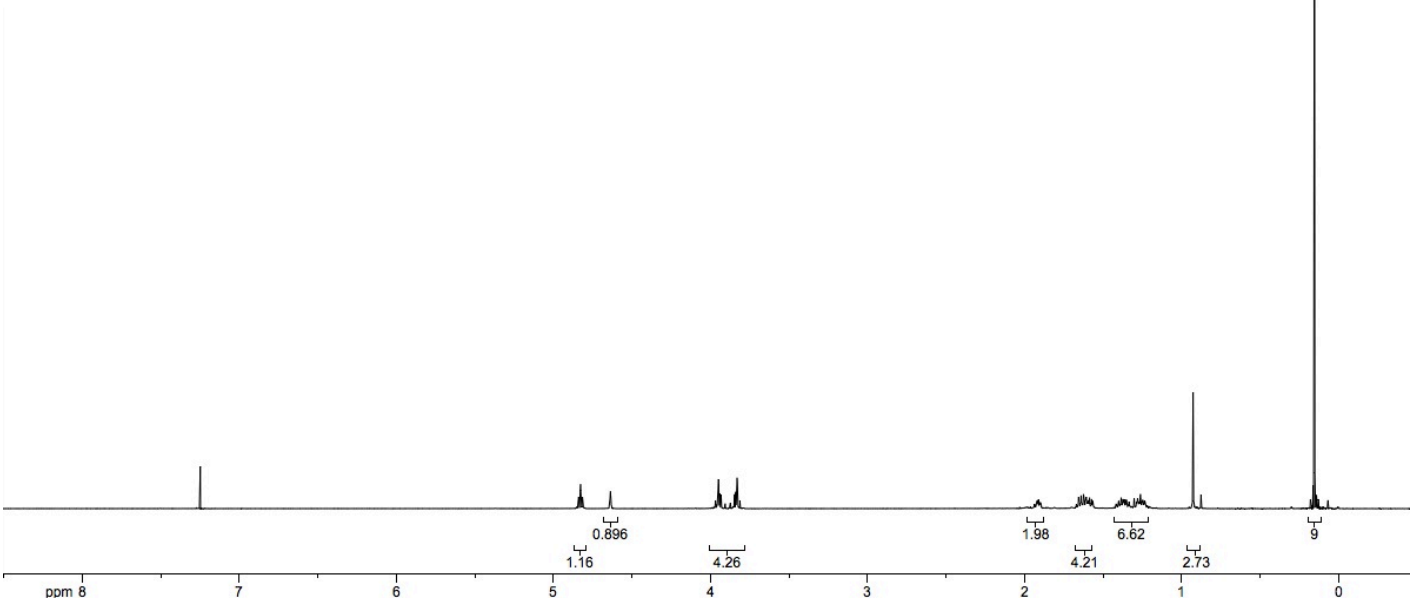
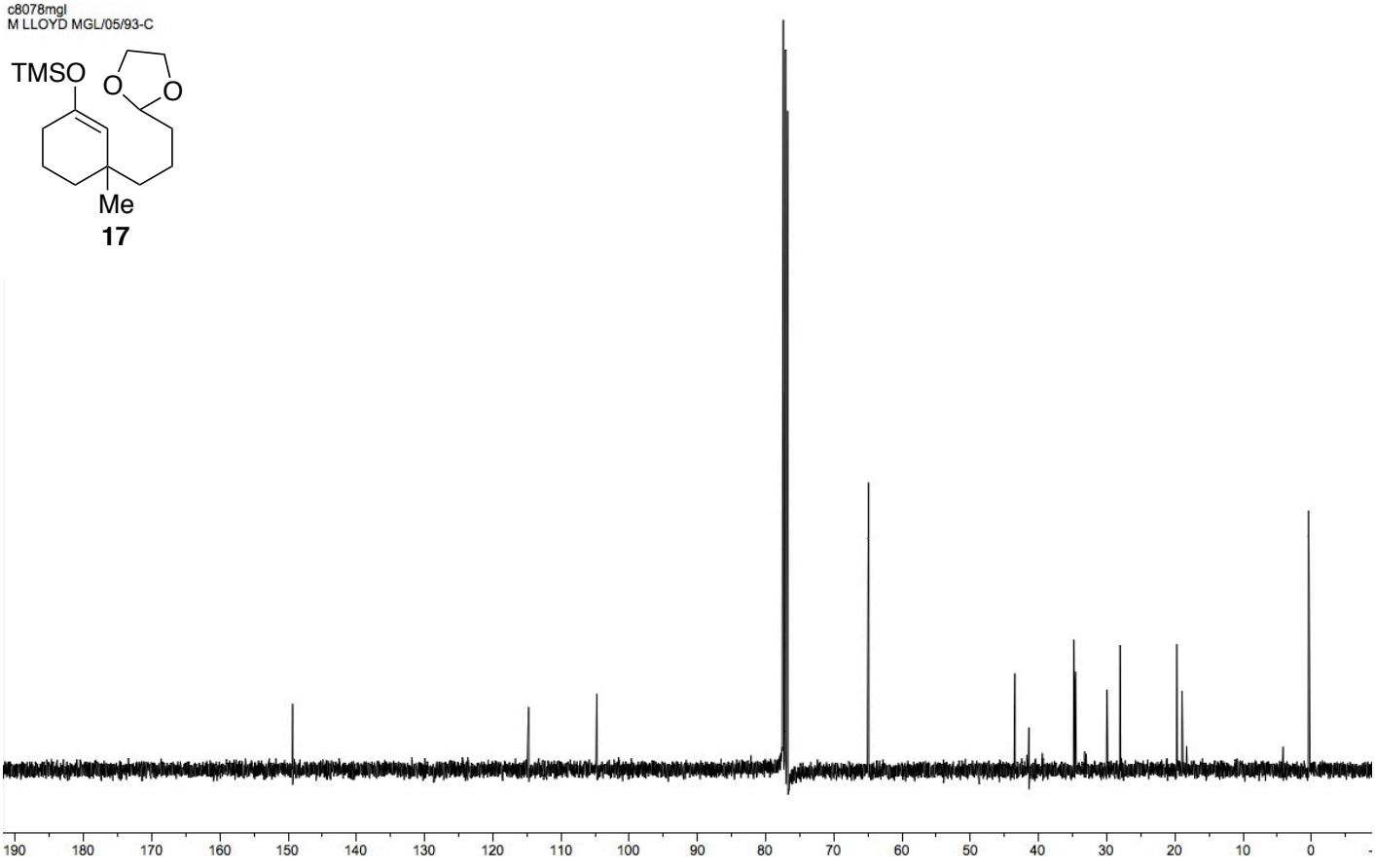


c8078mgl
M LLOYD MGL/05/93-C

17



c8475mgl
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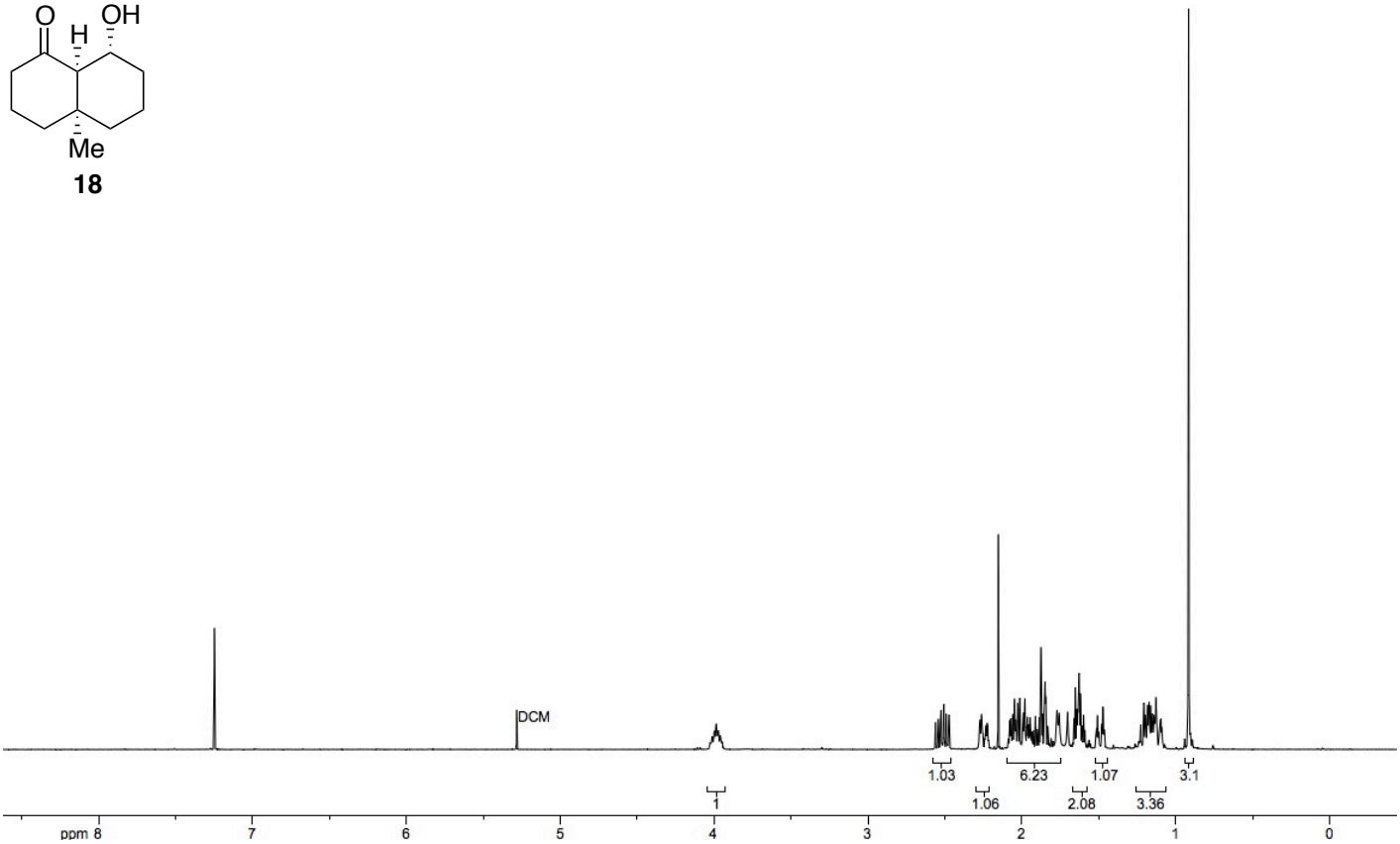
18



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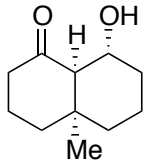

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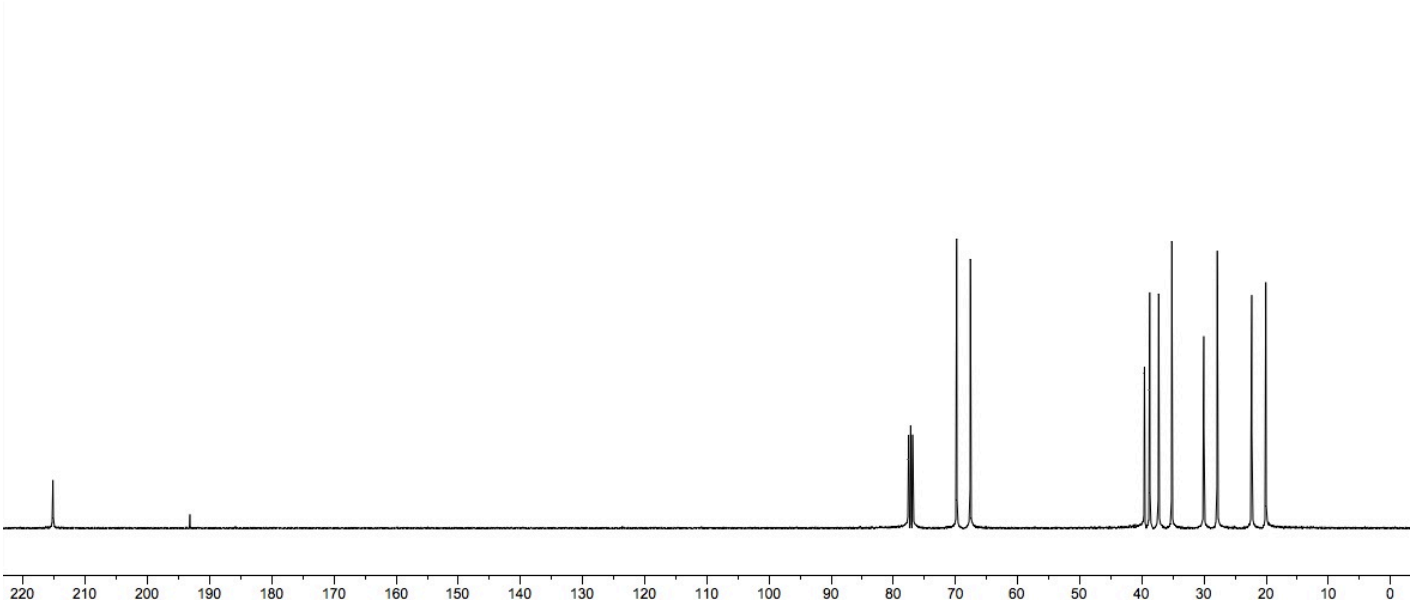

n3836mgl
M LLOYD MGL/06/28-P

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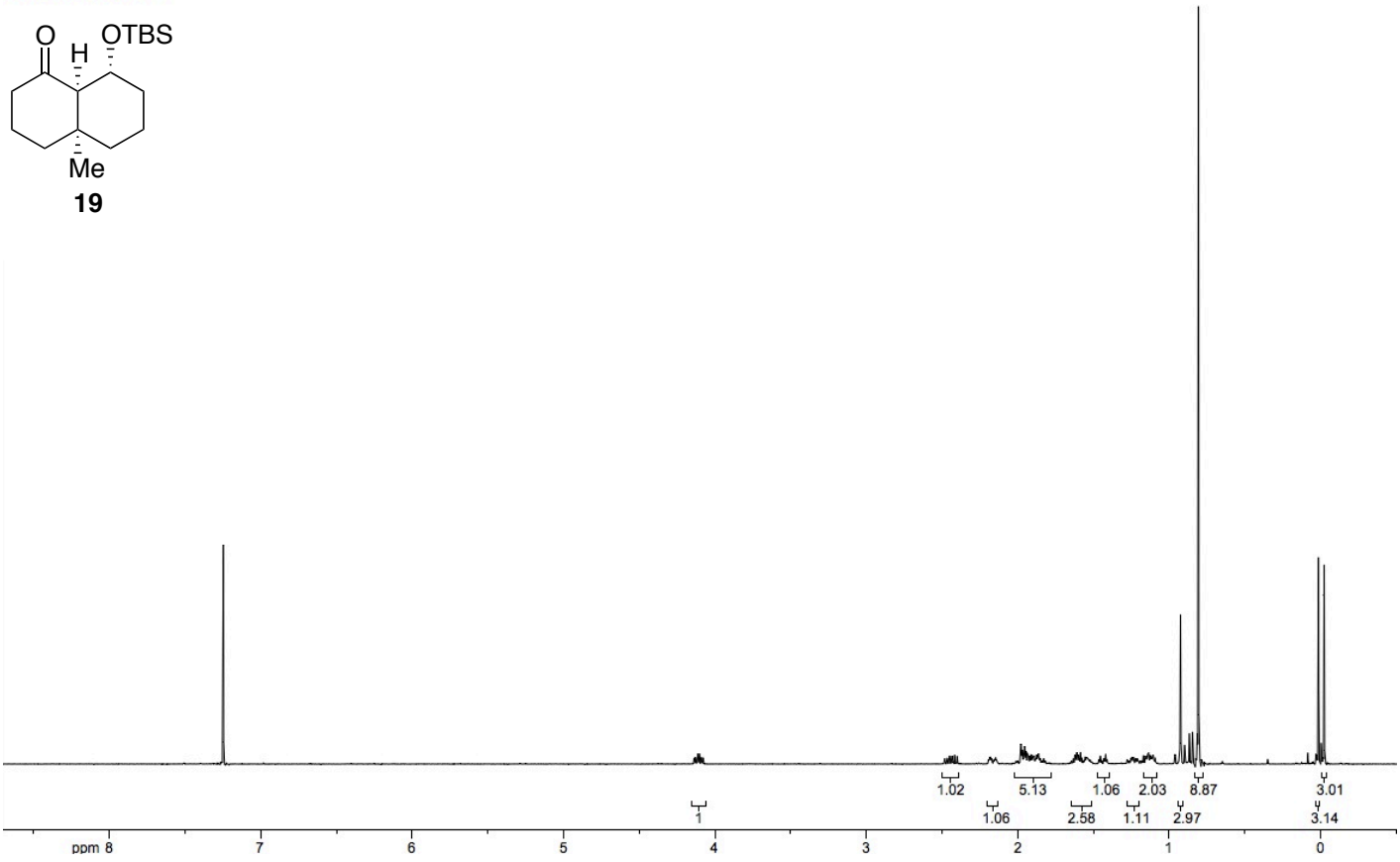

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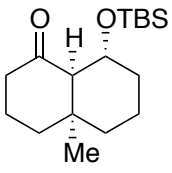

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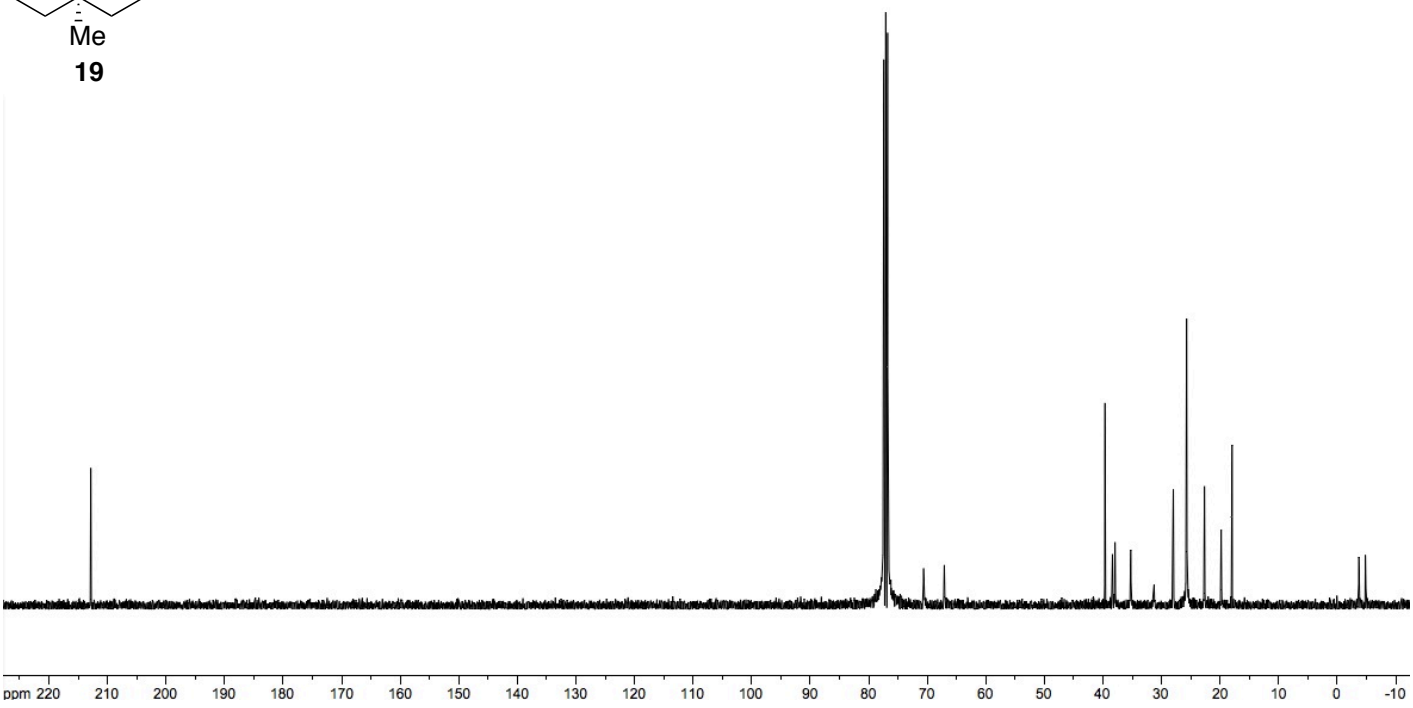

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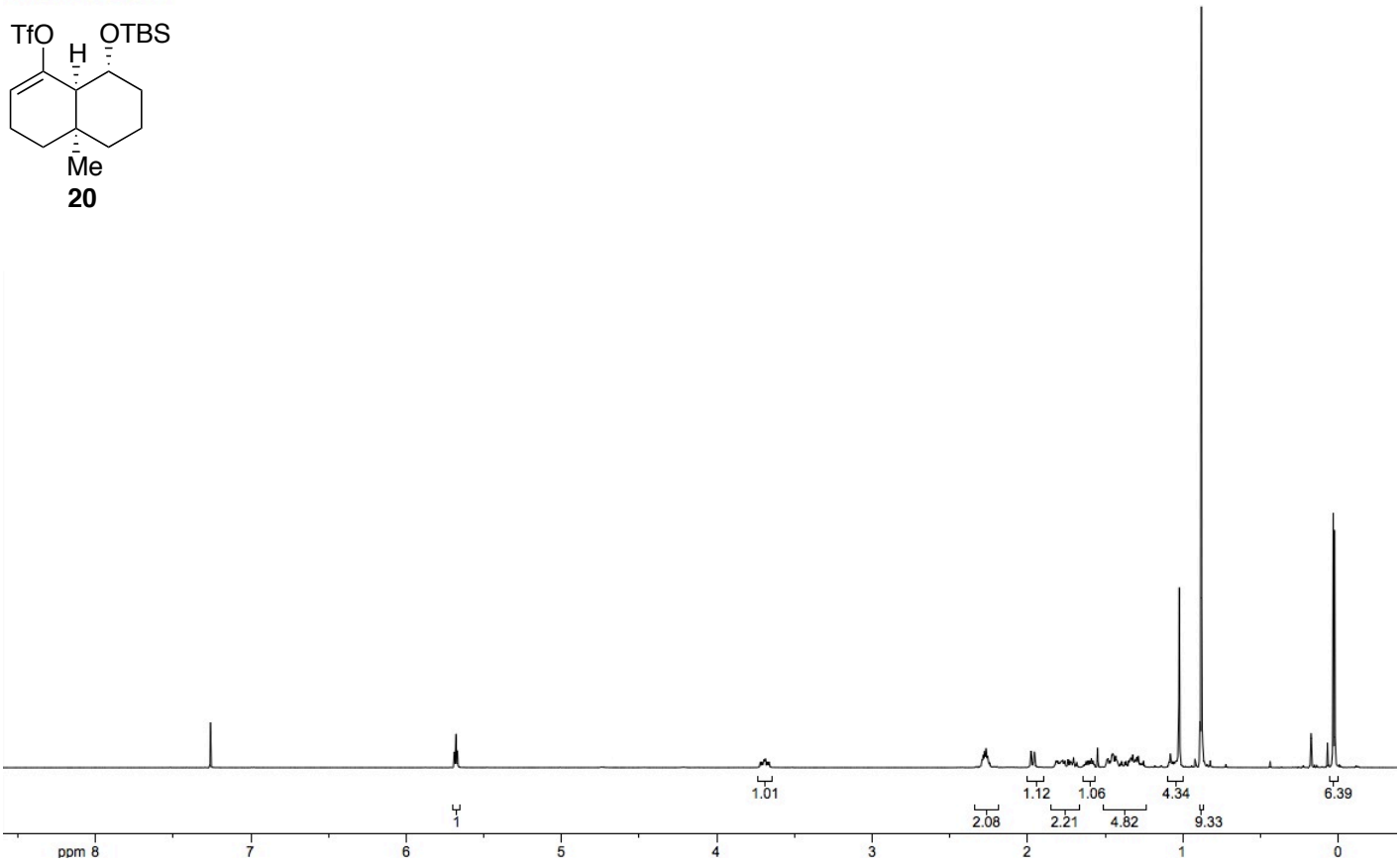

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M LLOYD MGL/07/30-P

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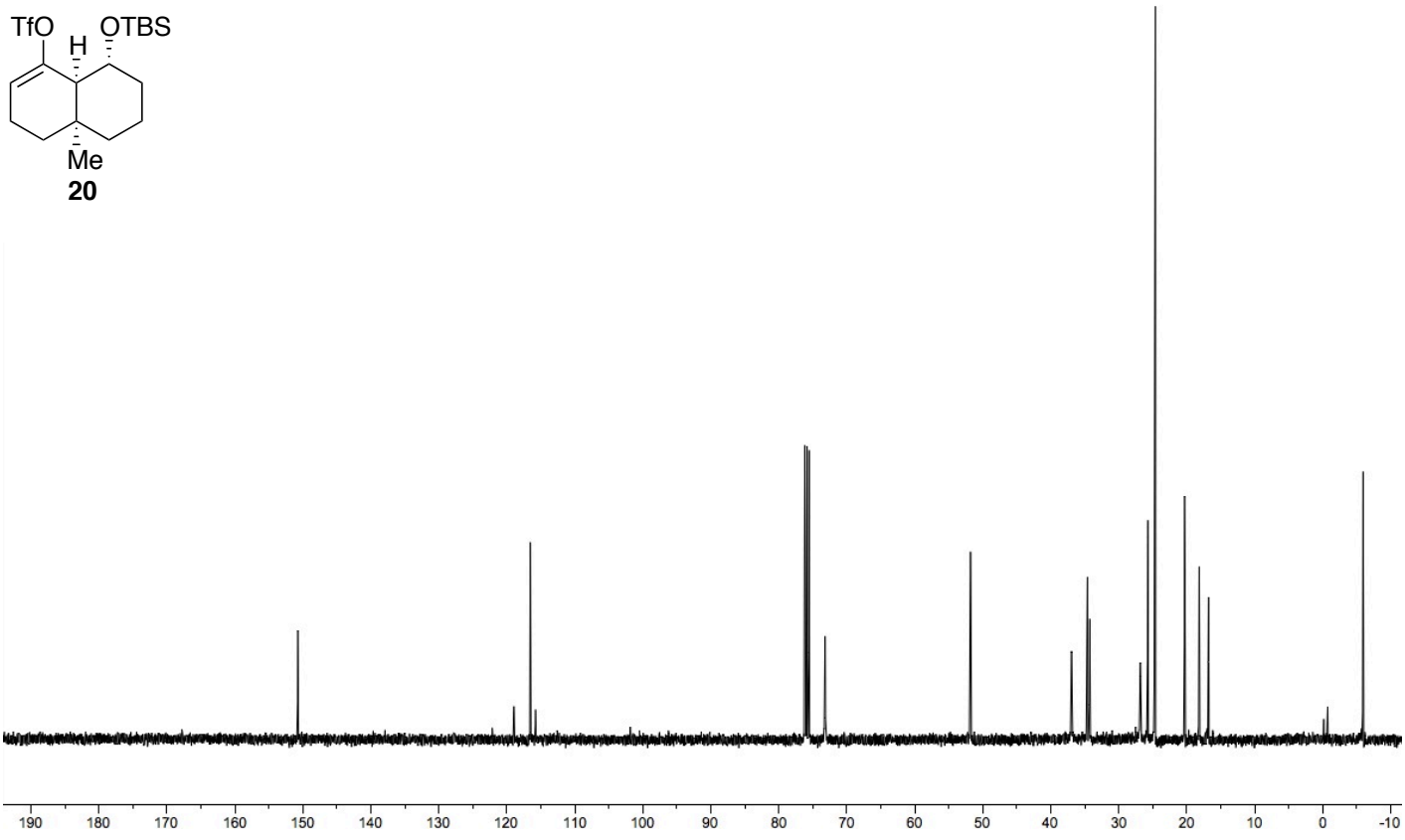

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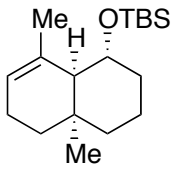

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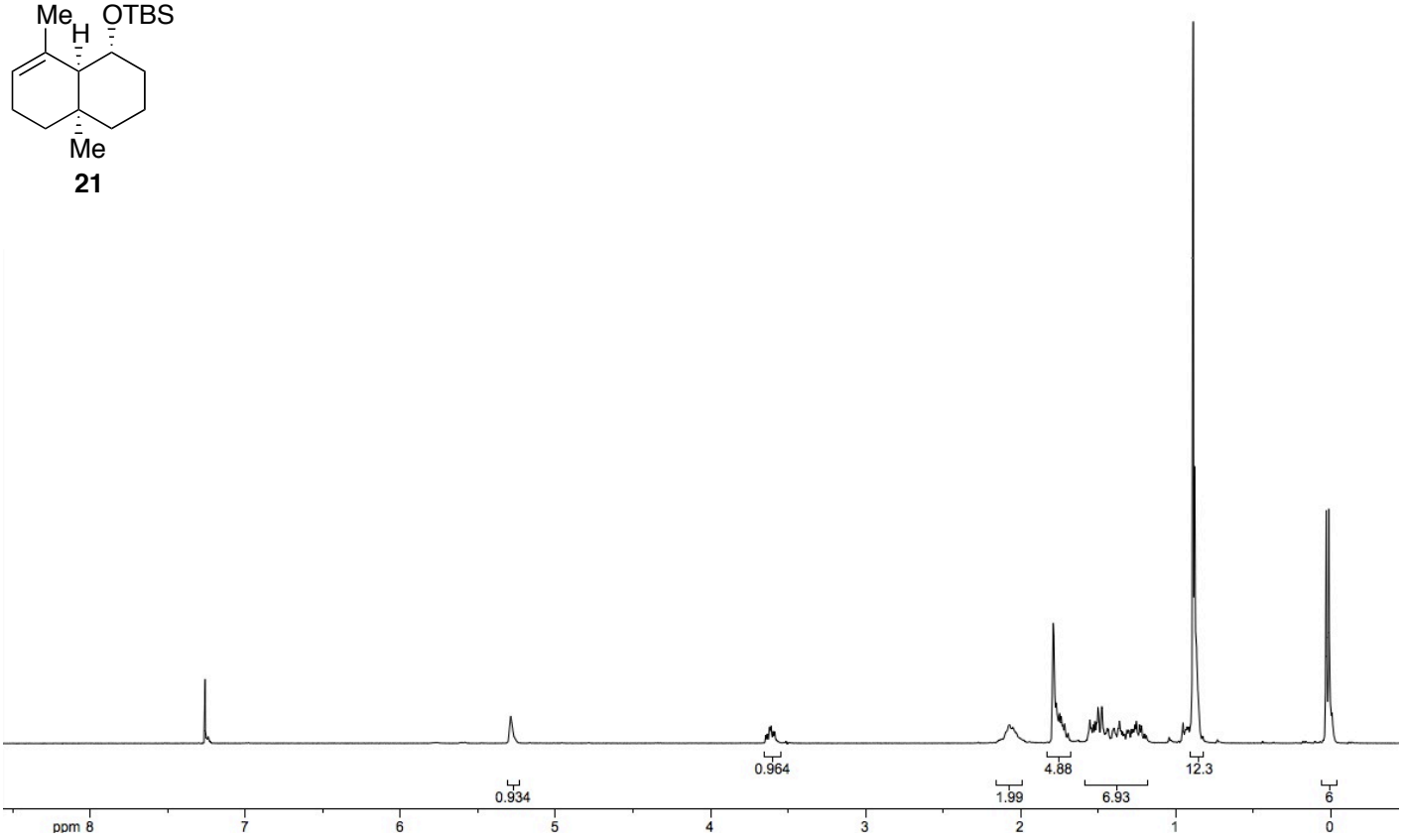

p0105mgl
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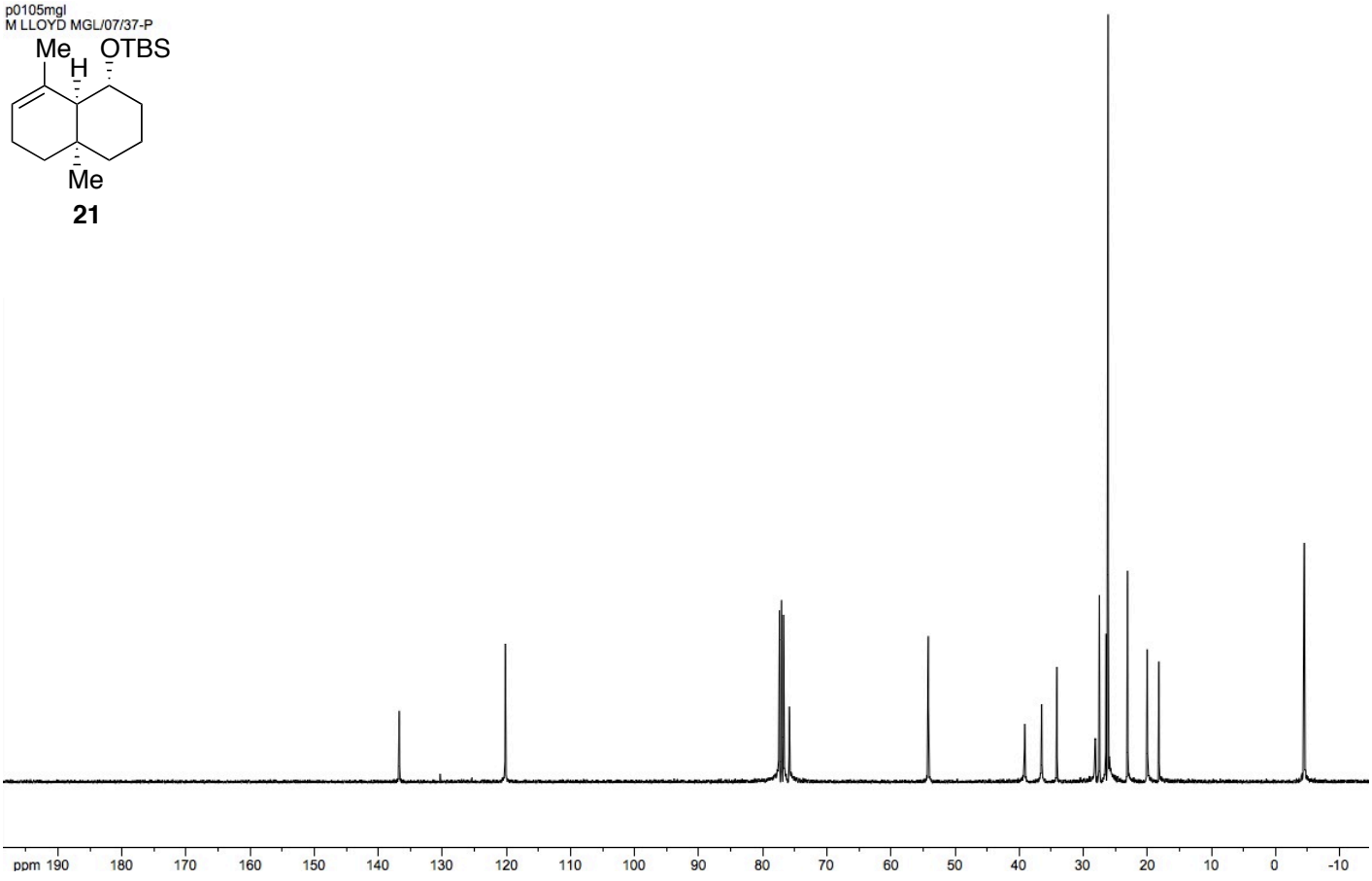

p0249mgl
M LLOYD MGL/07/38-P

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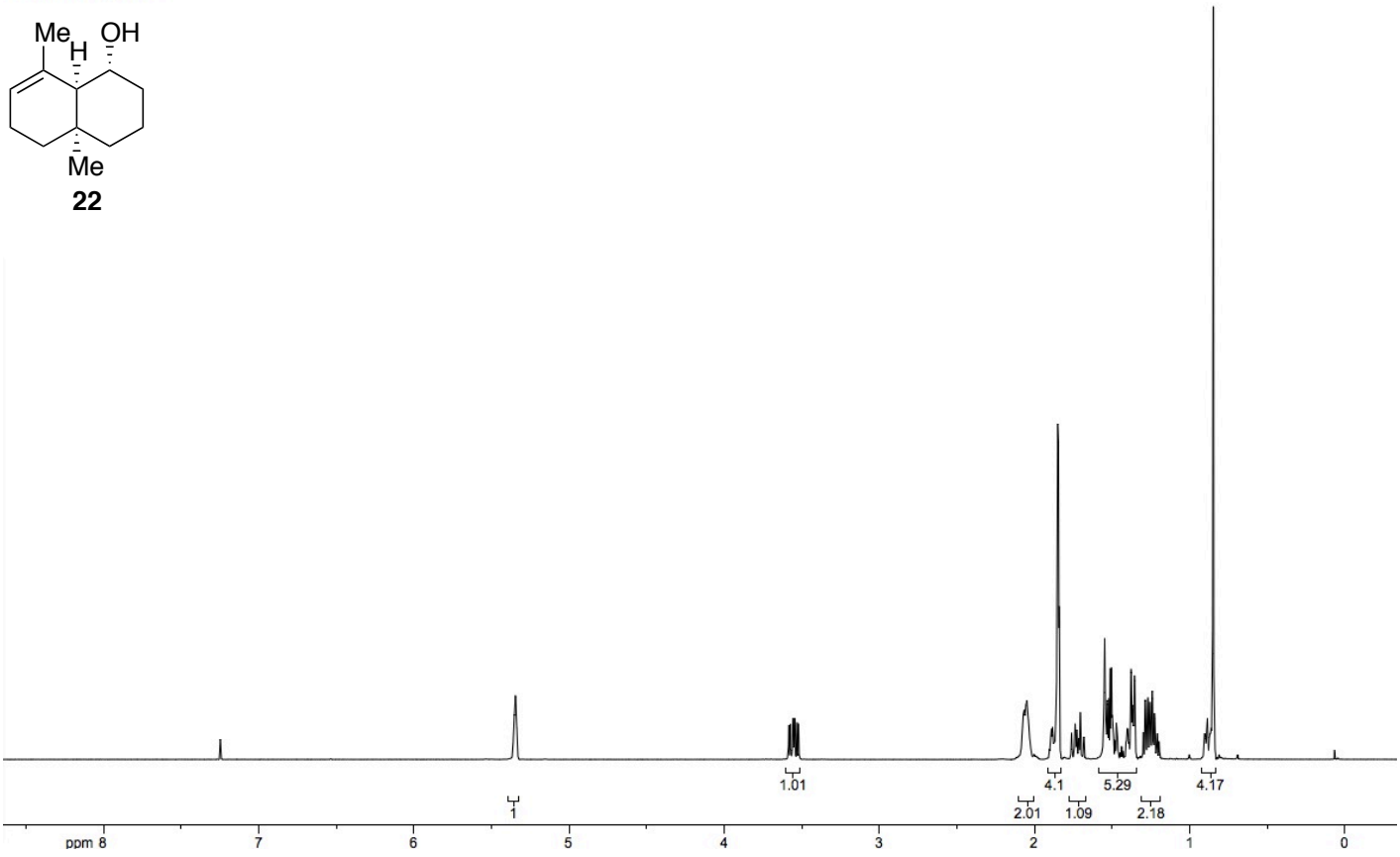
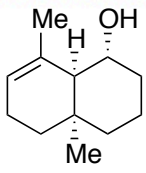


p0271mgl
M LLOYD MGL/07/38-P



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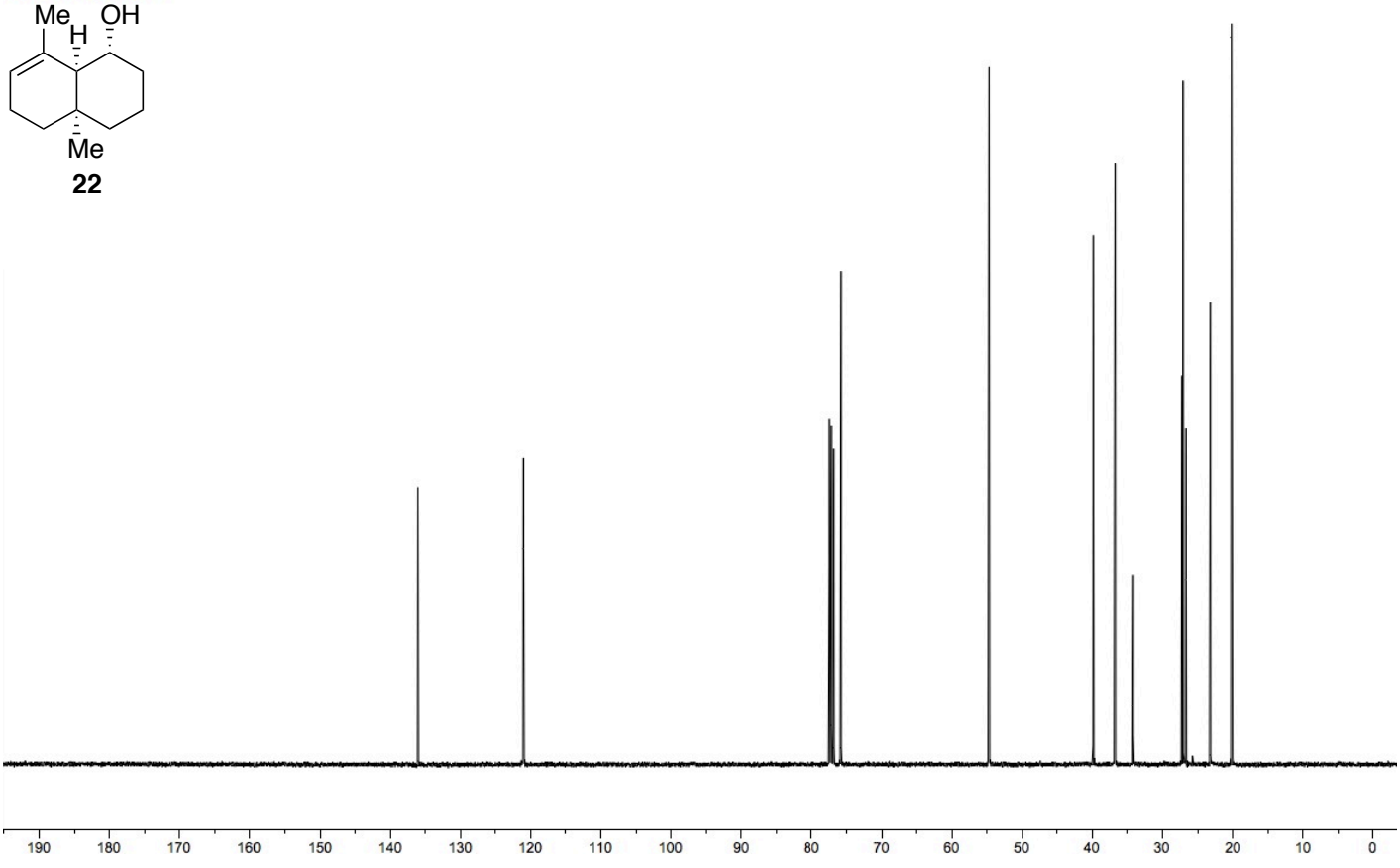

p0426mgl
M LLOYD MGL/07/41-P

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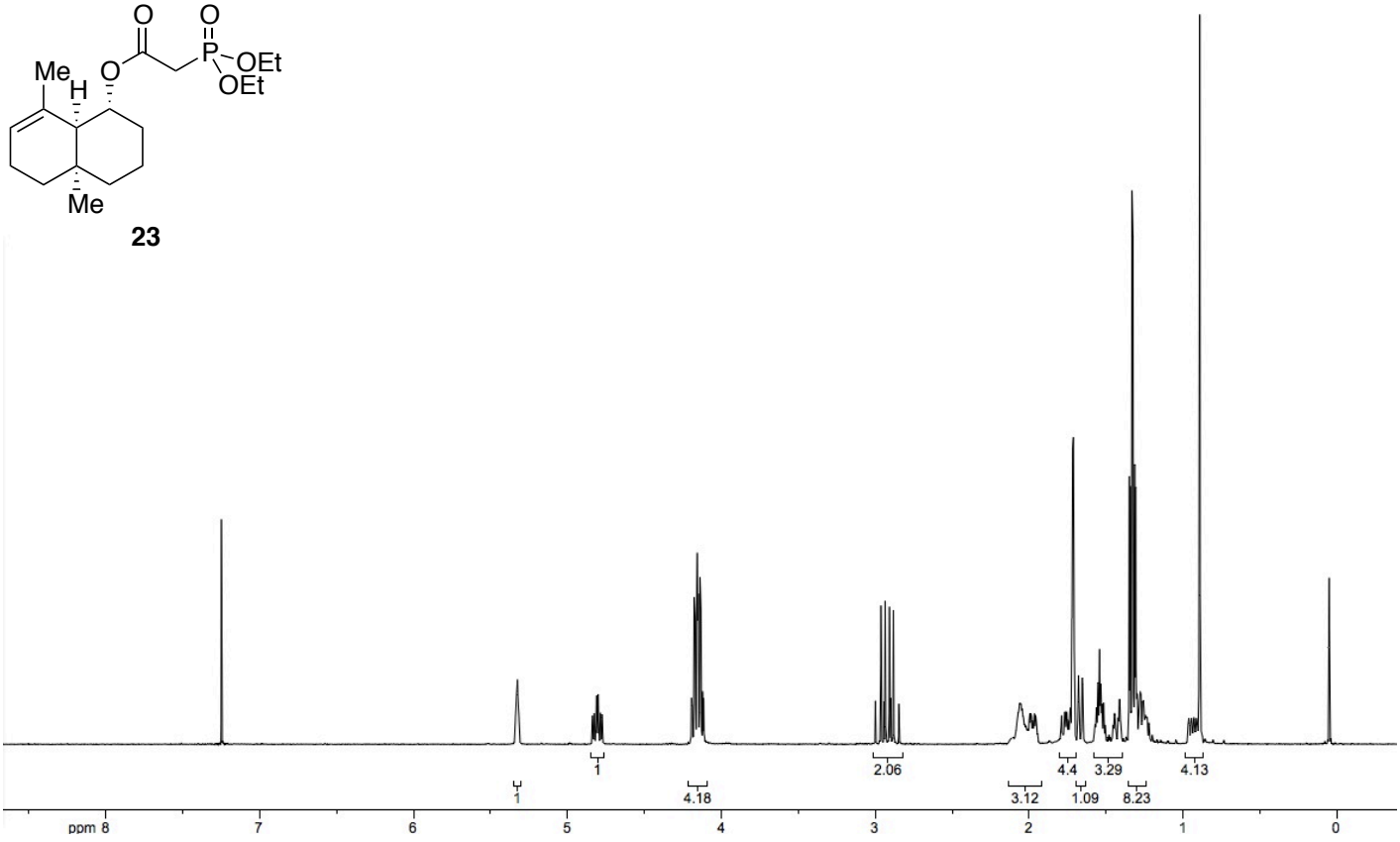

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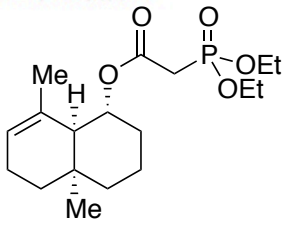

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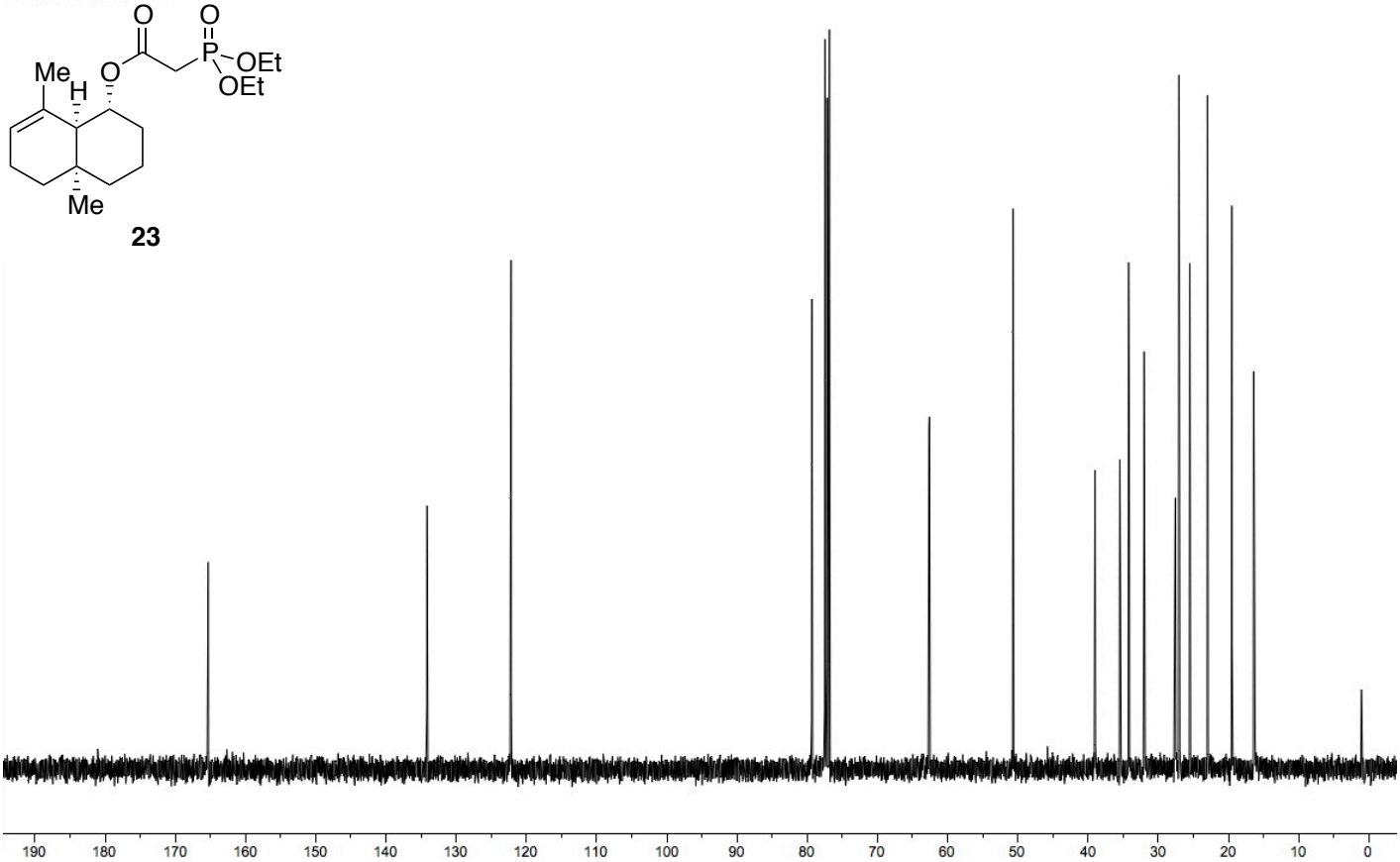

p0448mgl
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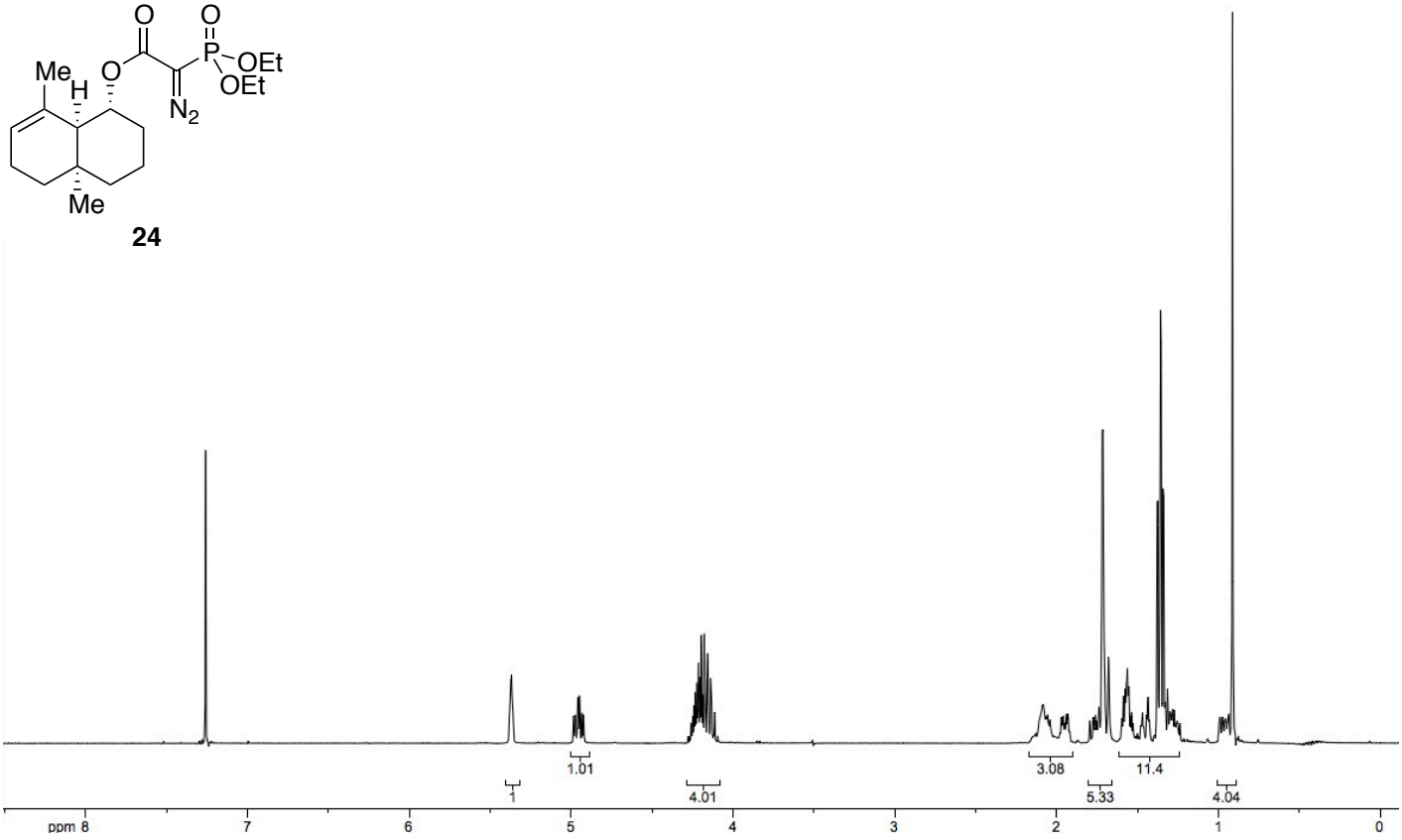
24



p0474mgl
M LLOYD MGL/07/42-P

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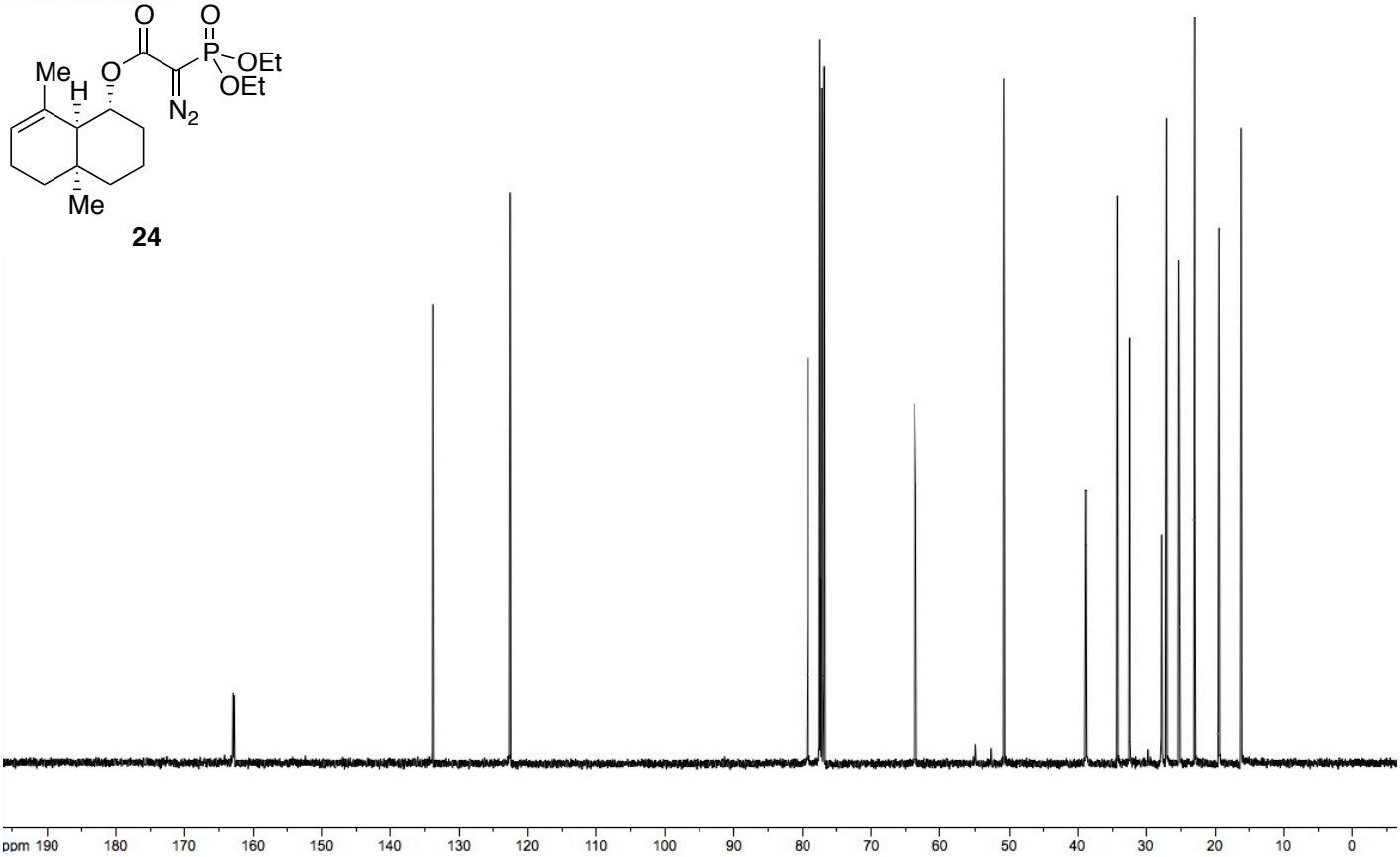

p1847mgl
M LLOYD MGL/07/43-P

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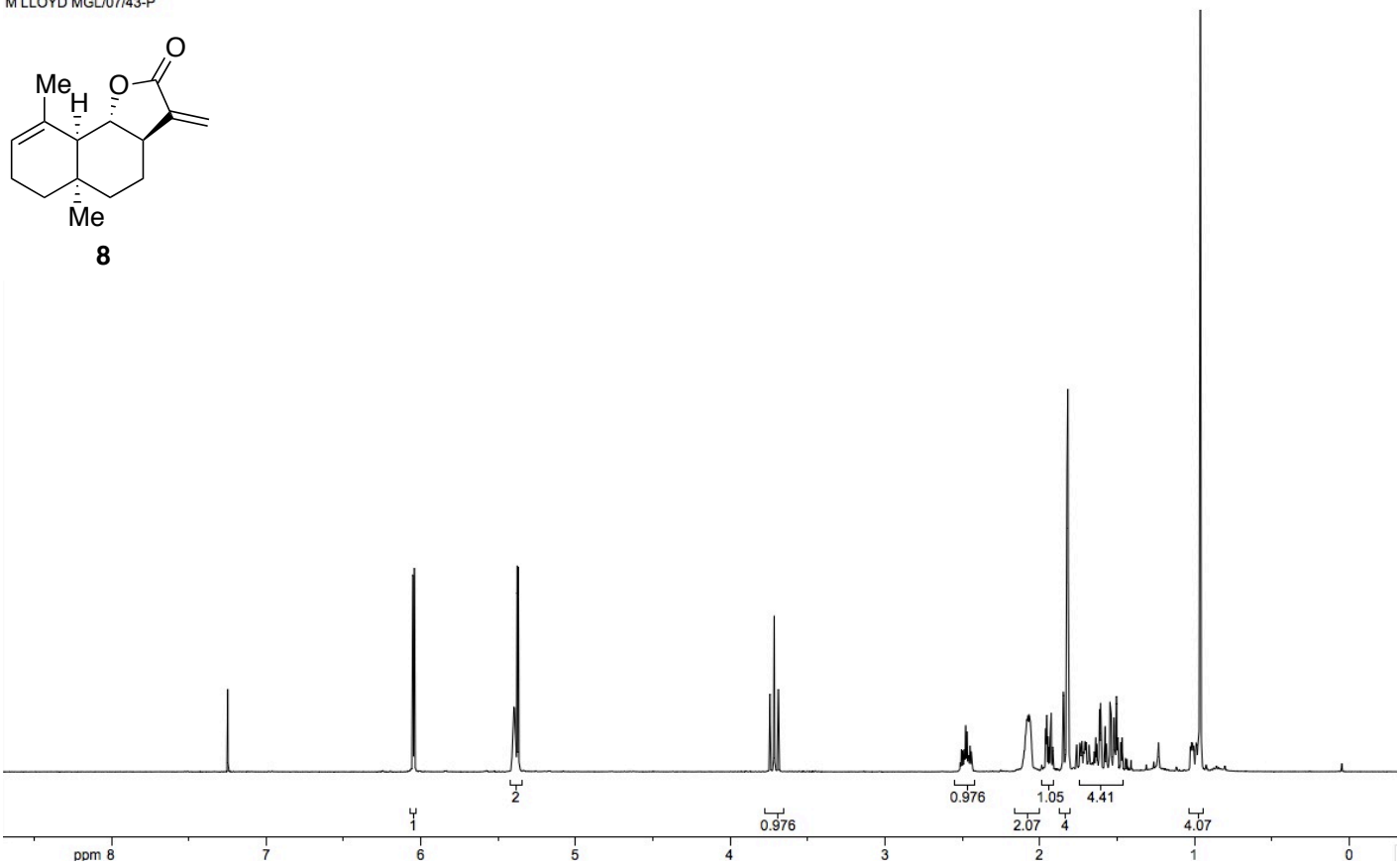

p0567mgl
M LLOYD MGL/07/43-P

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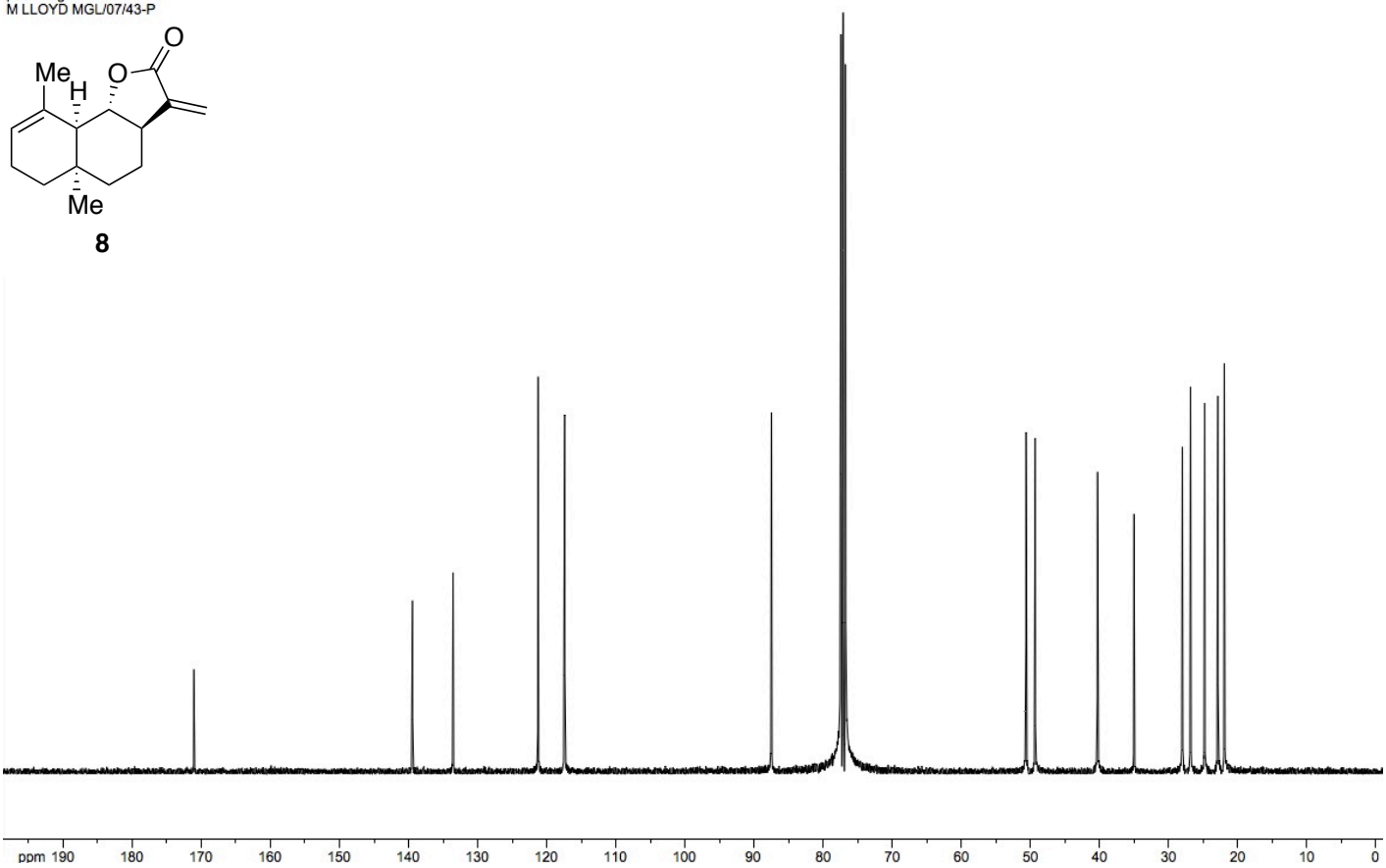
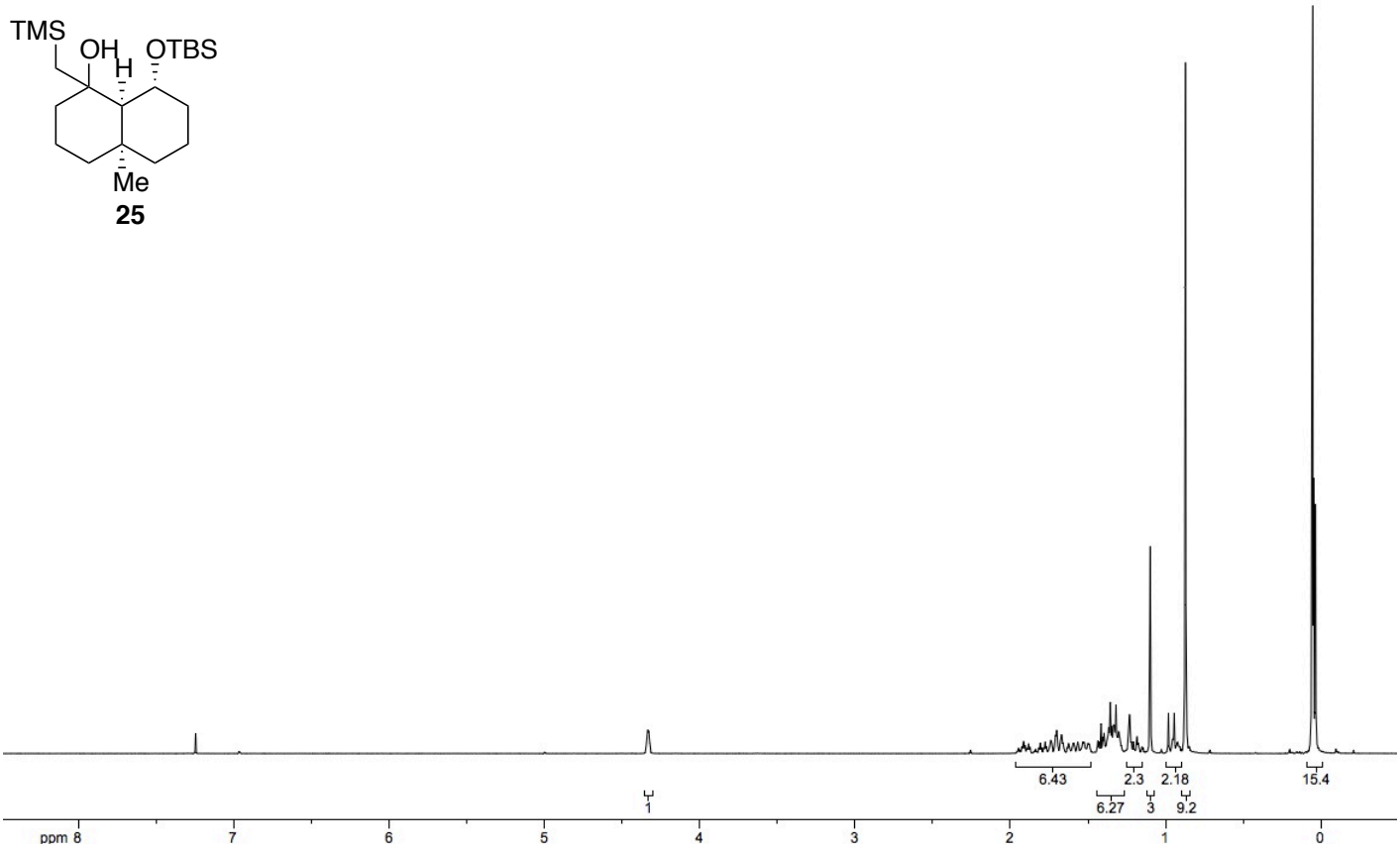


n3880mgl
M LLOYD MGL/06/29-C

25



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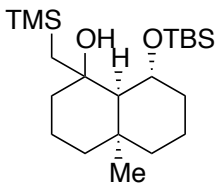

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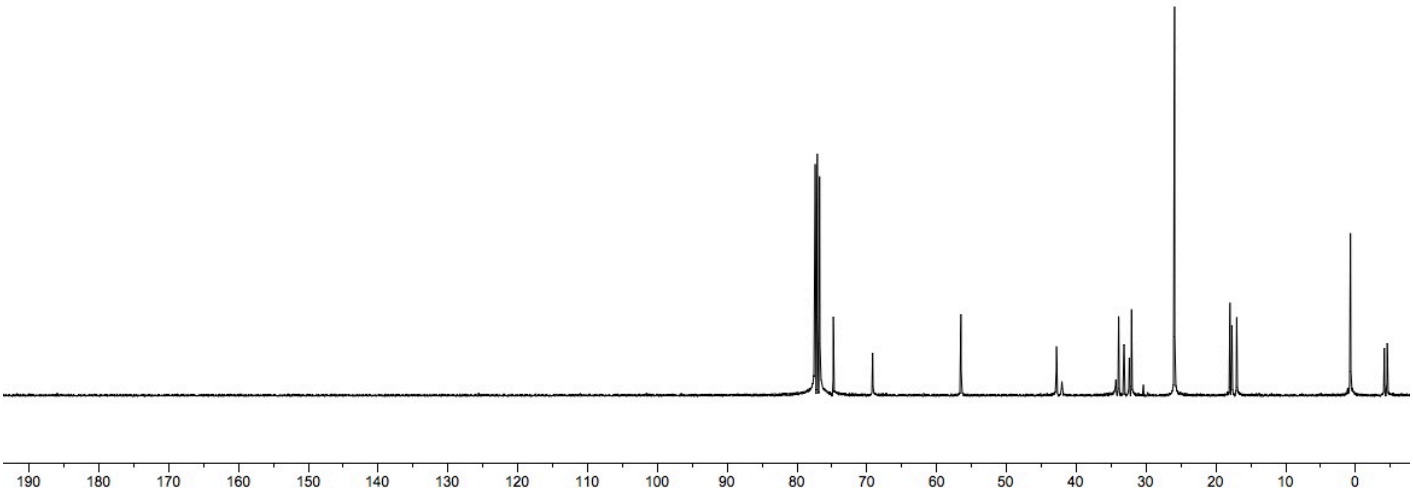

d2683mgl
M LLOYD MGL/06/36-P

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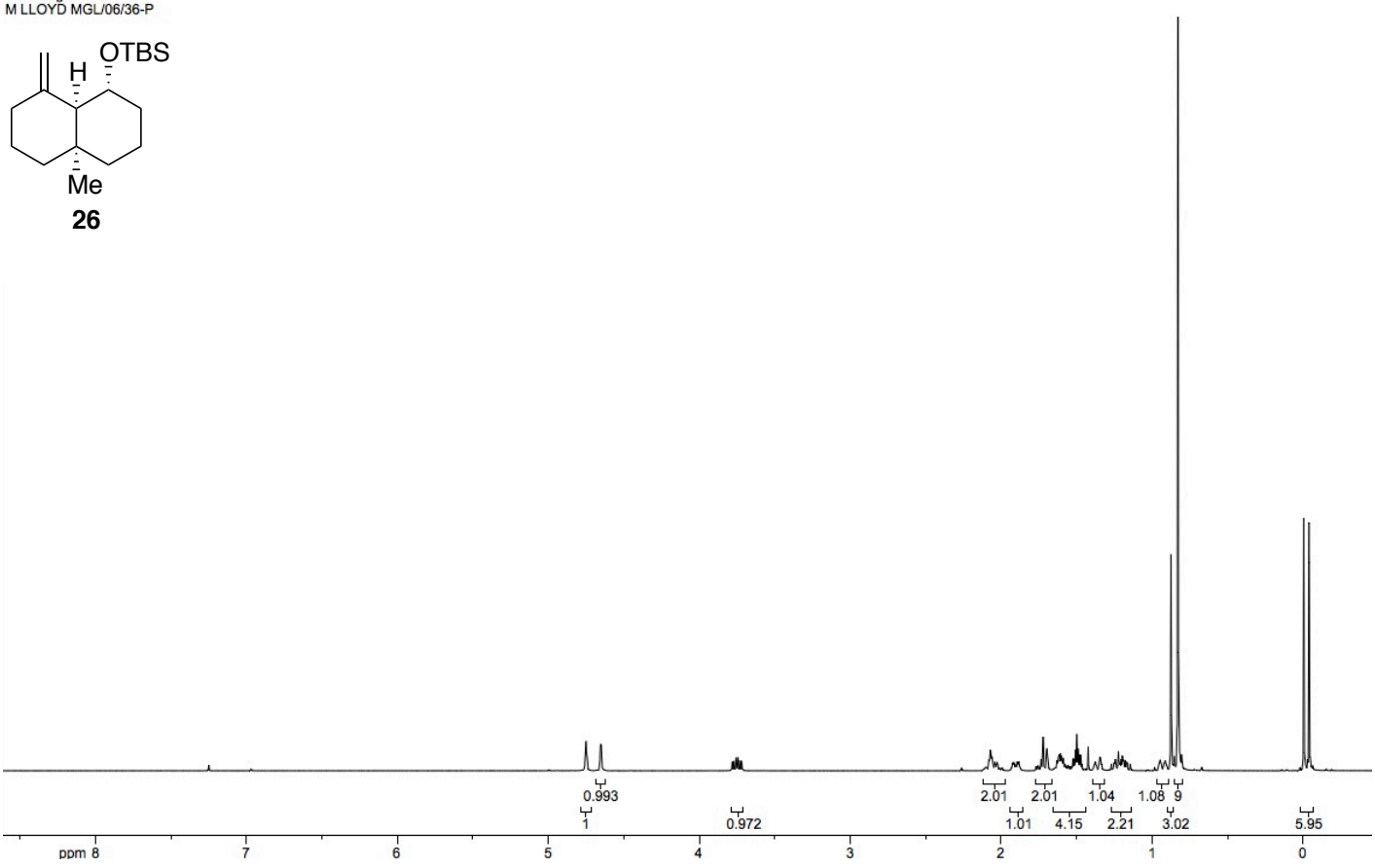
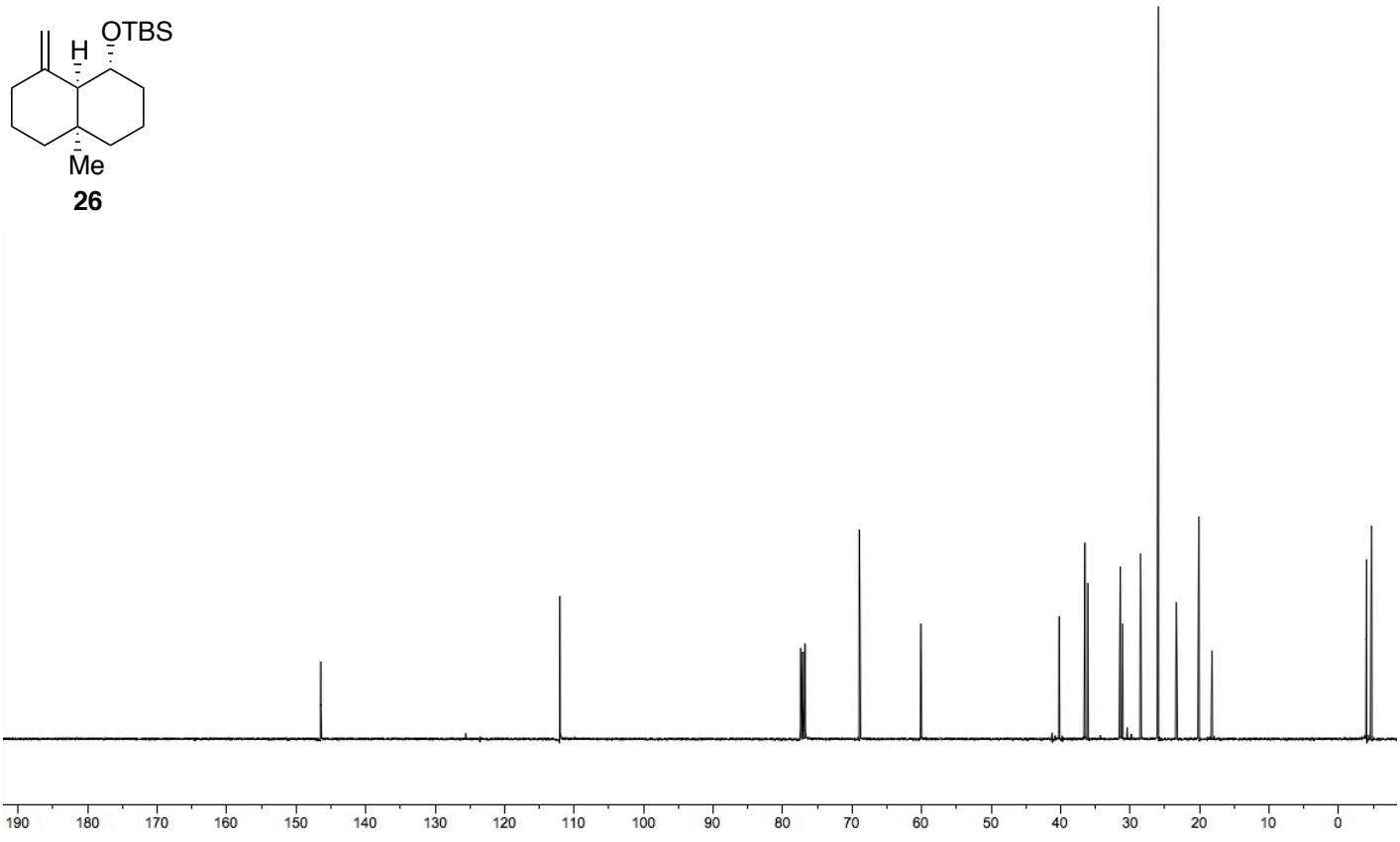


d2713mgl
M LLOYD MGL/06/36-P

26



d2754mgl
M LLOYD MGL/06/37-P

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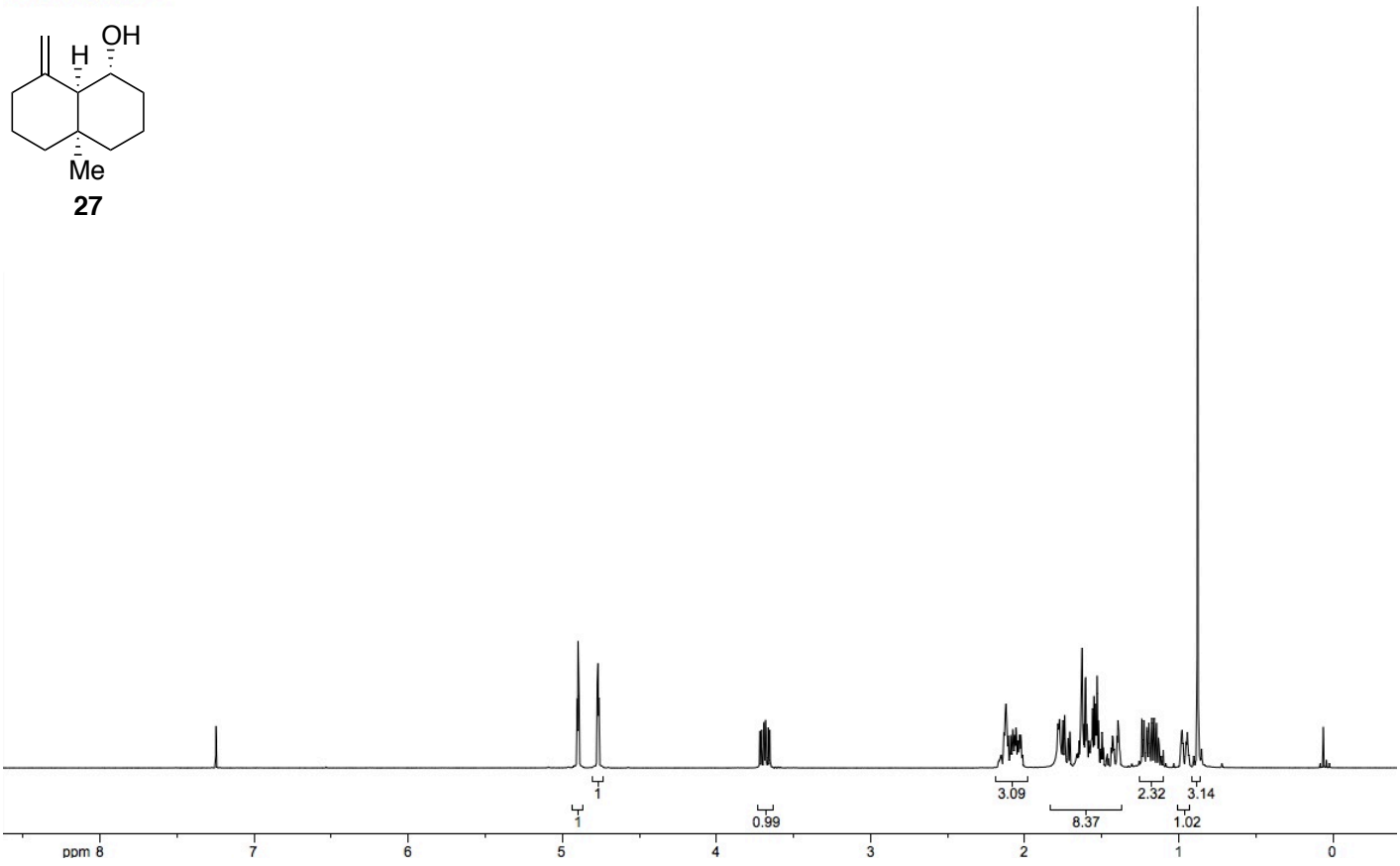
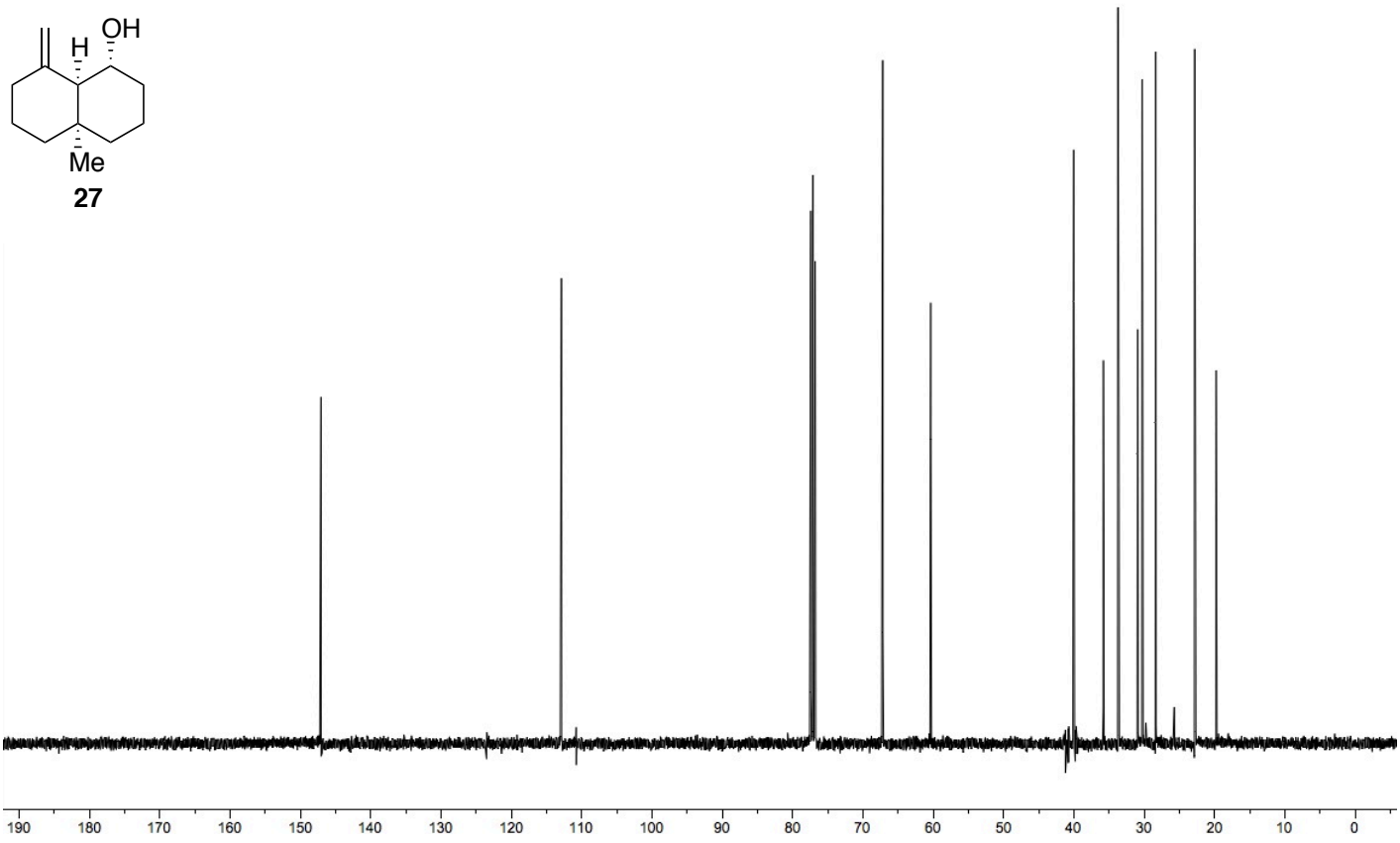


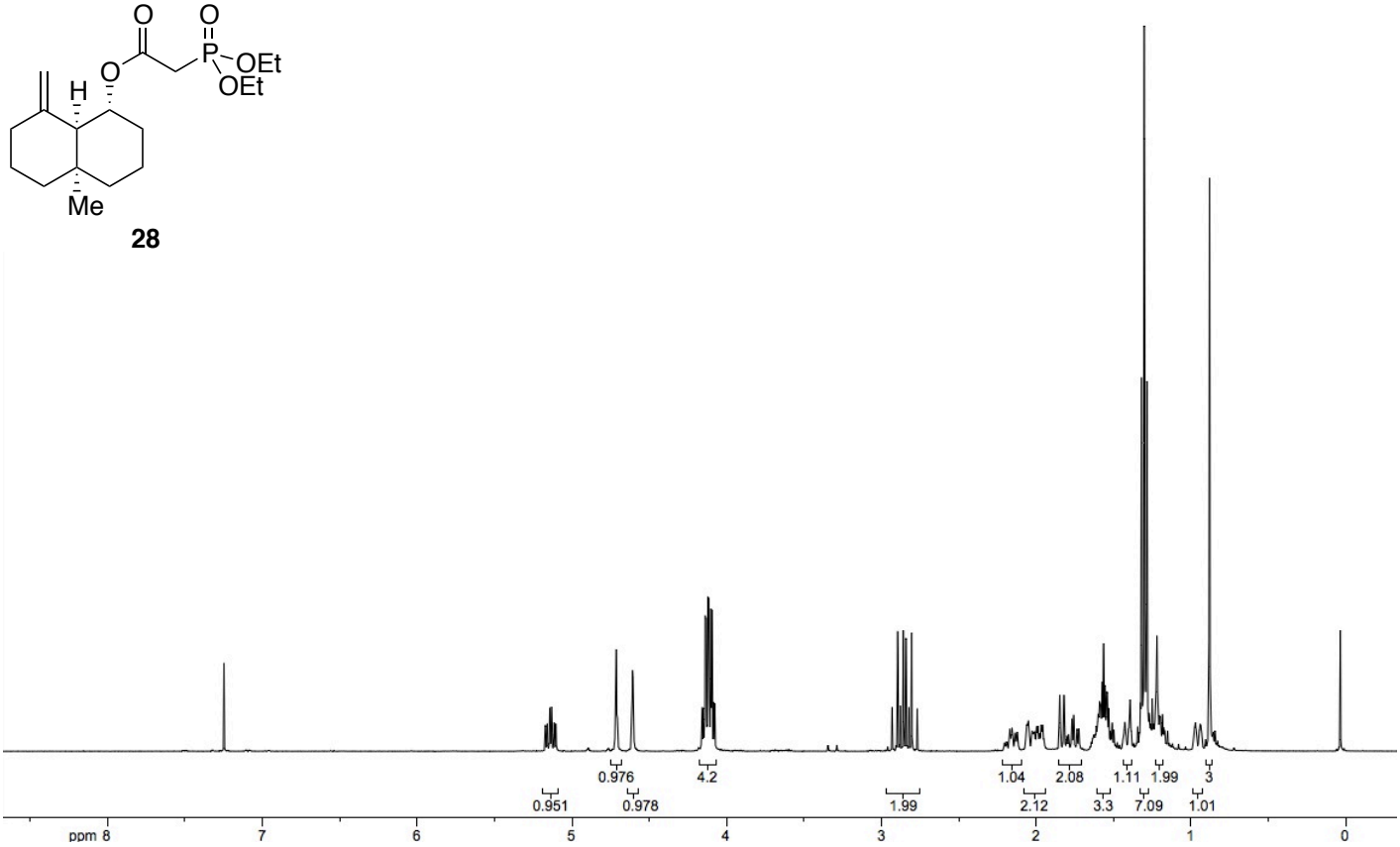
d2774mgl
M LLOYD MGL/06/37-P

27



d2805mgl
M LLOYD MGL/06/38-P

28



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M LLOYD MGL/06/38-P

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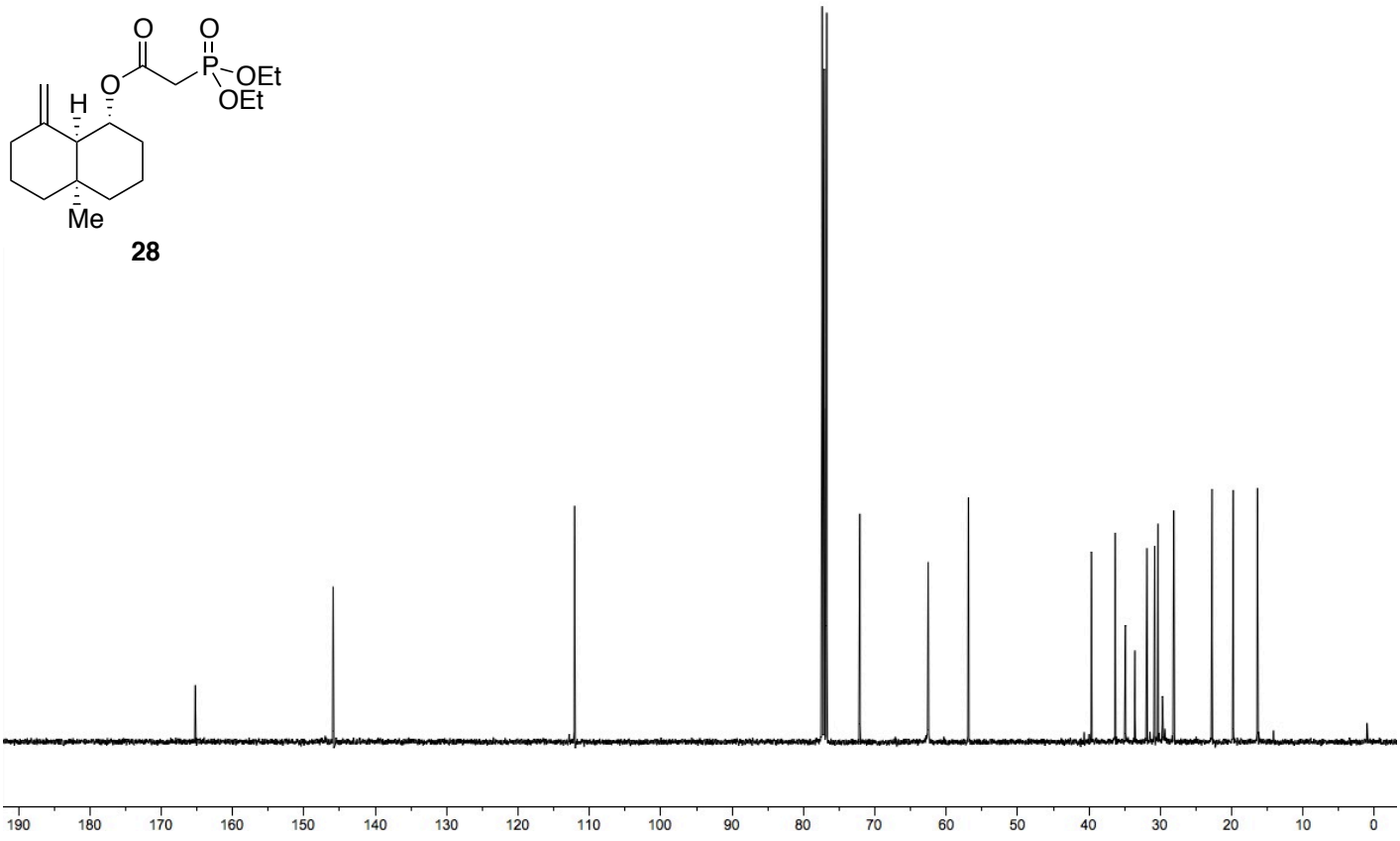

d2870mgl
M LLOYD MGL/06/39-P

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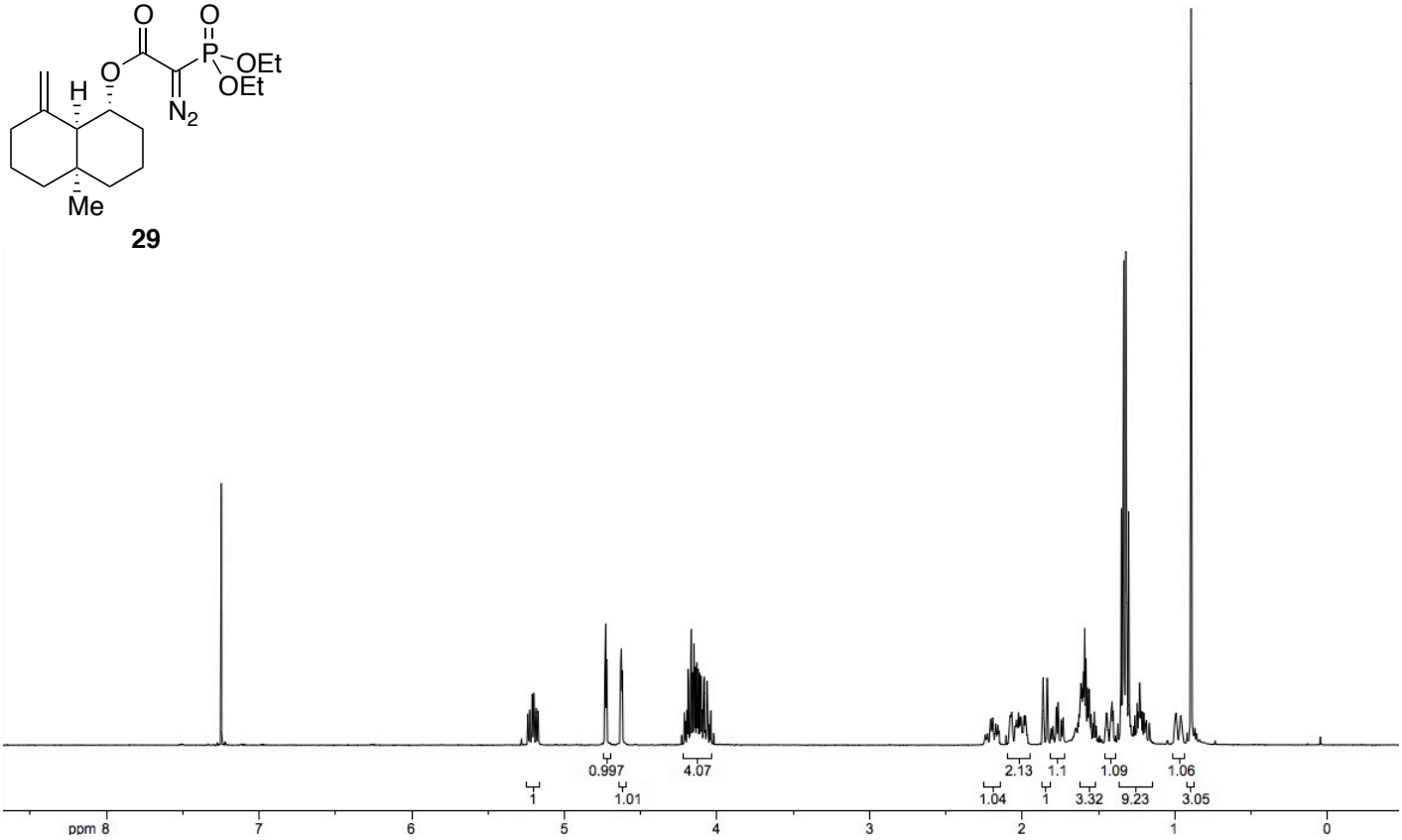

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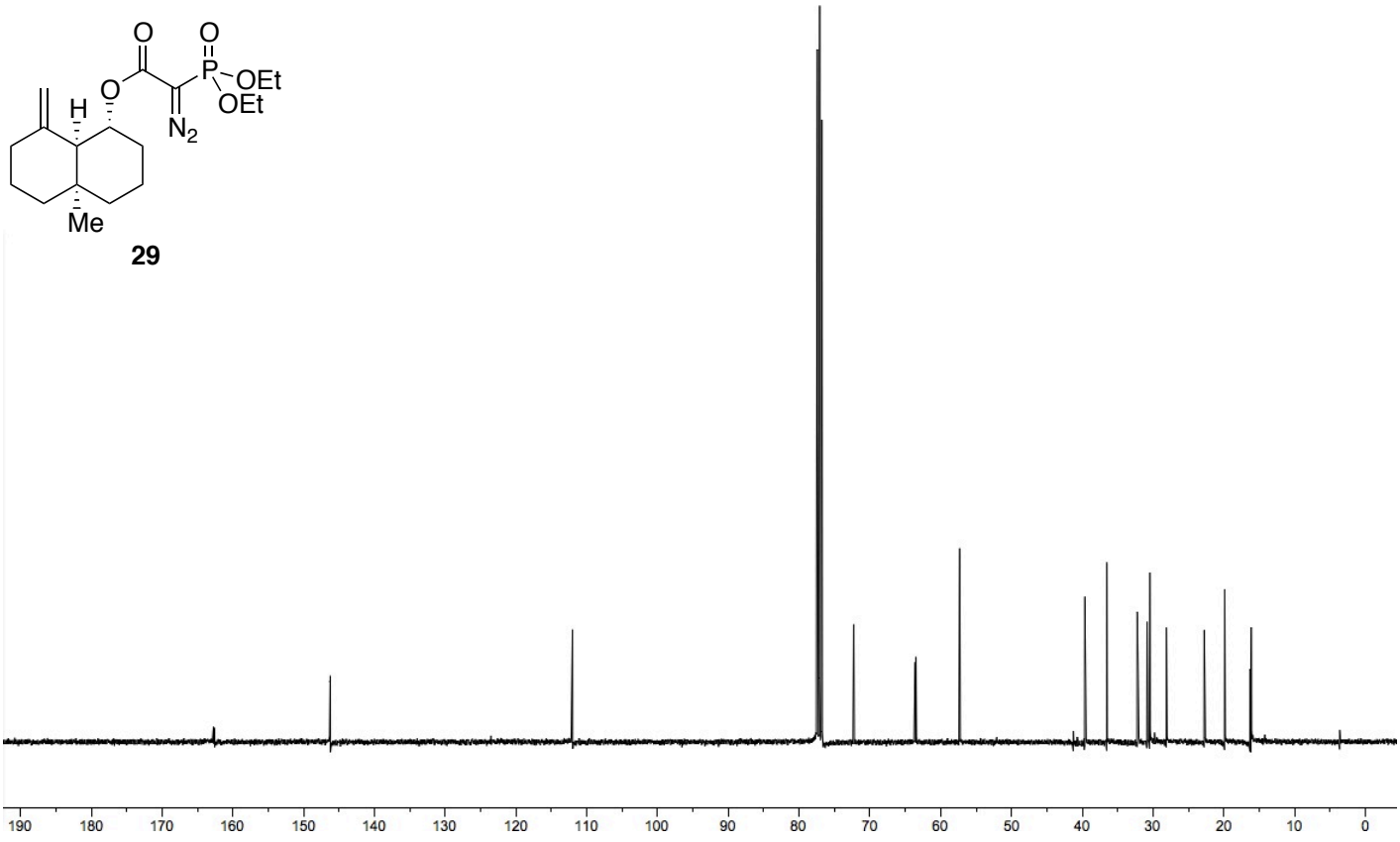

d4279mgl
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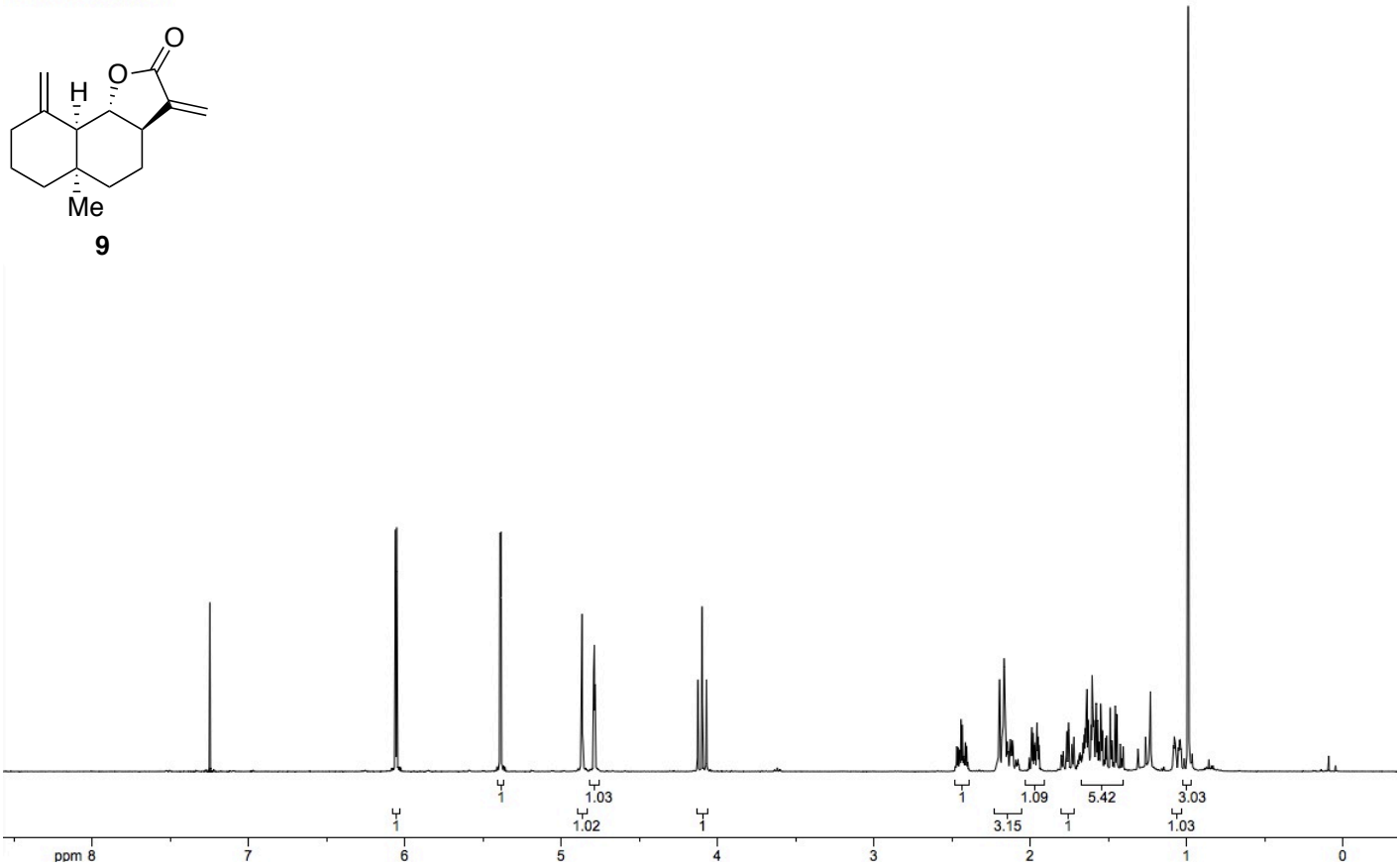

d4279mgl
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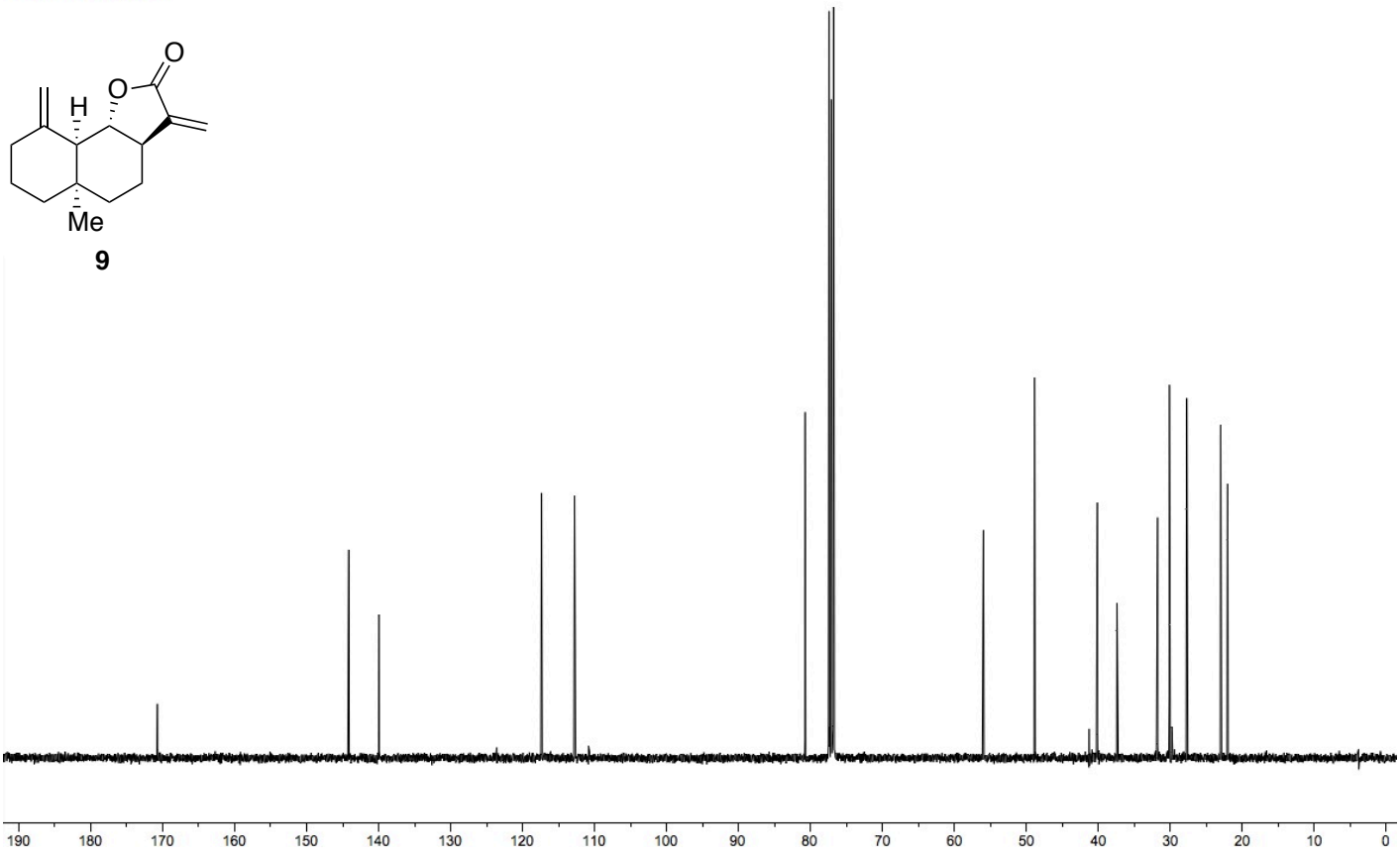
9



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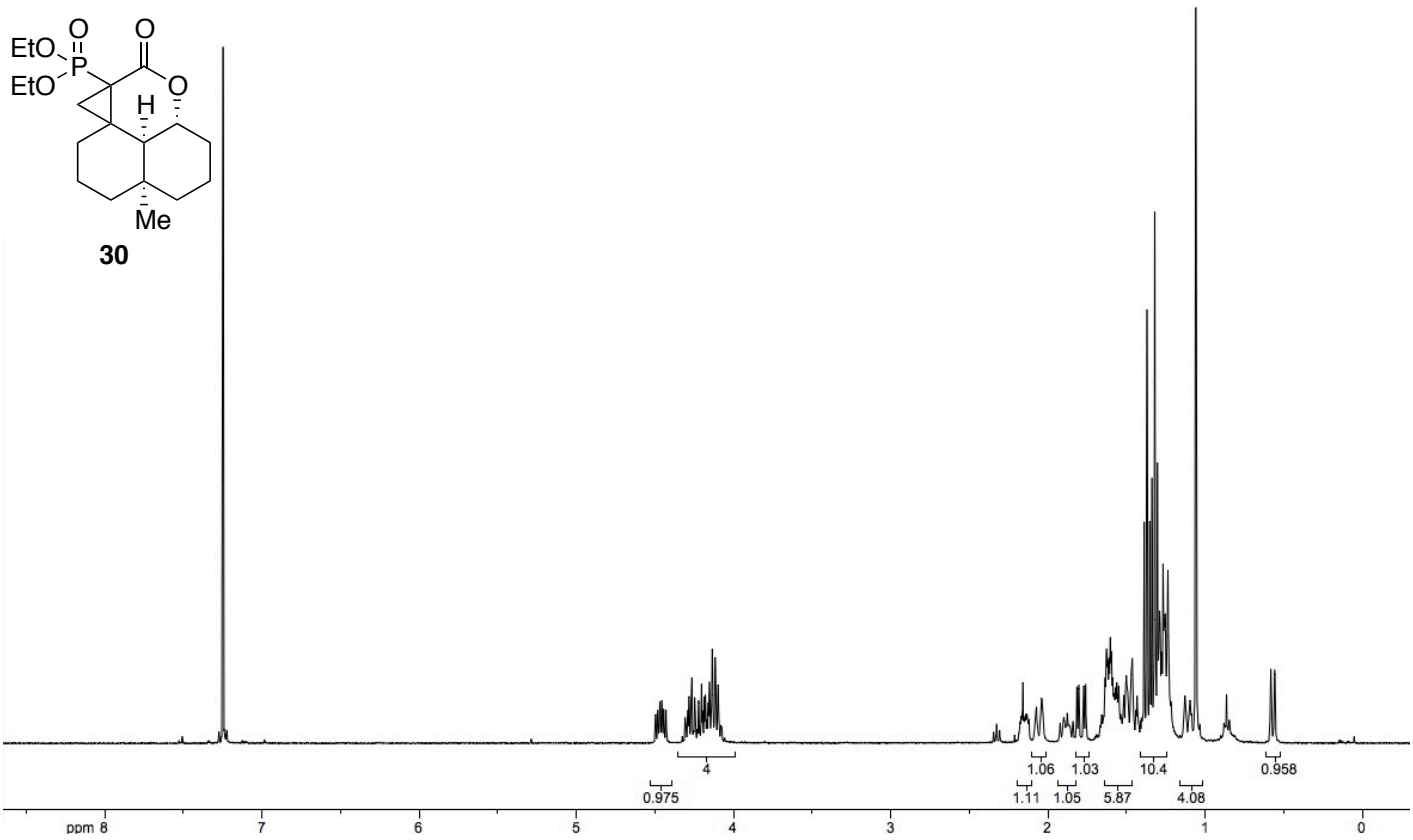
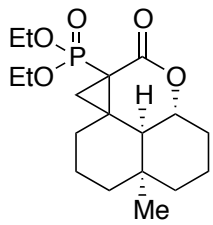
30



d4280mgl
M LLOYD MGL/06/58-P2



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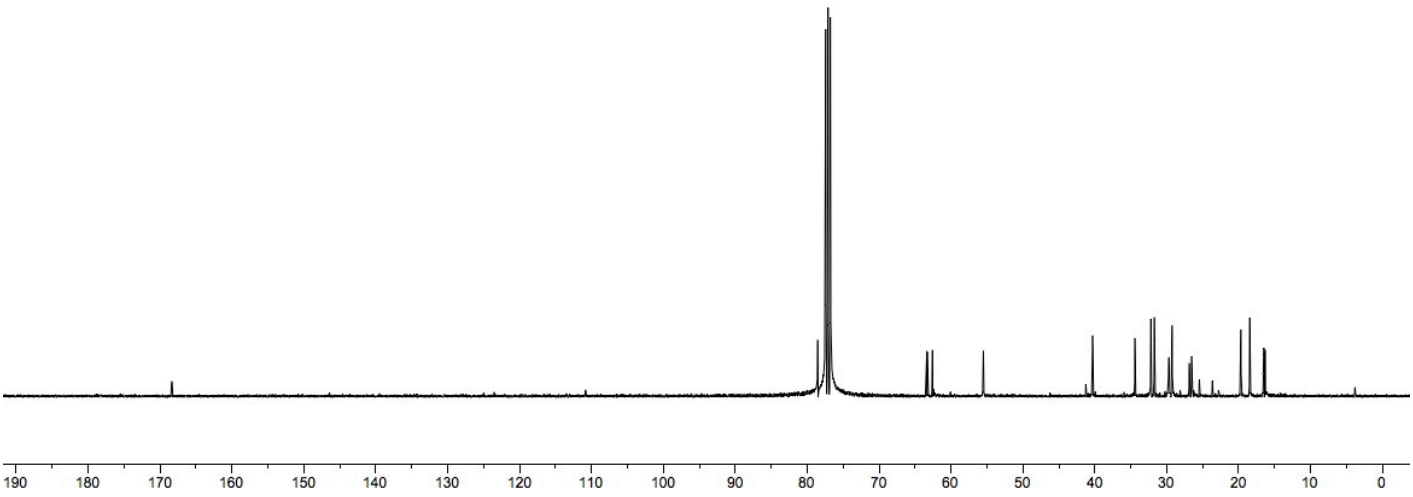
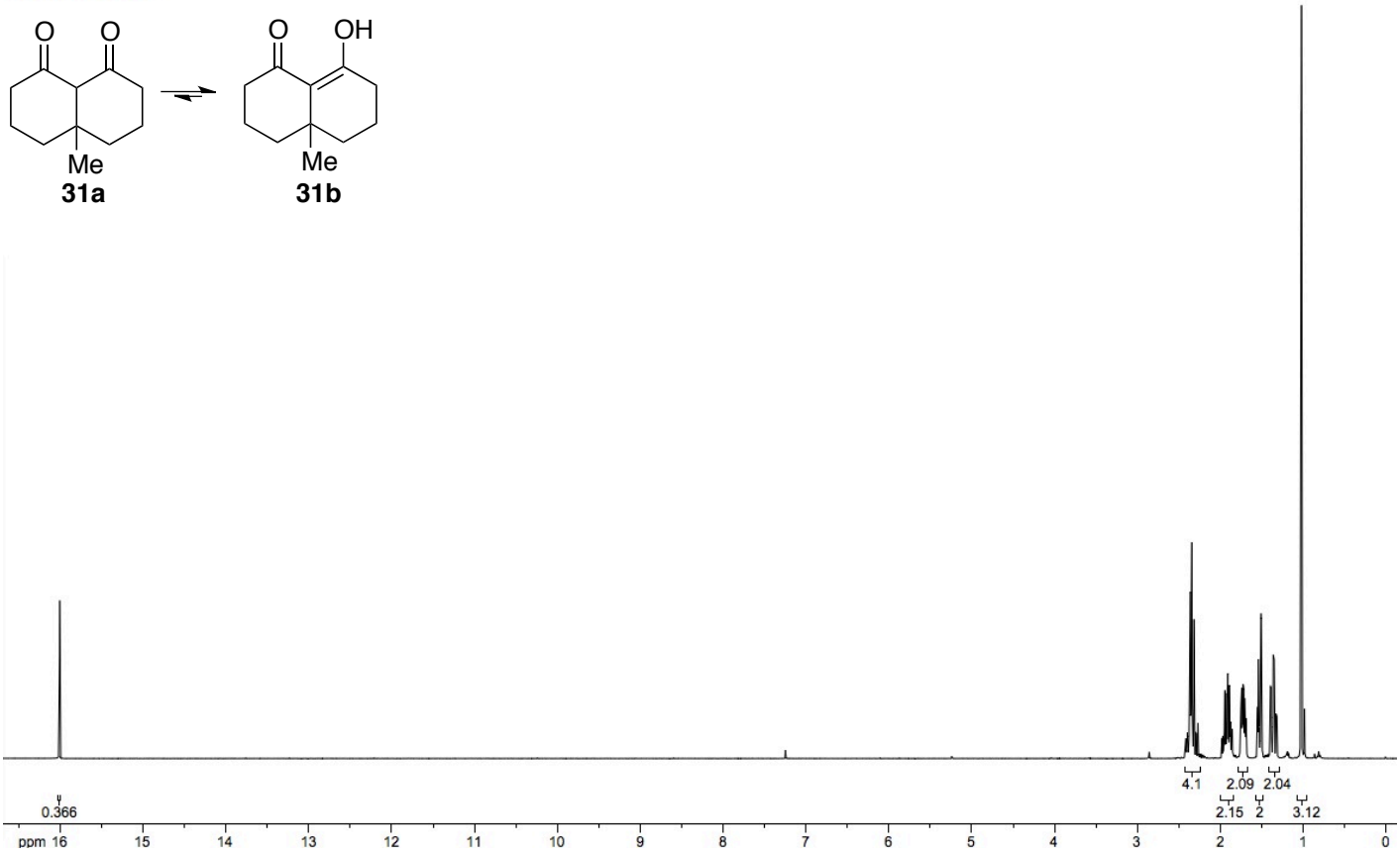


d6657mgl
M LLOYD MGL/06/87-P

31a

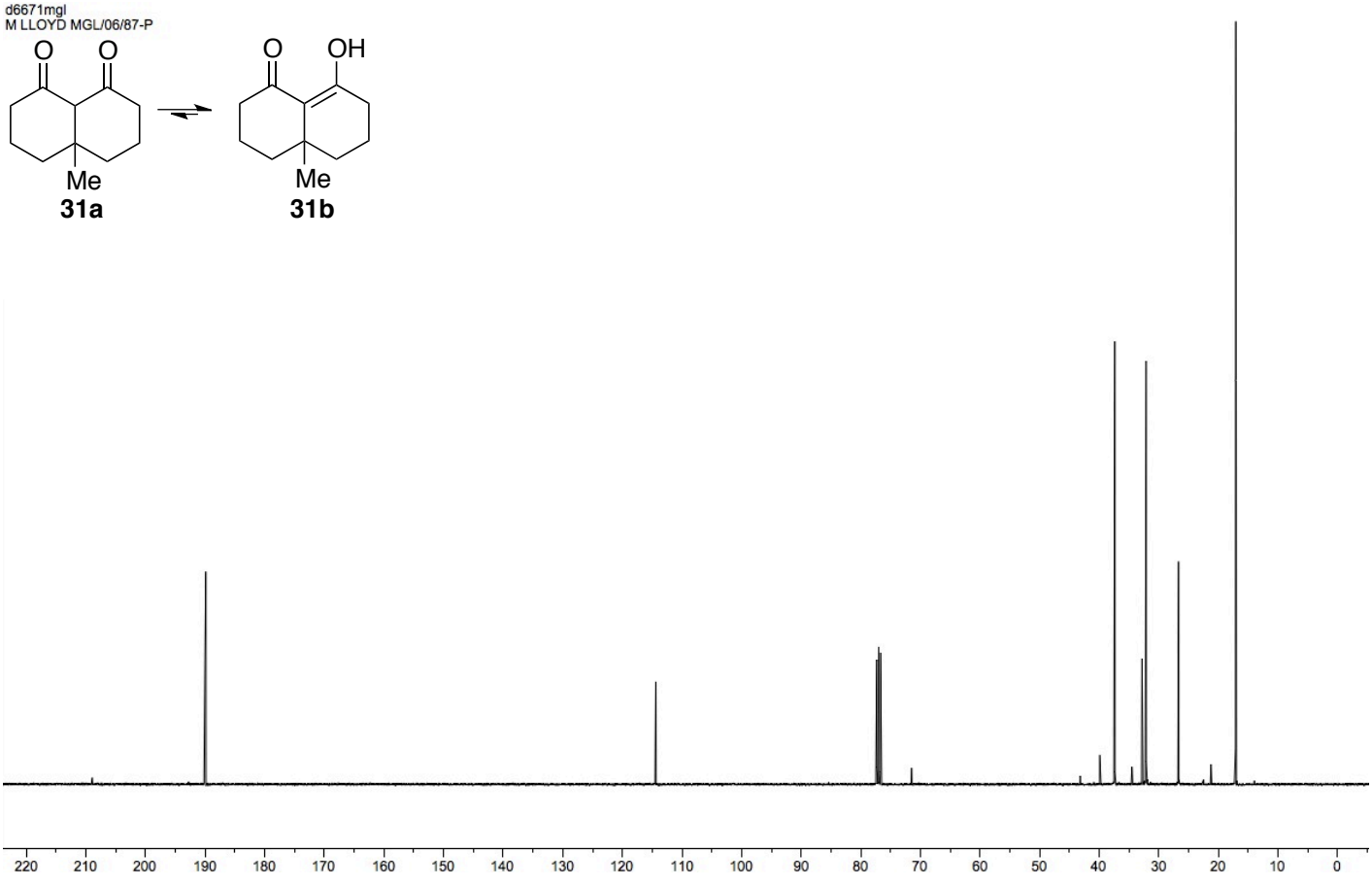
31b



d6671mgl
M LLOYD MGL/06/87-P

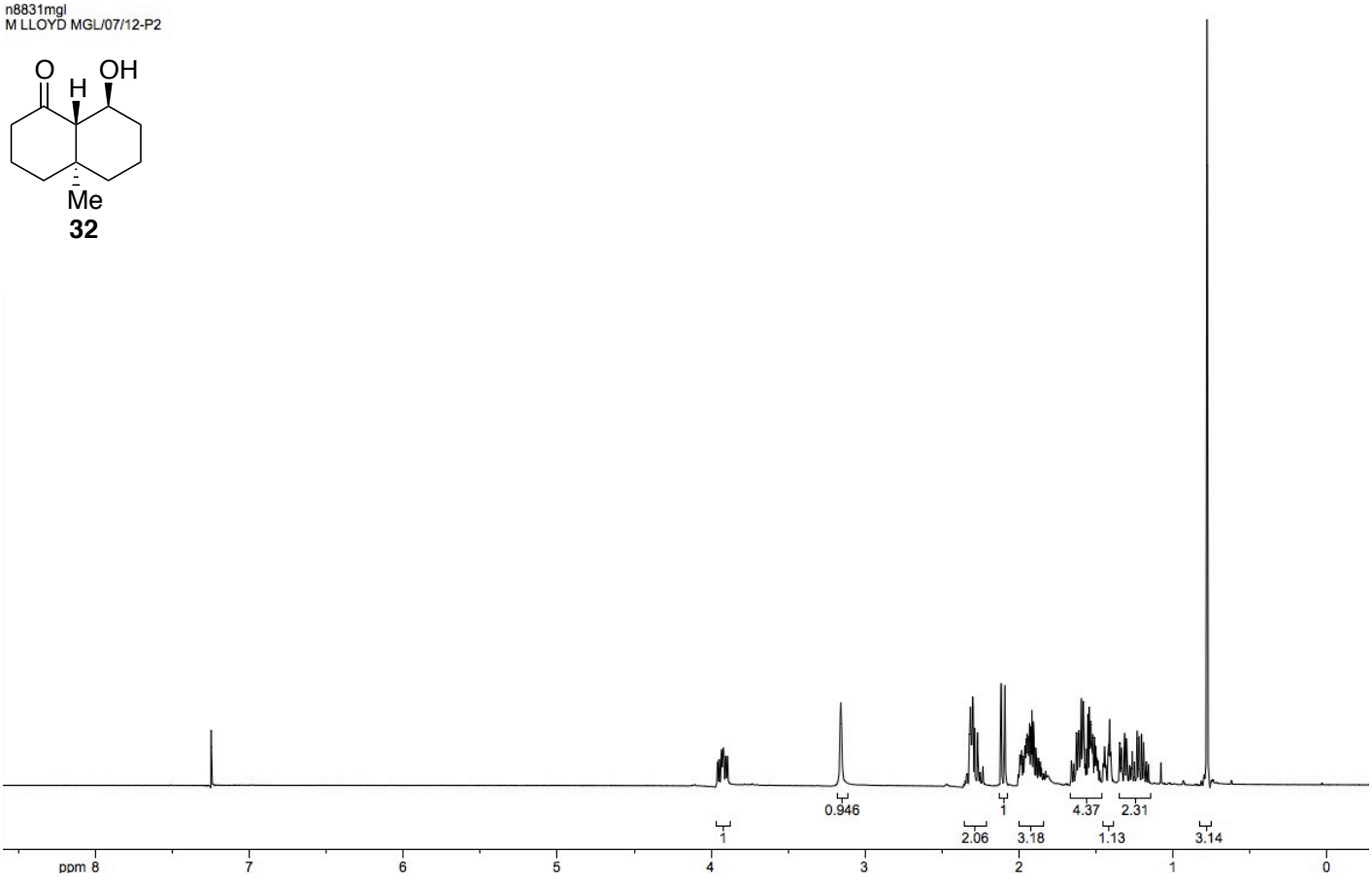
31a

31b

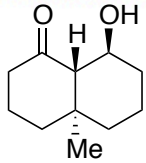


n8831mgl
M LLOYD MGL/07/12-P2

32



n8862mgl
M LLOYD MGL/07/12-P2



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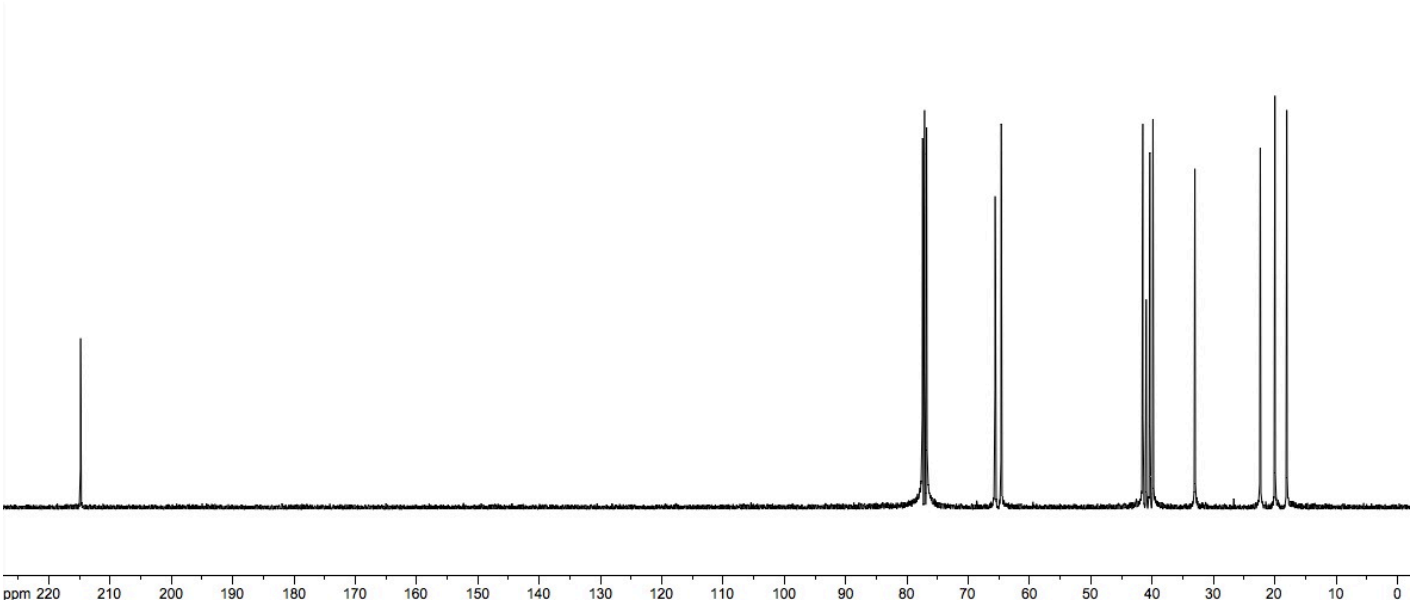
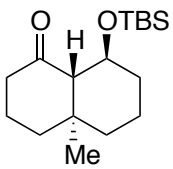
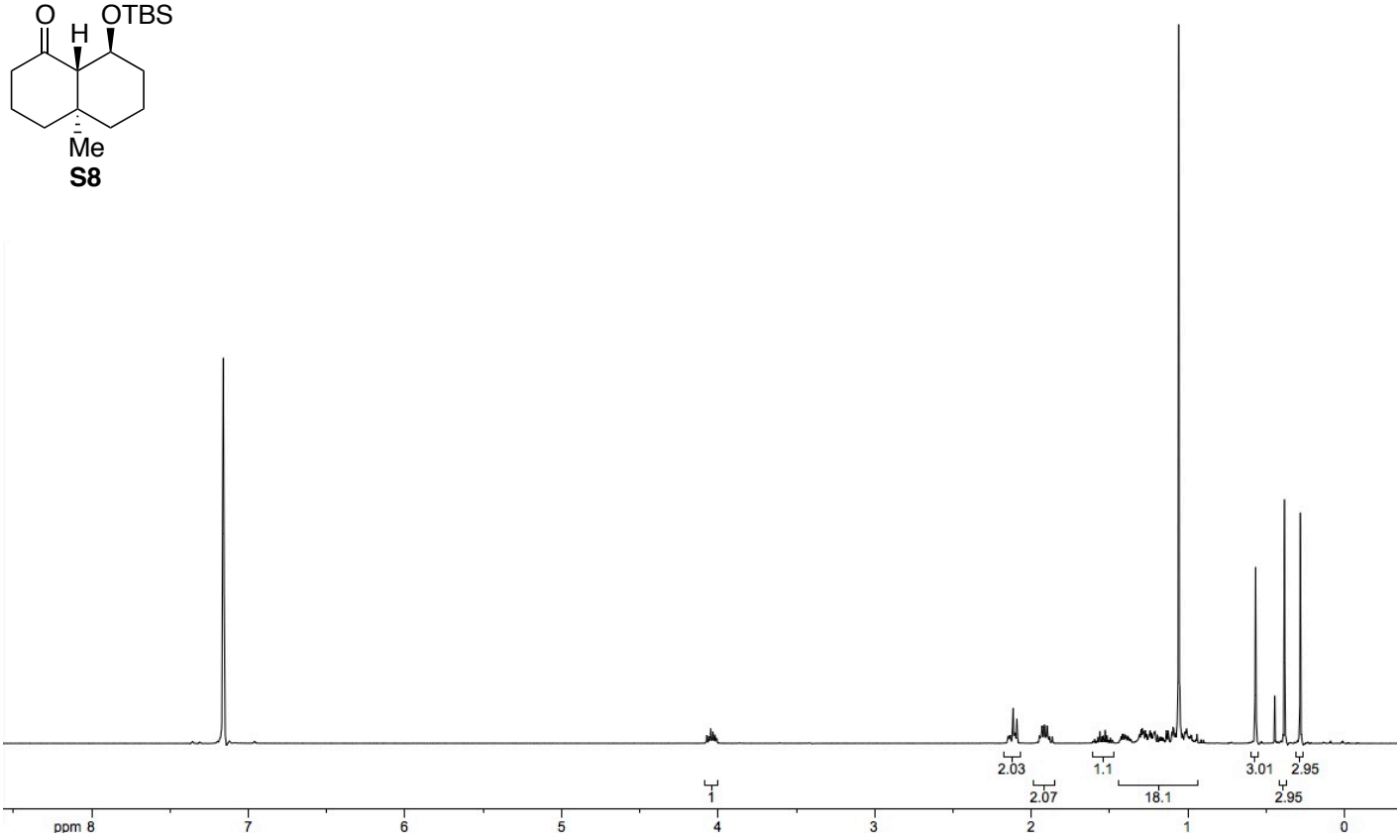


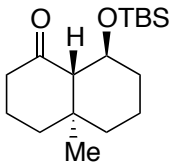
p0549mgl
M LLOYD MGL/07/40-P C6D6



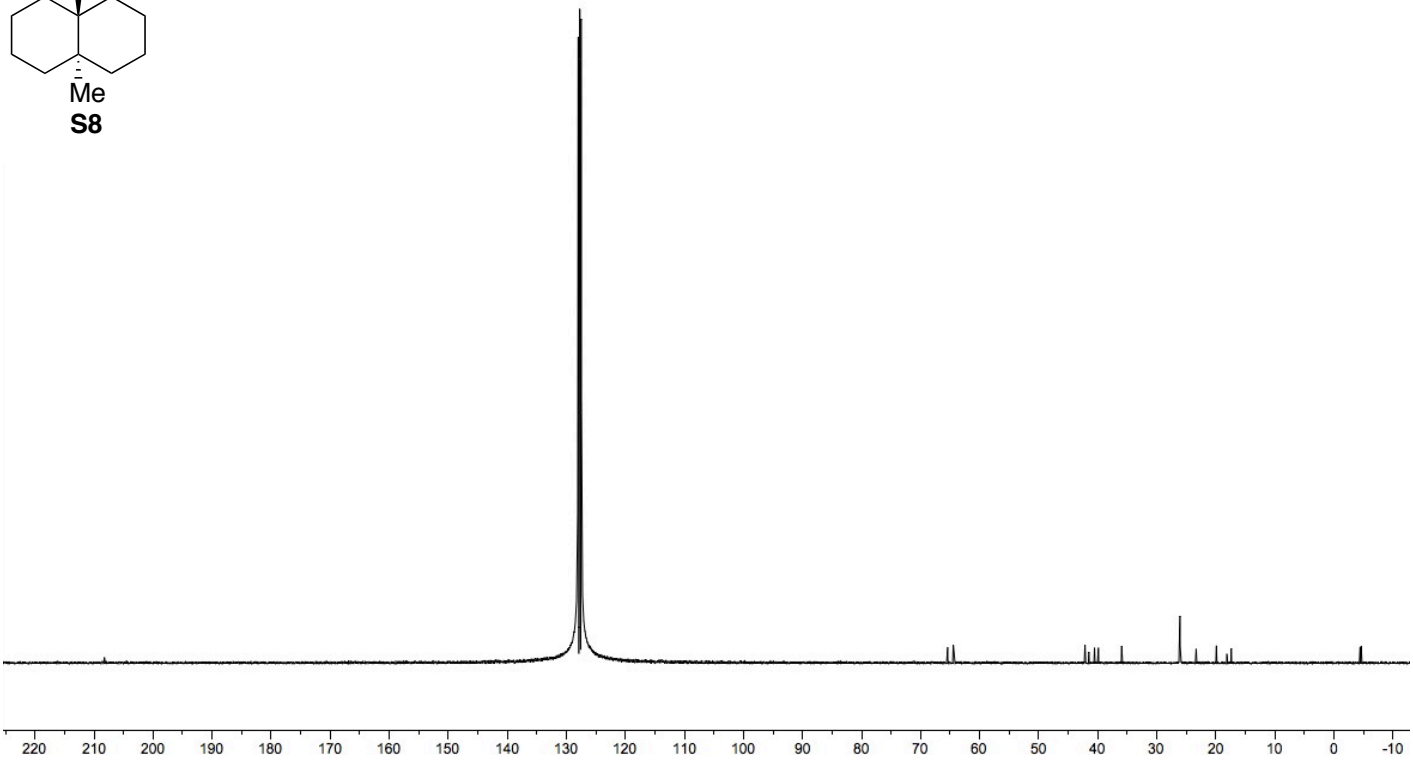
S8



p0566mgl
M LLOYD MGL/07/40-P

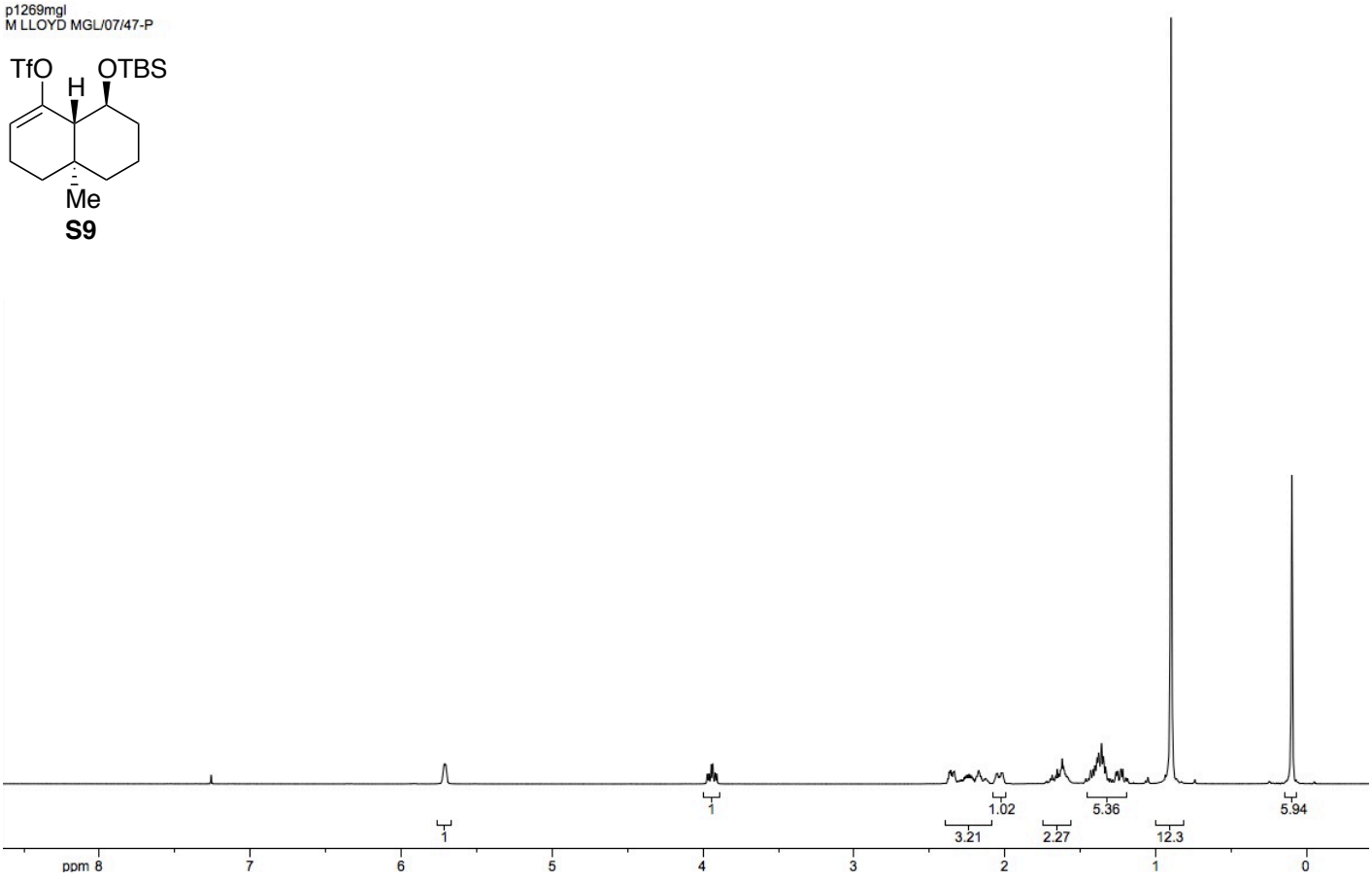


S8



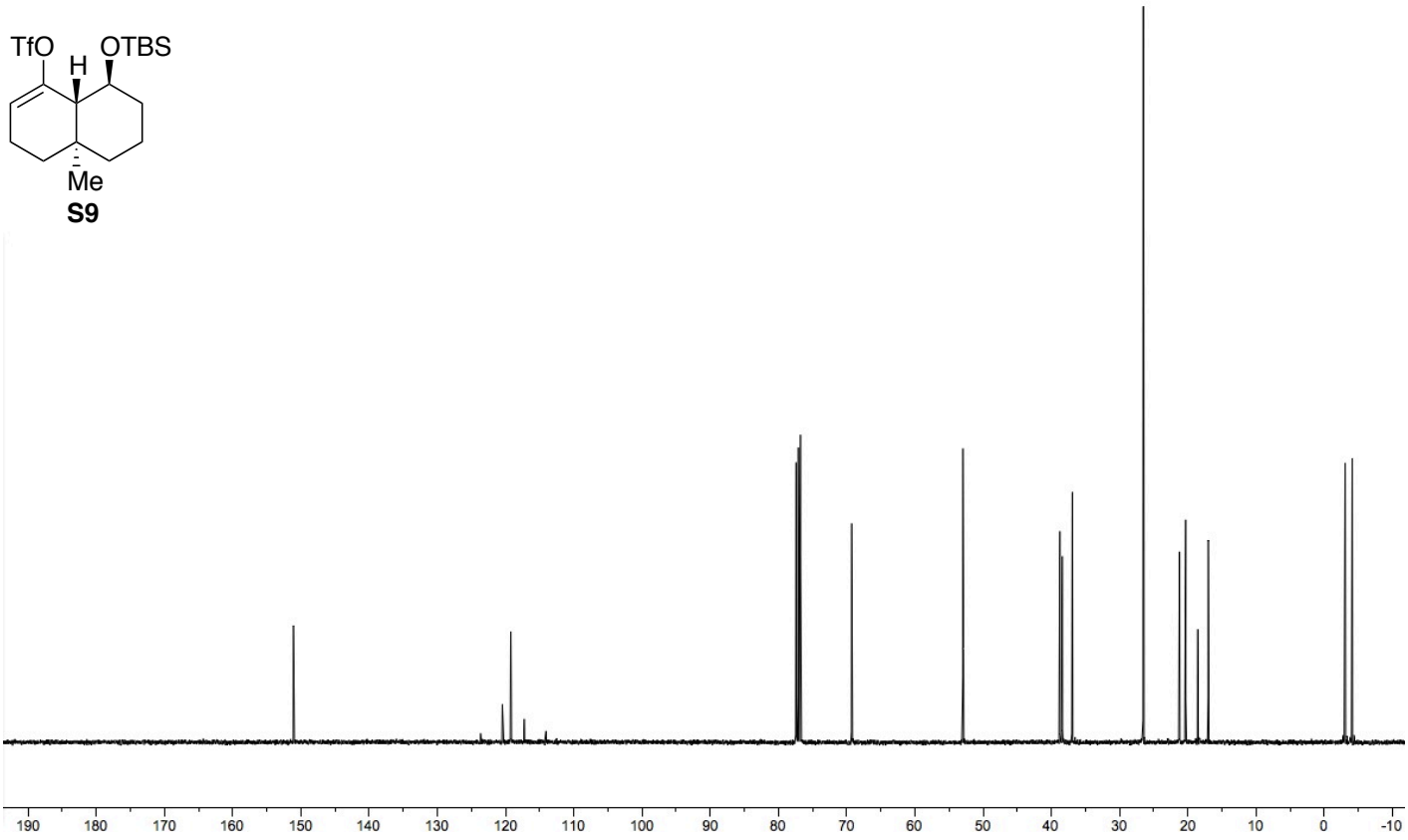
p1269mgl
M LLOYD MGL/07/47-P

S9



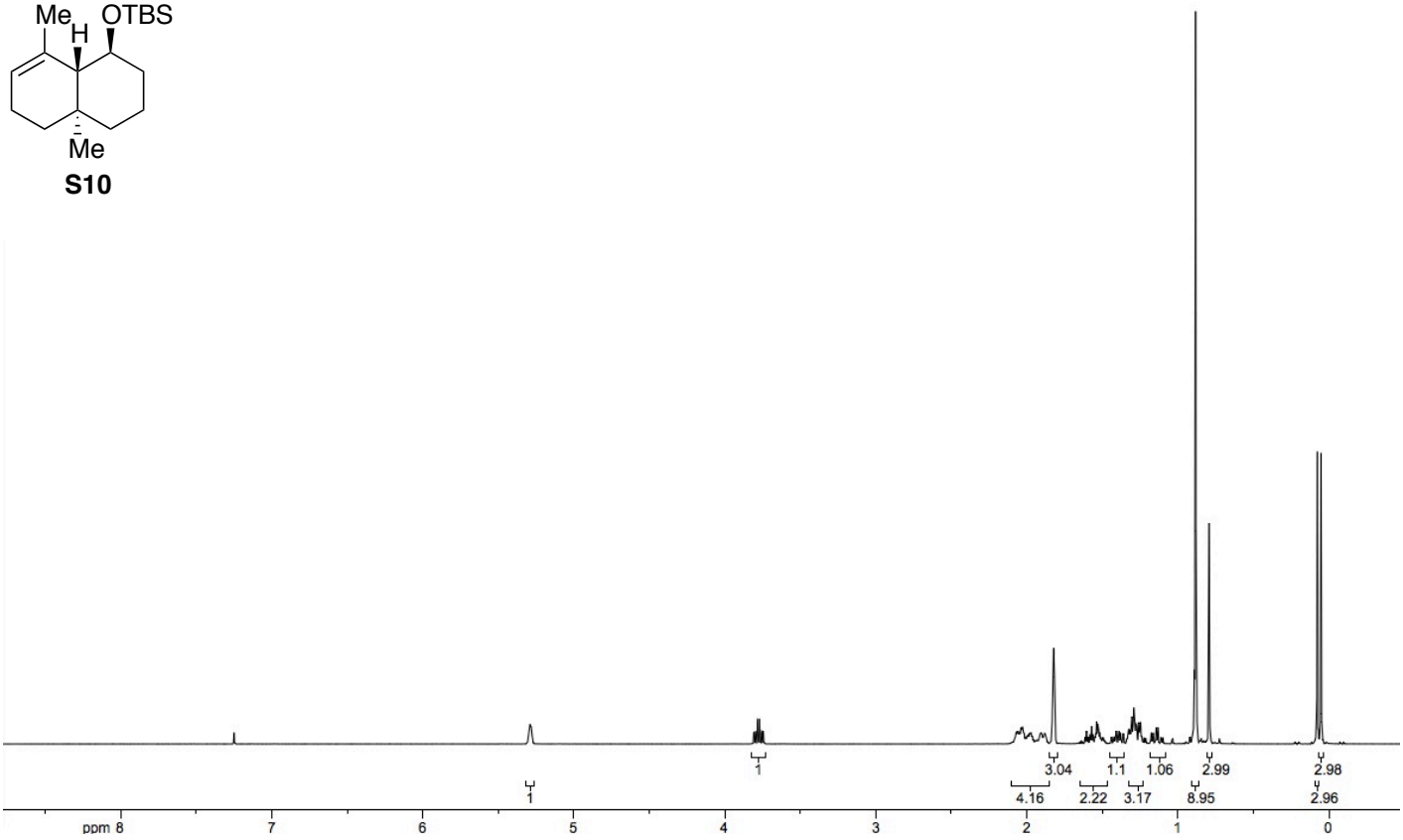
p1269mgl
M LLOYD MGL/07/47-P

S9



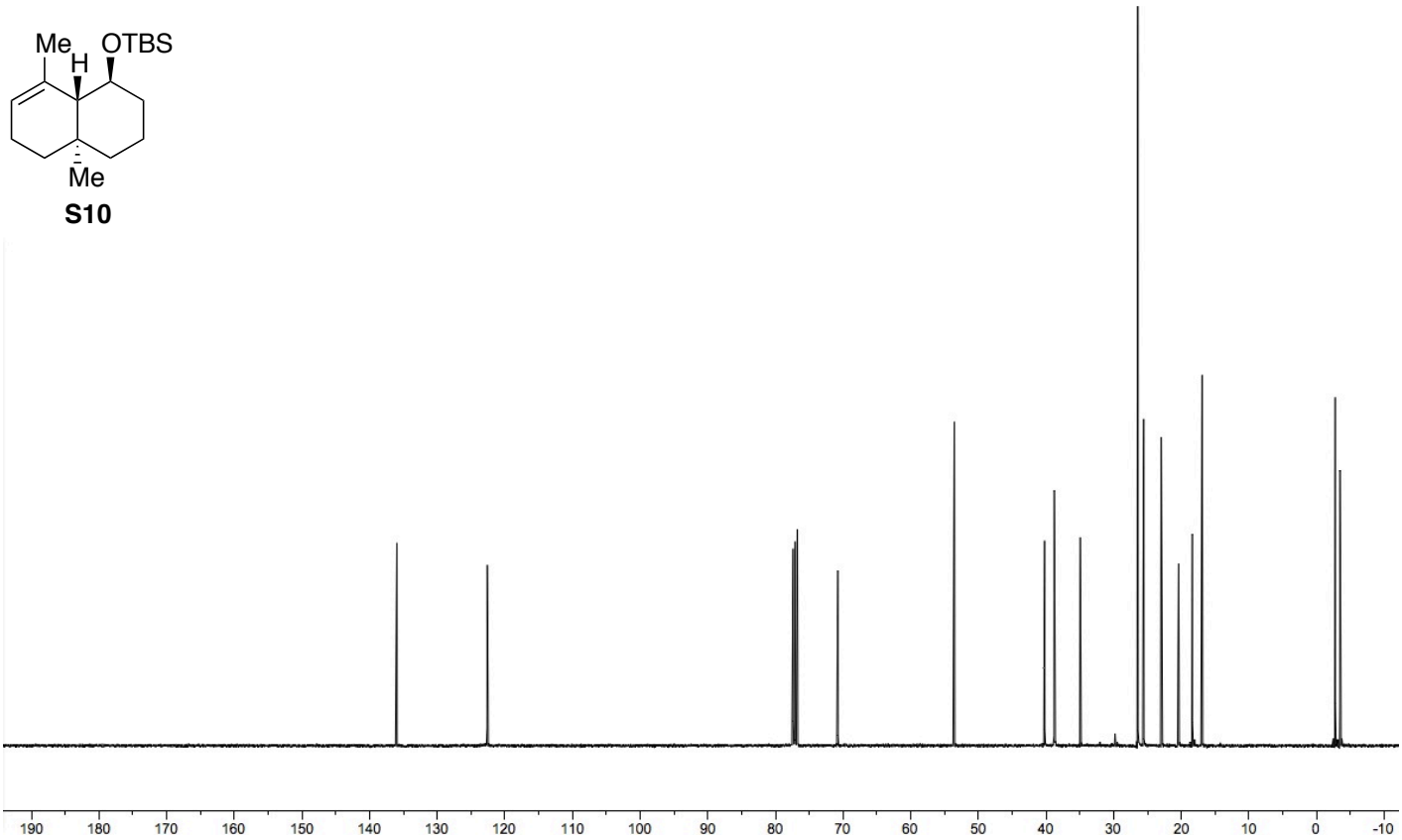
p1431mgl
M LLOYD MGL/07/48-P

S10



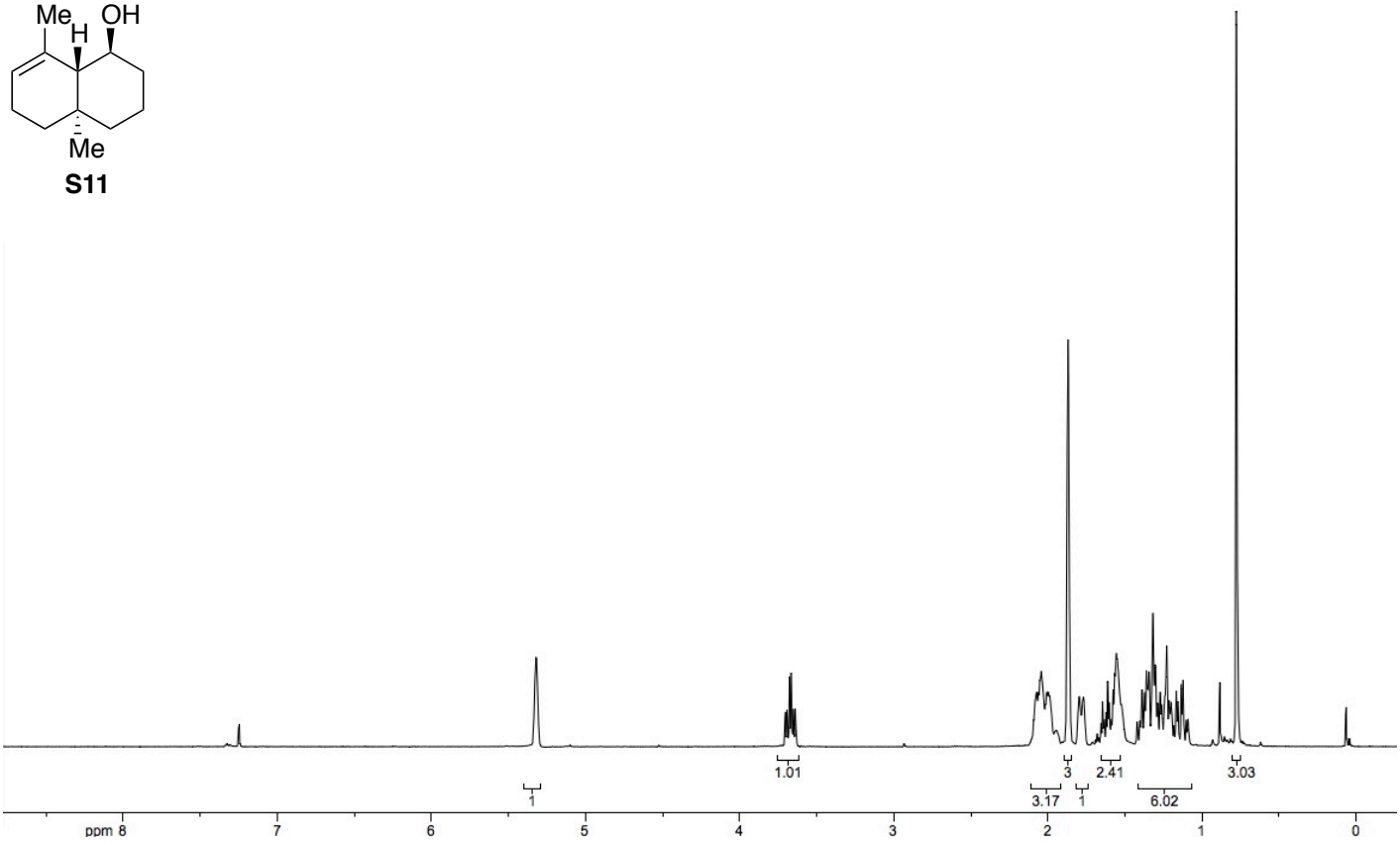
p1431mgl
M LLOYD MGL/07/48-P

S10



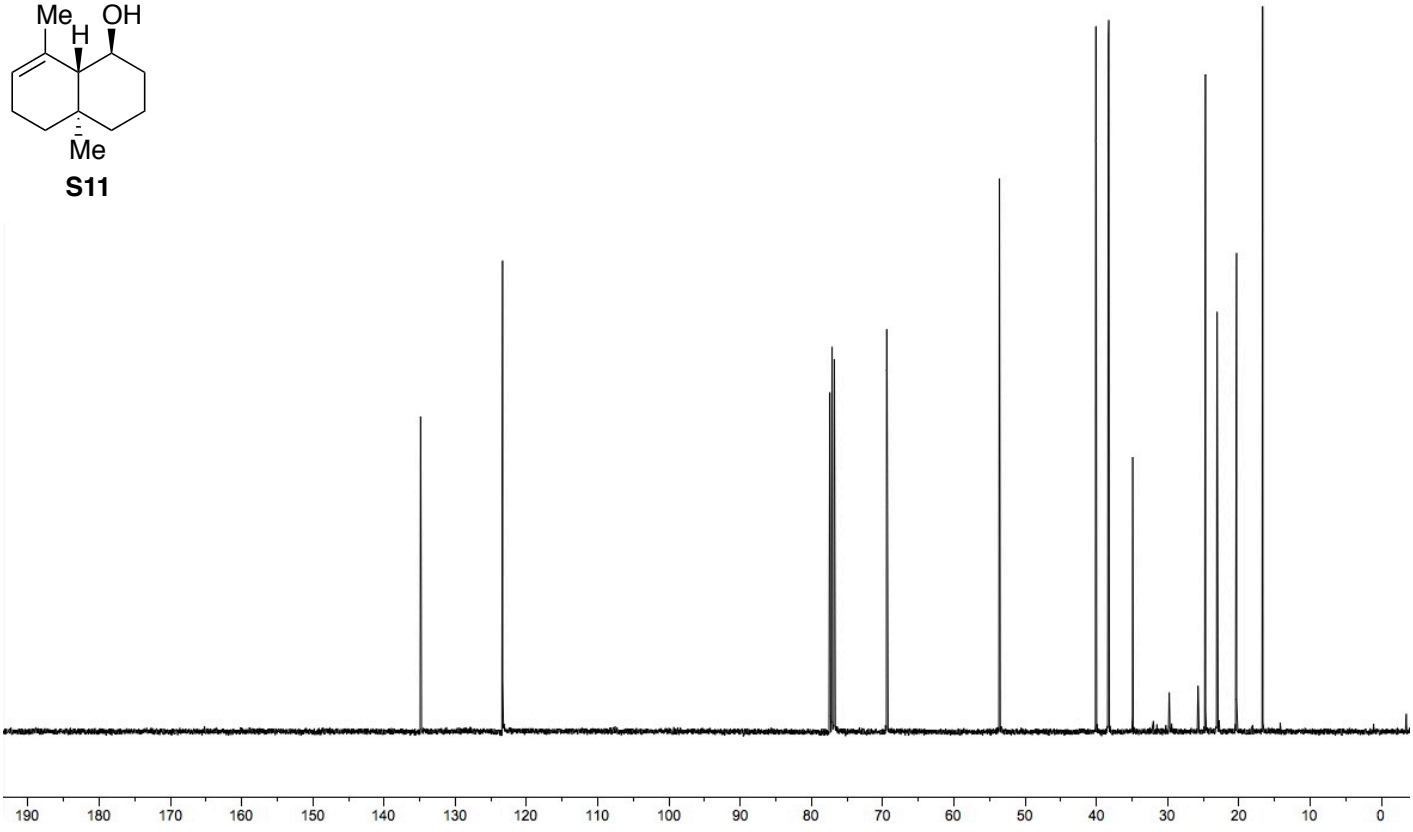
p1486mgl
M LLOYD MGL/07/49-P

S11



p1486mgl
M LLOYD MGL/07/49-P

S11



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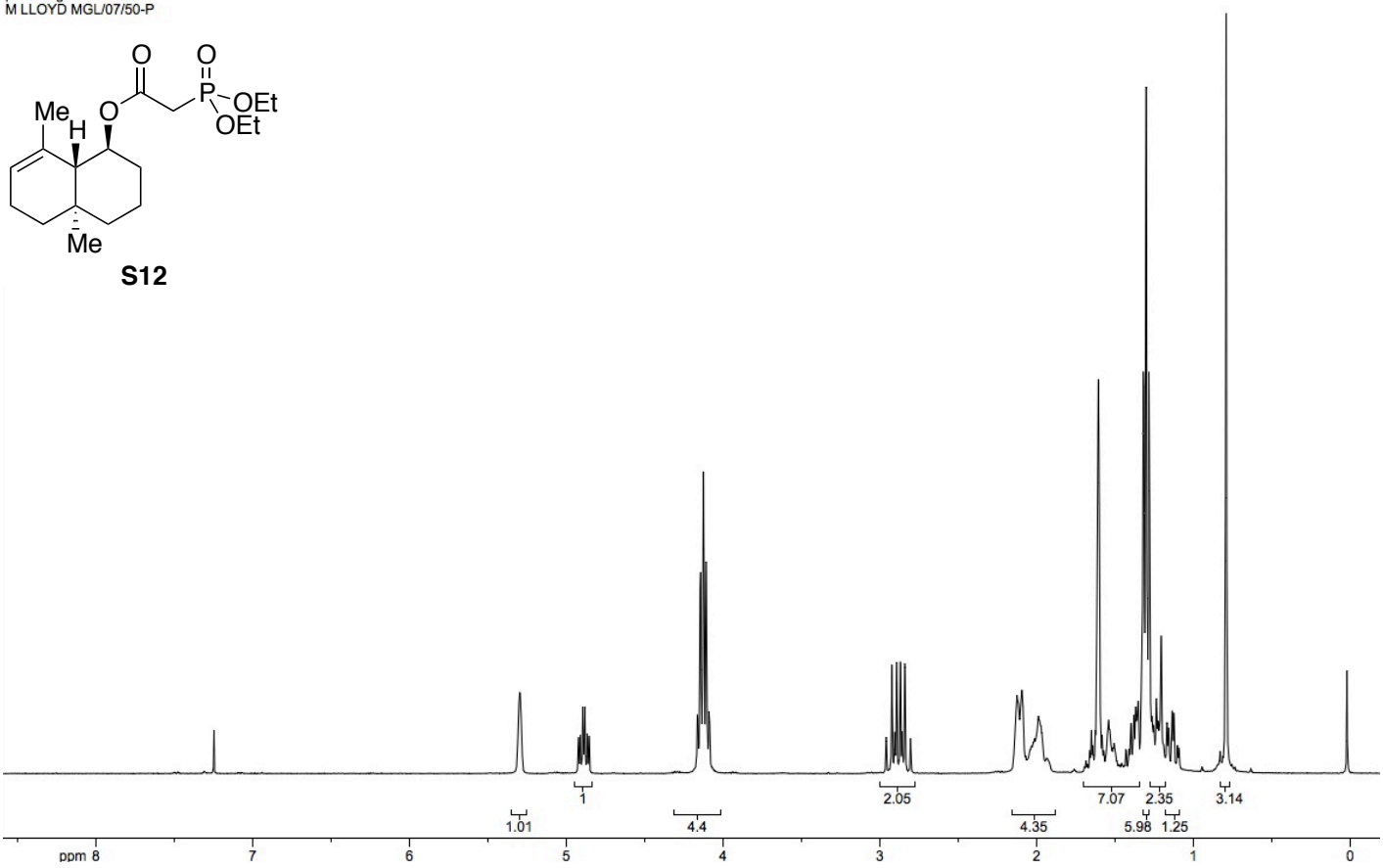
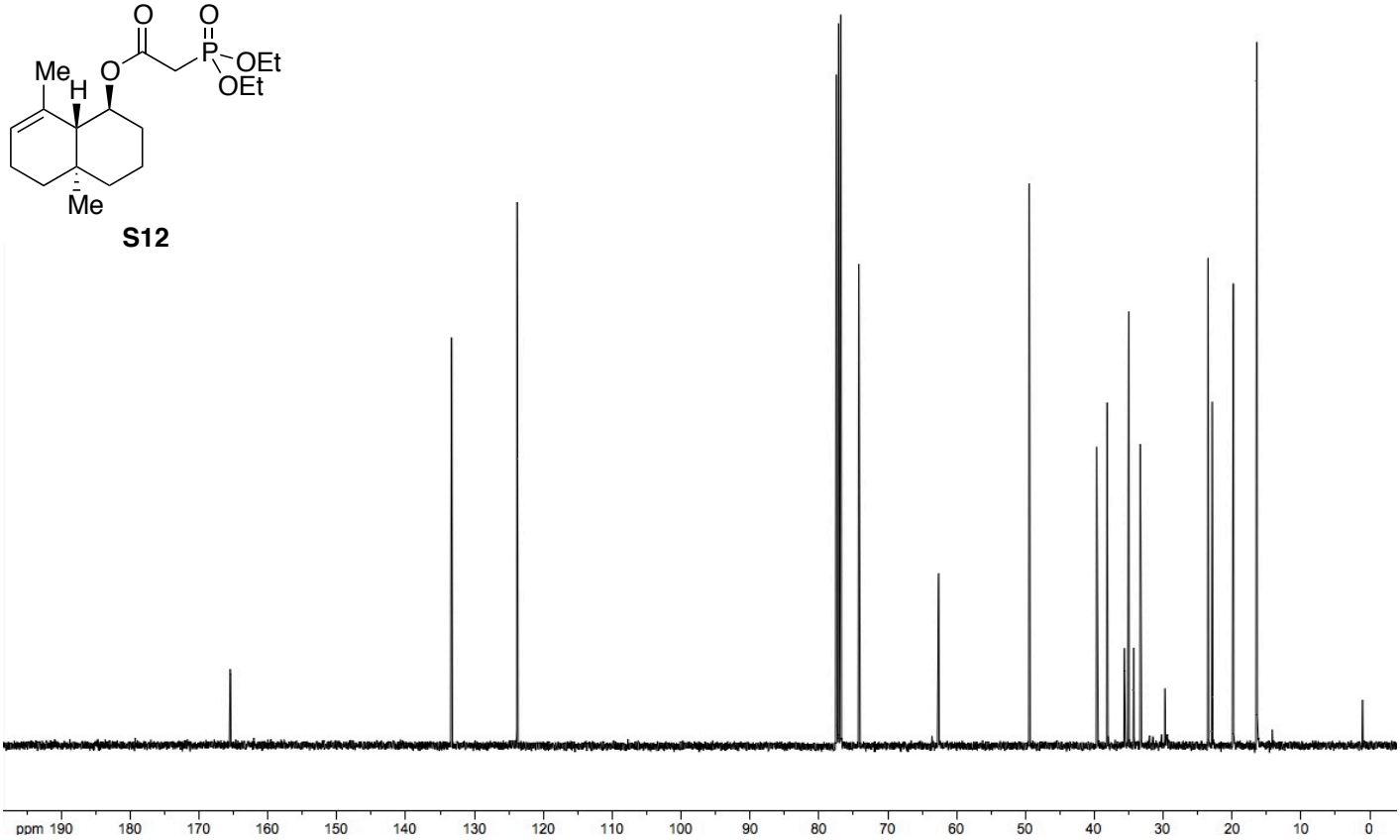
S12



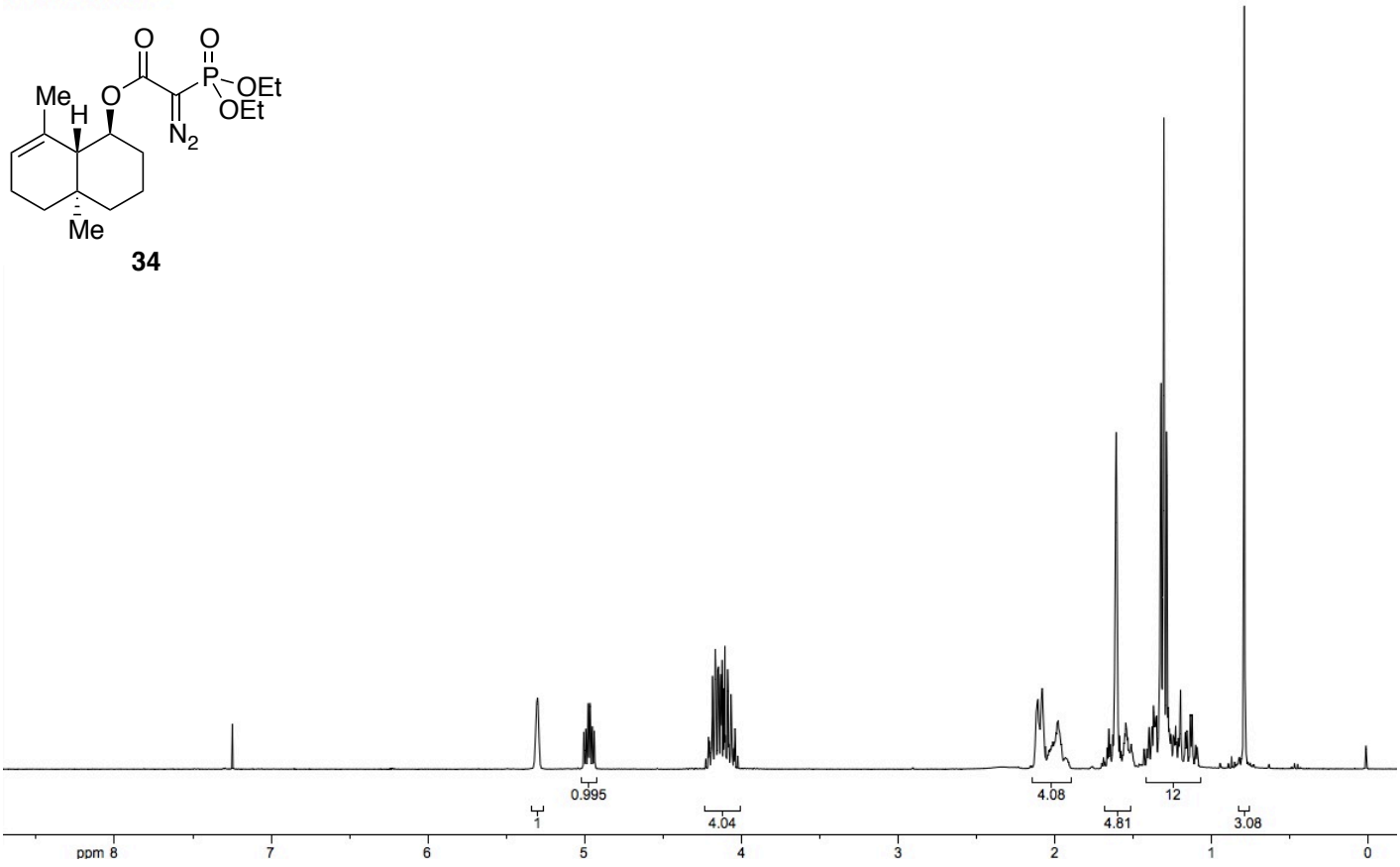
p1557akc
MGL/07/50-P

S12



p1608mgl
M LLOYD MGL/07/51-P

34



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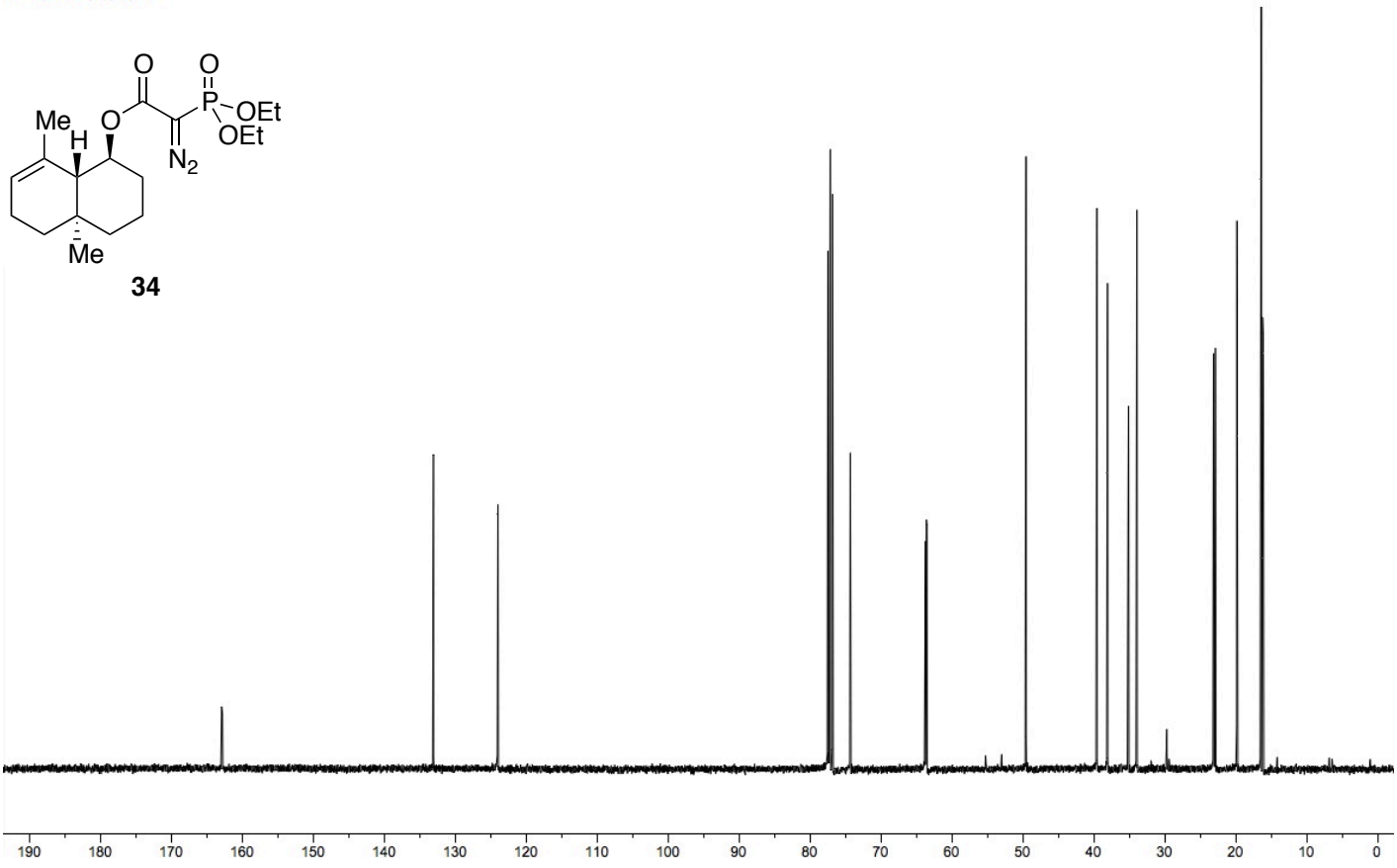
34



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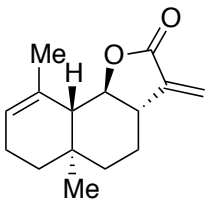
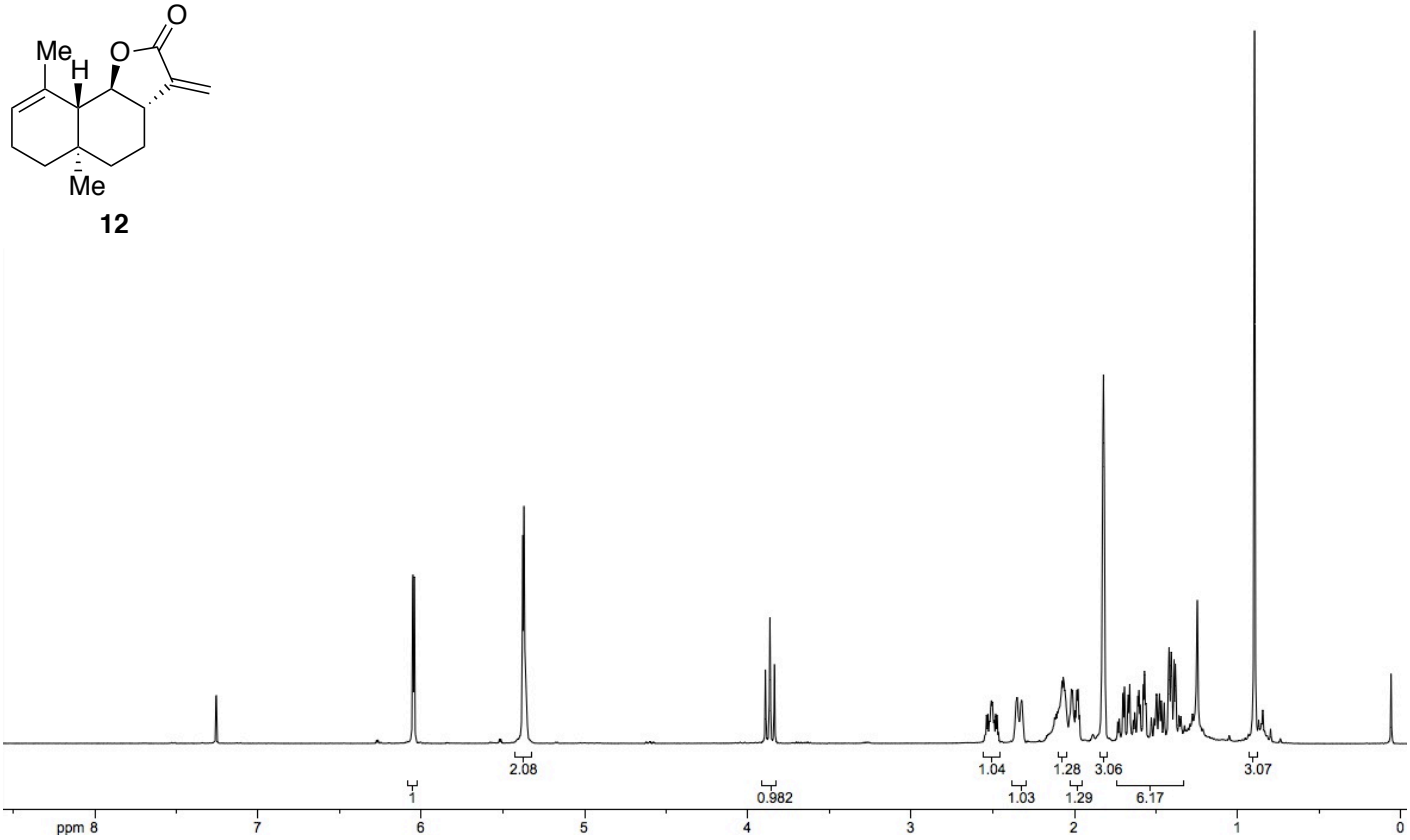


12



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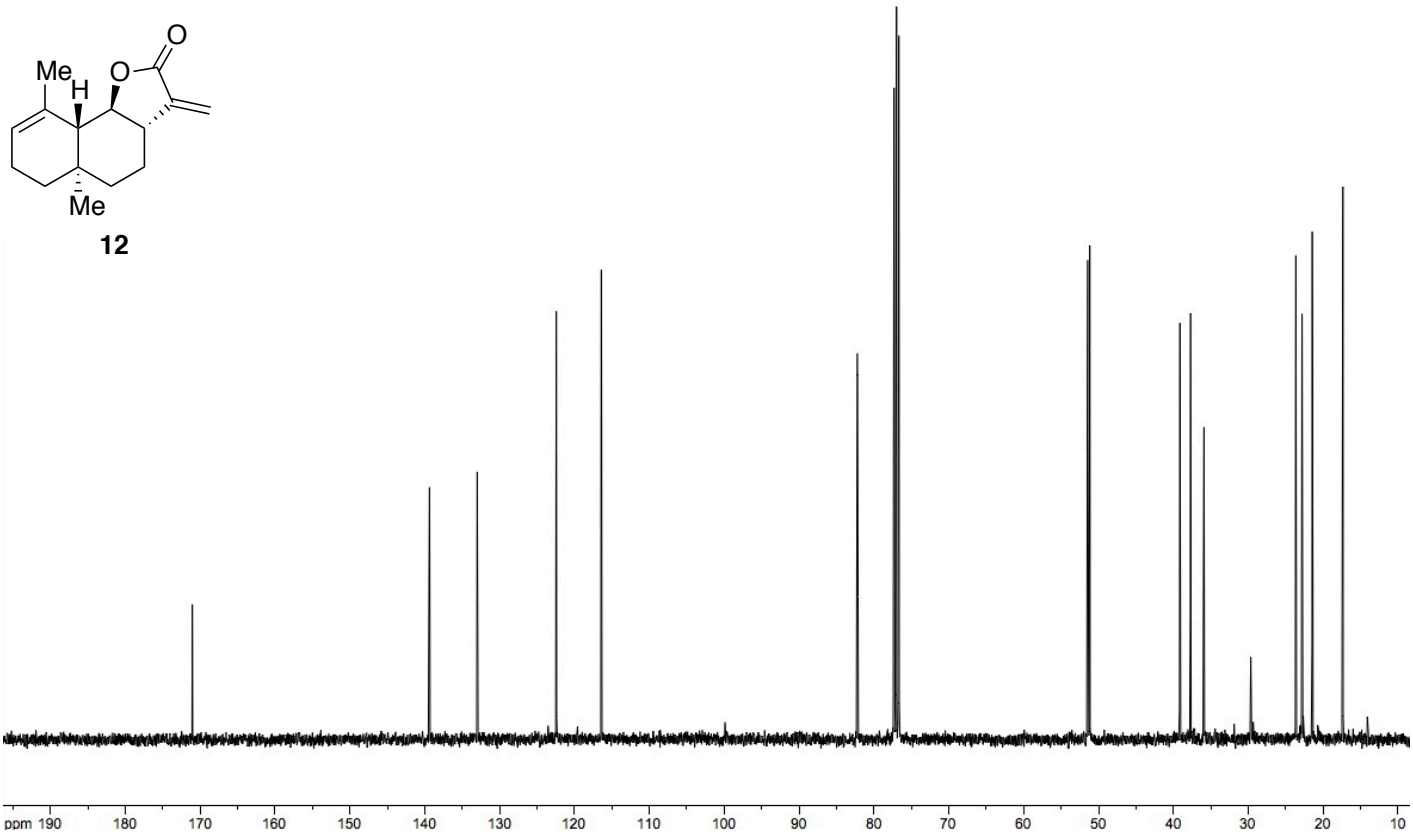
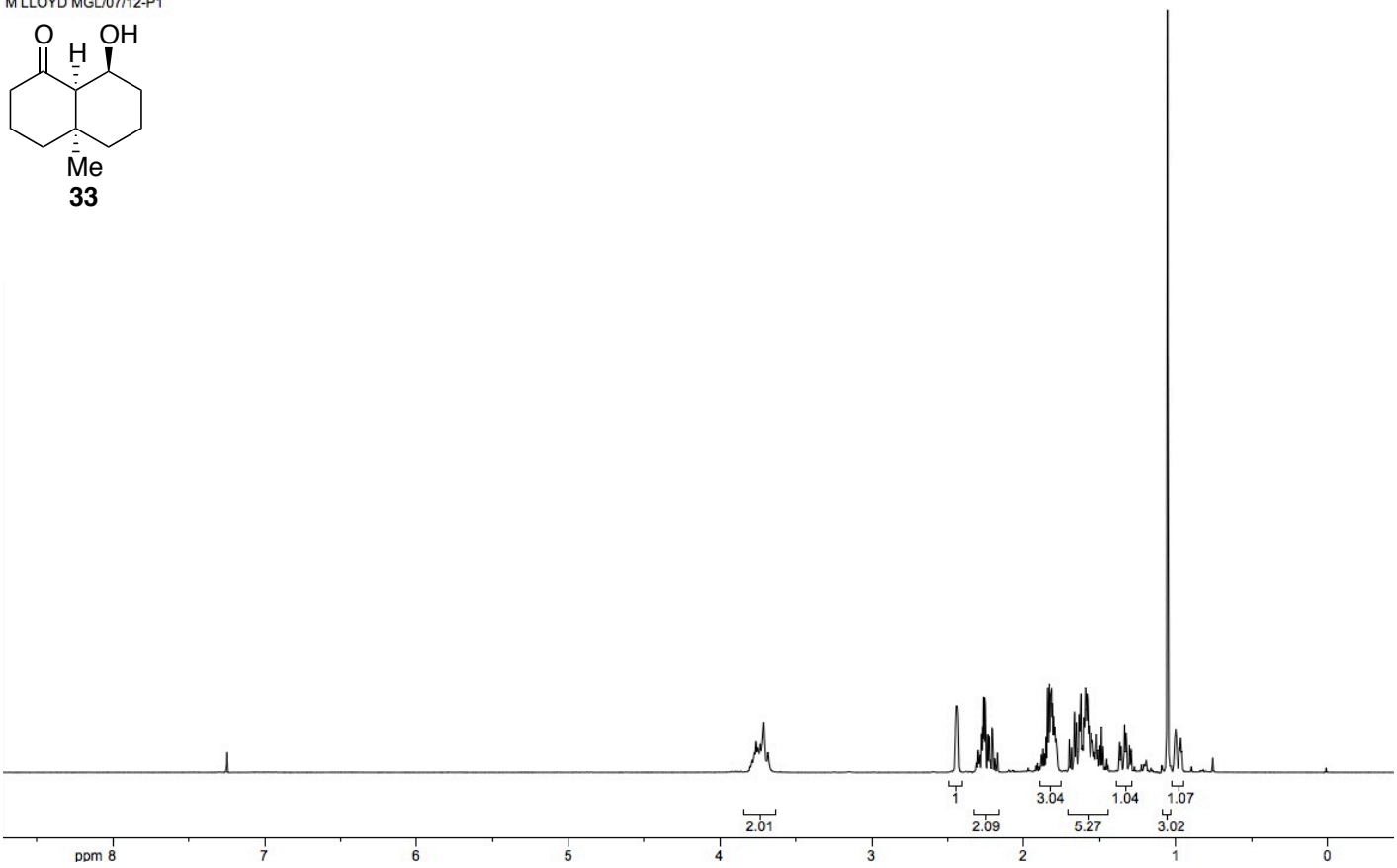
M LLOYD MGL/07/52-P

12



n8404mgl
M LLOYD MGL/07/12-P1

33



n8491mgl
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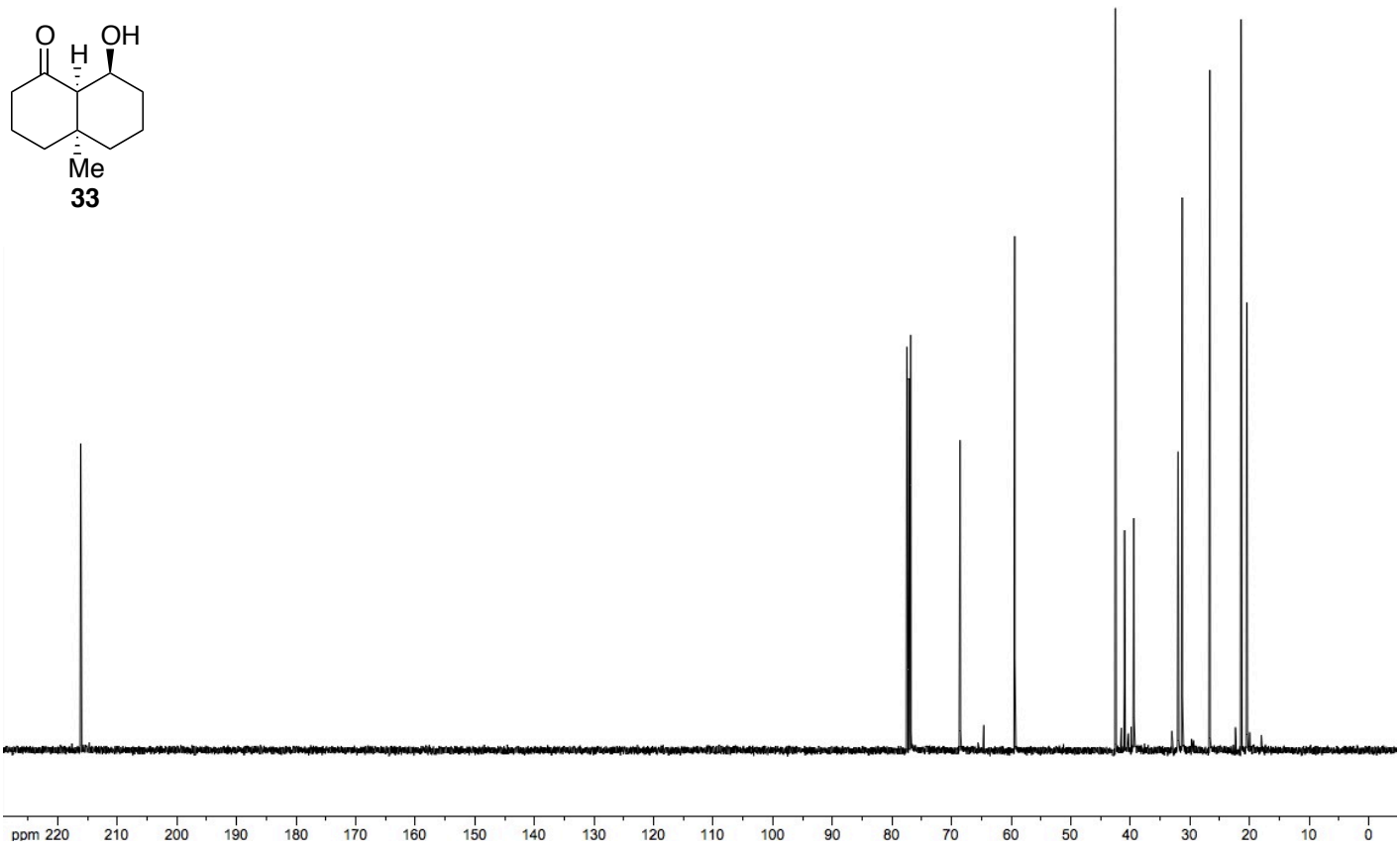
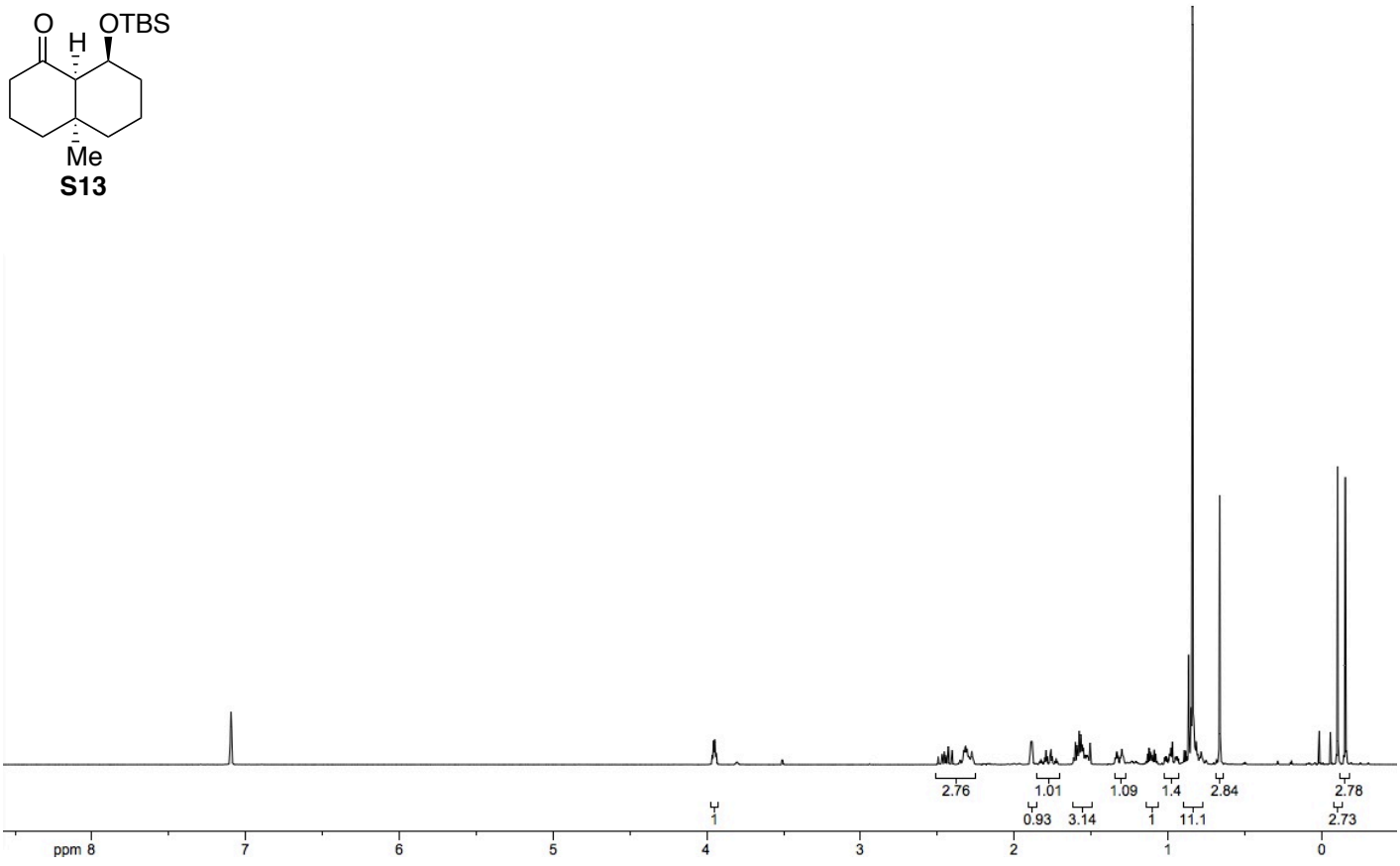
33



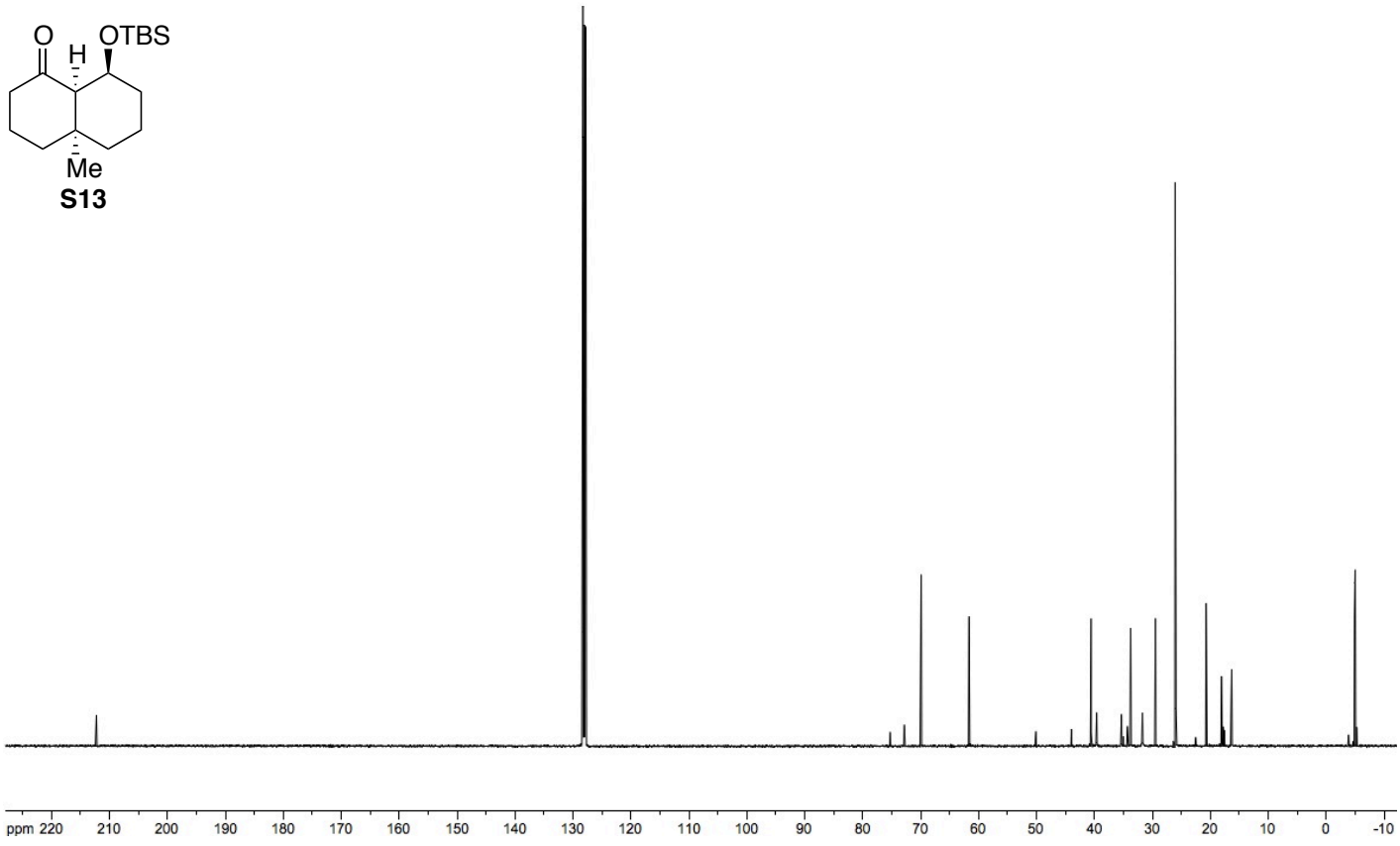
p1659mgl
M LLOYD MGL/07/39-P

S13



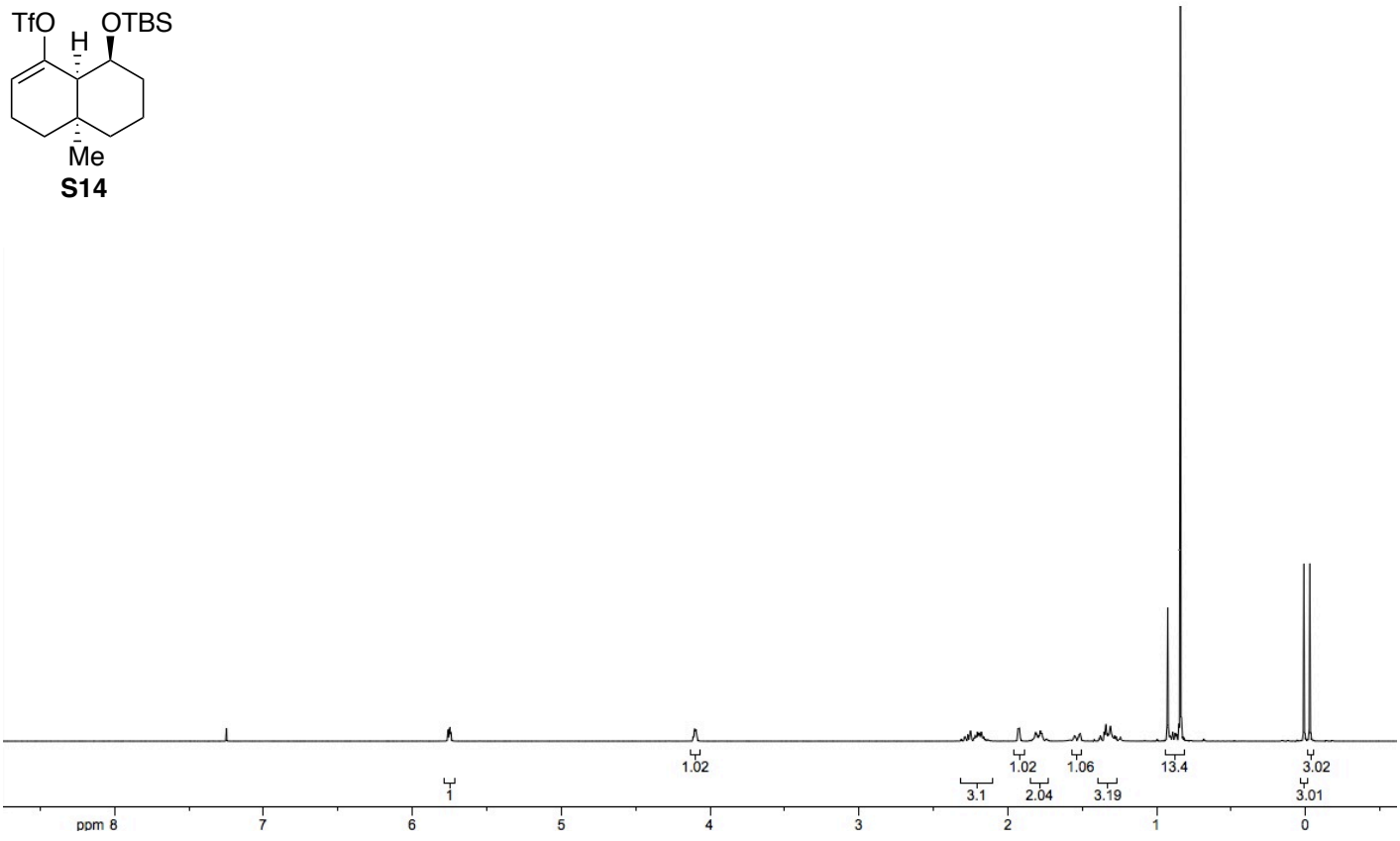
p1659mgl
M LLOYD MGL/07/39-P

S13



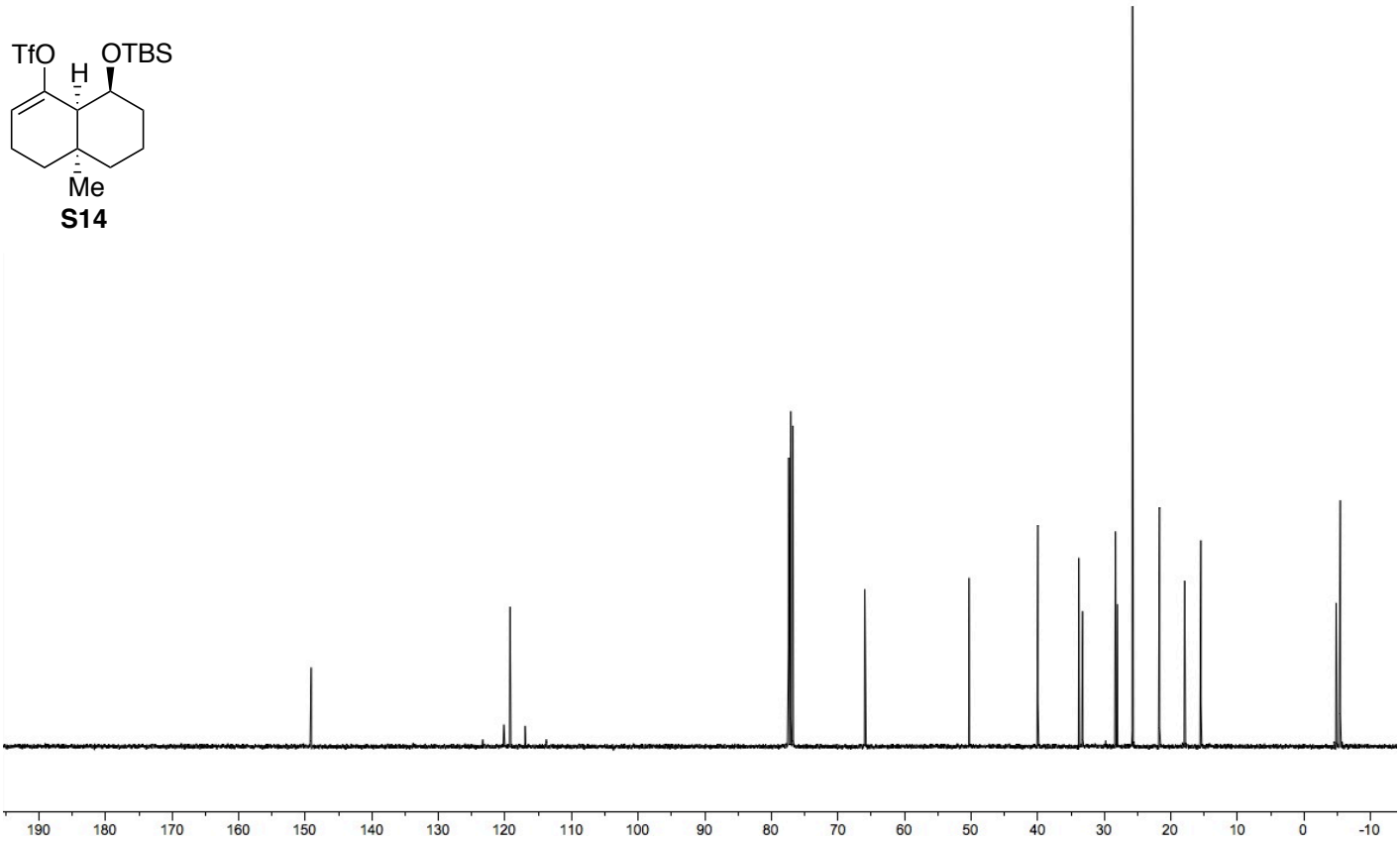
a1158mgl
M LLOYD MGL/07/55-P

S14



p1885mgl
M LLOYD MGL/07/55-P

S14



p2024mgl
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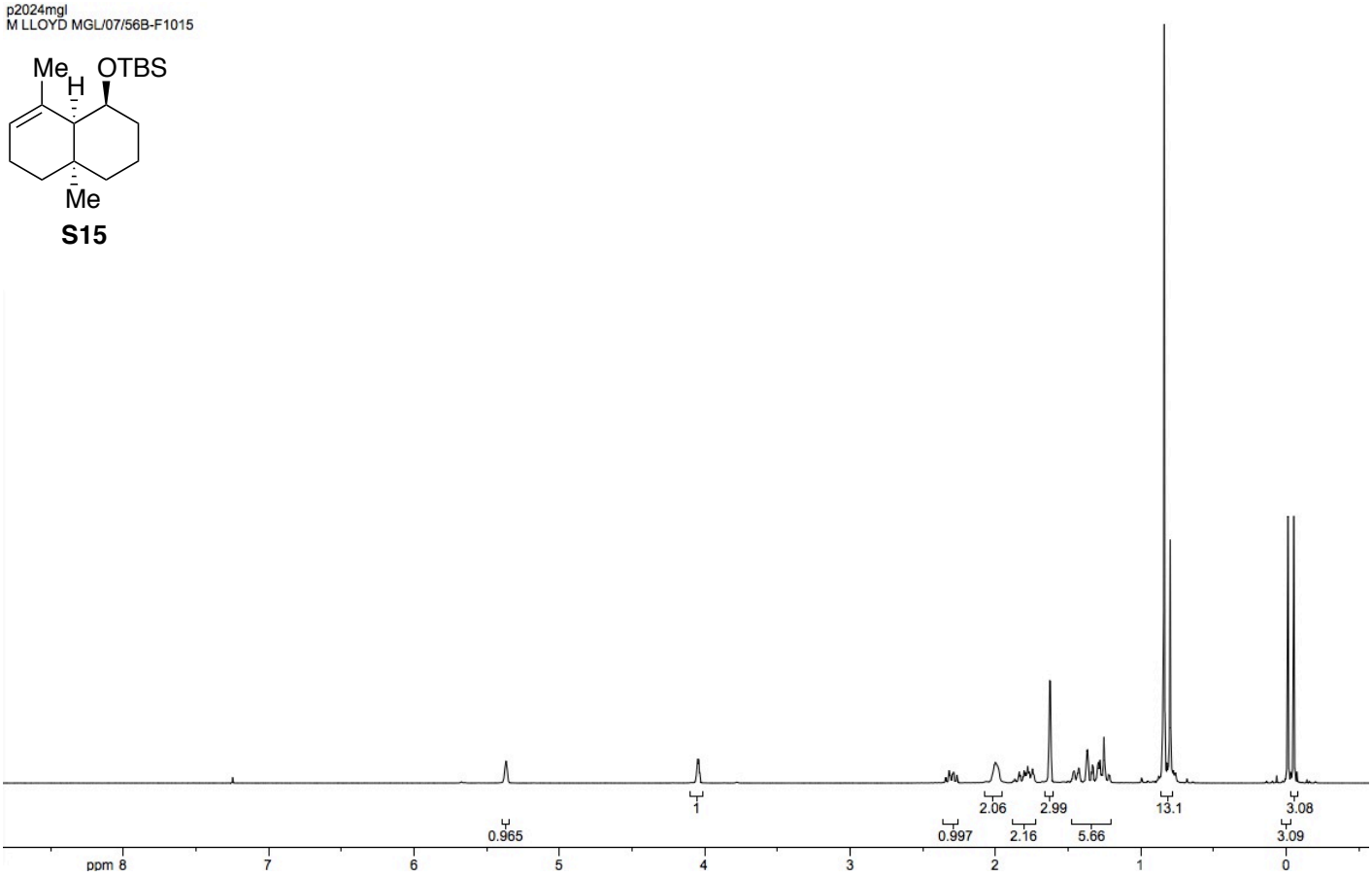
S15



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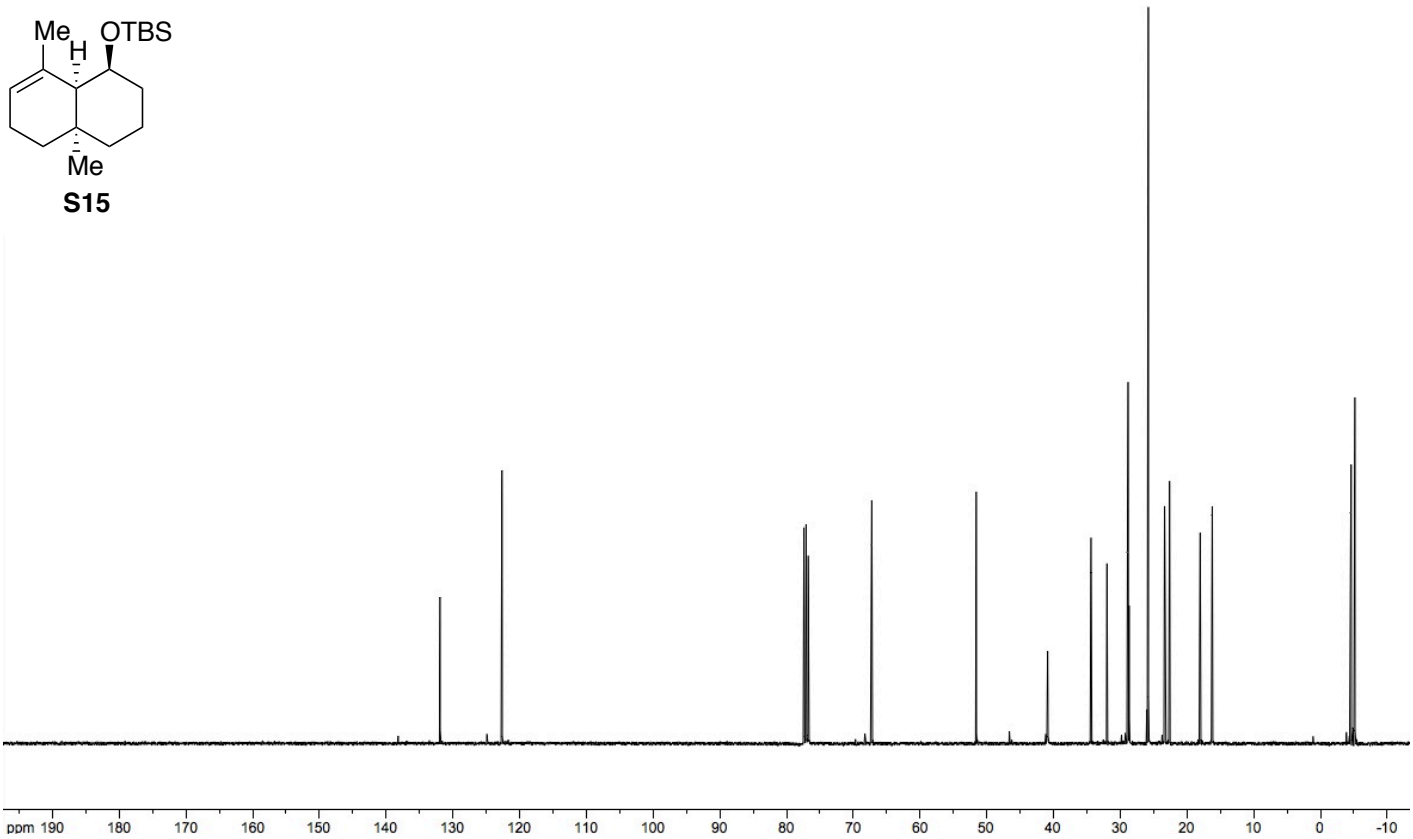
M LLOYD MGL/07/56-P

S15



p2205mgl
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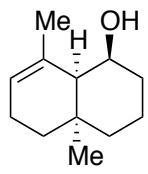
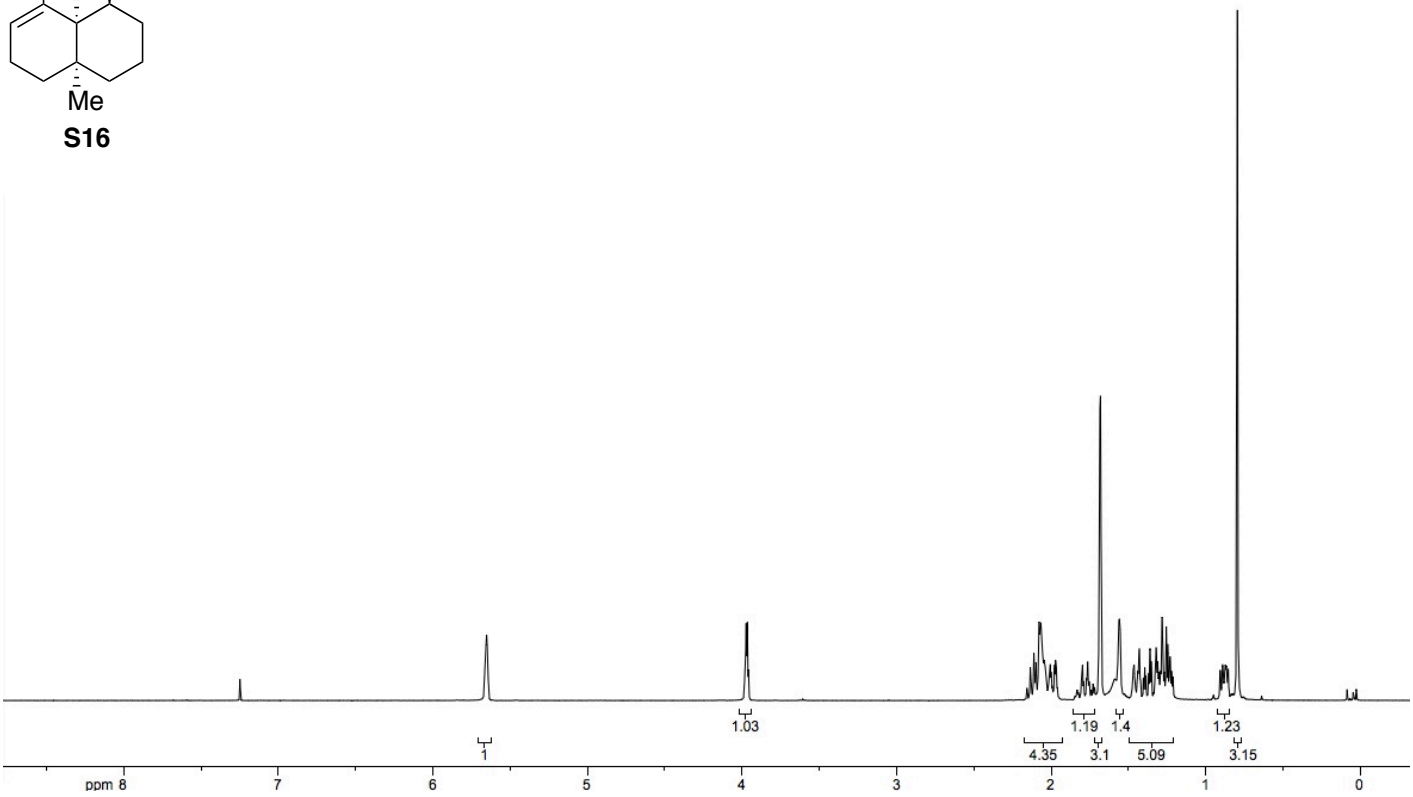


S16



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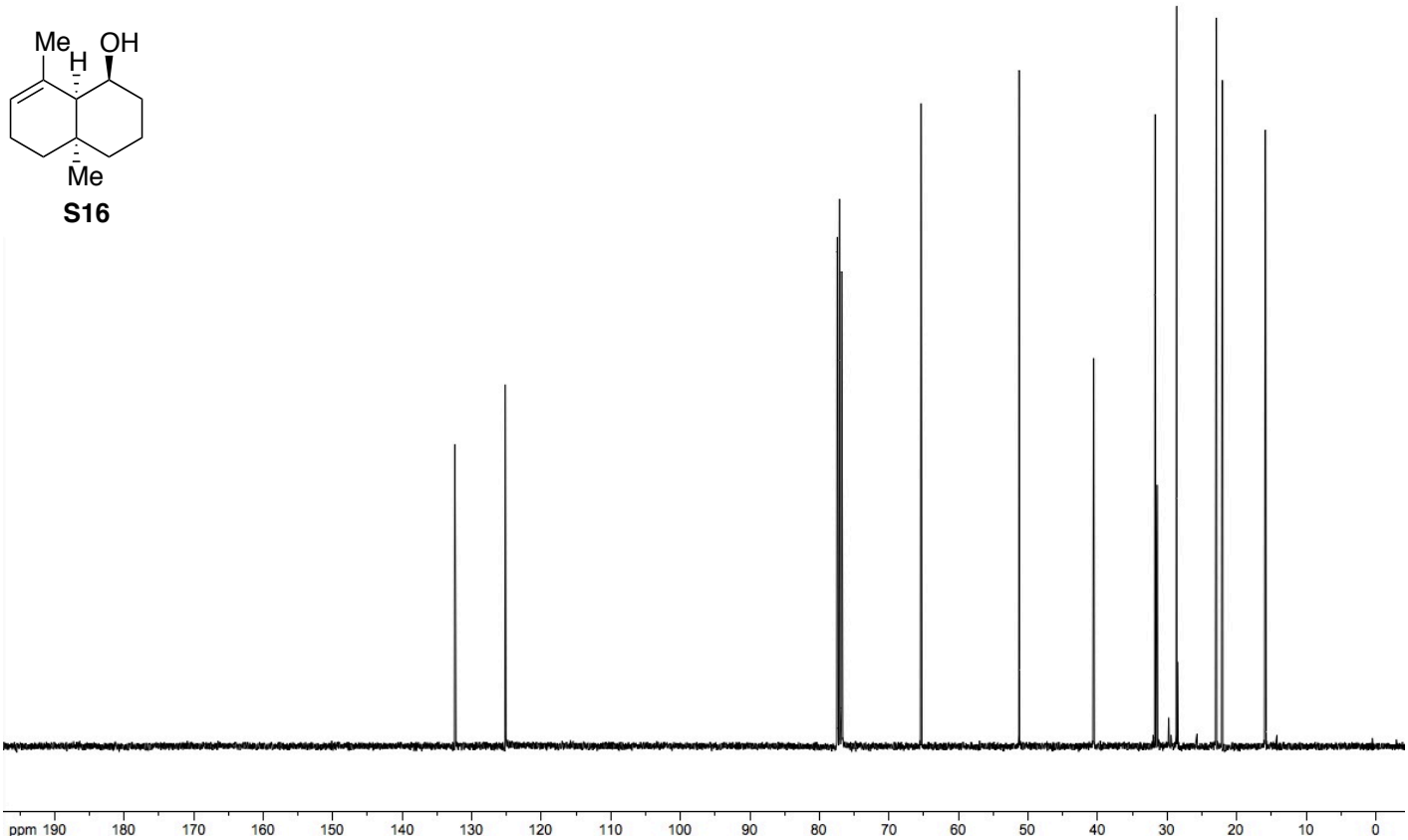
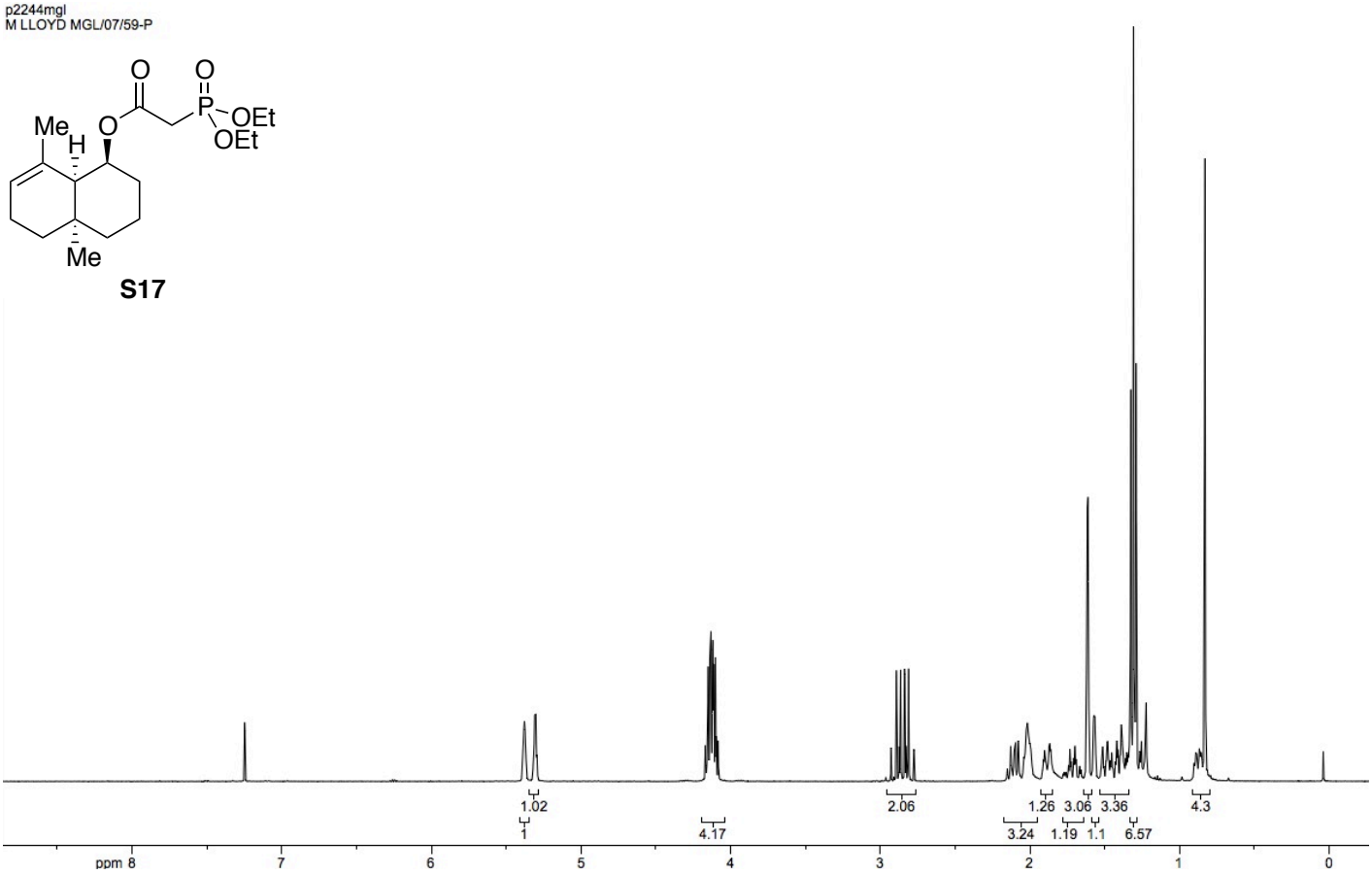
M LLOYD MGL/07/58-P

S16



p2244mgl
M LLOYD MGL/07/59-P

S17



p2262mgl
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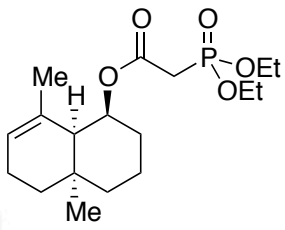
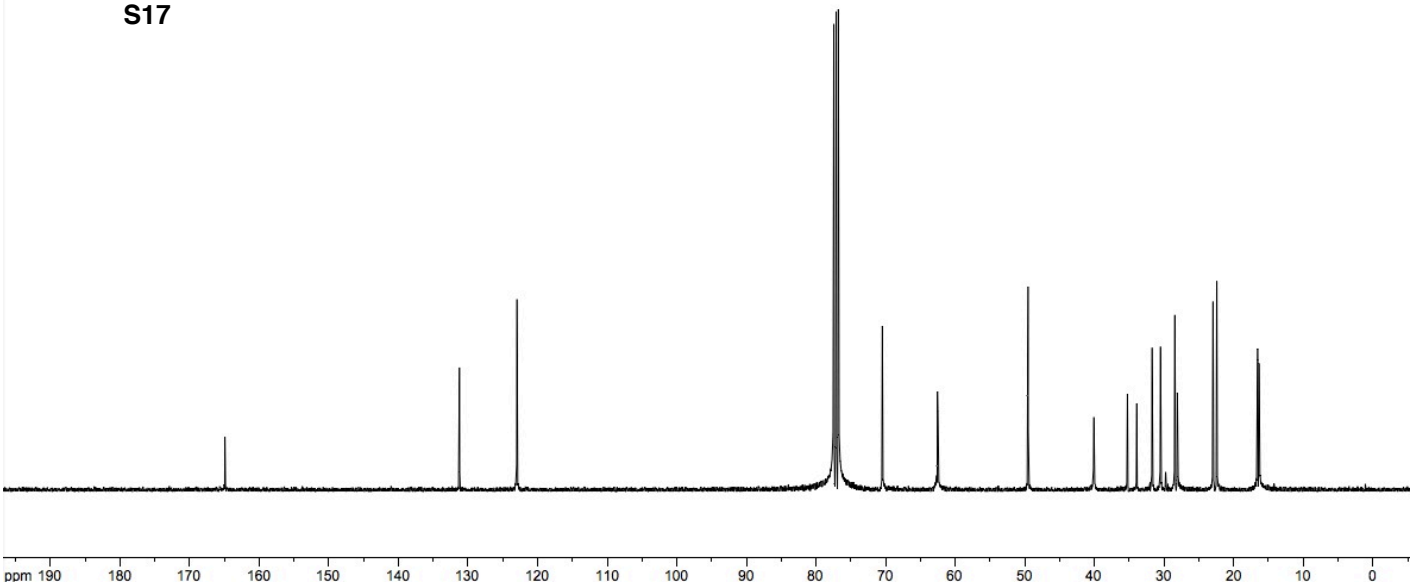
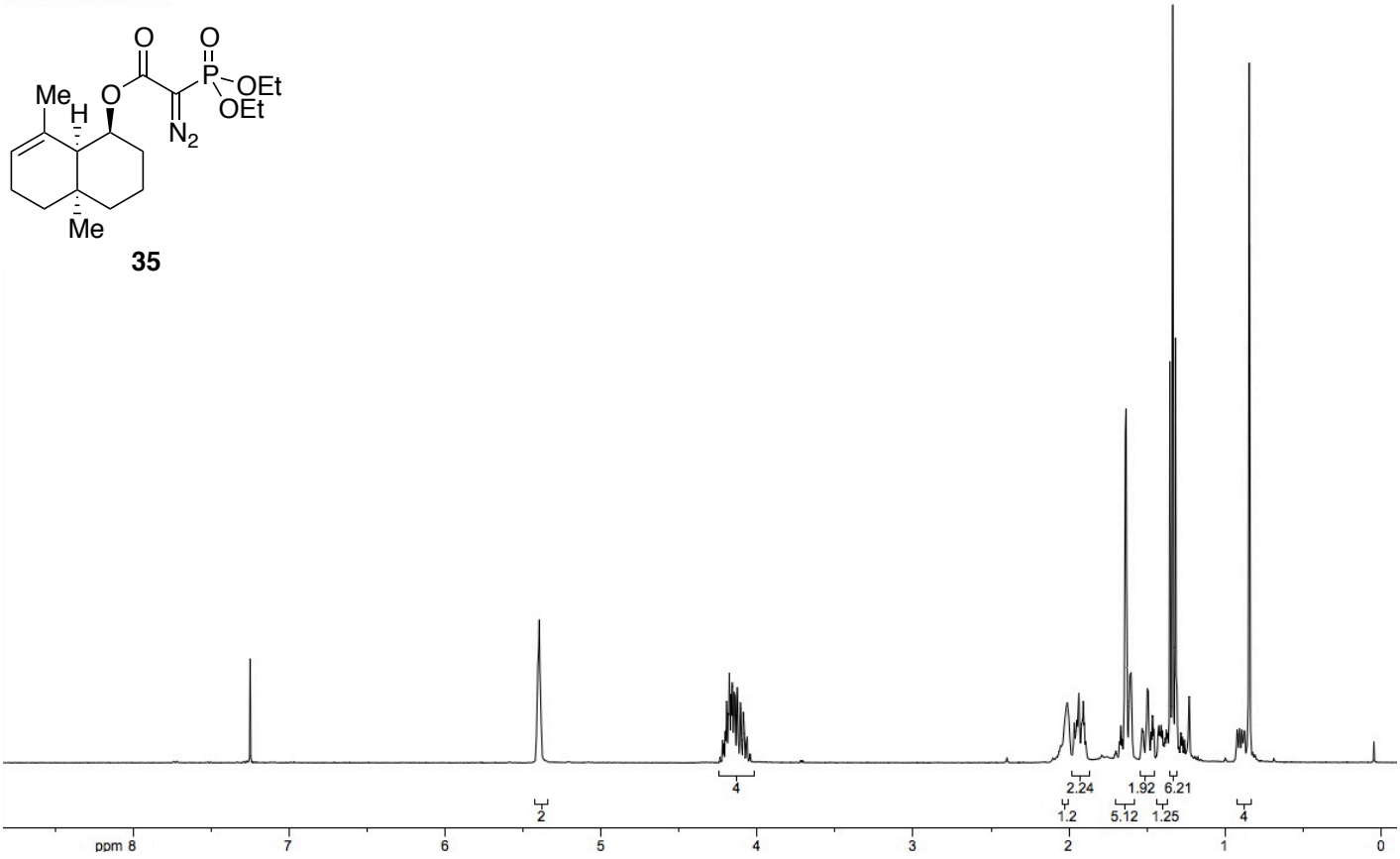


S17



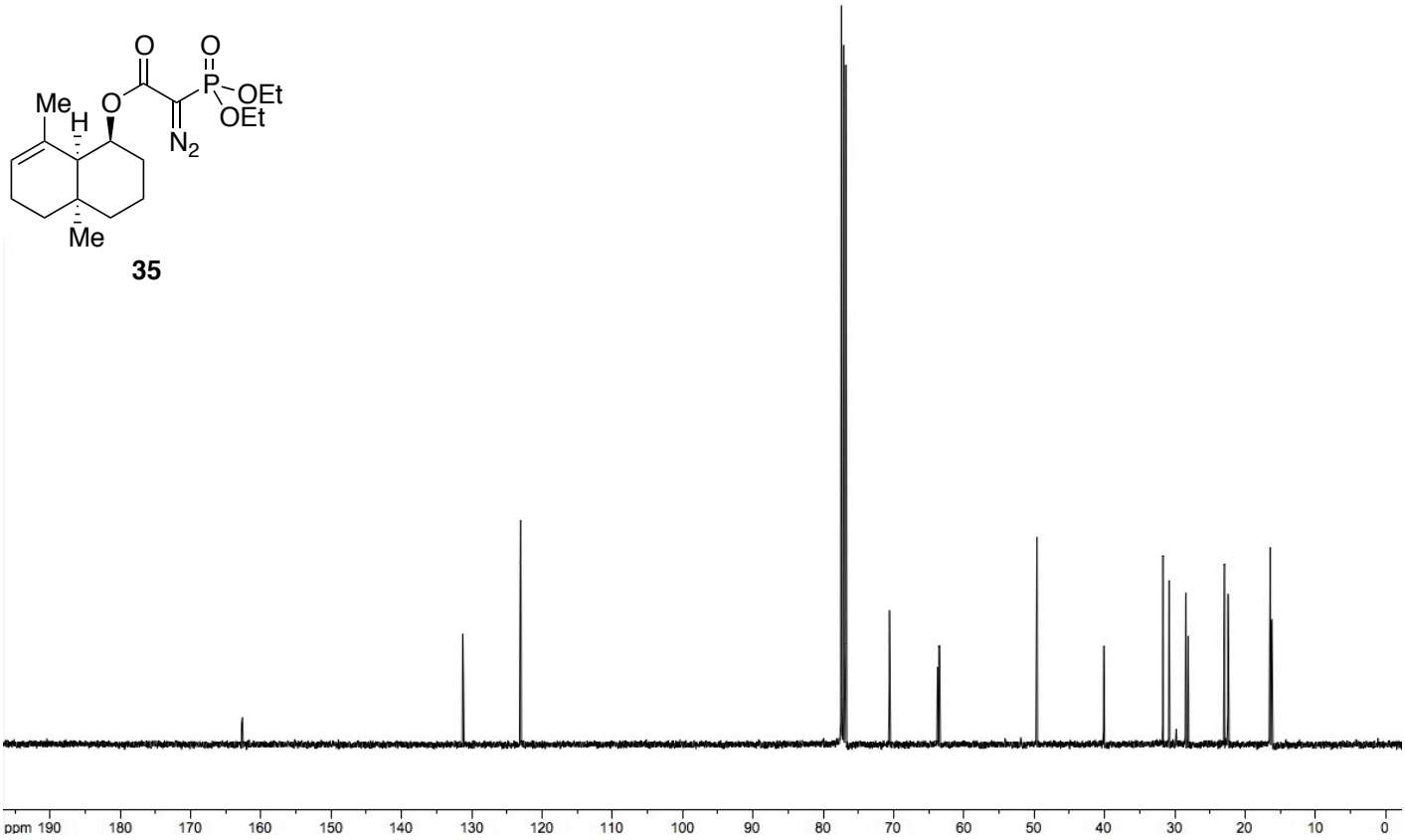
p2310mgl
M LLOYD MGL/07/60-P

35



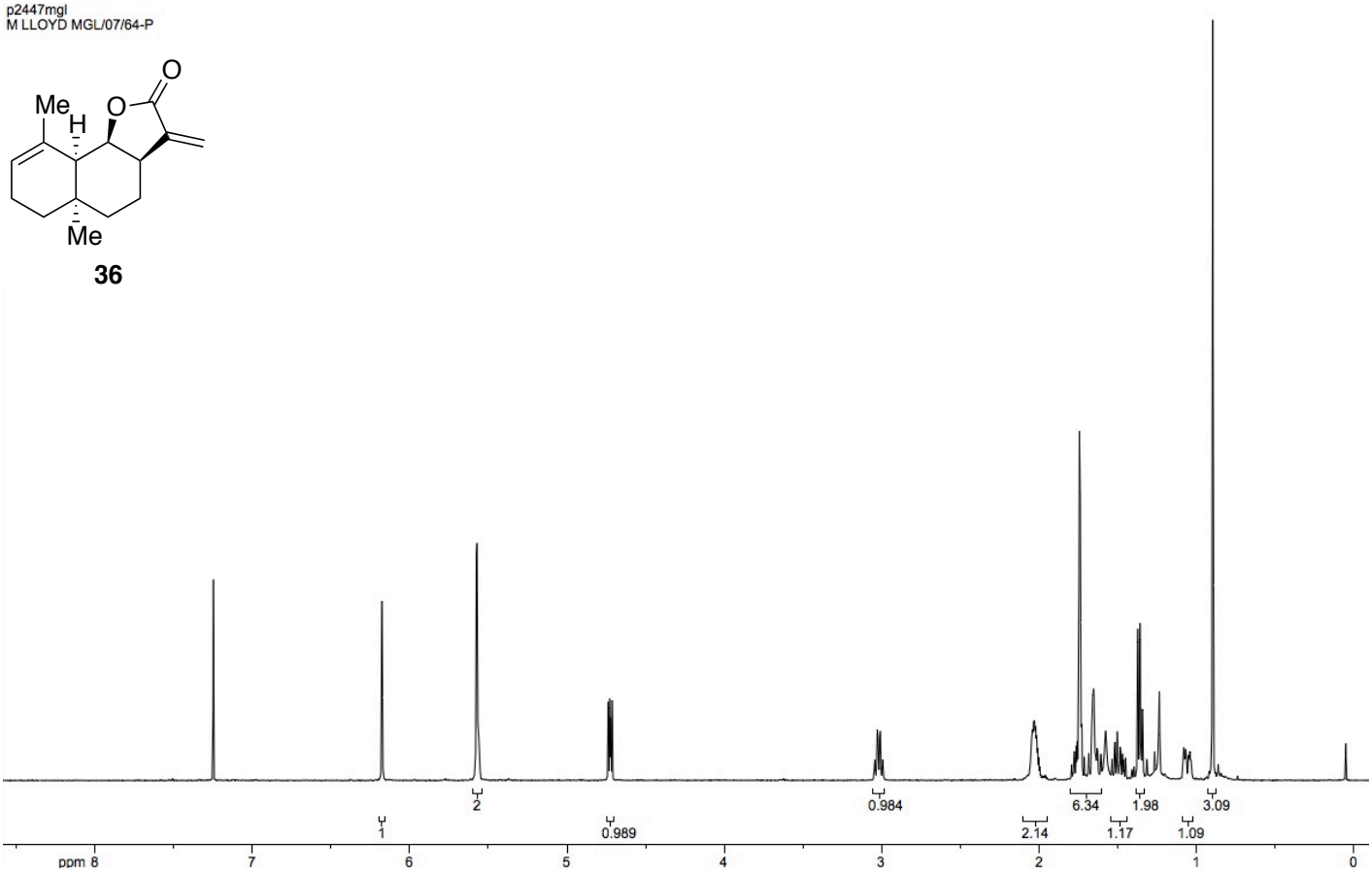
p2332mgl
M LLOYD MGL/07/60-P

35



p2447mgl
M LLOYD MGL/07/64-P

36



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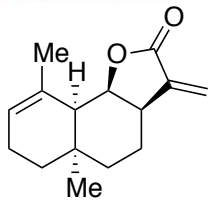

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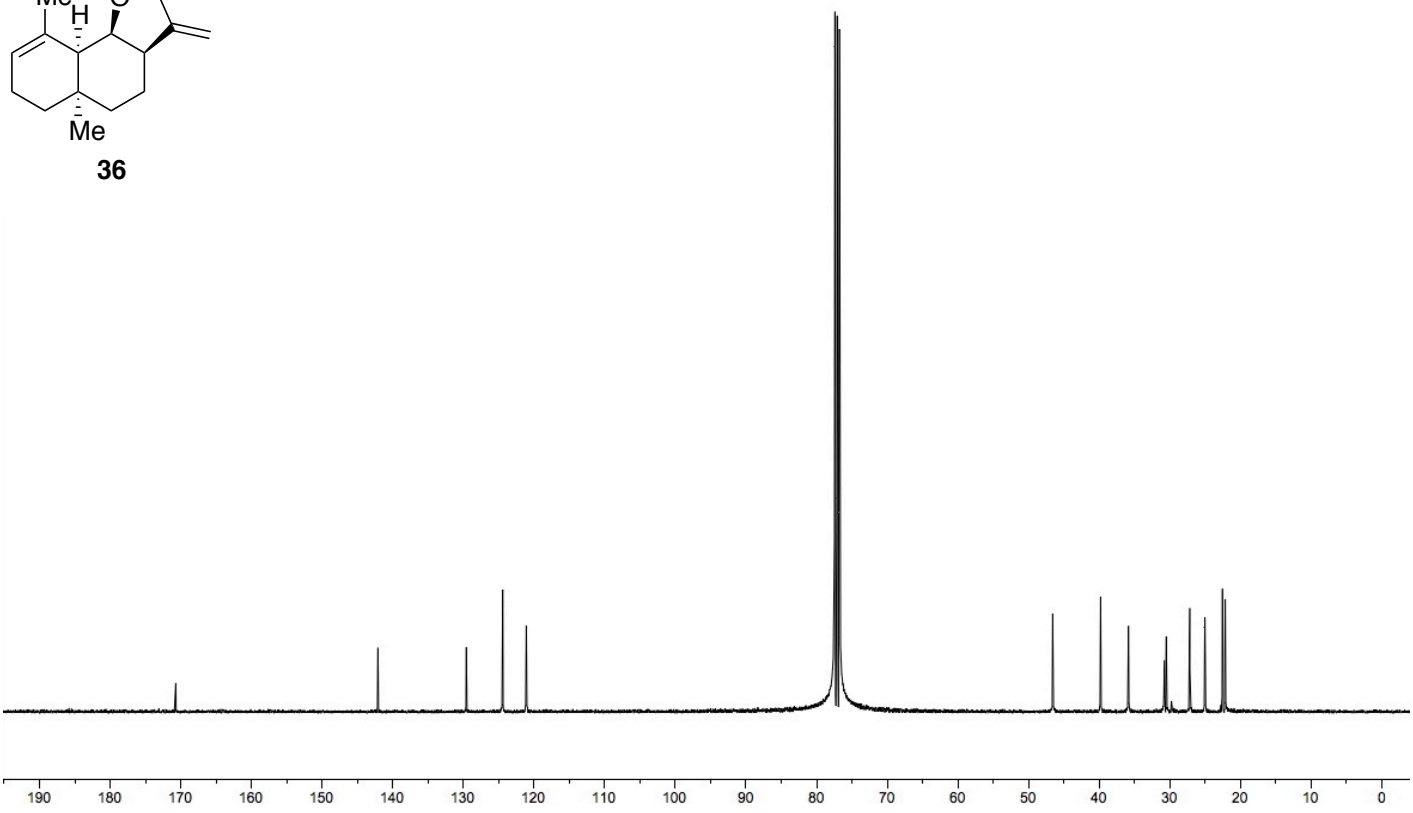

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