Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

IBX as a Catalyst for Dehydration of Hydroperoxides: Green Entry to α,β-Unsaturated Ketones via Oxygenative Allylic Transposition

Tetsuya Kuga, Yusuke Sasano, and Yoshiharu Iwabuchi

Department of Organic Chemistry, Graduate School of Pharmaceutical Sciences, Tohoku University,

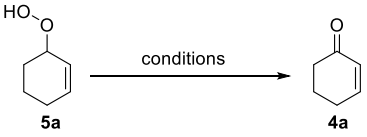
6-3 Aoba, Aramaki, Aoba-ku, Sendai 980-8578, Japan

General Methods and Materials

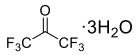
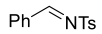
All reactions were carried out with dehydrated solvents under argon atmosphere, unless otherwise noted. Dehydrated THF and CH_2Cl_2 were purchased from Kanto Chemical Co.,Inc. Other solvents were dehydrated and distilled according to standard prorocols. Reagents were obtained from commercial suppliers and used without further purification, unless otherwise noted. Reactions were monitored by thin-layer chromatography (TLC) carried out on silica gel plates (Merck Kieselgel 60 F_{254}). Open column chromatography was performed on Silica gel 60 N (Kanto Chemical Co.,Inc., spherical, neutral, 63-210 μm) and flash column chromatography was performed on Silica gel 60N (Kanto Chemical Co.,Inc., spherical, neutral, 40-50 μm). All melting points were determined with Yazawa Micro Melting Point BY-2 and are reported uncorrected. Optical rotations were measured on a JASCO P-2200 Polarimeter at rt, using the sodium D line. IR spectra were recorded on a JASCO FT/IR-410 Fourier Transform Infrared Spectrophitimeter. ^{1}H-NMR (400 MHz) and ^{13}C-NMR spectra (100 MHz) were recorded on JEOL JNM-AL-400 spectrometers, respectively. For ^{1}H-NMR spectra, chemical shifts (δ) are given from TMS (0.00 ppm) in $CDCl_3$ as an internal standard. Multiplicities are reported using the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br s, broad singlet; br d, broad doublet; dd, double doublet; dt, double triplet). For ^{13}C-NMR spectra, chemical shifts (δ) are given from $^{13}CDCl_3$ (77.0 ppm) as an internal standard. Mass spectra were recorded on JEOL JMS-DX303, JEOL JNM-AL500, JEOL JMS-700 and Thermo Scientific Exactive Mass Spectrometers.

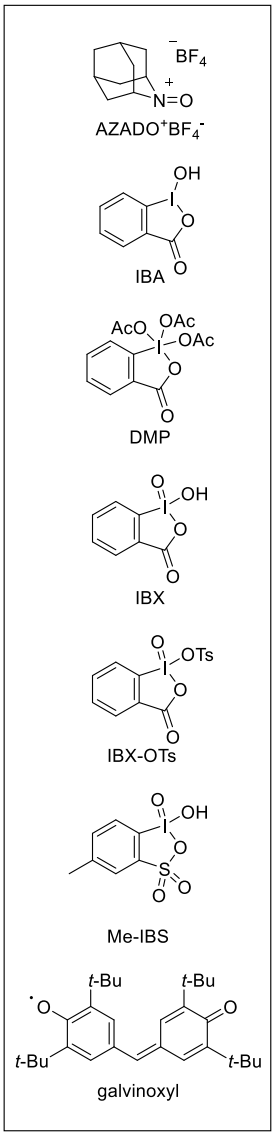
1. Optimization of Reaction Conditions

Table S1. Optimization of Reaction Conditions



5a **4a**

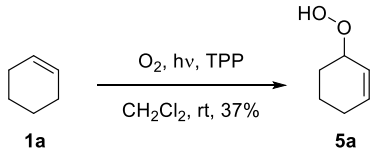
	conditions				
entry	catalyst (10 mol%)	additive	solvent	time (h)	yield (%)
1	Et_3N		CH_2Cl_2 (0.2 M)	12	N. R.
2	DBU		CH_2Cl_2 (0.2 M)	12	trace
3	K_2CO_3		CH_2Cl_2 (0.2 M)	12	trace
4	KO*t*-Bu		CH_2Cl_2 (0.2 M)	12	trace
5	$(PhO)_2P(O)OH$		CH_2Cl_2 (0.2 M)	12	N. R.
6	*p*-TsOH·H_2O		CH_2Cl_2 (0.2 M)	12	N. R.
7	H_2SO_4		CH_2Cl_2 (0.2 M)	12	dec.
8			CH_2Cl_2 (0.2 M)	12	trace
9			CH_2Cl_2 (0.2 M)	12	N. R.
10	AZADO$^+BF_4^-$		CH_2Cl_2 (0.2 M)	12	8
11	$PhI(OAc)_2$		CH_2Cl_2 (0.2 M)	12	12
12	$PhI(OAc)_2$		CH_2Cl_2 (0.2 M)	24	20
13	PhIO		CH_2Cl_2 (0.2 M)	12	11
14	PhI(OH)OTs		CH_2Cl_2 (0.2 M)	12	dec.
15	$PhIO_2$		CH_2Cl_2-DMSO (20:1) (0.2 M)	12	26
16	DMP		CH_2Cl_2 (0.2 M)	12	12
17	IBX		CH_2Cl_2-DMSO (20:1) (0.2 M)	12	59
18	IBX-OTs[1]		CH_2Cl_2-DMSO (20:1) (0.2 M)	12	57
19	Me-IBS[2]		CH_2Cl_2-DMSO (20:1) (0.2 M)	12	dec.
20	I_2O_5		CH_2Cl_2-DMSO (20:1) (0.2 M)	12	22
21	IBX		DMSO (0.5 M)	12	68
22	IBX		DMSO-H_2O (20:1) (0.5 M)	12	43
23	IBX		DMSO-HFIP (20:1) (0.5 M)	12	70
24	IBX		DMSO-AcOH (20:1) (0.5 M)	12	65
25	IBX		DMSO-TFA (20:1) (0.5 M)	6	85
26	IBX	TFA (20 mol%)	DMSO (0.5 M)	12	83
27	IBX	$(PhO)_2P(O)OH$ (20 mol%)	DMSO (0.5 M)	12	77
28	IBX	*p*-TsOH·H_2O (20 mol%)	DMSO (0.5 M)	4	82
29	IBX	*p*-TsOH·H_2O (10 mol%)	DMSO (0.5 M)	4	83
30	IBX (5 mol%)	*p*-TsOH·H_2O (5 mol%)	DMSO (0.5 M)	12	70
31	IBX-OTs		DMSO (0.5 M)	6	68
32	IBX	*p*-TsOH·H_2O (10 mol%) galvinoxyl (20 mol%)	DMSO (0.5 M)	4	84



* Reactions ran at room temperature.
Yield was determined by ^{1}H-NMR analysis using mesitylene as an internal standard.

2. Preparation of Substrates

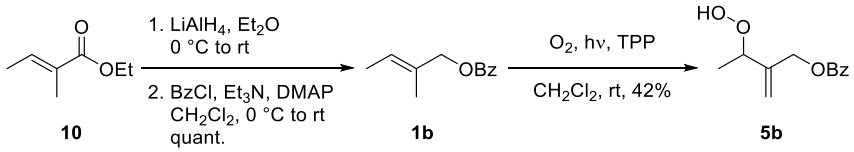
· 3-Hydroperoxycyclohex-1-ene (5a)



To a solution of cyclohexene (**1a)** (1.63 g, 19.8 mmol) in CH_2Cl_2 (30 mL) was added TPP (21 mg, 36 μmol). The mixture was stirred at room temperature under O_2 atmosphere (balloon) with irradiation (100 V, 22 W fluorescent lamp). After 24 h, the solvent was removed under reduced pressure and the residue was purified with flash column chromatography (CH_2Cl_2) to afford **5a** (829 mg, 7.27 mmol, 37%) as a colorless oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.86 (m, 1H), 6.02 (m, 1H), 5.76 (m, 1H), 4.50 (m, 1H), 2.11-1.91 (m, 3H), 1.80-1.55 (m, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 134.4, 124.0, 78.4, 26.3, 25.3, 18.3; IR (neat, cm^{-1}): 3373, 3032; MS (EI): *m/z* 114 (M^+), 81 (100%); HRMS (EI): calcd. for $C_6H_{10}O_2$ (M^+) 114.0681, found 114.0676.

· 3-Hydroperoxy-2-methylenebutyl benzoate (5b)



(*E*)-2-Methylbut-2-en-1-yl benzoate (1b)

To a suspension of $LiAlH_4$ (460 mg, 12.1 mmol) in Et_2O (20 mL) was added a solution of ethyl tiglate (**10**) (1.28 g, 10.0 mmol) in Et_2O (10 mL) dropwise at 0 °C. After stirring for 30 min at room temperature, the mixture was quenched with 28% aqueous NH_4OH at 0 °C and filtered through Celite®. Solvent was removed under reduced pressure, and the residue was used in the next reaction without further purification.

To a solution of the residue in CH_2Cl_2 (20 mL) was added Et_3N (1.7 mL, 12 mmol), DMAP (24 mg, 0.20 mmol) and BzCl (1.3 mL, 11 mmol) at 0 °C. The mixture was gradually warmed up to room

temperature. After stirring for 50 min, the mixture was quenched with saturated aqueous $NaHCO_3$ at 0 °C and extracted with CH_2Cl_2. The combined organics were dried over $MgSO_4$. Concentration and flash column chromatography (hexane : AcOEt = 15 : 1) provided **1b** (2.00 g, 10.5 mmol, quant.) as a colorless oil.

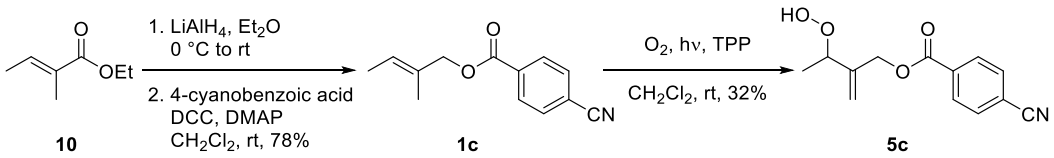
^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.06 (d, *J* = 7.6 Hz, 2 H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.43 (dd, *J* = 7.6, 7.5 Hz, 2H), 5.65 (q, *J* = 6.6 Hz, 1H), 4.71 (s, 2H), 1.74 (s, 3H), 1.67 (d, *J* = 6.6 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 166.5, 132.8, 130.9, 130.5, 129.6, 128.3, 124.0, 70.6, 13.7, 13.2; IR (neat, cm^{-1}): 1719, 1272, 1114, 711; MS (EI): *m/z* 190 (M^+), 105 (100%); HRMS (EI): calcd. for $C_{12}H_{14}O_2$ (M^+) 190.0994, found 190.0992.

3-Hydroperoxy-2-methylenebutyl benzoate (5b)

To a solution of **1b** (573 mg, 3.01 mmol) in CH_2Cl_2 (6 mL) was added TPP (3.0 mg, 4.9 μmol). The mixture was stirred at room temperature under O_2 atmosphere (balloon) with irradiation (100 V, 22 W fluorescent lamp). After 4.5 h, the solvent was removed under reduced pressure and the residue was purified with flash column chromatography (hexane : AcOEt = 10 : 1 to 4 : 1) to afford **5b** (281 mg, 1.26 mmol, 42%) as a colorless oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.92 (s, 1H), 8.07 (d, *J* = 7.5 Hz, 2H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.46 (dd, *J* = 7.5, 7.5 Hz, 2H), 5.36 (s, 1H), 5.32 (s, 1H), 5.04 (d, *J* = 13.5 Hz, 1H), 4.82 (d, *J* = 13.5 Hz, 1H), 4.68 (q, *J* = 6.6 Hz, 1H), 1.34 (d, *J* = 6.6 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 166.7, 143.8, 133.3, 129.9, 129.7, 128.5, 115.9, 82.9, 63.6, 17.2; IR (neat, cm^{-1}): 3396, 1720, 1277, 711; MS (EI): *m/z* 221 (M^+-H), 105 (100%); HRMS (EI): calcd. for $C_{12}H_{13}O_4$ (M^+-H) 221.0814, found 221.0823.

· 3-Hydroperoxy-2-methylenebutyl 4-cyanobenzoate (5c)



(*E*)-2-Methylbut-2-en-1-yl 4-cyanobenzoate (1c)

To a suspension of $LiAlH_4$ (460 mg, 12.1 mmol) in Et_2O (20 mL) was added a solution of ethyl tiglate (**10**) (1.28 g, 10.0 mmol) in Et_2O (10 mL) dropwise at 0 °C. After stirring for 1.5 h at room temperature, the mixture was quenched with 28% aqueous NH_4OH at 0 °C and filtered through Celite®. Solvent was removed under reduced pressure, and the residue was used in the next reaction without further purification.

To a solution of the residue in CH_2Cl_2 (20 mL) was added 4-cyanobenzoic acid (1.00 g, 6.80 mmol), DCC (1.8 g, 8.7 mmol) and DMAP (16 mg, 0.13 mmol) at 0 °C. After stirring for 2 h at room temperature, the mixture was quenched with H_2O and extracted with CH_2Cl_2. The combined organics were dried over $MgSO_4$. Concentration and flash column chromatography (hexane : AcOEt = 30 : 1 to 10 : 1) provided **1c** (1.15 g, 5.35 mmol, 79%) as a white solid.

Colorless needle (hexane): mp 50-51 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.15 (d, *J* = 8.8 Hz, 2H), 7.75 (d, *J* = 8.8 Hz, 2H), 5.66 (q, *J* = 6.7 Hz, 1H), 4.74 (s, 2H), 1.74 (s, 3H), 1.68 (d, *J* = 6.7 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 164.8, 134.3, 132.2, 130.3, 130.1, 125.0, 118.0, 116.3, 71.3, 13.7, 13.3; IR (neat, cm^{-1}): 1723, 1274; MS (EI): *m/z* 215 (M^+), 130 (100%); HRMS (EI): calcd. for $C_{13}H_{13}NO_2$ (M^+) 215.0946, found 215.0945.

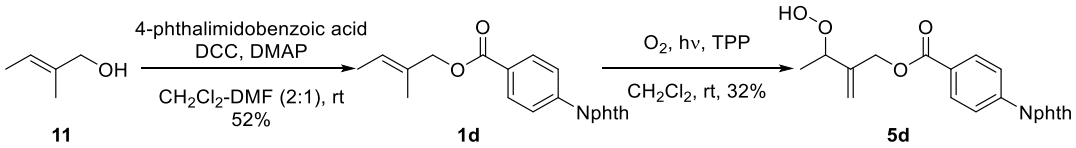
3-Hydroperoxy-2-methylenebutyl 4-cyanobenzoate (5c)

To a solution of **1c** (919 mg, 4.27 mmol) in CH_2Cl_2 (8 mL) was added TPP (7.9 mg, 13 μmol). The mixture was stirred at room temperature under O_2 atmosphere (balloon) with irradiation (100 V, 22 W fluorescent lamp). After 8 h, the solvent was removed under reduced pressure and the residue was purified with flash column chromatography (hexane : AcOEt = 4 : 1) to afford **5c** (337 mg, 1.36 mmol, 32%) as a white solid.

Colorless crystal (benzene-hexane): mp 54-55 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.60 (br, 1H),

8.17 (d, *J* = 8.2 Hz, 2H), 7.77 (d, *J* = 8.2 Hz, 2H), 5.35 (s, 2H), 5.05 (d, *J* = 13.8 Hz, 1H), 4.88 (d, *J* = 13.8 Hz, 1H), 4.68 (q, *J* = 6.8 Hz, 1H) 1.35 (d, *J* = 6.8 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 165.0, 143.2, 133.7, 132.3, 130.2, 117.8, 116.8, 116.4, 82.7, 64.3, 17.2; IR (neat, cm^{-1}): 3410, 2232, 1726, 1277, 1108; MS (EI): *m/z* 229 (M^+-H_2O), 130 (100%); HRMS (EI): calcd. for $C_{13}H_{11}NO_3$ (M^+-H_2O) 229.0739, found 229.0743.

· 3-Hydroperoxy-2-methylenebutyl 4-(1,3-dioxoisoindolin-2-yl)benzoate (5d)



(*E*)-2-Methylbut-2-en-1-yl 4-(1,3-dioxoisoindolin-2-yl)benzoate (1d)

To a solution of (*E*)-2-methylbut-2-en-1-ol[3] (**11**) (272 mg, 3.16 mmol) in CH_2Cl_2 (10 mL) was added 4-phthalimidobenzoic acid[4] (1.0 g, 3.7 mmol), DMF (5 mL), DCC (850 mg, 4.1 mmol) and DMAP (19 mg, 0.16 mmol) at 0 °C. After stirring for 3 h at room temperature, the mixture was quenched with H_2O at 0 °C and extracted with Et_2O. The combined organics were washed with brine and dried over $MgSO_4$. Concentration and flash column chromatography (hexane : AcOEt = 4 : 1 to 2 : 1) provide **1d** (553 mg, 1.65 mmol, 52%) as a white solid.

Colorless crystal (CH_2Cl_2-hexane): mp 110-112 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.19 (d, *J* = 8.7 Hz, 2H), 7.97 (dd, *J* = 5.3, 3.1 Hz, 2H), 7.81 (dd, *J* = 5.3, 3.1 Hz, 2H), 7.59 (d, *J* = 8.7 Hz, 2H), 5.66 (q, *J* = 6.6 Hz, 1H), 4.74 (s, 2H), 1.74 (s, 3H), 1.68 (d, *J* = 6.6 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 166.8, 165.7, 135.8, 134.6, 131.7, 130.8, 130.4, 129.7, 125.9, 124.2, 123.9, 70.9, 13.7, 13.3; IR (neat, cm^{-1}): 1716, 1376, 1273; MS (EI): *m/z* 335 (M^+), 250 (100%); HRMS (EI): calcd. for $C_{20}H_{17}NO_4$ (M^+) 335.1157, found 335.1117.

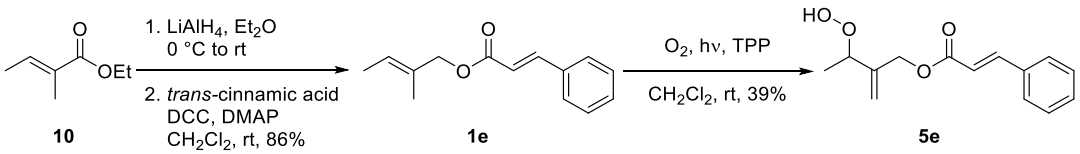
3-Hydroperoxy-2-methylenebutyl 4-(1,3-dioxoisoindolin-2-yl)benzoate (5d)

To a solution of **1d** (553 mg, 1.65 mmol) in CH_2Cl_2 (3 mL) was added TPP (2.9 mg, 4.7 μmol). The mixture was stirred at room temperature under O_2 atmosphere (balloon) with irradiation (100 V, 22 W fluorescent lamp). After 7 h, the solvent was removed under reduced pressure and the residue

was purified with flash column chromatography (hexane : AcOEt = 4 : 1 to 2 : 1) to afford **5d** (185 mg, 0.505 mmol, 31%) as a white solid.

Colorless crystal (CH_2Cl_2-hexane): mp 117-118 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.84 (s, 1H), 8.21 (d, *J* = 8.2 Hz, 2H), 7.98 (br s, 2H), 7.82 (br s, 2H), 7.63 (d, *J* = 8.2 Hz, 2H), 5.37 (s, 1H), 5.34 (s, 1H), 5.05 (d, *J* = 13.5 Hz, 1H), 4.86 (d, *J* = 13.5 Hz, 1H), 4.68 (q, *J* = 6.4 Hz, 1H), 1.36 (d, *J* = 6.4 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 166.7, 165.9, 143.7, 136.3, 134.7, 131.6, 130.5, 129.0, 126.0, 124.0, 116.0, 82.9, 63.5, 17.2; IR (neat, cm^{-1}): 1717, 1373, 1274; MS (EI): *m/z* 349 (M^+-H_2O), 250 (100%); HRMS (EI): calcd. for $C_{20}H_{15}NO_5$ (M^+-H_2O) 349.0950, found 349.0956.

· 3-Hydroperoxy-2-methylenebutyl cinnamate (5e)



(*E*)-2-Methylbut-2-en-1-yl cinnamate (1e)

To a suspension of $LiAlH_4$ (460 mg, 12.1 mmol) in Et_2O (20 mL) was added a solution of ethyl tiglate (**10**) (1.28 g, 10.0 mmol) in Et_2O (10 mL) dropwise at 0 °C. After stirring for 1 h at room temperature, the mixture was quenched with 28% aqueous NH_4OH at 0 °C and filtered through Celite®. Solvent was removed under reduced pressure, and the residue was used in the next reaction without further purification.

To a solution of the residue in CH_2Cl_2 (30 mL) was added *trans*-cinnamic acid (1.48 g, 10.0 mmol), DCC (2.1 g, 10 mmol) and DMAP (120 mg, 0.98 mmol) at 0 °C. After stirring for 1 h at room temperature, the mixture was diluted with Et_2O and filtered through Celite®. The filtrate was washed with H_2O and brine, and dried over $MgSO_4$. Concentration and flash column chromatography (hexane : AcOEt = 30 : 1) provided **1e** (1.85 g, 8.56 mmol, 86%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 16.2 Hz, 1H), 7.52 (m, 2H), 7.39-7.37 (m, 3H), 6.46 (d, *J* = 16.2 Hz, 1H), 5.61 (q, *J* = 6.6 Hz, 1H), 4.60 (s, 2H), 1.71 (s, 3H), 1.66 (d, *J* = 6.6 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 168.9, 144.7, 134.5, 130.9, 130.2, 128.9, 128.1, 124.1, 118.2, 70.3, 13.7, 13.2; IR (neat, cm^{-1}): 1713, 1165; MS (EI): *m/z* 216 (M^+), 131 (100%); HRMS (EI): calcd. for

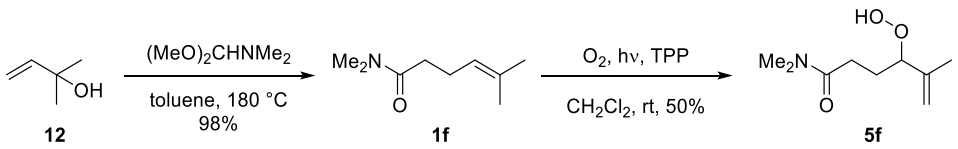
$C_{14}H_{16}O_2$ (M^+) 216.1150, found 216.1146.

3-Hydroperoxy-2-methylenebutyl cinnamate (5e)

To a solution of **1e** (655 mg, 3.03 mmol) in CH_2Cl_2 (6 mL) was added TPP (5.9 mg, 9.6 μmol). The mixture was stirred at room temperature under O_2 atmosphere (balloon) with irradiation (100 V, 22 W fluorescent lamp). After 8 h, the solvent was removed under reduced pressure and the residue was purified with flash column chromatography (hexane : AcOEt = 10 : 1 to 8 : 1 to 4 : 1) to afford **5e** (295 mg, 1.19 mmol, 39%) as a yellow oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.98 (s, 1H), 7.75 (d, *J* = 15.9 Hz, 1H), 7.54 (m, 2H), 7.41-7.39 (m, 3H), 6.49 (d, *J* = 15.9 Hz, 1H), 5.33 (s, 1H), 5.31 (s, 1H), 4.93 (d, *J* = 13.5 Hz, 1H), 4.70 (d, *J* = 13.5 Hz, 1H), 4.65 (q, *J* = 6.8 Hz, 1H), 1.32 (d, *J* = 6.8 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 167.1, 145.9, 143.9, 134.2, 130.6, 128.9, 128.2, 117.5, 115.9, 82.9, 62.8, 17.2; IR (neat, cm^{-1}): 3380, 1700, 1635, 1173; HRMS (ESI-pos): calcd. for $C_{14}H_{16}O_4Na$ (M^++Na) 271.0941, found 271.0950.

· 4-Hydroperoxy-*N*,*N*,5-trimethylhex-5-enamide (5f)



12 **1f** **5f**

***N*,*N*,5-Trimethylhex-4-enamide (1f)**

To a solution of 2-methyl-3-buten-1-ol (**12**) (2.52 g, 29.3 mmol) in toluene (15 mL) was added *N*,*N*-dimethylacetamide dimethyl acetal (5.1 mL, 35 mmol) at room temperature. The mixture was heated to 180 °C in a sealed tube. After stirring for 5 h, reaction mixture was purified with column chromatography (hexane : AcOEt = 15 : 1 to 4 : 1 to 1 : 1) to afford **1f** (4.45 g, 28.6 mmol, 98%) as a yellow oil.

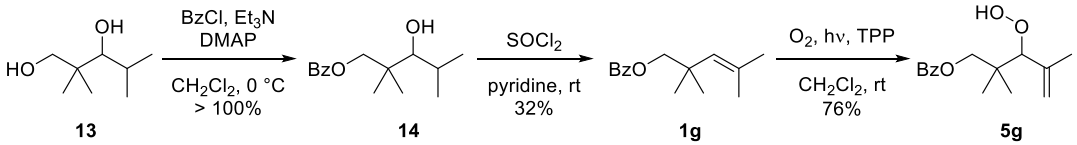
^{1}H-NMR (400 MHz, $CDCl_3$): δ 5.14 (br s, 1H), 3.00 (s, 3H), 2.94 (s, 3H), 2.32 (m, 4H), 1.69 (s, 3H), 1.63 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 172.7, 132.4, 123.2, 37.2, 35.3, 33.4, 25.6, 23.8, 17.6; IR (neat, cm^{-1}): 2927, 1643, 772; HRMS (ESI-pos): calcd. for $C_9H_{17}NONa$ (M^++Na) 178.1202, found 178.1211.

4-Hydroperoxy-*N*,*N*,5-trimethylhex-5-enamide (5f)

To a solution of **1f** (498 mg, 3.21 mmol) in CH_2Cl_2 (6 mL)was added TPP (5.8 mg, 9.4 μmol). The mixture was stirred at room temperature under O_2 atmosphere (balloon) with irradiation (100 V, 22 W fluorescent lamp). After 7 h, the solvent was removed under reduced pressure and the residue was purified with flash column chromatography (hexane : AcOEt = 2 : 1 to 1 : 2 to 0 : 1) to afford **5f** (301 mg, 1.61 mmol, 50%) as a brown oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 10.19 (s, 1H), 5.00 (s, 1H), 4.94 (s, 1H), 4.33 (t, *J* = 5.6 Hz, 1H), 3.02 (s, 3H), 2.99 (s, 3H), 2.46 (ddd, *J* = 16.9, 8.0, 4.3 Hz, 1H), 2.35 (ddd, *J* = 16.9, 8.0, 4.3 Hz, 1H), 2.23 (m, 1H), 2.00 (m, 1H), 1.79 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 173.7, 143.2, 112.8, 86.8, 37.2, 35.8, 28.2, 23.9, 19.5; IR (neat, cm^{-1}): 3253, 2938, 1626, 1403; HRMS (ESI-pos): calcd. for $C_9H_{17}NO_3Na$ (M^++Na) 210.1101, found 210.1103.

· 3-Hydroperoxy-2,2,4-trimethylpent-4-en-1-yl benzoate (5g)



13 **14** **1g** **5g**

3-Hydroxy-2,2,4-trimethylpentyl benzoate (14)

To a solution of 2,2,4-trimethyl-1,3-pentandiol (**13**) (1.45 g, 9.92 mmol) in CH_2Cl_2 (10 mL) was added Et_3N (1.8 mL, 13 mmol), DMAP (36 mg, 0.29 mmol) and BzCl (1.4 mL, 12 mmol) at 0 °C. After stirring for 2 h, the mixture was quenched with saturated aqueous $NaHCO_3$, and extracted with CH_2Cl_2. The combined organics were dried over $MgSO_4$. Concentration and column chromatography (hexane : AcOEt = 10 : 1) provided **14** (3.01 g, > 100%) as a colorless oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.04 (d, *J* = 7.5 Hz, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.45 (dd, *J* = 7.5, 7.5 Hz, 2H), 4.38 (d, *J* = 10.7 HZ, 1H), 4.03 (d, *J* = 10.7 Hz, 1H), 3.37 (dd, *J* = 6.0, 2.4 Hz, 1H), 1.98 (m, 1H), 1.87 (d, *J* = 6.0 Hz, 1H), 1.07 (s, 3H), 1.05 (s, 3H), 1.02 (d, *J* = 6.8 Hz, 3H), 0.97 (d, *J* = 6.3 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 166.7, 133.0, 130.3, 12.9.5, 128.4, 79.4, 71.9, 39.6, 28.8, 23.5, 22.1, 20.5, 16.8; IR (neat, cm^{-1}): 3521, 2964, 1718, 1275, 711; MS (EI): *m/z* 207 (M^+-C_3H_7), 123 (100%); HRMS (EI): calcd. for $C_{12}H_{15}O_3$ (M^+-C_3H_7) 207.1021, found 207.1027.

2,2,4-Trimethylpent-3-en-1-yl benzoate (1g)

To a solution of **14** (2.51 g, 10.0 mmol) in pyridine (20 mL) was added $SOCl_2$ (1.0 mL, 14 mmol) at 0 °C. After stirring for 3 h at room temperature, the mixture was quenched with H_2O and 2 M HCl, and extracted with CH_2Cl_2. The combined organics were dried over $MgSO_4$. Concentration and flash column chromatography (hexane : AcOEt = 15 : 1 to 10 : 1) provided **1g** (750 mg, 3.23 mmol, 32%) as a colorless oil.

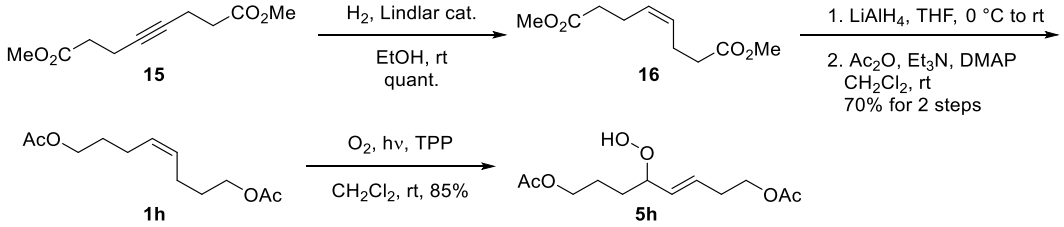
^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.05 (d, *J* = 7.3 Hz, 2H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.44 (dd, *J* = 7.3, 7.3 Hz, 2H), 5.19 (s, 1H), 4.15 (s, 2H), 1.77 (s, 3H), 1.71 (s, 3H), 1.23 (s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 166.7, 133.1, 132.8, 130.6, 130.1, 129.6, 128.3, 73.2, 36.1, 28.1, 25.9, 19.2; IR (neat, cm^{-1}): 2968, 1720, 1272, 711; MS (EI): *m/z* 232 (M^+), 97 (100%); HRMS (EI): $C_{15}H_{20}O_2$ (M^+) 232.1463, found 232.1455.

3-Hydroperoxy-2,2,4-trimethylpent-4-en-1-yl benzoate (5g)

To a solution of **1g** (582 mg, 2.51 mmol) in CH_2Cl_2 (5 mL) was added TPP (4.5 mg, 7.4 μmol). The mixture was stirred at room temperature under O_2 atmosphere (balloon) with irradiation (100 V, 22 W fluorescent lamp). After 13 h, the solvent was removed under reduced pressure and the residue was purified with flash column chromatography (hexane : AcOEt = 10 : 1) to afford **5g** (501 mg, 1.90 mmol, 76%) as a yellow solid.

Colorless crystal (CH_2Cl_2-hexane): mp 56-57 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.07 (d, *J* = 7.5 Hz, 2H), 7.98 (s, 1H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.46 (dd, *J* = 7.5, 7.5 Hz, 2H), 5.20 (s, 1H), 5.08 (s, 1H), 4.41 (s, 1H), 4.27 (d, *J* = 10.9 Hz, 1H), 4.08 (d, *J* = 10.9 Hz, 1H), 1.86 (s, 3H), 1.09 (s, 3H), 1.04 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 166.5, 142.3, 133.0, 130.3, 129.6, 128.4, 115.7, 92.2, 70.8, 38.7, 21.9, 21.0, 20.8; IR (neat, cm^{-1}): 3395, 2972, 1720, 1702, 1274, 712; HRMS (ESI-pos): calcd. for $C_{15}H_{20}O_4Na$ (M^++Na) 287.1254, found 287.1275.

· (*E*)-5-Hydroperoxyoct-3-ene-1,8-diyl diacetate (5h)



Dimethyl (*Z*)-oct-4-enedioate (16)

To a solution of dimethyl oct-4-ynedioate[5] (**15**) (371 mg, 1.87 mmol) in EtOH (5 mL) was added Lindlar catalyst (37 mg) at room temperature. Then the reaction flask was purged with H_2. After stirring for 1 h under H_2 atmosphere (balloon), the reaction mixture was filtered through Celite®. The filtrate was concentrated under reduced pressure, and the residue was purified with flash column chromatography (hexane : AcOEt = 4 : 1) to afford **16** (378 mg, 1.88 mmol, quant.) as a colorless oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 5.40 (m, 2H), 3.68 (s, 6H), 2.41-2.34 (m, 8H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 173.5, 129.0, 51.5, 34.0, 22.7; IR (neat, cm^{-1}): 1736; MS (EI): *m/z* 200 (M^+), 136 (100%); HRMS (EI): calcd. for $C_{10}H_{16}O_4$ (M^+) 200.1049, found 200.1030.

(*Z*)-Oct-4-ene-1,8-diyl diacetate (1h)

To a solution of **16** (454 mg, 2.27 mmol) in THF (11 mL) was added $LiAlH_4$ (206 mg, 5.4 mmol) portionwise at 0 °C. After stirring for 40 min at room temperature, the reaction mixture was quenched with 28% aqueous NH_4OH and filtered through Celite®. The filtrate was concentrated under reduced pressure. The residue was used next reaction without further purification.

To a solution of the residue in CH_2Cl_2 (11 mL) was added Et_3N (1.9 mL, 13.7 mmol), DMAP (14 mg, 0.12 mmol) and Ac_2O (0.86 mL, 9.1 mmol) at 0 °C. After stirring overnight at room temperature, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ at 0 °C, and extracted with CH_2Cl_2. The combined organics were dried over $MgSO_4$. Concentration and flash column chromatography (hexane : AcOEt = 8 : 1 to 4 : 1) provided **1h** (362 mg, 1.59 mmol, 70%) as a colorless oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 5.40 (t, *J* = 4.8 Hz, 2H), 4.06 (t, *J* = 6.9 Hz, 4H), 2.11 (m, 4H), 2.05

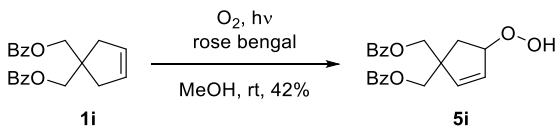
(s, 6H), 1.69 (tt, *J* = 6.9, 6.9 Hz, 4H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 171.1, 129.4, 63.9, 28.5, 23.5, 20.9; IR (neat, cm^{-1}): 1739, 1241; MS (EI): *m/z* 168 (M^+-AcOH), 93 (100%); HRMS (EI): calcd. for $C_{10}H_{16}O_2$ (M^+-AcOH) 168.1150, found 168.1137.

(*E*)-5-Hydroperoxyoct-3-ene-1,8-diyl diacetate (5h)

To a solution of **1h** (324 mg, 1.42 mmol) in CH_2Cl_2 (3 mL) was added TPP (2.8 mg, 4.6 μmol). The mixture was stirred at room temperature under O_2 atmosphere (balloon) with irradiation (100 V, 22 W fluorescent lamp). After 6 h, the solvent was removed under reduced pressure and the residue was purified with flash column chromatography (hexane : AcOEt = 8 : 1 to 4 : 1 to 2 : 1) to afford **5h** (314 mg, 1.21 mmol, 85%) as a colorless oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.96 (s, 1H), 5.78 (dt, *J* = 15.2, 7.0 Hz, 1H), 5.50 (br dd, *J* = 15.2, 7.8 Hz, 1H), 4.32 (m, 1H), 4.16 (t, *J* = 6.6 Hz, 2H), 4.08 (t, *J* = 6.0 Hz, 2H), 2.42 (dt, *J* = 6.6, 6.0 Hz, 2H), 2.05 (s, 6H), 1.75-1.68 (m, 3H), 1.55 (m, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 171.2, 171.1, 131.7, 131.1, 85.8, 64.1, 63.3, 31.8, 28.9, 24.6, 20.9; IR (neat, cm^{-1}): 3402, 2959, 1737, 1241; MS (EI): *m/z* 243 (M^+-OH), 107 (100%); HRMS (EI): calcd. for $C_{12}H_{19}O_5$ (M^+-OH) 243.1232, found 243.1239.

· (4-Hydroperoxycyclopent-2-ene-1,1-diyl)bis(methylene) dibenzoate (5i)



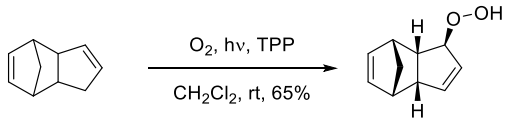
1i **5i**

To a solution of cyclopent-3-ene-1,1-diylbis(methylene) dibenzoate[6] (**1i**) in MeOH (6 mL) was added rose bengal (15 mg, 15 μmol) at room temperature. The mixture was stirred at room temperature under O_2 atmosphere (balloon) with irradiation (100 V, 22 W fluorescent lamp). After 16 h, the reaction mixture was quenched with H_2O and extracted with Et_2O. The combined organics were washed with brine and dried over $MgSO_4$. Concentration and flash column chromatography (hexane : AcOEt = 4 : 1 to 2 : 1) provided **5i** (474 mg, 1.29 mmol, 42%) as a colorless oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.11 (s, 1H), 8.05 (d, *J* = 7.3 Hz, 2H), 8.01 (d, *J* = 7.3 Hz, 2H), 7.57 (t, *J* = 7.6 Hz, 2H), 7.44 (dd, *J* = 7.6, 7.3 Hz, 4H), 6.14 (d, *J* = 5.9 Hz, 1H), 6.06 (dd, *J* = 5.9, 2.0 Hz,

1H), 5.25 (m, 1H), 4.57 (d, *J* = 11.2 Hz, 1H), 4.48 (d, *J* = 10.7 Hz, 1H), 4.40 (d, *J* = 10.7 Hz, 1H), 4.33 (d, *J* = 11.2 Hz, 1H), 2.20 (dd, *J* = 14.9, 7.1 Hz, 1H), 2.13 (dd, *J* = 14.9, 3.2 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 166.6, 166.3, 139.0, 133.2, 132.1, 129.80, 129.77, 129.7, 129.6, 128.6, 128.5, 128.4, 89.4, 67.7, 67.6, 53.0, 35.0; IR (neat, cm^{-1}): 3402, 1719, 1270, 710; HRMS (ESI-pos): calcd. for. $C_{21}H_{20}O_6Na$ (M^++Na) 391.1152, found 391.1177.

(1*S,3a*R**,4*S**,7*R**,7a*S**)-1-Hydroperoxy-3a,4,7,7a-tetrahydro-1*H*-4,7-methanoindene (5j)**

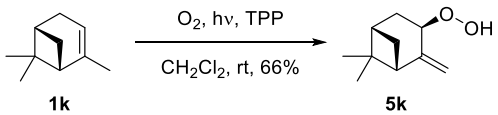


1j **5j**

To a solution of dicyclopentadiene (**1j**) (1.32 g, 10.0 mmol) in CH_2Cl_2 (20 mL) was added TPP (20 mg, 0.033 mmol). The mixture was stirred at room temperature under O_2 atmosphere (balloon) with irradiation (100 V, 22 W fluorescent lamp). After 18 h, the solvent was removed under reduced pressure and the residue was purified with flash column chromatography (hexane : CH_2Cl_2 = 2 : 1 to 0 : 1) to afford **5j** (1.07 g, 6.49 mmol, 65%) as a colorless oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.73 (s, 1H), 5.98-5.94 (m, 2H), 5.85 (m, 1H), 5.61 (m, 1H), 4.46 (br s, 1H), 3.38 (m, 1H), 3.04 (br s, 1 H), 2.84 (br s, 1H), 2.72 (m, 1H), 1.59 (d, *J* = 9.3 Hz, 1H), 1.44 (d, *J* = 9.3 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 141.4, 135.4, 132.3, 129.6, 92.8, 54.4, 51.1, 48.1, 44.8, 44.6; IR (neat, cm^{-1}): 3378, 2967, 1339, 731; MS (EI): *m/z* 146 (M^+-H_2O), 66 (100%); HRMS (EI): calcd. for $C_{10}H_{10}O$ (M^+-H_2O) 146.0732, found 146.0726.

· (1*S*,3*R*,5*S*)-3-Hydroperoxy-6,6-dimethyl-2-methylenebicyclo[3.1.1]heptane (5k)



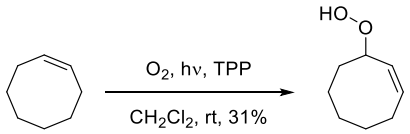
1k **5k**

To a solution of α-pinene (**1k**) (1.36 g, 10.0 mmol) in CH_2Cl_2 (20 mL) was added TPP (10 mg, 0.016 mmol). The mixture was stirred at room temperature under O_2 atmosphere (balloon) with irradiation (100 V, 22 W fluorescent lamp). After 10 h, the solvent was removed under reduced pressure and the residue was purified with flash column chromatography (hexane : AcOEt = 15 : 1

to 10 : 1) to afford **5k** (1.12 g, 6.44 mmol, 66%) as a colorless oil.

$[\alpha]_D^{29}$ = -23.3 (*c* = 0.51, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.90 (s, 1H), 5.14 (s, 1H), 5.01 (s, 1H), 4.62 (d, *J* = 8.3 Hz, 1H), 2.50 (t, *J* = 5.4 Hz, 1H), 2.35 (m, 1H), 2.24 (m, 1H), 1.98-1.91 (m, 2H), 1.52 (d, *J* = 10.2 Hz, 1H), 1.28 (s, 3H), 0.69 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 148.5, 115.0, 80.7, 50.5, 41.2, 39.4, 30.7, 27.6, 26.0, 21.9; IR (neat, cm^{-1}): 3393, 2921, 903, 774; MS (EI): *m/z* 150 (M^+-H_2O), 108 (100%); HRMS (EI): calcd. for $C_{10}H_{14}O$ (M^+-H_2O) 150.1045, found 150.041.

· (*Z*)-3-Hydroperoxycyclooct-1-ene (5l)

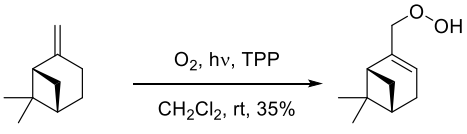


1l **5l**

To a solution of cyclooctene (**1l**) (1.11 g, 10.1 mmol) in CH_2Cl_2 (20 mL) was added TPP (20 mg, 0.033 mmol). The mixture was stirred at room temperature under O_2 atmosphere (balloon) with irradiation (100 V, 22 W fluorescent lamp). After 8 h, the solvent was removed under reduced pressure and the residue was purified with flash column chromatography (hexane : CH_2Cl_2 = 2 : 1 to hexane : AcOEt = 10 : 1 to 8 : 1) to afford **5l** (449 mg, 3.16 mmol, 31%) as a colorless oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.44 (br, 1H), 5.74 (ddt, *J* = 10.1, 1.4, 9.0 Hz, 1H), 5.61 (dd, *J* =10.1, 7.2 Hz, 1H), 4.94 (m, 1H), 2.24-2.08 (m, 2H), 1.95 (m, 1H), 1.70-1.31 (m, 7H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 131.3, 130.4, 83.2, 32.7, 28.7, 26.3, 26.1, 23.4; IR (neat, cm^{-1}): 3374, 2928; MS (EI): *m/z* 124 (M^+-H_2O), 81 (100%); HRMS (EI): calcd. for $C_8H_{12}O$ (M^+-H_2O) 124.0888, found 124.0867.

· (1*R*,5*S*)-2-(Hydroperoxymethyl)-6,6-dimethylbicyclo[3.1.1]hept-2-ene (5m)



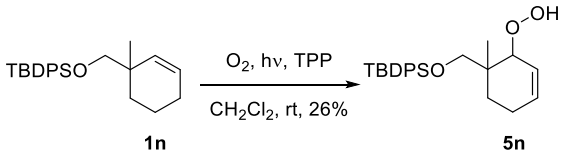
1m **5m**

To a solution of β-pinene (**1m**) (1.36 g, 10.0 mmol) in CH_2Cl_2 (20 mL) was added TPP (10 mg,

0.016 mmol). The mixture was stirred at room temperature under O_2 atmosphere (balloon) with irradiation (100 V, 22 W fluorescent lamp). After 12 h, the solvent was removed under reduced pressure and the residue was purified with flash column chromatography (hexane : AcOEt = 15 : 1 to 10 : 1) to afford **5m** (596 mg, 3.54 mmol, 35%) as a colorless oil.

$[\alpha]_D^{28}$ = -30.8 (*c* = 0.597, $CHCl_3$); (^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.76 (s, 1H), 5.65 (m, 1H), 4.40 (dd, *J* = 12.1, 1.2 Hz, 1H), 4.35 (dd, *J* = 12.1, 1.5 Hz, 1H), 2.43 (ddd, *J* = 8.5, 5.6, 5.6 Hz, 1H), 2.33 (br s, 1H), 2.30 (br s, 1H), 2.25 (m, 1H), 2.13 (m, 1H), 1.31 (s, 3H), 1.18 (d, *J* = 8.8 Hz, 1H), 0.86 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 143.3, ,123.9, 80.3, 43.7, 40.7, 38.0, 31.6, 31.4, 26.1, 21.1; IR (neat, cm^{-1}): 3401, 2916; MS (EI): *m/z* 168 (M^+), 79 (100%); HRMS (EI): calcd. for $C_{10}H_{16}O_2$ (M^+) 168.1150, found 168.1164.

· *tert*-Butyl((2-hydroperoxy-1-methylcyclohex-3-en-1-yl)methoxy)diphenylsilane (5n)

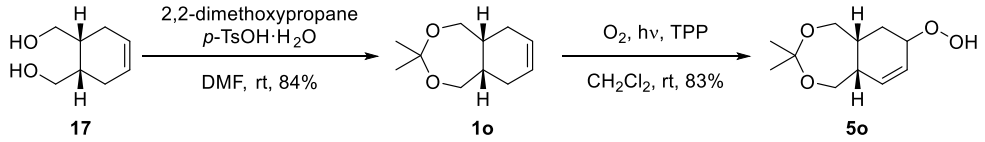


To a solution of tert-butyl((1-methylcyclohex-2-en-1-yl)methoxy)diphenylsilane[7] (**1n**) (601 mg, 1.65 mmol) in CH_2Cl_2 (3 mL) was added TPP (3.1 mg, 5.0 μmol). The mixture was stirred at room temperature under O_2 atmosphere (balloon) with irradiation (100 V, 22 W fluorescent lamp). After 55 h, the solvent was removed under reduced pressure and the residue was purified with flash column chromatography (hexane : AcOEt = 15 : 1) to afford **5n** (169 mg, 0.426 mmol, 26%, dr 3:2) as a colorless oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.95 (m, 0.6H), 8.89 (m, 0.4H), 7.71-7.64 (m, 4H), 7.45-7.39 (m, 6H), 5.94 (br d, *J* = 9.8 Hz, 0.6H), 5.82-5.78 (m, 1H), 5.71 (br d, *J* = 10.2 Hz, 0.4H), 4.67 (br s, 0.4H), 4.17 (br d, *J* = 2.9Hz, 0.6H), 3.66 (br s, 1.2H), 3.60 (d, *J* = 9.8 Hz, 0.4H), 3.52 (d, *J* = 9.8Hz, 0.4H), 2.07-1.96 (m, 2H), 1.78 (m, 0.6H), 1.65-1.60 (m, 1H), 1.32 (m, 0.4H), 1.09 (s, 9H), 0.87 (s, 1.2H), 0.85 (s, 1.8H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 135.81, 135.76, 135.7, 133.3, 133.2, 132.9, 132.8, 132.2, 129.9, 129.8, 129.74, 129.67, 127.8, 127.7, 125.4, 123.8, 84.6, 84.3, 70.9, 69.9, 38.8, 38.7, 29.8, 27.2, 27.0, 22.3, 22.2, 20.7, 19.4, 15.2; IR (neat, cm^{-1}): 3411, 2930, 2857, 1111, 702; MS

(EI): *m/z* 321 (M^+-C_4H_9-H_2O), 81 (100%); HRMS (EI): calcd. for $C_{20}H_{21}O_2Si$ (M^+-C_4H_9-H_2O) 321.1311, found 321.1303.

·(5a*R,9a*S**)-7-Hydroperoxy-3,3-dimethyl-1,5,5a,6,7,9a-hexahydrobenzo[*e*][1,3]dioxepine (5o)**



17 1o 5o

(5a*R,9a*S**)-3,3-Dimethyl-1,5,5a,6,9,9a-hexahydrobenzo[*e*][1,3]dioxepine (1o)**

To a solution of ((1*R**,2*S**)-cyclohex-4-ene-1,2-diyl)dimethanol[8] (**17**) (430 mg, 3.02 mmol) in DMF (7 mL) was added 2,2-dimethoxypropane (1.85 mL, 15 mmol) and *p*-TsOH·H_2O (57 mg, 0.30 mmol) at room temperature. After stirring for 2 h, the mixture was quenched with solid K_2CO_3 and H_2O at 0 °C, and extracted with Et_2O. The combined organics were washed with H_2O and brine, and dried over $MgSO_4$. Concentration and flash column chromatography (hexane : AcOEt = 8 : 1) provided **1o** (465 mg, 2.55 mmol, 84%) as a yellow oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 5.60 (s, 2H), 3.62 (dd, *J* = 11.5, 6.3 Hz, 2H), 3.56 (br d, *J* = 11.5 Hz, 2H), 2.14 (m, 4H), 1.96 (br s, 2H), 1.34 (s, 3H), 1.32 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 124.9, 100.9, 64.6, 36.5, 25.22, 25.16, 25.1; IR (neat, cm^{-1}): 2938, 1218; MS (EI): *m/z* 182 (M^+), 79 (100%); HRMS (EI): calcd. for $C_{11}H_{18}O_2$ (M^+) 182.1307, found 182.1285.

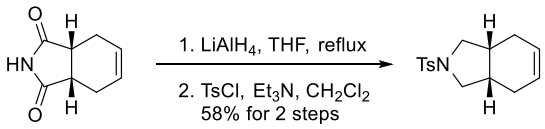
(5a*R,9a*S**)-7-Hydroperoxy-3,3-dimethyl-1,5,5a,6,7,9a-hexahydrobenzo[*e*][1,3]dioxepine (5o)**

To a solution of **1o** (366 mg, 2.01 mmol) in CH_2Cl_2 (4 mL) was added TPP (3.8 mg, 6.1 μmol). The mixture was stirred at room temperature under O_2 atmosphere (balloon) with irradiation (100 V, 22 W fluorescent lamp). After 11 h, the solvent was removed under reduced pressure and the residue was purified with flash column chromatography (hexane : AcOEt = 4 : 1) to afford **5o** (356 mg, 1.66 mmol, 83%, dr 4:1) as a yellow oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.87-7.85 (m, 1H), 5.89-5.83 (m, 1.8H), 5.73 (m, 0.2H), 4.60 (m, 0.2H), 4.51 (m, 0.8H), 3.98 (d, *J* = 12.1 Hz, 0.8H), .3.90 (d, *J* = 12.6 Hz, 0.2H), 3.66-3.47 (m, 3H), 2.46-2.42 (m, 1H), 2.05-1.92 (m, 3H), 1.34 (s, 3H), 1.31 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ

133.9, 125.1, 101.80, 101.75, 77.6, 77.2, 64.8, 64.6, 62.4, 61.4, 40.7, 40.6, 35.7, 32.5, 26.8, 26.1, 24.7, 24.6; IR (neat, cm^{-1}): 3330, 2941, 1372, 1219; HRMS (ESI-posi): calcd. for $C_{11}H_{18}O_4Na$ (M^++Na) 237.1097, found 237.1093.

· (3a*R,7a*S**)-2-Tosyl-2,3,3a,4,7,7a-hexahydro-1*H*-isoindole (1q)**



18 **1q**

To a solution of *cis*-1,2,3,6-tetrahydrophthalimide (**18**) (1.00 g, 6.62 mmol) in THF (20 mL) was added $LiAlH_4$ (1.1 g, 28 mmol) at 0 °C. The mixture was refluxed for 3 h. Then the mixture was quenched with 28% aqueous NH_4OH at 0 °C, and filtered through Celite®. The filtrate was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was used in the next reaction without further purification.

To a solution of the residue in CH_2Cl_2 (15 mL) was added Et_3N (1.8 mL, 13 mmol) and TsCl (1.3 g, 6.6 mmol) at 0 °C. After stirring for 1 h at room temperature, the mixture was quenched with saturated aqueous $NaHCO_3$ and extracted with CH_2Cl_2. The combined organics were dried over $MgSO_4$. Concentration and flash column chromatography (hexane : AcOEt = 8 : 1) provided a brown oil. The oil was solidified from Et_2O-hexane to afford **1q** (1.07 g, 3.87 mmol, 58%) as a light brown solid.

Colorless crystal (Et_2O-hexane): mp 69-70 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.72 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 5.31 (s, 2H), 3.38 (dd, *J* = 9.4, 6.5 Hz, 2H), 3.07 (dd, *J* = 9.4, 5.6 Hz, 2H), 2.43 (s, 3H), 2.20 (m, 2H), 2.10 (m, 2H), 1.66 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 143.1, 134.8, 129.8, 127.3, 124.0, 52.7, 34.3, 24.2, 21.5; IR (neat, cm^{-1}): 2887, 1340, 1160, 662; MS (EI): *m/z* 277 (M^+, 100%); HRMS (EI): calcd. for $C_{15}H_{19}NO_2S$ (M^+) 277.1137, found 277.1121.

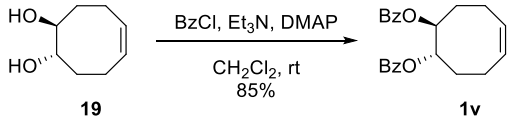
· ((1*S,2*S**)-Cyclohex-4-ene-1,2-diyl)bis(methylene) dibenzoate (1r),**

Cyclohept-4-en-1-yl benzoate (1t)

and Cyclohept-4-ene-1,1-diylbis(methylene) dibenzoate (1u)

These compounds were synthesized according to the literature's procedure.[6]

· (1*S,2*S**,*Z*)-Cyclooct-5-ene-1,2-diyl dibenzoate (1v)**

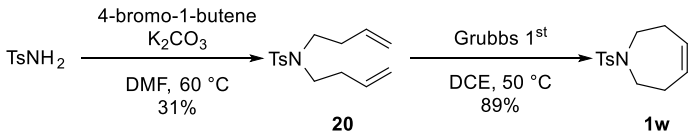


19 **1v**

To a solution of (1*S**,2*S**,*Z*)-cyclooct-5-ene-1,2-diol[9] (**19**) (379 mg, 2.66 mmol) in CH_2Cl_2 (10 mL) was added Et_3N (1.5 mL, 10.8 mmol), BzCl (0.77 mL, 6.7 mmol) and DMAP (10 mg, 0.082 mmol) at 0 °C. After stirring for 24 h at room temperature, the mixture was quenched with H_2O, and extracted with CH_2Cl_2. The combined organics were dried over $MgSO_4$. Concentration and flash column chromatography (hexane : AcOEt = 15 : 1) provided **1v** (789 mg, 2.25 mmol, 85%) as a white solid.

Colorless crystal ($CHCl_3$-hexane): mp 105-106 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.86 (d, *J* = 8.0 Hz, 4H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.23 (dd, *J* = 8.0, 7.6 Hz, 4H), 5.76 (t, *J* = 4.3 Hz, 2H), 5.55 (t, *J* = 3.9 Hz, 2H), 2.55 (m, 2H), 2.34-2.18 (m, 4H), 2.04 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 165.8, 132.7, 130.1, 129.5, 129.0, 128.1, 74.3, 30.3, 22.9; IR (neat, cm^{-1}): 2939, 1719, 1281, 1115, 710; MS (EI): *m/z* 350 (M^+), 105 (100%); HRMS (EI): calcd. for $C_{22}H_{22}O_4$ (M^+) 350.1518, found 350.1514.

· 1-Tosyl-2,3,6,7-tetrahydro-1*H*-azepine (1w)



20 **1w**

***N*,*N*-Di(but-3-en-1-yl)-4-methylbenzenesulfonamide (20)**

To a solution of *p*-toluenesulfonamide (1.71 g, 10 mmol) in DMF (30 mL) was added K_2CO_3 (4.2 g, 30 mmol) and 4-bromo-1-butene (2.4 mL, 24 mmol) at room temperature. After stirring for 2

days at 60 °C, the mixture was quenched with H_2O and extracted with Et_2O. The combined organics were washed with H_2O and brine, and dried over $MgSO_4$. Concentration and flash column chromatography (hexane : AcOEt = 8 : 1 to 4 : 1) provided **20** (857 mg, 3.07 mmol, 31%) as a colorless oil.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.70 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 5.72 (ddt, *J* = 17.2, 10.3, 6.9 Hz, 2H), 5.08-5.02 (m, 4H), 3.19 (t, *J* = 7.5 Hz, 4H), 2.42 (s, 3H), 2.30 (dt, *J* = 6.9, 7.5 Hz, 4H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 143.1. 137.1. 134.7. 129.6. 127.1. 117.0. 47.8. 33.2. 21.4; IR (neat, cm^{-1}): 1339, 1157; MS (EI): *m/z* 279 (M^+), 238 (100%); HRMS (EI): calcd. for $C_{15}H_{21}NO_2S$ (M^+) 279.1293, found 279.1287.

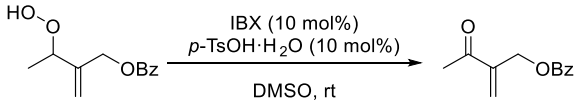
1-Tosyl-2,3,6,7-tetrahydro-1*H*-azepine (1w)

To a solution of **20** (706 mg, 2.53 mmol) in degassed DCE (20 mL) was added Grubbs 1st catalyst (20 mg, 24 μmol) at room temperature. After stirring for 3 days at 50 °C, the mixture was concentrated under reduced pressure. The residue was purified with flash column chromatography (hexane : AcOEt = 15 : 1 to 10 : 1) to afford **1w** (567 mg, 2.26 mmol, 89%) as a white solid.

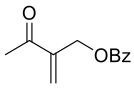
Colorless needle (CH_2Cl_2-hexane): mp 65-66 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 5.75 (t, *J* = 3.1 Hz, 2H), 3.28 (t, *J* = 5.3 Hz, 4H), 2.42 (s, 3H), 2.31 (m, 4H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 143.0, 136.3, 130.1, 129.6, 127.0, 48.2, 29.8, 21.4; IR (neat, cm^{-1}): 1332, 1160; MS (EI): *m/z* 251 (M^+, 100%); HRMS (EI): calcd. for $C_{13}H_{17}NO_2S$ (M^+) 251.0980, found 251.0971.

3. General Procedure and Characterization

General procedure for Scheme 5

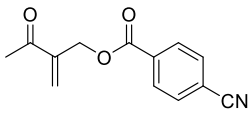


To a solution of **5b** (111 mg, 0.500 mmol) in DMSO (1 mL) was added *p*-TsOH·H_2O (9.5 mg, 0.050 mmol) and IBX (14.3 mg, 0.051 mmol) at room temperature. After stirring for 24 h at same temperature, the reaction mixture was quenched with H_2O and extracted with Et_2O. The combined organics were washed with H_2O and brine, and dried over $MgSO_4$. Concentration and flash column chromatography (hexane : AcOEt = 10 : 1) provided **4b** (88.8 mg, 0.435 mmol, 87%) as a white solid.



2-Methylene-3-oxobutyl benzoate (4b)

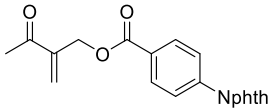
Colorless plate (Et_2O-hexane): mp 37-38 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.06 (d, *J* = 7.5 Hz, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.45 (dd, *J* = 7.5, 7.5 Hz, 2H), 6.23 (s, 1H), 6.10 (s, 1H), 5.08 (s, 2H), 2.40 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 197.9, 165.9, 143.3, 133.1, 129.9, 129.6, 128.4, 126.4, 62.3, 25.8; IR (neat, cm^{-1}): 1723, 1676, 1273, 711; MS (EI): *m/z* 204 (M^+), 105 (100%); HRMS (EI): calcd. for $C_{12}H_{12}O_3$ (M^+) 204.0786, found 204.0772.



2-Methylene-3-oxobutyl 4-cyanobenzoate (4c)

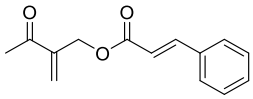
Coloeless crystal (Et_2O-hexane): mp 56-57 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.15 (d, *J* = 8.0 HZ, 2H), 7.75 (d, *J* = 8.0 Hz, 2H), 6.27 (s, 1H), 6.12 (s, 1H), 5.10 (s, 2H), 2.42 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 197.7, 164.3, 142.9, 133.7, 132.2, 130.1, 127.2, 117.8, 116.5, 63.1, 25.7; IR (neat, cm^{-1}): 2235, 1719, 1664, 1278; MS (EI): *m/z* 229 (M^+), 130 (100%); HRMS (EI): calcd. for

$C_{13}H_{11}NO_3$ (M^+) 229.0739, found 229.0725.



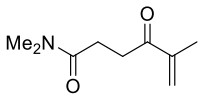
2-Methylene-3-oxobutyl 4-(1,3-dioxoisoindolin-2-yl)benzoate (4d)

Colorless crystal ($CHCl_3$-hexane): mp 155-156 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.21 (d, *J* = 8.8 Hz, 2H), 7.98 (dd, *J* = 5.5, 3.3 Hz, 2H), 7.82 (dd, *J* = 5.5, 3.3 Hz, 2H), 7.62 (d, *J* = 8.8 Hz, 2 H), 6.25 (s, 1H), 6.11 (s, 1H), 5.11 (s, 2H), 2.42 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 197.9, 166.7, 165.2, 143.3, 136.1, 134.7, 131.6, 130.5, 129.0, 126.5, 126.0, 123.9, 62.3, 25.8; IR (neat, cm^{-1}): 1714, 1669, 1384; MS (EI): *m/z* 349 (M^+), 250 (100%); HRMS (EI): calcd. for $C_{20}H_{15}NO_5$ (M^+) 349.0950, found 349.0916.



2-Methylene-3-oxobutyl cinnamate (4e)

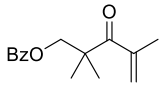
Colorless crystal (Et_2O-hexane): mp 53-54 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 15.9 Hz, 1H), 7.53 (m, 2H), 7.40-7.38 (m, 3H), 6.48 (d, *J* = 15.9 Hz, 1H), 6.22 (s, 1H), 6.07 (s, 1H), 4.96 (s, 2H), 2.39 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 198.0, 166.3, 145.3, 143.4, 134.2, 130.4, 128.9, 128.1, 126.5, 117.5, 62.0, 25.8; IR (neat, cm^{-1}): 1715, 1676, 1636, 1169; HRMS (ESI-pos): calcd. for $C_{14}H_{14}O_3Na$ (M^++Na) 253.0835, found 253.0845.



***N*,*N*,5-Trimethyl-4-oxohex-5-enamide (4f)**

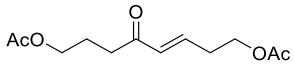
Yellow oil; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.07 (s, 1H), 5.78 (s, 1H), 3.08-3.05 (m, 5H), 2.95 (s, 3H), 2.64 (t, *J* = 6.5 Hz, 2H), 1.89 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 200.7, 171.8, 144.2, 124.7, 37.1, 35.5, 32.6, 27.2, 17.6; IR (neat, cm^{-1}): 2930, 1702, 1634; HRMS (ESI-pos): calcd. for

$C_9H_{15}NO_2Na$ (M^++Na) 192.0995, found 192.0992.



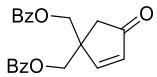
2,2,4-Trimethyl-3-oxopent-4-en-1-yl benzoate (4g)

Colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.98 (d, *J* =7.5 Hz, 2H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.43 (dd, *J* = 7.5, 7.5 Hz, 2H), 5.43 (m, 2H), 4.45 (s, 2H), 1.92 (s, 3H), 1.36 (s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 208.5, 166.2, 144.0, 133.1, 129.9, 129.5, 128.4, 118.3, 71.0, 47.8, 23.0, 21.0; IR (neat, cm^{-1}): 1722, 1687, 1272, 1113, 712; MS (EI): *m/z* 246 (M^+), 105 (100%); HRMS (EI): calcd. for $C_{15}H_{18}O_3$ (M^+), 246.1256, found 246.1240.



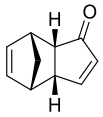
(*E*)-5-Oxooct-3-ene-1,8-diyl diacetate (4h)

Colorless oil; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.80 (dt, *J* = 15.9, 6.7 Hz, 1H), 6.18 (d, *J* = 15.9 Hz, 1H), 4.20 (t, *J* = 6.4 Hz, 2H), 4.10 (t, *J* = 6.5 Hz, 2H), 2.64 (t, *J* = 6.9 Hz, 2H), 2.56 (dt, *J* = 6.7, 6.4 Hz, 2H), 2.06 (s, 3H), 2.05 (s, 3H), 1.97 (tt, *J* =6.9, 6.5 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 198.7, 171.0, 170.9, 142.1, 131.9, 63.7, 62.2, 36.5, 31.6, 23.0, 20.9, 20.8; IR (neat, cm^{-1}): 1739, 1239, 1039; MS (EI): *m/z* 242 (M^+), 99 (100%); HRMS (EI): calcd. for $C_{12}H_{18}O_5$ (M^+) 242.1154, found 242.1125.



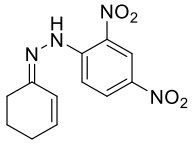
(4-Oxocyclopent-2-ene-1,1-diyl)bis(methylene) dibenzoate (4i)

Colorless crystal (CH_2Cl_2-hexane): mp 82-83 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.99 (d, *J* = 7.2 Hz, 4H), 7.64 (d, *J* = 5.8 Hz, 1H), 7.59 (t, *J* = 7.4 Hz, 2H), 7.45 (dd, *J* = 7.4, 7.2 Hz, 4 H), 6.35 (d, *J* = 5.8 Hz, 1H), 4.60 (d, *J* = 11.1 Hz, 2H), 4.46 (d, *J* = 11.1 Hz, 2H), 2.55 (s, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 206.3, 166.0, 163.2, 136.2, 133.4, 129.6, 129.3, 128.6, 66.3, 49.7, 41.6; IR (neat, cm^{-1}): 1719, 1269, 1111, 710; HRMS (ESI-pos): calcd. for $C_{21}H_{18}O_5Na$ (M^++Na) 373.1046, found 373.1072.



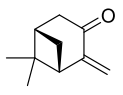
(3a*R,4*S**,7*R**,7a*S**)-3a,4,7,7a-Tetrahydro-1*H*-4,7-methanoinden-1-one (4j)**

Colorless crystal (Et_2O-hexane): mp 45-46 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.37 (dd, *J* = 5.7, 2.7 Hz, 1H), 5.97-5.93 (m, 2H), 5.78 (dd, *J* = 5.7, 2.9 Hz, 1H), 3.41 (m, 1H), 3.23 (br s, 1H), 2.97 (br s, 1H), 2.80 (dd, *J* = 5.1, 5.1 Hz, 1H), 1.76 (br d, *J* = 8.3 Hz, 1H), 1.62 (br d, *J* = 8.3 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 210.6, 164.5, 136.9, 132.5, 132.3, 52.7, 50.2, 48.2, 45.0, 44.0; IR (neat, cm^{-1}): 2977, 1696; MS (EI): *m/z* 146 (M^+, 100%); HRMS (EI): calcd. for $C_{10}H_{10}O$ (M^+) 146.0732, found 146.0713.



1-(Cyclohex-2-en-1-ylidene)-2-(2,4-dinitrophenyl)hydrazine (4a')

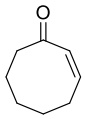
Red plate (CH_2Cl_2-hexane): mp 163-164 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 11.24 (br, 1H), 9.13 (d, *J* = 2.4 Hz, 1H), 8.31 (dd, *J* = 9.7, 2.4 Hz, 1H), 8.00 (d, *J* = 9.7 Hz, 1H), 6.45 (dt, *J* = 9.8, 4.7 Hz, 1H), 6.35 (d, *J* = 9.8 Hz, 1H), 2.61 (t, *J* = 6.4 Hz, 2H), 2.30 (m, 2H), 1.96 (tt, *J* = 6.4, 6.4 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 154.1, 144.7, 138.9, 137.8, 129.9, 129.3, 127.2, 123.4, 116.4, 24.8, 24.2, 21.0; IR (neat, cm^{-1}): 1616, 1591, 1334, 1311, 1287; MS (EI): *m/z* 276 (M^+, 100%); HRMS (EI): calcd. for $C_{12}H_{12}N_4O_4$ (M^+) 276.0856, found 276.0854.



(1*S*,5*S*)-6,6-Dimethyl-2-methylenebicyclo[3.1.1]heptan-3-one (4k)

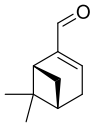
$[\alpha]_D^{29}$ = -50.6 (*c* = 0.577, $CHCl_3$) [lit. $[\alpha]_D^{20}$ = -60.0 (*c* = 2, $CHCl_3$), J. Karolak-Wojciechowska *et al. Tetrahedron Asymm.* **2006**, *17*, 434.]; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 5.97 (d, *J* = 1.5 Hz, 1H), 5.02 (d, *J* = 1.5 Hz, 1H), 2.77 (t, *J* = 5.9 Hz, 1H), 2.73-2.65 (m, 2H), 2.53 (dd, *J* = 19.0, 2.9 Hz, 1H),

2.21 (m, 1H), 1.37 (s, 3H), 1.31 (d, *J* = 10.4 Hz, 1H), 0.82 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 199.9, 149.1, 117.4, 48.3, 42.5, 40.8, 38.6, 32.4, 26.0, 21.5; IR (neat, cm^{-1}): 2929, 1707, 1626; HRMS (ESI-pos): calcd. for $C_{10}H_{14}ONa$ (M^++Na) 173.0937, found 173.0961.



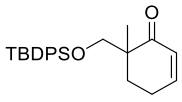
(*Z*)-Cyclooct-2-en-1-one (4l)

^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.35 (dt, *J* = 12.6, 7.1 Hz, 1H), 6.01 (d, *J* = 12.6 Hz, 1H), 2.67 (t, *J* = 6.8 Hz, 2H), 2.52 (m, 2H), 1.83 (m, 2H), 1.67-1.55 (m, 4H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 206.0, 141.5, 132.3, 42.7, 28.5, 25.1, 23.1, 22.5; IR (neat, cm^{-1}): 2931, 1660; MS (EI): *m/z* 124 (M^+), 80 (100%); HRMS (EI): calcd. for $C_8H_{12}O$ (M^+) 124.0888, found 124.0891.



(1*R*,5*S*)-6,6-Dimethylbicyclo[3.1.1]hept-2-ene-2-carbaldehyde (4m)

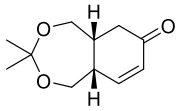
Yellow oil; $[\alpha]_D^{28}$ = -0.23 (*c* = 0.565, $CHCl_3$) [lit. $[\alpha]_D$ = -10.7 (neat), I. A. Dvornikova *et al. Russian J. Org. Chem.* **2007**, *43*, 352.]; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.44 (s, 1H), 6.70 (br s, 1H), 2.87 (dd, *J* = 5.6, 5.6 Hz, 1H), 2.63-2.55 (m, 2H), 2.49 (ddd, *J* = 9.2, 5.6, 5.6 Hz, 1H), 2.19 (br s, 1H), 1.34 (s, 3H), 1.06 (d, *J* = 9.2 Hz, 1H), 0.75 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 191.2, 151.6, 147.6, 40.7, 38.1, 37.6, 33.0, 31.1, 25.7, 20.9; IR (neat, cm^{-1}): 2931, 1681; MS (EI): *m/z* 150 (M^+), 79 (100%); HRMS (EI): calcd. for $C_{10}H_{14}O$ (M^+) 150.1045, found 150.1035.



6-(((*tert*-Butyldiphenylsilyl)oxy)methyl)-6-methylcyclohex-2-en-1-one (4n)

Yellow oil; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.71-7.63 (m, 4H), 7.42-7.35 (m, 6H), 6.88 (dt, *J* = 9.3, 4.5 Hz, 1H), 5.94 (d, *J* = 9.3 Hz, 1H), 3.88 (d, *J* = 9.7 Hz, 1H), 3.49 (d, *J* = 9.7 Hz, 1H), 2.35 (m,

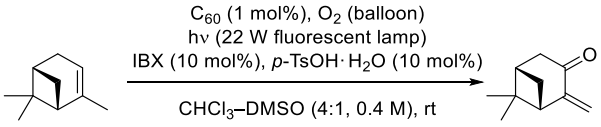
2H), 2.28 (dt, *J* = 13.4, 6.8 Hz, 1H), 1.83 (dt, *J* = 13.4, 5.3 Hz, 1H), 1.09 (s, 3H), 1.04 (s, 9H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 202.4, 149.1, 135.7, 135.6, 133.6, 133.4, 129.62, 129.59, 129.1, 127.6, 68.2, 47.2, 31.0, 26.8, 23.1, 19.4, 19.3; IR (neat, cm^{-1}): 2930, 2857, 1674, 1111, 702; MS (EI): *m/z* 321 (M^+-C_4H_9), 81 (100%); HRMS (EI): calcd. for $C_{35}H_{30}O_2Si$ (M^+-C_4H_9) 321.1311, found 321.1347.



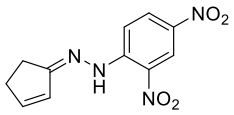
(5a*R,9a*S**)-3,3-Dimethyl-1,5a,6,9a-tetrahydrobenzo[*e*][1,3]dioxepin-7(5*H*)-one (4o)**

Yellow oil; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.79 (dd, *J* = 10.2, 4.2 Hz, 1H), 6.05 (dd, *J* = 10.2, 1.4 Hz, 1H), 3.82-3.76 (m, 2H), 3.70 (dd, *J* = 12.6, 2.9 Hz, 1H), 3.58 (dd, *J* = 12.6, 5.3 Hz, 1H), 2.72-2.65 (m, 2H), 2.46-2.39 (m, 2H), 1.35 (s, 3H), 1.32 (s, 3H); ^{13}C-NMR (100MHz, $CDCl_3$): δ 199.1, 148.9, 130.4, 102.2, 63.3, 61.2, 41.2, 38.4, 38.0, 24.8, 24.7; IR (neat, cm^{-1}): 2938, 1678, 1218, 1090; MS (EI): *m/z* 181 (M^+-CH_3), 166 (100%); HRMS (EI): calcd. for $C_{10}H_{13}O_3$ (M^+-CH_3) 181.0865, found 181.0866.

General procedure for Scheme 6

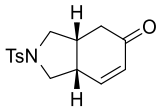


To a solution of α-pinene (**1k**) (137 mg, 1.01 mmol) in $CHCl_3$ (2 mL) was added C_{60} (6.9 mg, 9.6 μmol) at room temperature. The mixture was stirred until almost all C_{60} was dissolved. Then to the mixture was added DMSO (0.5 mL), *p*-TsOH·H_2O (19 mg, 0.099 mmol) and IBX (28 mg, 0.10 mmol). The reaction mixture was stirred at room temperature under O_2 atmosphere (balloon) with irradiation (100 V, 22 W fluorescent lamp). After 10 h, the mixture was quenched with H_2O and extracted with Et_2O. The combined organics were washed with H_2O and brine, and dried over $MgSO_4$. Concentration and flash column chromatography (hexane : Et_2O = 12 : 1) provided **4k** (117 mg, 0.779 mmol, 77%) as a colorless oil.



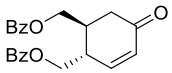
1-(Cyclopent-2-en-1-ylidene)-2-(2,4-dinitrophenyl)hydrazine (4p')

Red crystal (CH_2Cl_2-hexane): mp 164-166 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 10.85 (s, 1H), 9.12 (d, *J* = 2.3 Hz, 1H), 8.29 (dd, *J* = 9.5, 2.3 Hz, 1H), 7.93 (d, *J* = 9.5 Hz, 1H), 6.86 (m, 1H), 6.44 (m, 1H), 2.81 (m, 2H), 2.72 (br t, *J* = 4.3 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 167.8, 149.5, 144.9, 137.7, 131.2, 129.9, 129.1, 123.6, 116.3, 31.3, 25.5; IR (neat, cm^{-1}): 1617, 1588, 1513, 1333, 1311; MS (EI): *m/z* 262 (M^+, 100%); HRMS (EI): calcd. for $C_{11}H_{10}N_4O_4$ (M^+) 262.0702, found 262.0675.



(3a*R,7a*S**)-2-Tosyl-1,2,3,3a,4,7a-hexahydro-5*H*-isoindol-5-one (4q)**

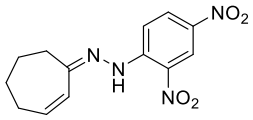
Colorless needle (CH_2Cl_2-hexane): mp 126-127 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.70 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 6.52 (dd, *J* = 10.3, 3.4 Hz, 1H), 5.89 (dd, *J* = 10.3, 1.7 Hz, 1H), 3.61 (dd, *J* = 10.3, 7.7 Hz, 1H), 3.50 (dd, *J* = 10.0, 7.7 Hz, 1H), 3.37 (dd, *J* = 10.3, 4.6 Hz, 1H), 3.06 (dd, *J* = 10.0, 7.5 Hz, 1H), 2.96 (m, 1H), 2.79 (m, 1H), 2.50 (dd, *J* = 17.0, 5.6 Hz, 1H), 2.44 (s, 3H), 2.29 (dd, *J* = 17.0, 6.3 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 196.4, 147.7, 143.8, 138.8, 130.3, 129.8, 127.4, 52.6, 51.3, 38.3, 37.3, 37.2, 21.5; IR (neat, cm^{-1}): 1678, 1342, 1160, 667; MS (EI): *m/z* 291 (M^+), 136 (100%); HRMS (EI): calcd. for $C_{15}H_{17}NO_3S$ (M^+) 291.0929, found 291.0923.



((1*S,2*S**)-5-Oxocyclohex-3-ene-1,2-diyl)bis(methylene) dibenzoate (4r)**

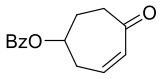
Colorless crystal (Et_2O-hexane): mp 85-86 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.01-7.98 (m, 4H), 7.59-7.55 (m, 2H), 7.45-7.41 (m, 4H), 6.96 (dd, *J* = 10.1, 2.9 Hz, 1H), 6.17 (dd, *J* = 10.1, 2.4 Hz, 1H), 4.63 (dd, *J* = 11.5, 5.1 Hz, 1H), 4.76 (dd, *J* = 11.5, 5.3 Hz, 1H), 4.53 (dd, *J* = 11.6, 5.3 Hz, 1H),

4.42 (dd, *J* = 11.6, 4.8 Hz, 1H), 2.99 (m, 1H), 2.76 (dd, *J* = 15.8, 4.1 Hz, 1H), 2.70 (m, 1H), 2.56 (dd, *J* = 15.8, 10.1 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 197.5, 166.22, 166.19, 149.2, 133.34, 133.25, 130.7, 129.63, 129.58, 129.5, 128.50, 128.47, 65.8, 64.7, 39.7, 38.4, 36.5; IR (neat, cm^{-1}): 1718, 1682, 1271, 1112, 710; MS (EI): *m/z* 242 (M^+-BzOH), 105 (100%); HRMS (EI): calcd. for $C_{15}H_{14}O_3$ (M^+-BzOH) 242.0943, found 242.0950.



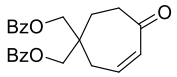
1-(Cyclohept-2-en-1-ylidene)-2-(2,4-dinitrophenyl)hydrazine (4s')

Orange plate (CH_2Cl_2-hexane): mp 137-139 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 11.20 (s, 0.5H), 11.17 (s, 0.5H), 9.13 (m, 1H), 8.31 (m, 1H), 8.01 (d, *J* = 9.7 Hz, 0.5 H), 7.98 (d, *J* = 11.1 Hz, 0.5H), 6.84 (dt, *J* = 12.2, 5.6 Hz, 0.5H), 6.35 (d, *J* = 12.2 Hz, 0.5H), 6.32 (d, *J* = 12.2 Hz, 0.5H), 6.14 (dt, *J* = 12.2, 5.0 Hz, 0.5H), 2.71 (t, *J* = 6.0 Hz, 2H), 2.43 (m, 2H), 1.95-1.75 (m, 4H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 158.0, 157.7, 144.8, 144.6, 138.1, 129.9, 129.8, 128.9, 123.5, 123.4, 120.7, 116.6, 116.5, 36.2, 31.3, 30.3, 29.7, 26.4, 26.3, 26.2, 23.3; IR (neat, cm^{-1}): 1615, 1591, 1333, 1305; MS (EI): *m/z* 290 (M^+, 100%); HRMS (EI): calcd. for $C_{13}H_{14}N_4O_4$ (M^+) 290.1015, found 290.1002.



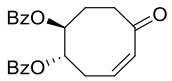
5-Oxocyclohept-3-en-1-yl benzoate (4t)

Yellow oil; ^{1}H-NMR (400MHz, $CDCl_3$): δ 8.01 (d, *J* = 7.6 Hz, 2H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.44 (dd, *J* = 7.6, 7.6 Hz, 2H), 6.47 (dt, *J* = 12.1, 5.9 Hz, 1H), 6.13 (d, *J* = 12.1 Hz, 1H), 5.44 (m, 1H), 2.91-2.75 (m, 3H), 2.65 (ddd, *J* = 16.7, 8.9, 3.7 Hz, 1H), 2.28 (m, 1H), 2.14 (m, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 202.4, 165.6, 139.9, 133.4, 133.1, 130.0, 129.5, 128.4, 71.6, 38.8, 34.7, 27.5; IR (neat, cm^{-1}): 1715, 1670, 1273, 1112, 711; MS (EI): *m/z* 230 (M^+), 105 (100%); HRMS (EI): calcd. for $C_{14}H_{14}O_3$ (M^+) 230.0943, found 230.0943.



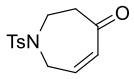
(5-Oxocyclohept-3-ene-1,1-diyl)bis(methylene) dibenzoate (4u)

Yellow oil; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.02 (d, *J* = 7.6 Hz, 4H), 7.58 (t, *J* = 7.6 Hz, 2H), 7.44 (dd, *J* = 7.6, 7.6 Hz, 4H), 6.65 (dt, *J* = 11.3, 7.1 Hz, 1H), 6.16 (d, *J* = 11.3 Hz, 1H), 4.37 (d, *J* = 11.1 Hz, 2H), 4.34 (d, *J* = 11.1 Hz, 2H), 2.68 (t, *J* = 5.7 Hz, 2H), 2.57 (d, *J* = 7.1 Hz, 2H), 1.90 (t, *J* = 5.7 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 202.8, 166.1, 141.8, 134.1, 133.1, 129.5, 129.4, 128.4, 67.6, 41.4, 38.6, 30.9, 25.7; IR (neat, cm^{-1}): 1719, 1670, 1269, 710; MS (EI): *m/z* 256 (M^+-BzOH), 105 (100%); HRMS (EI): calcd. for $C_{16}H_{16}O_3$ (M^+-BzOH) 256.1099, found 256.1094.



(1*S,2*S**,*Z*)-6-Oxocyclooct-4-ene-1,2-diyl dibenzoate (4v)**

Yellow oil; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.95-7.51 (m, 4H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.38-7.34 (m, 4H), 6.40 (dt, *J* = 12.6, 7.2 Hz, 1H), 6.15 (d, *J* = 12.6 Hz, 1H), 5.55 (dt, *J* = 8.2, 3.1 Hz, 1H), 5.48 (dt, *J* = 8.2, 3.1 Hz, 1H), 3.05-2.90 (m, 3H), 2.73 (m, 1H), 2.38 (m, 1H), 2.24 (m, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 202.5, 165.6, 165.5, 136.2, 133.23, 133.17, 132.8, 129.7, 129.64, 129.56, 129.5, 128.4, 128.3, 74.1, 72.1, 39.0, 31.8, 25.3; IR (neat, cm^{-1}): 1718, 1667, 1177, 711; MS (EI): *m/z* 242 (M^+-BzOH), 105 (100%); HRMS (EI): calcd. for $C_{15}H_{14}O_4$ (M^+-BzOH) 242.0943, found 2242.0950.

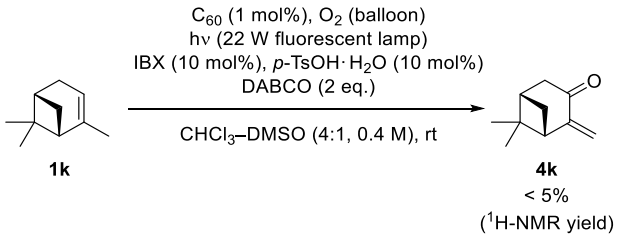


1-Tosyl-1,2,3,7-tetrahydro-4*H*-azepin-4-one (4w)

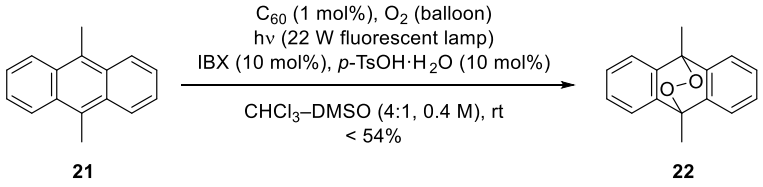
Colorless crystal (CH_2Cl_2-hexane): mp 92-93 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.69 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 6.29 (dt, *J* = 13.0, 3.7 Hz, 1H), 6.02 (br d, *J* = 13.0 Hz, 1H), 4.11 (m, 2H), 3.44 (t, *J* = 5.8 Hz, 2H), 2.82 (t, *J* = 5.8 Hz, 2H), 2.44 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 200.6, 143.9, 139.2, 134.9, 130.9, 129.9, 127.0, 50.9, 44.2, 42.7, 21.3; IR (neat, cm^{-1}): 1660, 1337, 1159; MS (EI): *m/z* 265 (M^+), 110 (100%); HRMS (EI): calcd. for $C_{13}H_{15}NO_3S$ (M^+) 265.0773, found 265.0771.0

4. Mechanistic Studies

4-1. Quenching Experiment of Singlet Oxygen



4-2. Trapping Experiment of Singlet Oxygen

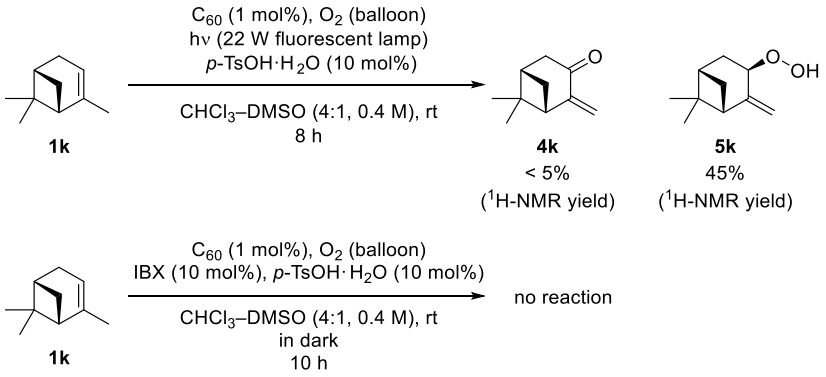


To a solution of 9,10-dimethylanthracene (**21**) (104 mg, 0.505 mmol) in $CHCl_3$ (1 mL) was added C_{60} (3.9 mg, 5.2 μmol) at room temperature. The mixture was stirred until almost all C_{60} was dissolved. Then to the mixture was added DMSO (0.25 mL), *p*-TsOH·H_2O (11 mg, 0.058 mmol) and IBX (14 mg, 0.051 mmol). The reaction mixture was stirred at room temperature under O_2 atmosphere (balloon) with irradiation (100 V, 22 W fluorescent lamp). After 12 h, the solvent was removed under reduced pressure. The residue was purified by flash column chromatography (hexane : AcOEt = 8 : 1) to afford **22** with some impurities (65.3 mg, < 0.274 mmol, < 54%) as a yellow solid.

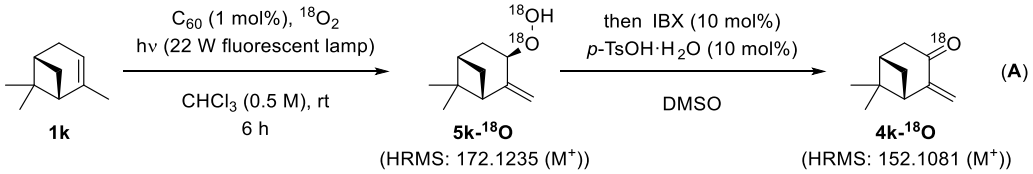
9,10-dimethyl-9,10-dihydro-9,10-epidioxyanthracene[10] (22)

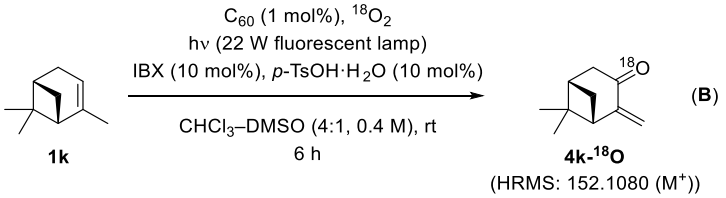
^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.39 (m, 4H), 7.26 (m, 4H), 2.14 (s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 140.8, 127.4, 120.6, 79.5, 13.7; MS (EI): *m/z* 238 (M^+), 209 (100%); HRMS (EI): calcd. for $C_{16}H_{14}O_2$ (M^+) 238.0994, found 238.0990.

4-3. Control Experiments

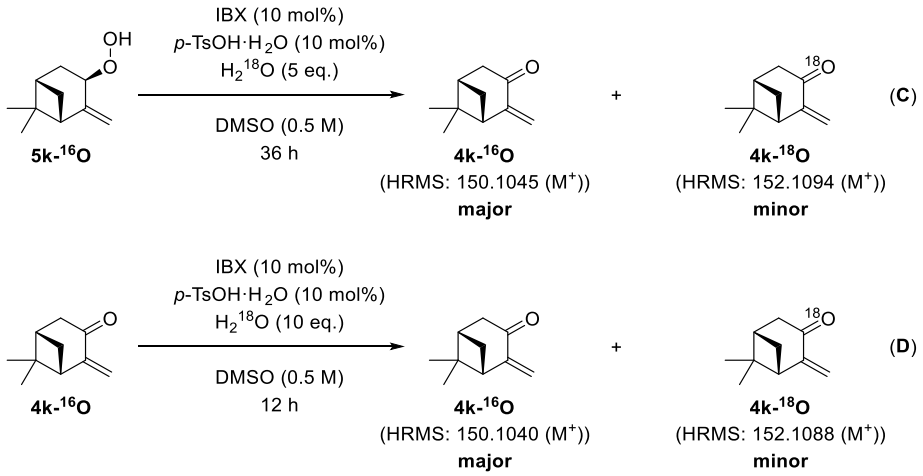


4-4. ^{18}O-Labeling Experiments

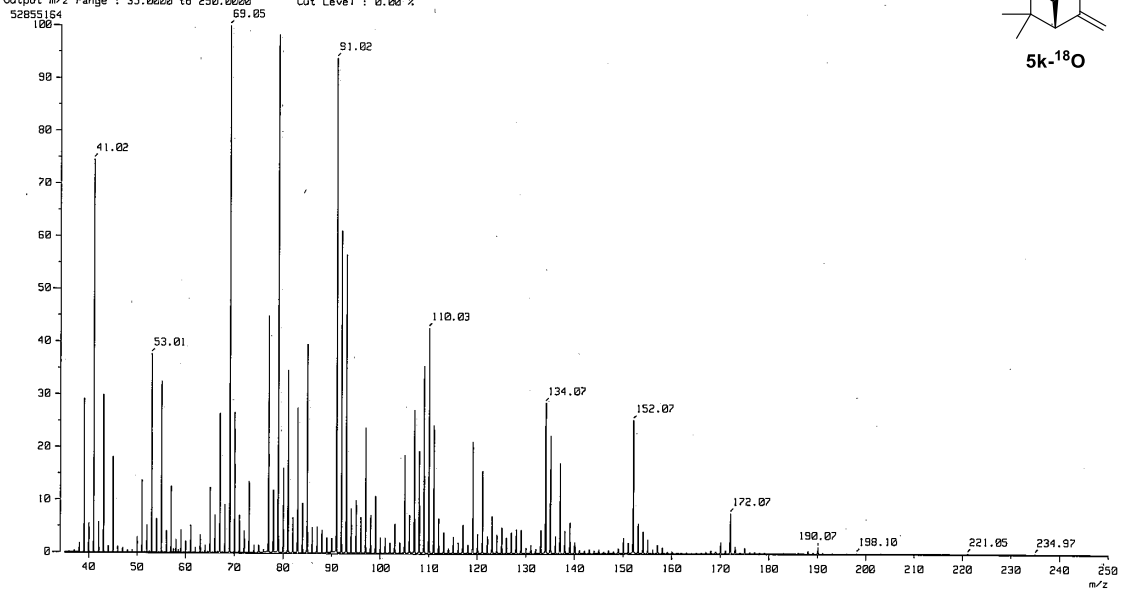


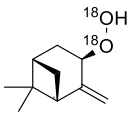


These results indicated that the oxygen atom of the product **4k** should come from molecular oxygen via its incorporation into hydroperoxide **5k**. However, **5k**-^{16}**O** or **4k**-^{16}**O** was also detected by EI-mass spectrometry as a minor peak in all cases. We considered that contamination of $^{16}O_2$ in $^{18}O_2$ and acid catalyzed oxygen atom exchange of the enone with water ($H_2{}^{16}O$) could generate **5k**-^{16}**O** and **4k**-^{16}**O**. The exchange of the oxygen atom was supported by the results shown below.



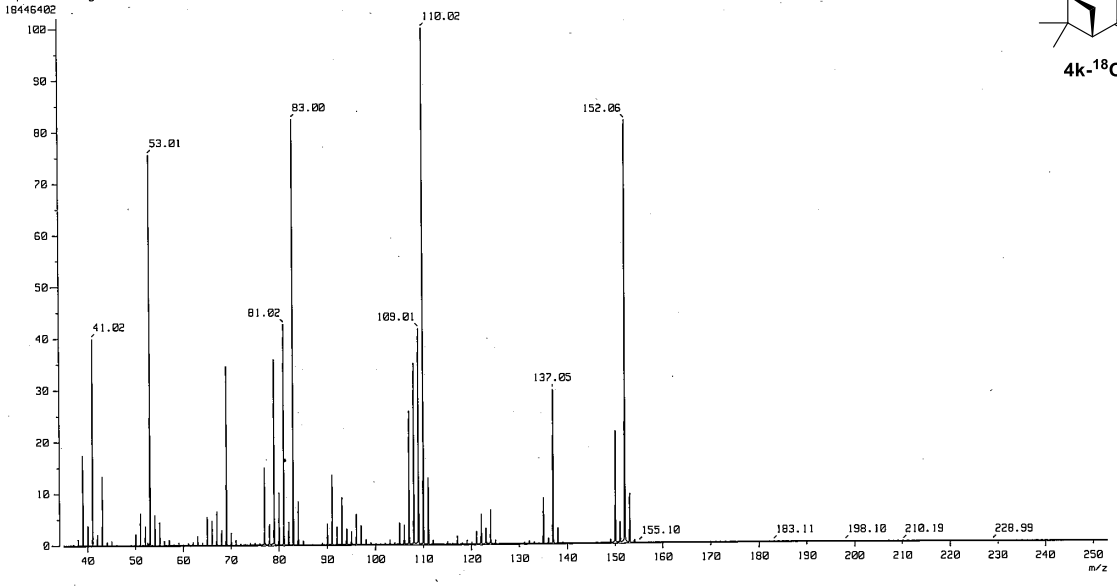
[Mass Spectrum]
Data : MS-2017-DEC-166 Date : 18-Dec-2017 10:09
Sample: GOS-7858
Note : JEOL JMS DX-303 mass spectrometer PHARM. TOHOKU UNIVERSITY
Inlet : Direct Ion Mode : EI+
Spectrum Type : Normal Ion [MF-Linear]
RT : 1.17 min Scan# : (28,44)
BP : m/z 69.0537 Int. : 296.51
Output m/z range : 35.0000 to 250.0000 Cut Level : 0.00 %



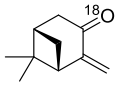


5k-^{18}O

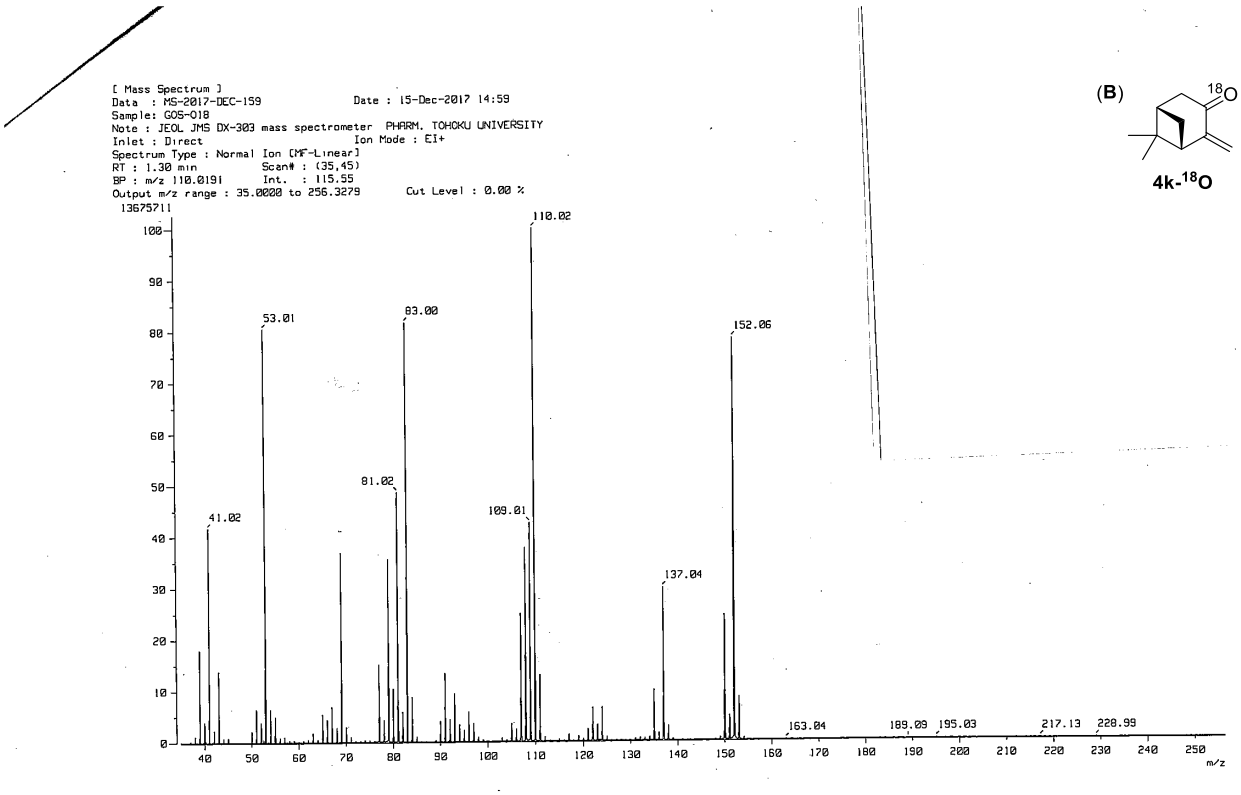
[Mass Spectrum]
Data : MS-2017-DEC-160 Date : 15-Dec-2017 15:39
Sample: GOS-7856
Note : JEOL JMS DX-303 mass spectrometer PHARM. TOHOKU UNIVERSITY
Inlet : Direct Ion Mode : EI+
Spectrum Type : Normal Ion [MF-Linear]
RT : 1.42 min Scan# : (39,48)
BP : m/z 110.0229 Int. : 172.42
Output m/z range : 35.0000 to 252.9228 Cut Level : 0.00 %



(**A**)

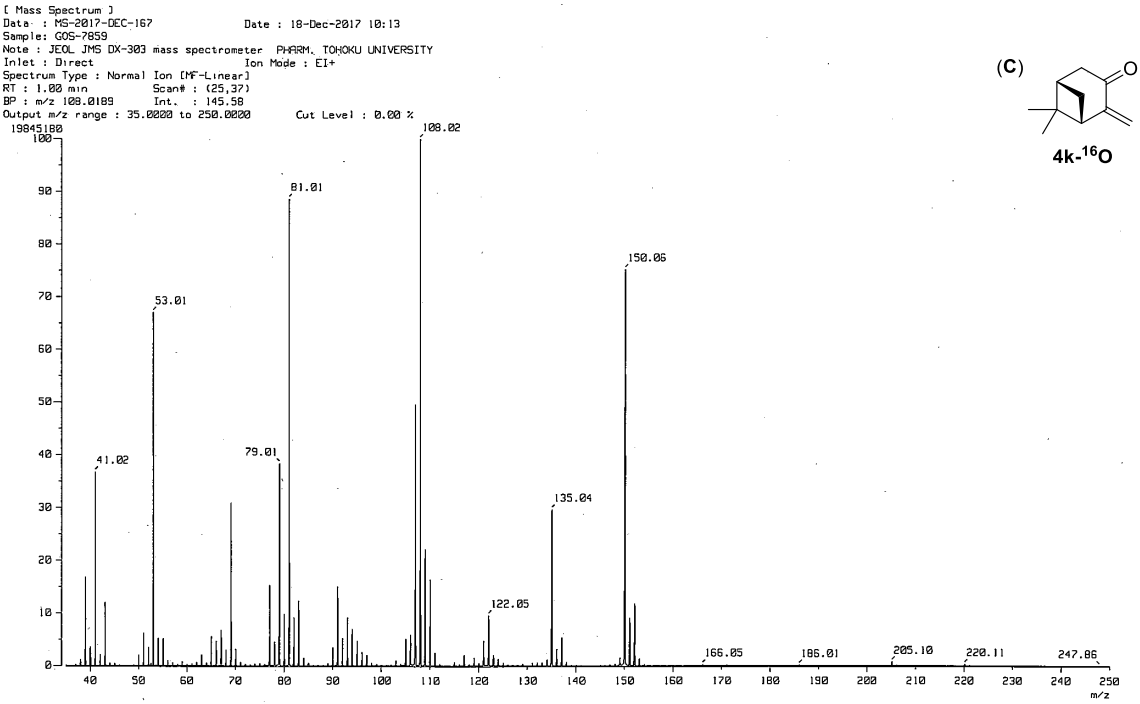


4k-^{18}O



(B)

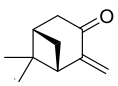
4k-^{18}O



(C)

4k-^{16}O

(**D**)



4k-^{16}O

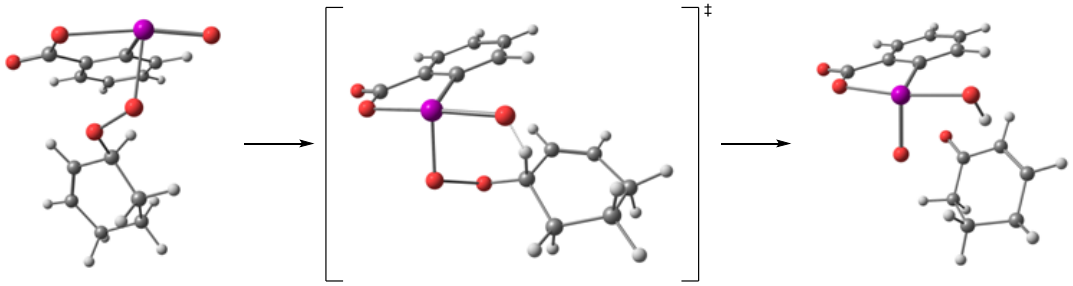
[Mass Spectrum]
Data : MS-2017-DEC-165 Date : 18-Dec-2017 10:04
Sample: GOS-7857
Note : JEOL JMS DX-303 mass spectrometer PHARM. TOHOKU UNIVERSITY
Inlet : Direct Ion Mode : EI+
Spectrum Type : Normal Ion [MF-Linear]
RT : 0.97 min Scan# : (24,36)
BP : m/z 108.0234 Int. : 202.17
Output m/z range : 35.0000 to 250.0000 Cut Level : 0.00 %
27559148
108.02
81.01
150.06
53.01
41.02
79.01
135.05
122.05
166.05
189.09
203.11
222.13
247.89
m/z

5. Computational Details

All DFT calculations were performed with the Gaussian09 program.[11] Structure optimization and frequency calculation were carried out with the B3LYP functional[12] including Grimme's D3 dispersion correction[13] with Becke–Johnson (BJ) damping corrections[14] (abbreviated as B3LYP-D3BJ) and the def2-SVP basis set.[15] Single point energy was obtained via calculation of the B3LYP-D3BJ geometries with the M06 functional[16] and the def2-TZVP basis set.[15] Gibbs free energy (kcal/mol) was calculated based on M06 single point energy and B3LYP-D3BJ frequency. Solvent effects were corrected by using Self-Consistent Reaction Field (SCRF) method using the Polarizable Continuum Model (PCM) model[17] together with dimethyl sulfoxide (DMSO) as a solvent.

The transition state (TS) models were designed on the basis of Goddard's model for IBX-promoted alcohol oxidation (see ref. 14b in the manuscript).

Scheme S1. A six-membered transition state for the proton transfer and O–O bond cleavage step



Scheme S2. A ten-membered transition state incorporating a DMSO molecule for the proton transfer and O–O bond cleavage step

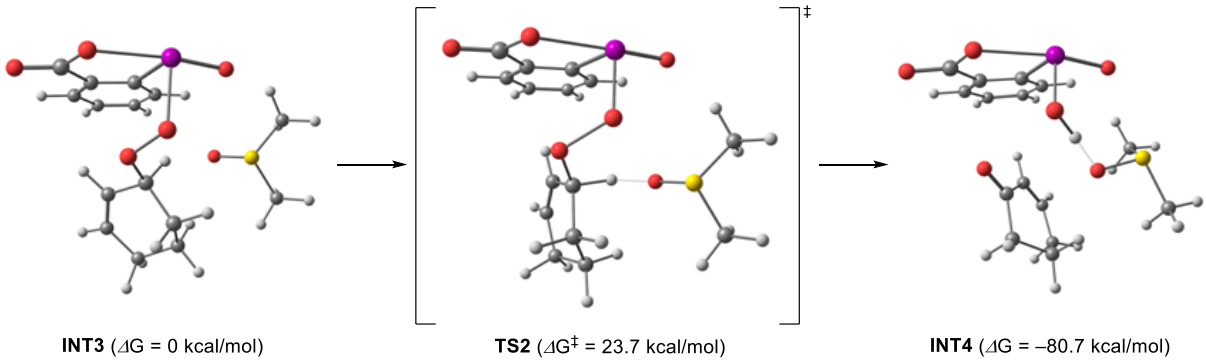


Table S2. Cartesian coordinates (Angstroms) for **INT1**

0 1

O	2.17968600	-1.65405900	-1.62698200
I	1.99486300	-0.84443700	0.01645200
O	1.45462500	0.28860600	1.92119300
C	0.75563600	1.37407600	1.76975600
O	0.28486100	2.04958700	2.67275500
C	1.06337200	0.93630200	-0.67551300
C	0.55372500	1.76188300	0.31990900
C	-0.14652000	2.90057200	-0.08797400
C	-0.30999600	3.16249300	-1.45234100
C	0.92210400	1.15073200	-2.03897500
C	0.21856900	2.29804500	-2.42227200
H	-0.56242700	3.56007400	0.67573100
H	-0.85983000	4.05118000	-1.76838500
H	1.33176300	0.43970400	-2.75963600
H	0.07925600	2.51510900	-3.48317000
C	-4.76850900	-0.50763400	-0.17981300
C	-3.96596900	0.42427200	0.68733200
C	-2.63596500	0.34976200	0.82753700
C	-1.81280500	-0.68774200	0.11753700
C	-2.64642300	-1.86649100	-0.37201000
C	-3.88400800	-1.34853500	-1.10847000
H	-5.50385600	0.07181900	-0.76329000
H	-5.37095000	-1.16526700	0.47566000
H	-4.51292100	1.20395500	1.22799800
H	-2.09493000	1.05933000	1.45909100
H	-1.26004500	-0.23530600	-0.72224700
H	-2.03289300	-2.51246200	-1.01668900
H	-2.94948000	-2.46053900	0.50675000
H	-4.45749300	-2.18996700	-1.52608900
H	-3.56253500	-0.73041800	-1.96501500
O	-0.81919900	-1.11654400	1.09554800
O	0.14619300	-1.88489600	0.49737700

Table S3. Cartesian coordinates (Angstroms) for **TS1**

0 1

O	-0.96195800	-1.01378800	-1.49138000
I	0.71673700	-1.31331100	-0.66976700

O	2.59555700	-1.34149400	0.56708700
C	3.09259900	-0.17872300	0.89515900
O	4.07052300	-0.01369100	1.60398100
C	1.22989300	0.74540800	-0.49857700
C	2.35473800	0.99059600	0.28118600
C	2.75001900	2.32094300	0.43888900
C	2.02577600	3.33822800	-0.19423700
C	0.49077400	1.71681700	-1.15656400
C	0.90961300	3.04291800	-0.98766900
H	3.62472900	2.53808500	1.05465200
H	2.33835000	4.37723500	-0.07287100
H	-0.37553200	1.44932000	-1.76361100
H	0.35860000	3.84637500	-1.48033500
C	-4.73208500	1.09614000	0.04880300
C	-3.48667700	1.91625800	0.25298400
C	-2.29674700	1.39853400	0.59177000
C	-2.12423200	-0.08948800	0.78812400
C	-3.42361200	-0.87029600	0.98322100
C	-4.45098000	-0.40878800	-0.05556100
H	-5.26633900	1.44888700	-0.84999400
H	-5.42162600	1.29812000	0.89098100
H	-3.57673200	3.00440200	0.16423800
H	-1.41729300	2.02286400	0.75681000
H	-1.74486200	-0.38166100	-0.30362400
H	-3.21210100	-1.94579000	0.88011900
H	-3.79512700	-0.70095100	2.00902800
H	-5.38737700	-0.97734000	0.05110900
H	-4.05825300	-0.63571500	-1.06197100
O	-1.11672500	-0.38660300	1.62158100
O	-0.09839200	-1.72562700	1.06097500

Table S4. Cartesian coordinates (Angstroms) for **INT2**

0 1

O	-0.84640100	-0.87348400	-2.01921700
I	0.46206900	-1.42539100	-0.58383800
O	2.06112400	-1.64285500	0.88324400
C	2.72818200	-0.55135800	1.20054200
O	3.58362300	-0.50627800	2.06278600
C	1.36391000	0.51273300	-0.60037700

C	2.35392200	0.64731400	0.36728400
C	2.98160300	1.88941700	0.49329700
C	2.61065200	2.93871200	-0.35348200
C	0.98121100	1.52059900	-1.47119600
C	1.62620600	2.75595300	-1.33270600
H	3.75856400	2.01086600	1.25025900
H	3.10051200	3.90960900	-0.25681200
H	0.21590000	1.34937500	-2.22795600
H	1.35469900	3.57922600	-1.99651900
C	-4.49982900	0.13325600	0.03181200
C	-3.62192900	0.97383800	-0.84474700
C	-2.44940900	1.50048500	-0.43332800
C	-1.95518900	1.34273500	0.95507100
C	-2.87947700	0.62051500	1.91713500
C	-3.74262400	-0.44188300	1.23141700
H	-4.96016700	-0.66900500	-0.56780600
H	-5.34458400	0.76842800	0.36490200
H	-3.97152700	1.18175600	-1.86219900
H	-1.84585300	2.12992500	-1.09178000
H	-1.55808800	-0.34889300	-1.59827100
H	-2.26603200	0.19893400	2.72560600
H	-3.52237800	1.40063000	2.36888500
H	-4.44870700	-0.88223500	1.95159400
H	-3.07925000	-1.24804400	0.88294200
O	-0.89333100	1.83336400	1.30678300
O	-0.76828300	-1.42183800	0.77093500

Table S5. Cartesian coordinates (Angstroms) for **INT3**

0 1

O	2.38449800	-0.32081100	1.28304000
I	-1.27065500	-1.66276900	-0.60947500
O	-2.99736600	-0.29972600	-1.23083900
C	-3.30351300	0.65843800	-0.40959600
O	-4.17041900	1.50083000	-0.58893500
C	-1.46470700	-0.29460800	1.00459400
C	-2.47120300	0.65438000	0.85523000
C	-2.63774300	1.58123200	1.88771700
C	-1.79689000	1.53301100	3.00432000
C	-0.59947700	-0.37531500	2.08656600

C	-0.78133300	0.57111700	3.10084100
H	-3.41996800	2.33595900	1.78958200
H	-1.92549200	2.26111100	3.80780000
H	0.21490800	-1.09983800	2.10458600
H	-0.11863000	0.55990400	3.96844200
C	2.47788600	3.85064800	-0.49791200
C	1.02856600	3.85688500	-0.09115600
C	0.21289600	2.80450800	-0.23767500
C	0.68258600	1.50244200	-0.81697400
C	1.95723500	1.65527300	-1.63964500
C	2.98608400	2.44058900	-0.82176900
H	3.08725500	4.30766500	0.30040800
H	2.60079400	4.51597400	-1.37397900
H	0.63380500	4.77833600	0.35008400
H	-0.82831100	2.84964100	0.09093100
H	0.85409000	0.76163000	-0.01843400
H	2.33705100	0.66074600	-1.91626600
H	1.71379700	2.19298700	-2.57192400
H	3.94479500	2.49290500	-1.36069900
H	3.16807800	1.89158800	0.11655200
O	-0.41841200	1.01194800	-1.63877800
O	-0.21904900	-0.30934600	-1.94606900
O	0.19593700	-2.57988600	0.03262300
C	3.09326800	-2.89122700	1.04441800
S	2.96846000	-1.27144600	0.22777300
C	4.75233600	-0.89267000	0.19071100
H	2.06137000	-3.24538500	1.14954100
H	3.67303100	-3.57663500	0.41014900
H	3.57360800	-2.74452900	2.02208200
H	5.27293700	-1.63277500	-0.43350500
H	4.85766000	0.10857200	-0.24654000
H	5.13111000	-0.90024400	1.22262100

Table S6. Cartesian coordinates (Angstroms) for **TS2**

0 1

O	2.47102900	-0.24147000	0.88145800
I	-1.27230500	-1.72498100	-0.30720900
O	-2.50487600	-0.44698600	-1.79597600
C	-2.97272900	0.66925300	-1.33905800

O	-3.61556400	1.49345100	-1.97766900
C	-1.91813700	-0.03794800	0.82485500
C	-2.67063100	0.89992500	0.12985400
C	-3.09494400	2.02976100	0.83561900
C	-2.74993800	2.17875700	2.18381700
C	-1.55173000	0.06507800	2.15761600
C	-1.98117400	1.20895600	2.84226200
H	-3.68366600	2.78289300	0.30894100
H	-3.07935200	3.06494000	2.73016300
H	-0.95032600	-0.71773200	2.62534100
H	-1.71366000	1.34182000	3.89250600
C	2.74324400	3.82244800	0.01467400
C	1.38462200	3.53007300	0.59503400
C	0.65094400	2.45612100	0.26321300
C	1.14064100	1.43249500	-0.72103600
C	2.34815000	1.87397200	-1.56399300
C	3.36371200	2.60275800	-0.67857300
H	3.41575200	4.19233800	0.80772200
H	2.65072000	4.66289100	-0.70037500
H	0.96793800	4.25663600	1.30126600
H	-0.33401200	2.28720100	0.69925600
H	1.64238000	0.62595800	0.03210200
H	2.80089800	0.99093400	-2.04296600
H	1.99300600	2.53629200	-2.37306800
H	4.23987700	2.90559800	-1.27295300
H	3.72137000	1.89902500	0.09011800
O	0.16968500	0.82593600	-1.41436800
O	0.28757800	-0.88252100	-1.19128200
O	-0.40671700	-2.56611800	1.09504800
C	2.69316500	-2.88199200	1.04507200
S	3.00728500	-1.43094400	0.02193000
C	4.80484200	-1.30282200	0.19580200
H	1.59608000	-2.95269400	1.11593800
H	3.11802300	-3.76074500	0.53971700
H	3.15018400	-2.72188000	2.03107700
H	5.26462000	-2.18493900	-0.27102700
H	5.11157100	-0.39188900	-0.33433800
H	5.05487200	-1.23689300	1.26311500

Table S7. Cartesian coordinates (Angstroms) for **INT4**

0 1

O	1.95655100	-0.94703400	-0.65704000
I	-1.56510800	-1.60809300	-0.25190500
O	-2.81226500	-0.16555500	-1.55468600
C	-2.96213200	1.03692000	-1.09802600
O	-3.52598800	1.95627200	-1.67768000
C	-1.72242600	0.18287900	0.90380100
C	-2.40262800	1.23024100	0.29707100
C	-2.55648300	2.41052800	1.02880300
C	-2.04047800	2.49727600	2.32615700
C	-1.20155800	0.22223900	2.18934600
C	-1.37057400	1.41200200	2.90770700
H	-3.08207000	3.24691600	0.56464400
H	-2.16313100	3.42091200	2.89568100
H	-0.69413000	-0.64704700	2.61003600
H	-0.97730100	1.48970000	3.92329300
C	3.83435000	2.47844500	0.15459100
C	2.57785700	2.42522000	0.97275800
C	1.35639100	2.21011700	0.44812000
C	1.14169600	2.06514800	-1.00458000
C	2.36020500	2.26344700	-1.88985100
C	3.66030800	1.82061000	-1.21708100
H	4.65796900	2.00514700	0.71521600
H	4.13092800	3.54060000	0.04540200
H	2.67295600	2.57814400	2.05371200
H	0.46778500	2.16272600	1.07785800
H	0.65701700	-1.14705000	-1.24322400
H	2.18130300	1.73915500	-2.84006600
H	2.39906700	3.34505000	-2.12356100
H	4.52342700	2.04530700	-1.86233000
H	3.61316900	0.73028900	-1.08464600
O	0.03096200	1.86656400	-1.47586900
O	-0.29583800	-1.24656000	-1.67971200
O	-0.42992500	-2.46509800	0.92992500
C	2.41823500	-1.45616100	1.91442800
S	2.49264200	-2.10823200	0.23020800
C	4.28491200	-2.03617100	-0.02466900
H	1.35079200	-1.44761600	2.15879900

H	2.96835300	-2.13015100	2.58540900
H	2.84175600	-0.44297200	1.91365800
H	4.75819700	-2.79423300	0.61521200
H	4.45853900	-2.27099400	-1.08280300
H	4.64978300	-1.02836200	0.21440600

6. References

(1) M. S. Yusubov, D. Y. Svitich, A. Yoshimura, V. N. Nemykin, V. V. Zhdankin *Chem. Commun.* **2013**, *49*, 11269.

(2) M. Uyanik, M. Akakura, K. Ishihara *J. Am. Chem. Soc.* **2009**, *131*, 251.

(3) E. Jecs, S. T. Diver *Org. Lett.* **2015**, *17*, 3510.

(4) L. M. Lima, P. Castro, A. L. Machado, C. A. M. Fraga, C. Lungnier, V. L. G. de Moraes, E. J. Barreiro *Bioorg. Med. Chem.* **2002**, *10*, 3067.

(5) I. Volchkov, D. Lee. *J. Am. Chem. Soc.* **2013**, *135*, 5324.

(6) S. Nagasawa, Y. Sasano, Y. Iwabuchi *Angew. Chem. Int. Ed.* **2016**, *55*, 13189.

(7) S. Pichlmair, M. de Lera Ruiz, K. Basu, L. A. Paquette *Tetrahedron* **2006**, *62*, 5178.

(8) G. L. Adams, P. J. Carroll, A. B. Smith III *J. Am. Chem. Soc.* **2013**, *135*, 519.

(9) O. R. Cromwell, J. Chung, Z. Guan *J. Am. Chem. Soc.* **2015**, *137*, 6492.

(10) W. Ding, L.-Q. Lu, Q.-Q. Zhou, Y. Wei, J.-R. Chen, W.-J. Xiao *J. Am. Chem. Soc.* **2017**, *139*, 63.

(11) Gaussian 09, Revision E.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, **2013**.

(12) (a) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648−5652. (b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B: Condens. Matter Mater. Phys.* **1988**, *37*, 785−789.

(13) S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104.

(14) S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* **2011**, *32*, 1456−1465.

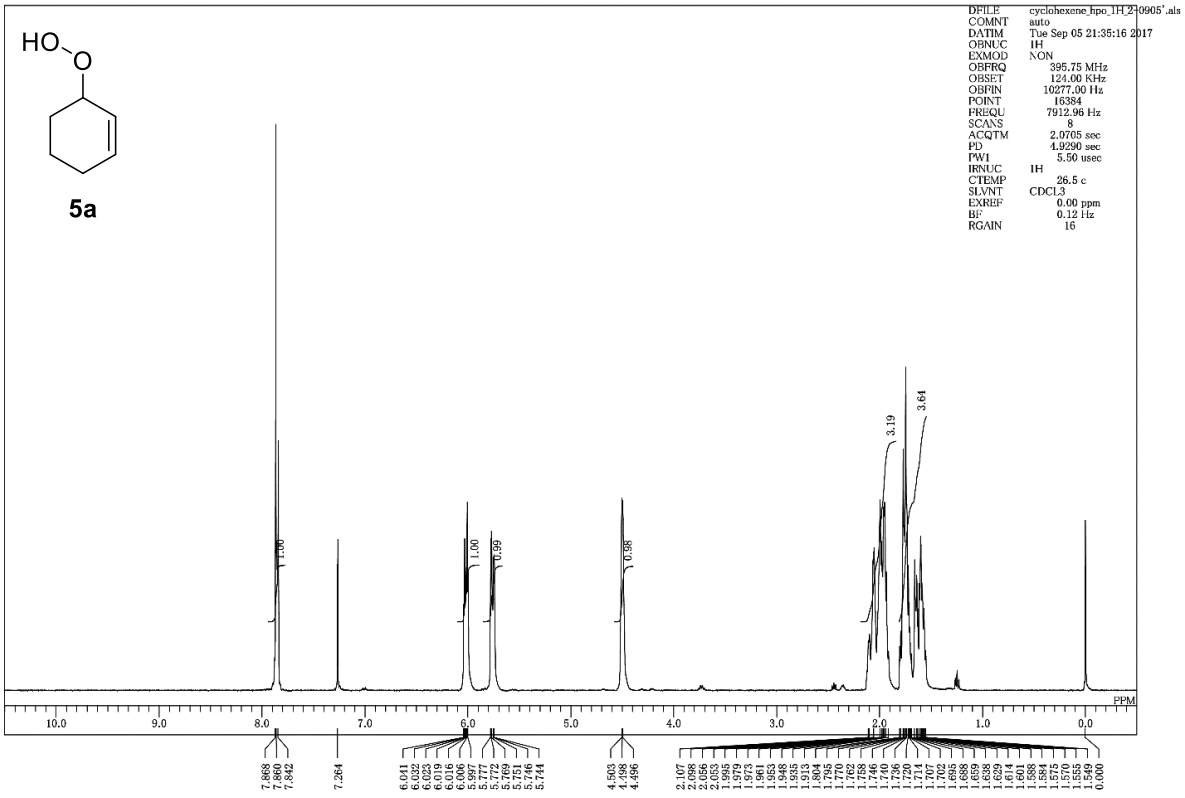
(15) F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305.

(16) Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.* **2008**, *120*, 215–241.

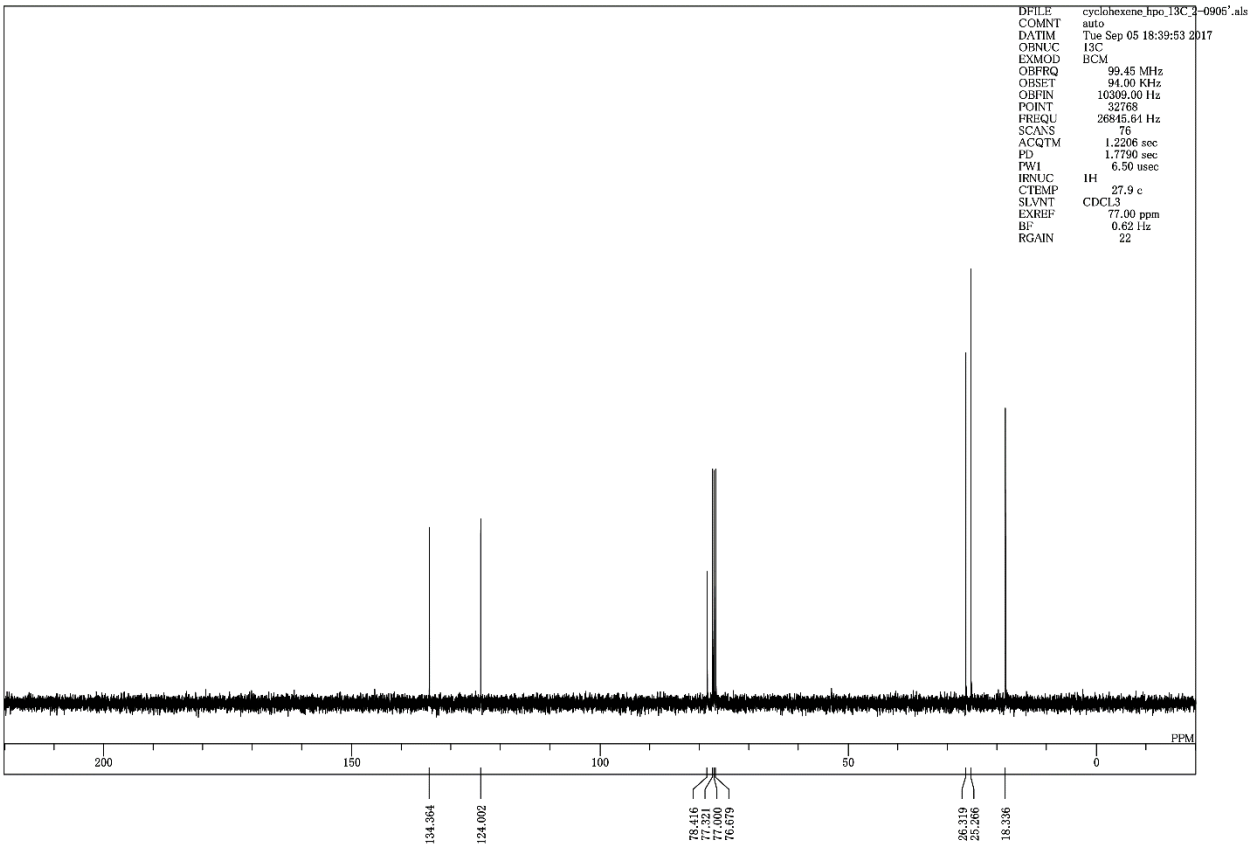
(17) J. Tomasi, B. Mennucci, R. Cammi, *Chem. Rev.* **2005**, *105*, 2999−3094.

7. ^{1}H and ^{13}C spectra

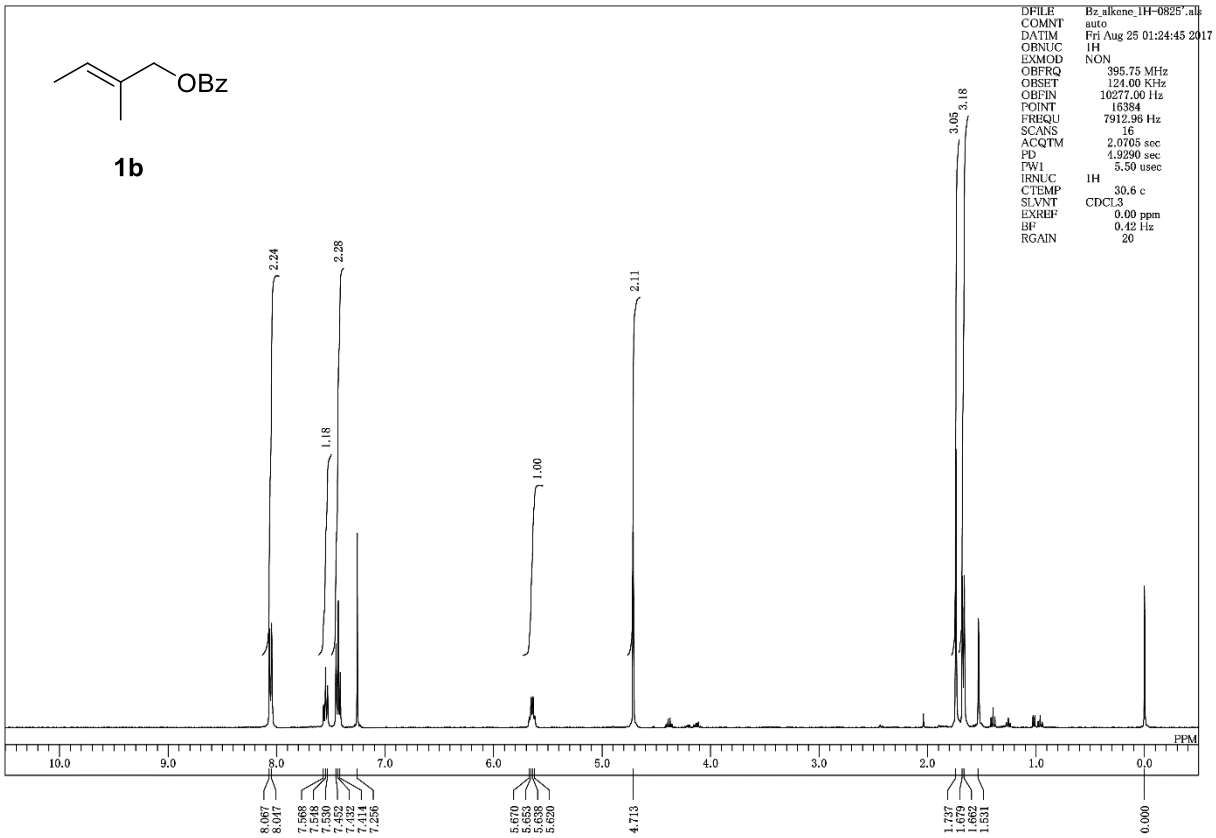
auto



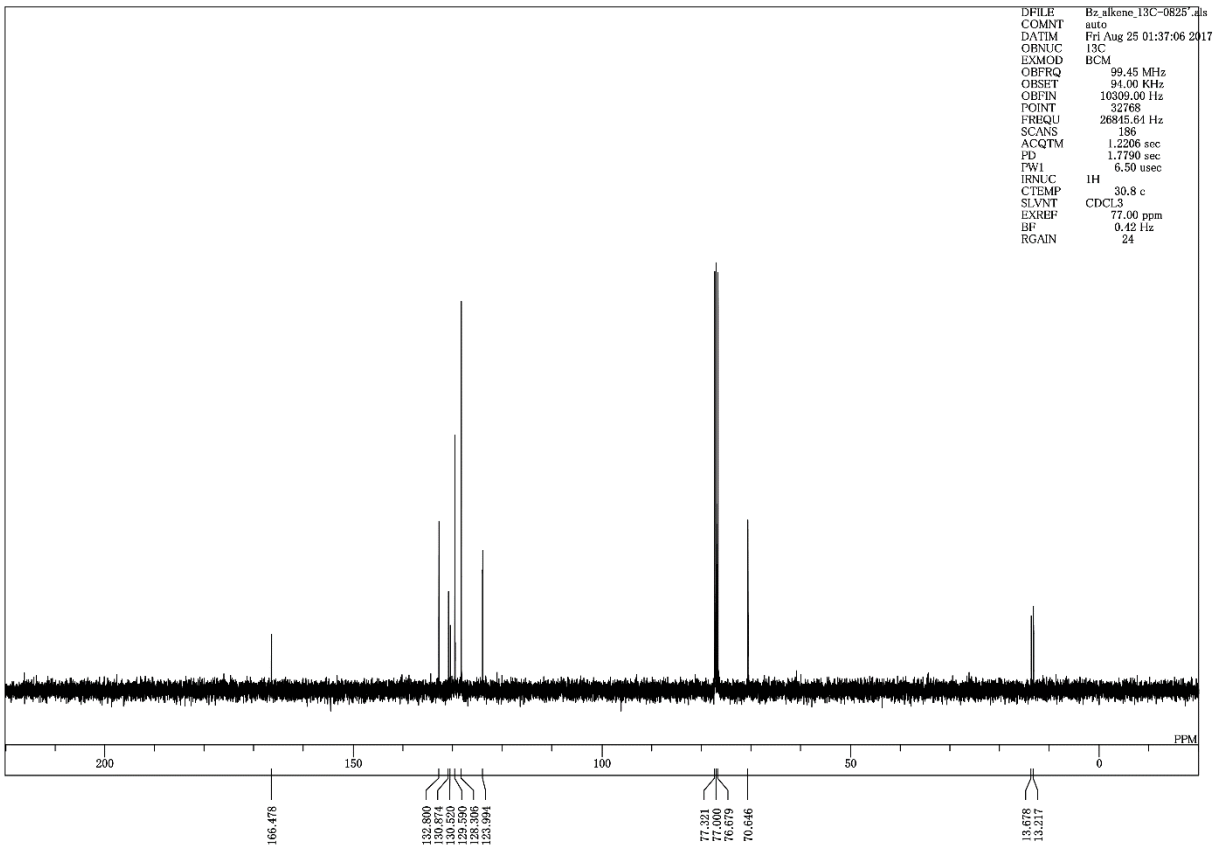
auto



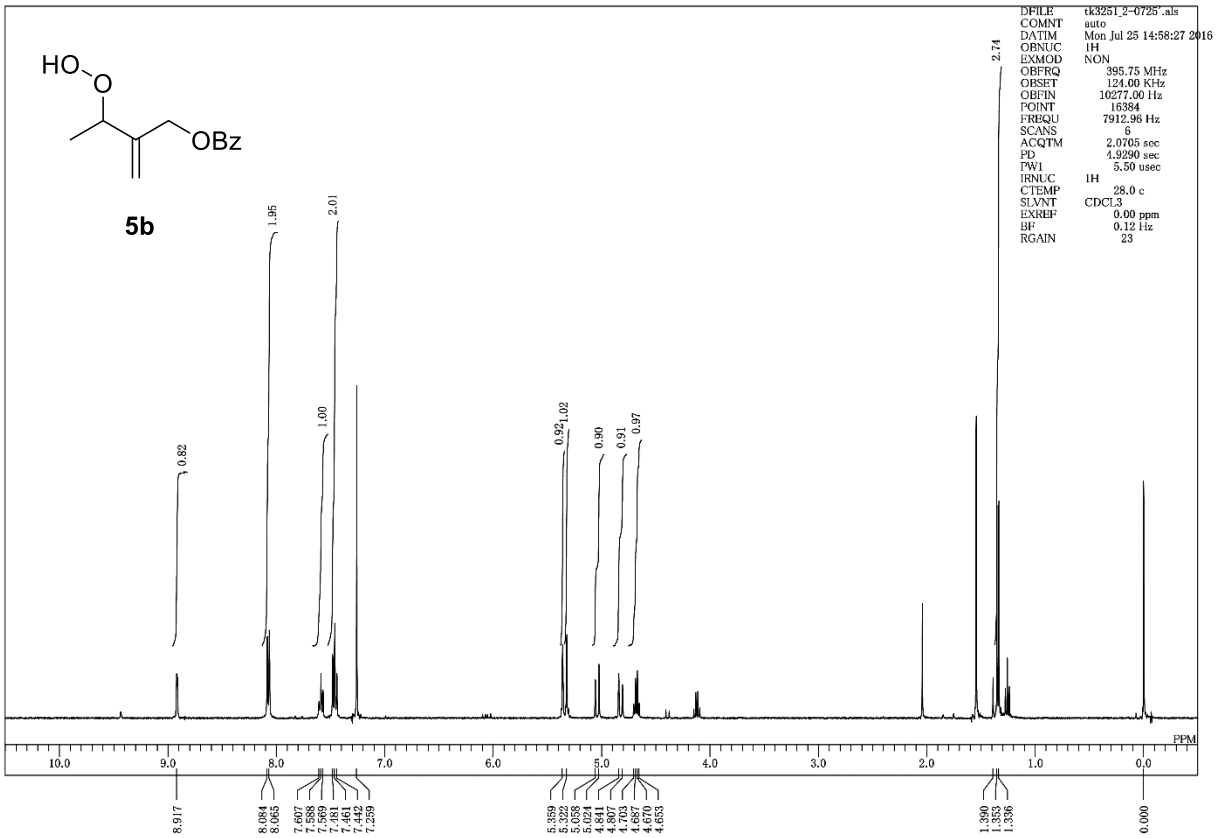
auto


OBz
1b
DFILE Bz_alkene_1H-0825'.als
COMNT auto
DATIM Fri Aug 25 01:24:45 2017
OBNUC 1H
EXMOD NON
OBFRQ 395.75 MHz
OBSET 124.00 KHz
OBFIN 10277.00 Hz
POINT 16384
FREQU 7912.96 Hz
SCANS 16
ACQTM 2.0705 sec
PD 4.9290 sec
PW1 5.50 usec
IRNUC 1H
CTEMP 30.6 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.42 Hz
RGAIN 20
2.24
2.28
1.18
1.00
2.11
3.05
3.18
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
8.067
8.047
7.568
7.548
7.530
7.462
7.432
7.414
7.256
5.670
5.653
5.638
5.620
4.713
1.737
1.679
1.662
1.531
0.000

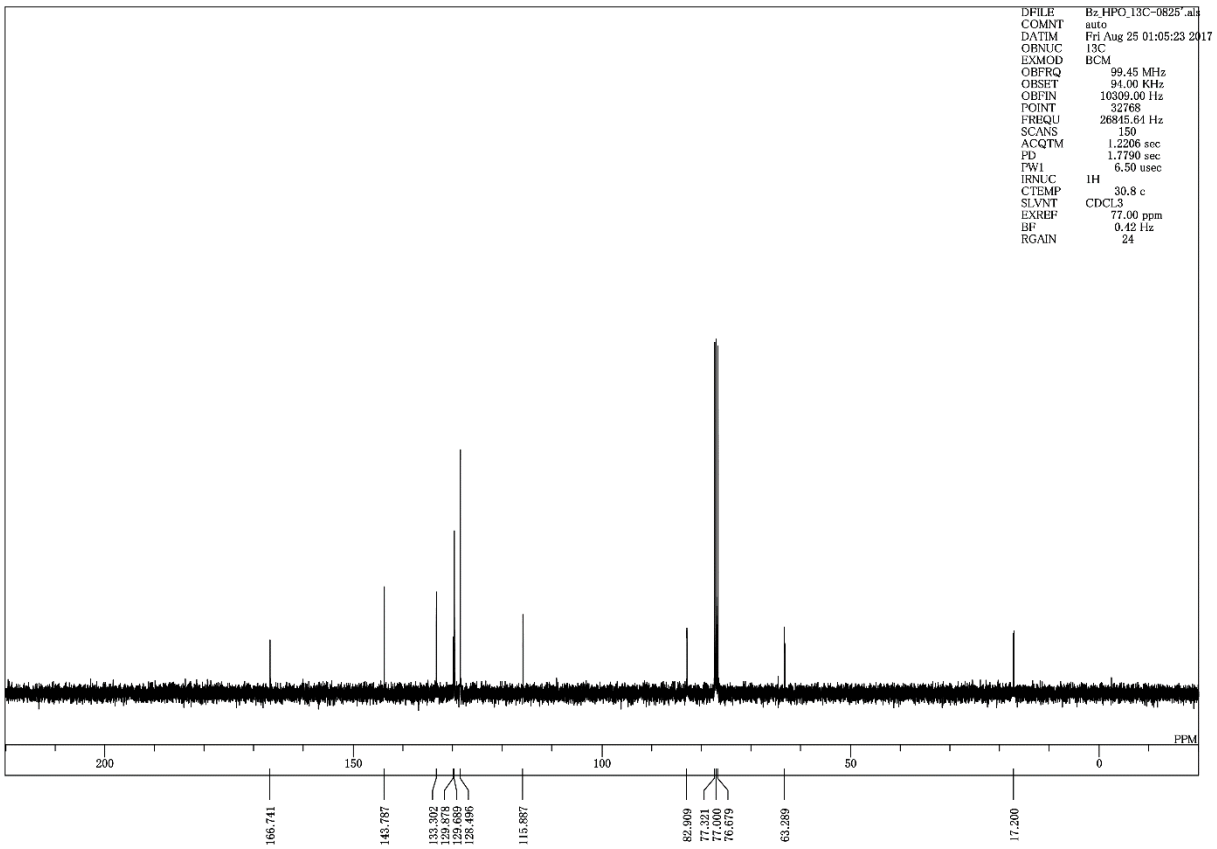
auto


DFILE Bz_alkene_13C-0825'.als
COMNT auto
DATIM Fri Aug 25 01:37:06 2017
OBNUC 13C
EXMOD BCM
OBFRQ 99.45 MHz
OBSET 94.00 KHz
OBFIN 10309.00 Hz
POINT 32768
FREQU 26845.64 Hz
SCANS 186
ACQTM 1.2206 sec
PD 1.7790 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 30.8 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.42 Hz
RGAIN 24
PPM
200
150
100
50
0
166.478
133.800
130.974
130.520
129.590
128.306
123.994
77.321
77.000
76.679
70.646
13.678
13.217

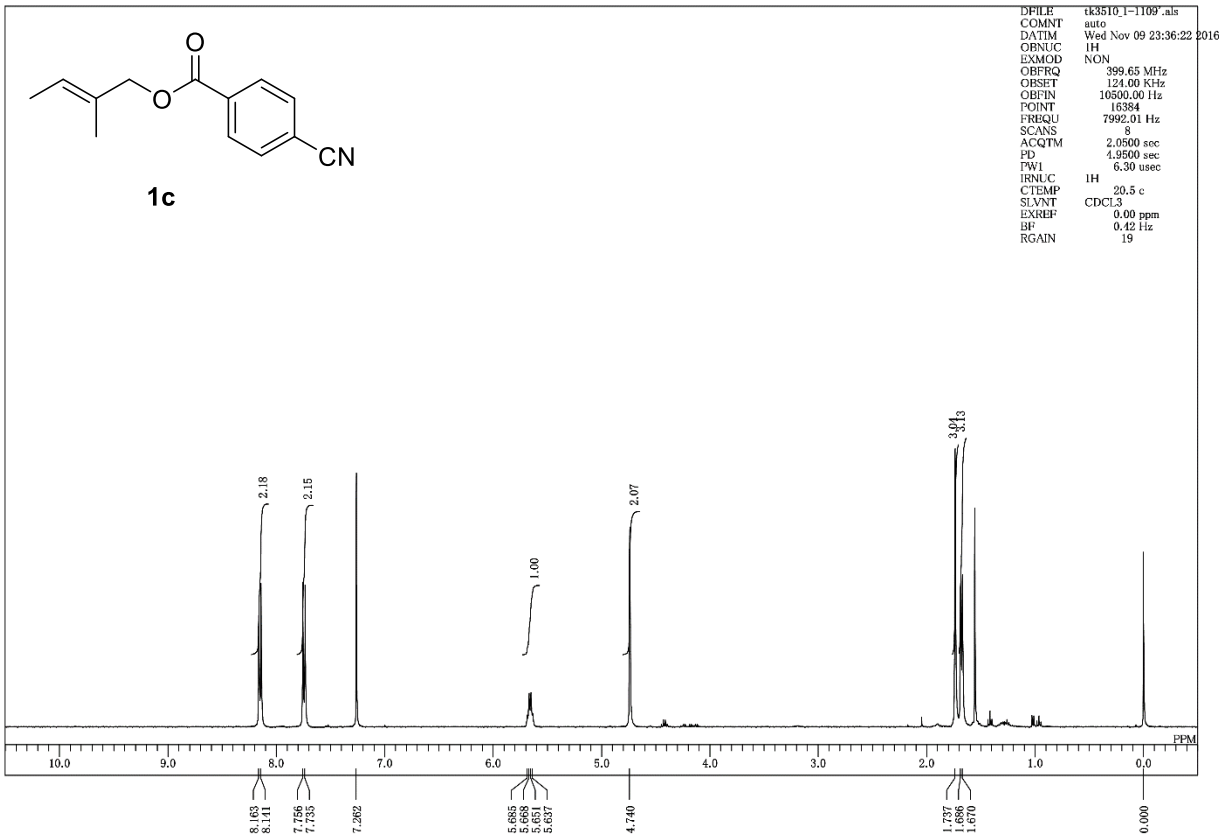
auto


HO
O
OBz
5b
DFILE tk3251_2-0725'.als
COMNT auto
DATIM Mon Jul 25 14:58:27 2016
OBNUC 1H
EXMOD NON
OBFRQ 395.75 MHz
OBSET 124.00 KHz
OBFIN 10277.00 Hz
POINT 16384
FREQU 7912.96 Hz
SCANS 6
ACQTM 2.0705 sec
PD 4.9290 sec
PW1 5.50 usec
IRNUC 1H
CTEMP 28.0 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 23
PPM

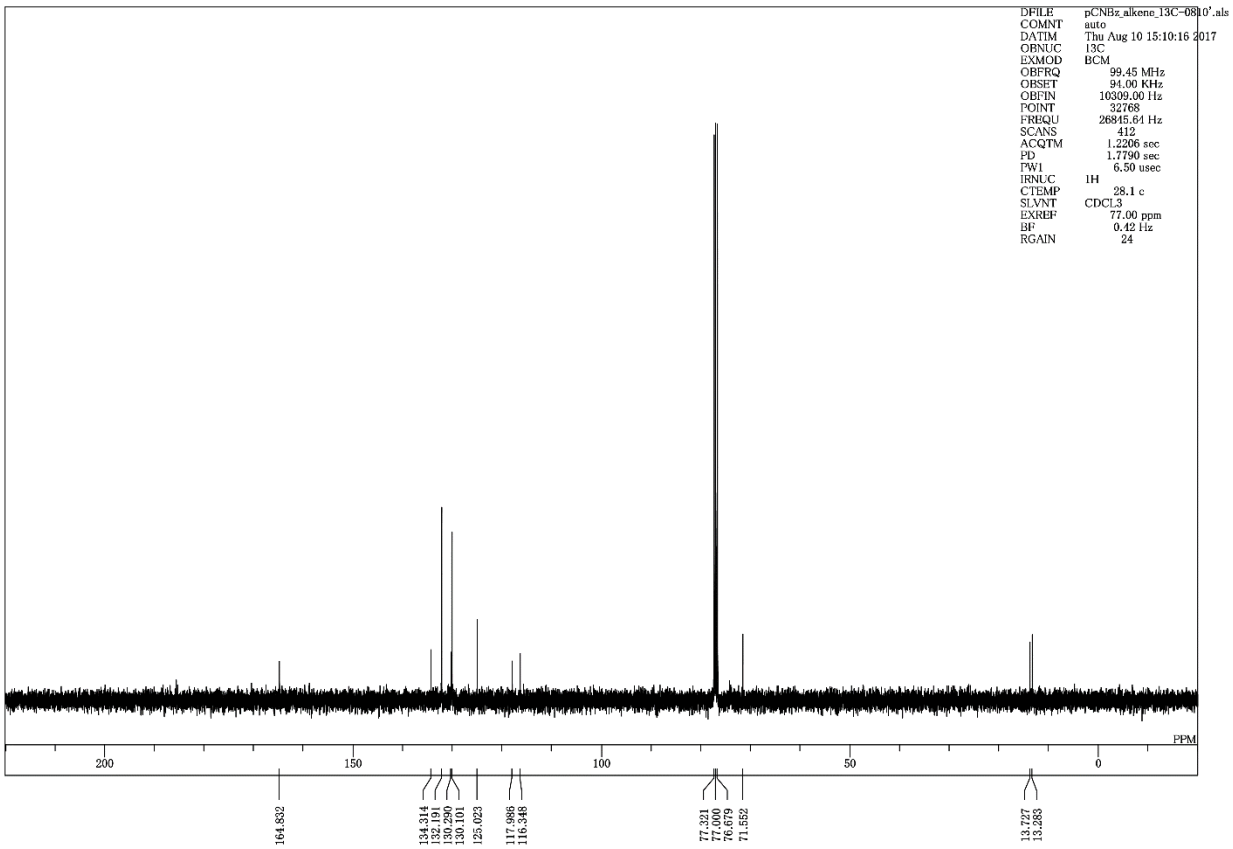
auto


DFILE Bz_HPO_13C-0825'.als
COMNT auto
DATIM Fri Aug 25 01:05:23 2017
OBNUC 13C
EXMOD BCM
OBFRQ 99.45 MHz
OBSET 94.00 KHz
OBFIN 10309.00 Hz
POINT 32768
FREQU 26845.64 Hz
SCANS 150
ACQTM 1.2206 sec
PD 1.7790 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 30.8 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.42 Hz
RGAIN 24
PPM

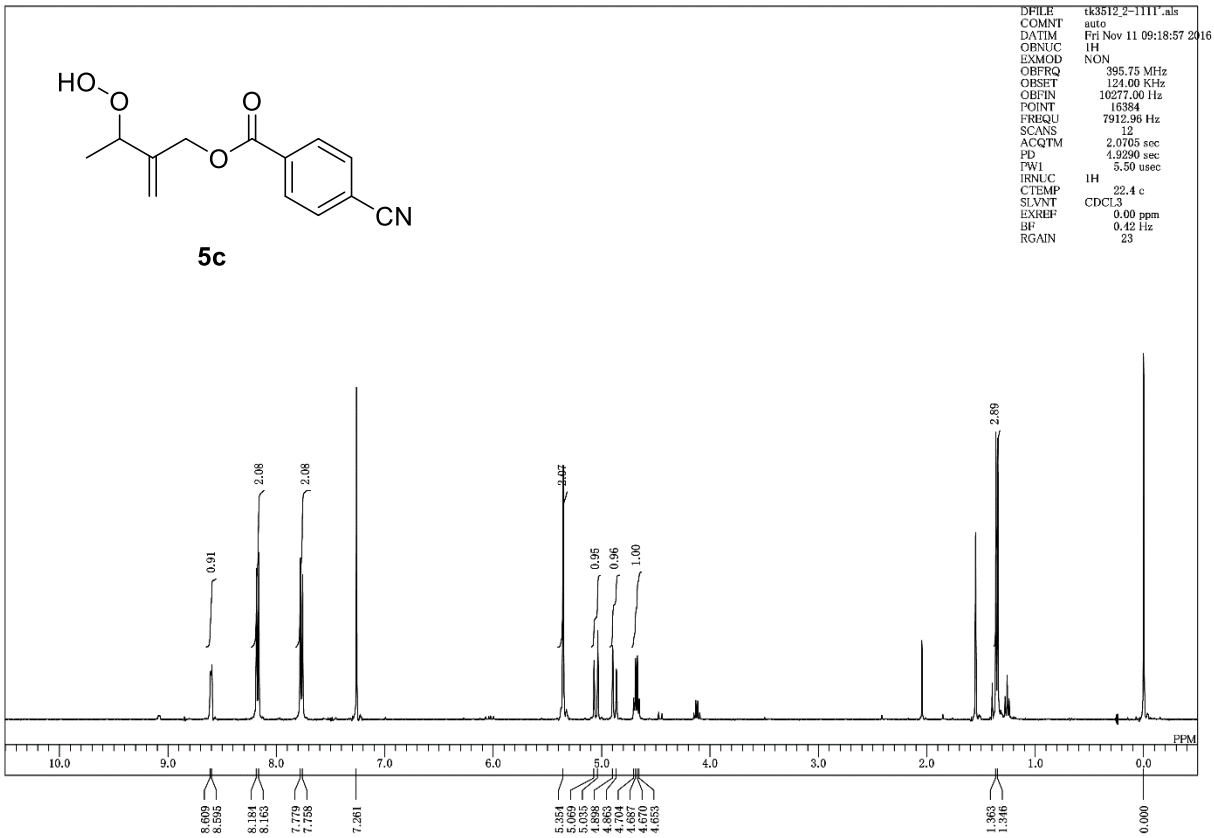
auto


O
O
CN
1c
DFILE tk3510_1-1109'.als
COMNT auto
DATIM Wed Nov 09 23:36:22 2016
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 16384
FREQU 7992.01 Hz
SCANS 8
ACQTM 2.0500 sec
PD 4.9500 sec
PW1 6.30 usec
IRNUC 1H
CTEMP 20.5 c
SLVNT CDCl3
EXREF 0.00 ppm
BF 0.42 Hz
RGAIN 19
2.18
2.15
1.00
2.07
3.04
3.13
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
8.163
8.141
7.756
7.735
7.282
5.655
5.648
5.643
5.637
4.740
1.737
1.686
1.670
0.000

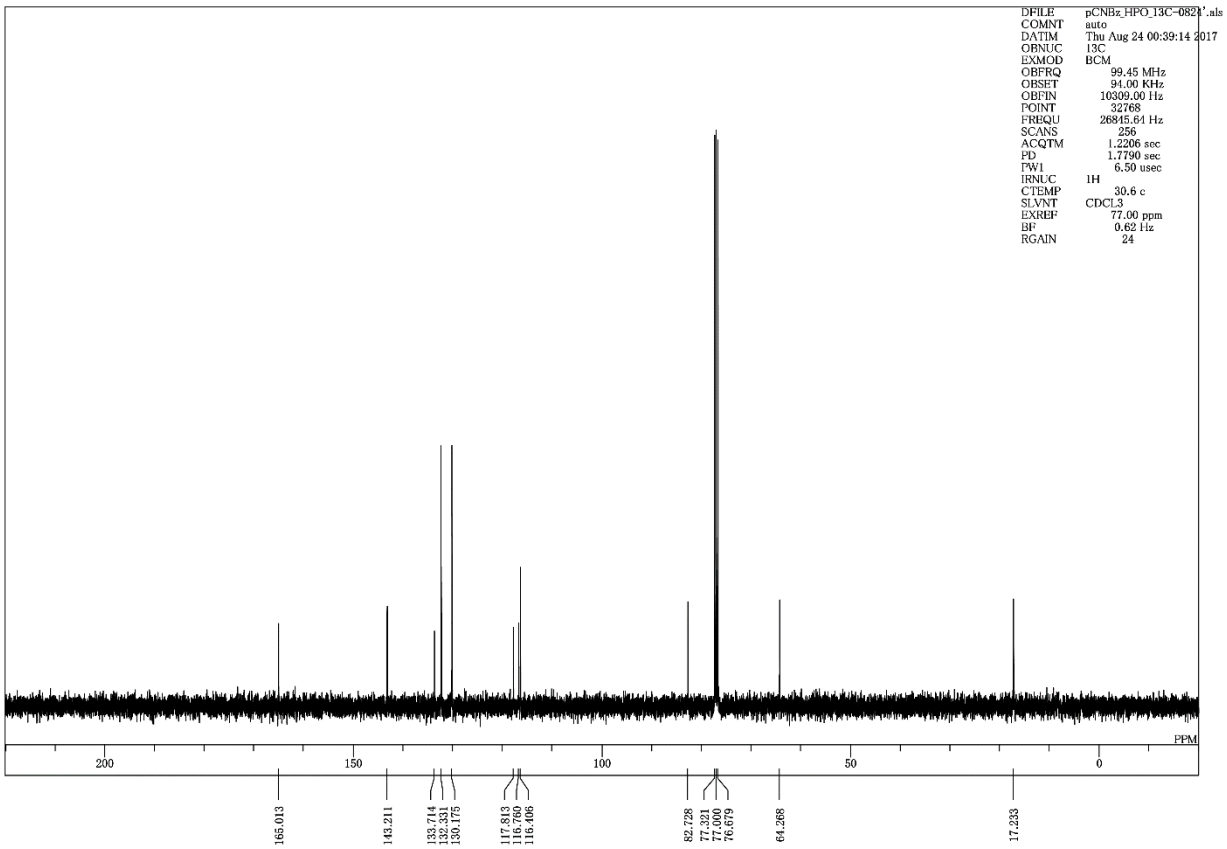
auto


DFILE pCNBz_alkene_13C-0810'.als
COMNT auto
DATIM Thu Aug 10 15:10:16 2017
OBNUC 13C
EXMOD BCM
OBFRQ 99.45 MHz
OBSET 94.00 KHz
OBFIN 10309.00 Hz
POINT 32768
FREQU 26845.64 Hz
SCANS 412
ACQTM 1.2206 sec
PD 1.7790 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 28.1 c
SLVNT CDCl3
EXREF 77.00 ppm
BF 0.42 Hz
RGAIN 24
PPM
200
150
100
50
0
164.832
134.314
132.191
130.290
130.101
125.023
117.998
116.348
77.321
77.000
76.679
71.552
13.727
13.283

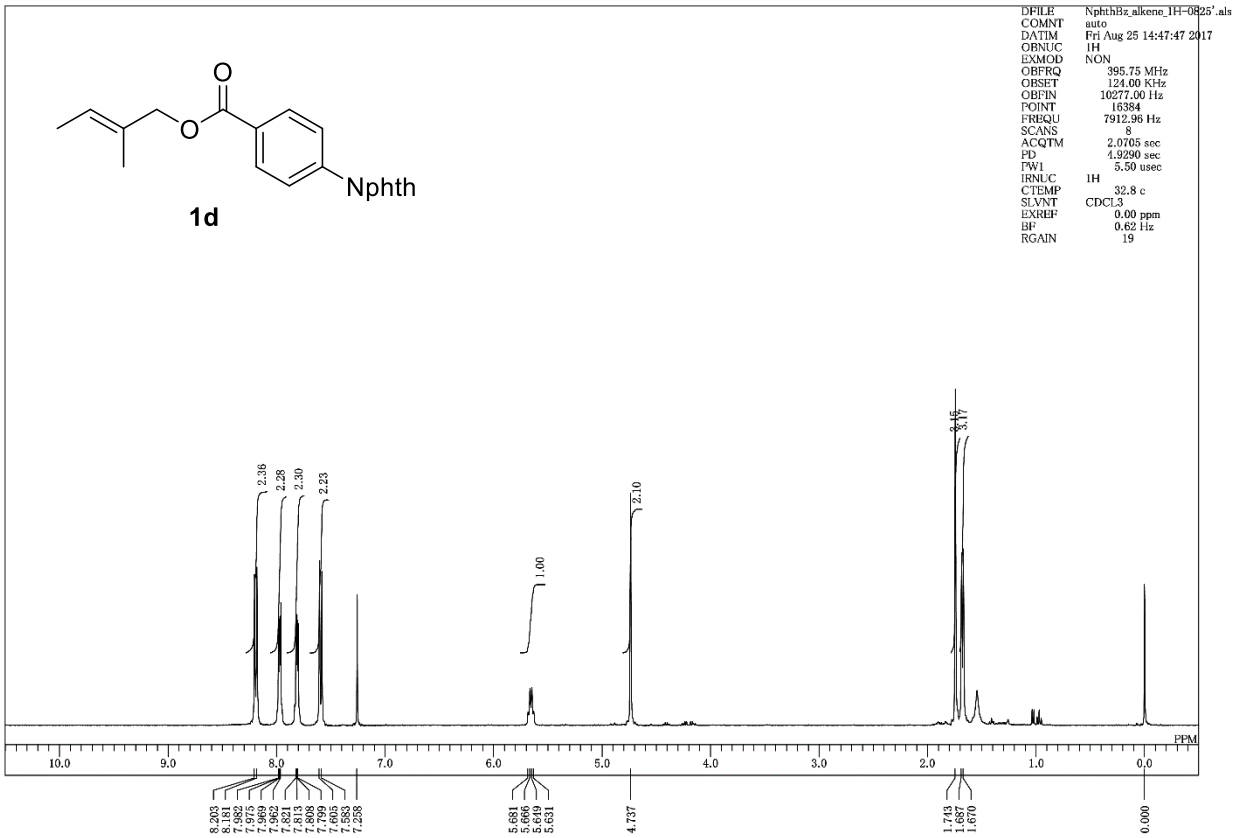
auto


HO
O
O
O
CN
5c
DFILE tk3512_2-1111'.als
COMNT auto
DATIM Fri Nov 11 09:18:57 2016
OBNUC 1H
EXMOD NON
OBFRQ 395.75 MHz
OBSET 124.00 KHz
OBFIN 10277.00 Hz
POINT 16384
FREQU 7912.96 Hz
SCANS 12
ACQTM 2.0705 sec
PD 4.9290 sec
PW1 5.50 usec
IRNUC 1H
CTEMP 22.4 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.42 Hz
RGAIN 23
0.91
2.08
2.08
2.07
0.95
0.96
1.00
2.89
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
8.609
8.595
8.184
8.163
7.779
7.758
7.261
5.354
5.069
5.035
4.898
4.885
4.704
4.687
4.670
4.653
1.363
1.346
0.000

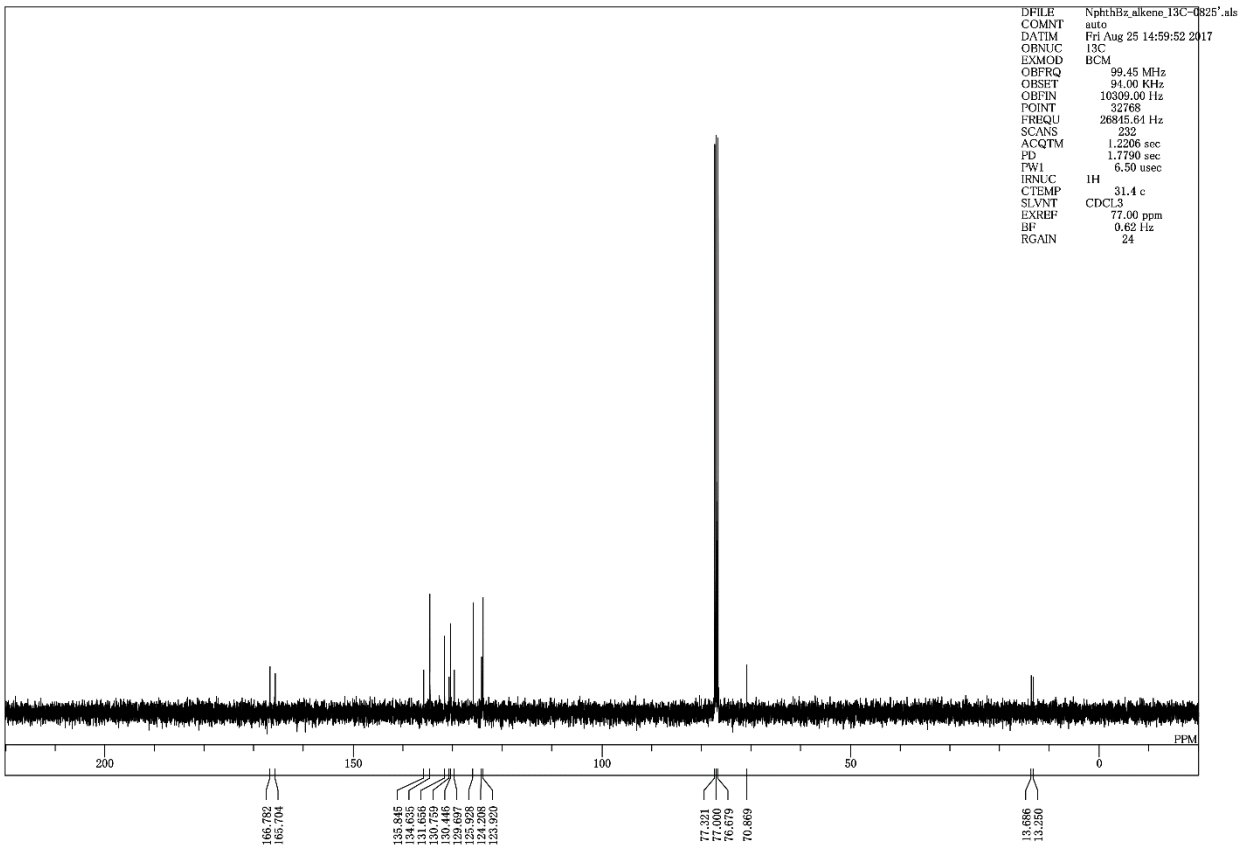
auto


DFILE pCNBz_HPO_13C-0823'.als
COMNT auto
DATIM Thu Aug 24 00:39:14 2017
OBNUC 13C
EXMOD BCM
OBFRQ 99.45 MHz
OBSET 94.00 KHz
OBFIN 10309.00 Hz
POINT 32768
FREQU 26845.64 Hz
SCANS 256
ACQTM 1.2206 sec
PD 1.7790 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 30.6 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.62 Hz
RGAIN 24
PPM
200
150
100
50
0
165.013
143.211
133.714
132.331
130.175
117.813
116.760
116.406
82.728
77.321
77.000
76.679
64.268
17.233

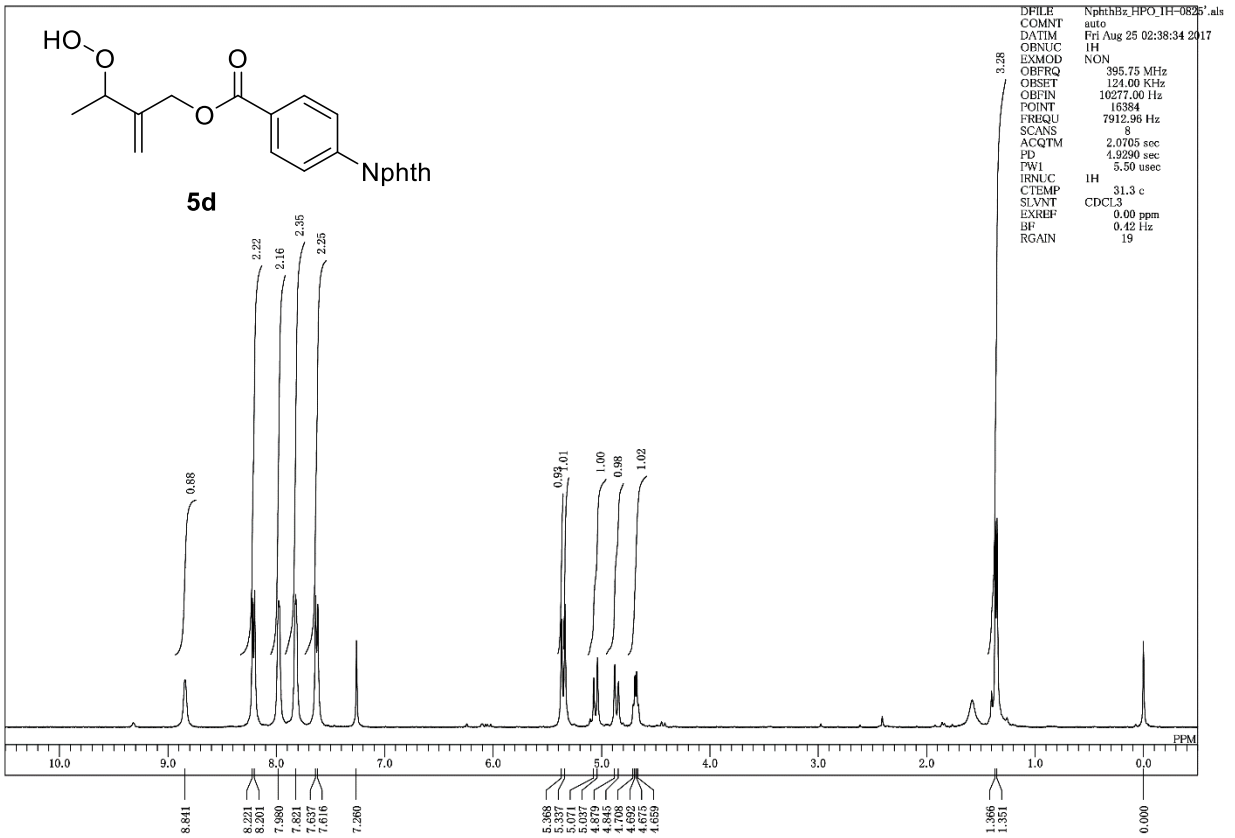
auto


DFILE NphthBz_alkene_1H-0825'.als
COMNT auto
DATIM Fri Aug 25 14:47:47 2017
OBNUC 1H
EXMOD NON
OBFRQ 395.75 MHz
OBSET 124.00 KHz
OBFIN 10277.00 Hz
POINT 16384
FREQU 7912.96 Hz
SCANS 8
ACQTM 2.0705 sec
PD 4.9290 sec
PW1 5.50 usec
IRNUC 1H
CTEMP 32.8 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.62 Hz
RGAIN 19
O
O
Nphth
1d
2.36
2.28
2.30
2.23
1.00
2.10
3.16
3.17
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
8.203
8.181
7.982
7.975
7.969
7.962
7.821
7.815
7.808
7.799
7.605
7.583
7.238
5.681
5.666
5.649
5.631
4.737
1.713
1.687
1.670
0.000

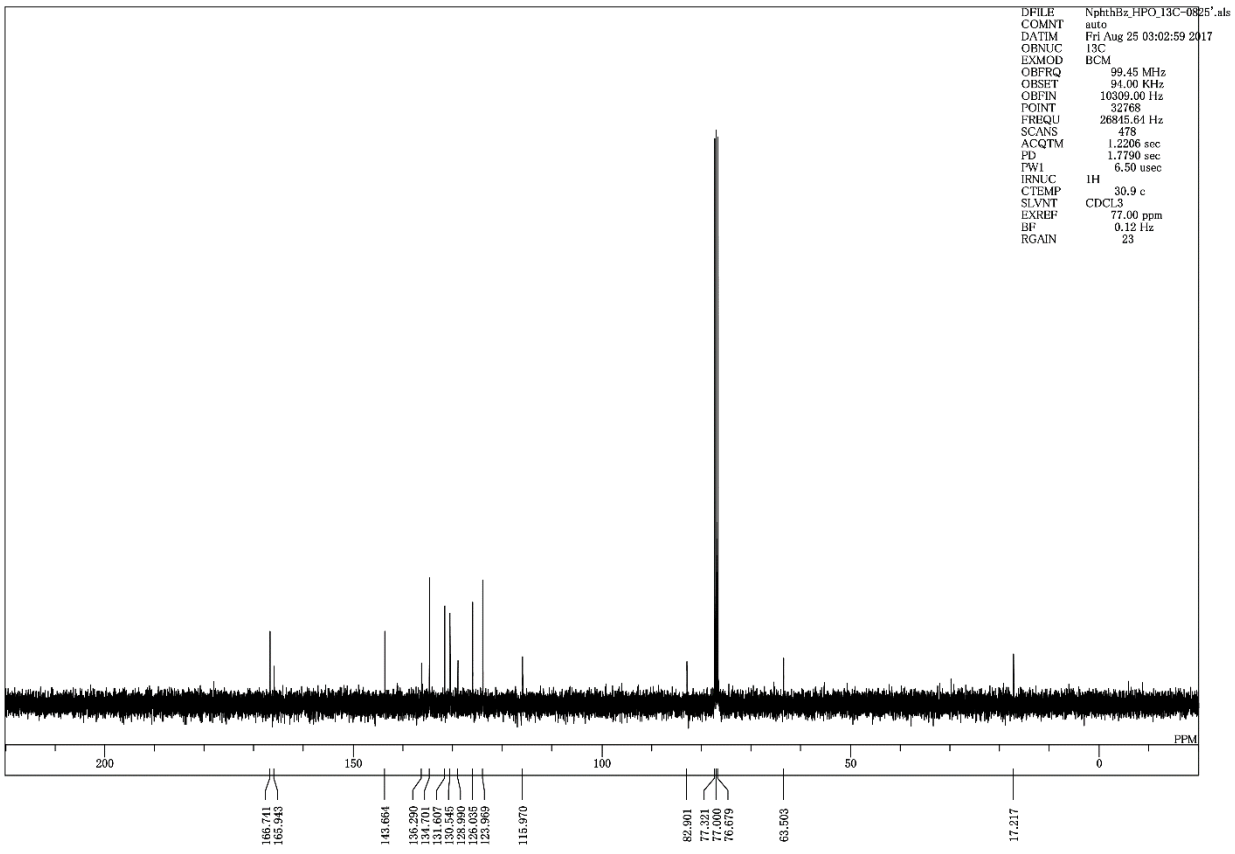
auto


DFILE NphthBz_alkene_13C-0825'.als
COMNT auto
DATIM Fri Aug 25 14:59:52 2017
OBNUC 13C
EXMOD BCM
OBFRQ 99.45 MHz
OBSET 94.00 KHz
OBFIN 10309.00 Hz
POINT 32768
FREQU 26845.64 Hz
SCANS 232
ACQTM 1.2206 sec
PD 1.7790 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 31.4 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.62 Hz
RGAIN 24
PPM
200
150
100
50
0
166.782
165.704
135.845
134.635
131.656
130.759
130.446
129.697
125.928
124.266
123.920
77.321
77.000
76.679
70.869
13.686
13.250

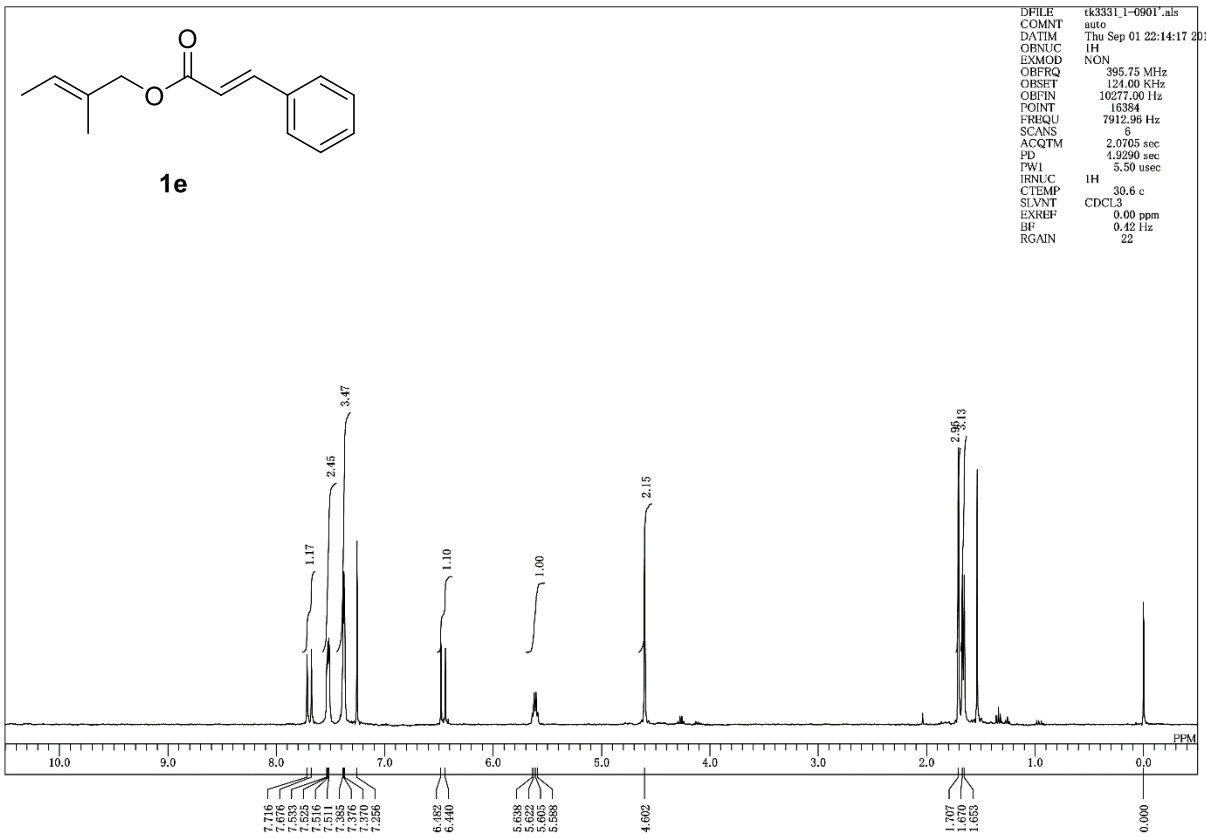
auto


HO
O
O
O
Nphth
5d
DFILE NphthBz_HPO_1H-0825'.als
COMNT auto
DATIM Fri Aug 25 02:38:34 2017
OBNUC 1H
EXMOD NON
OBFRQ 395.75 MHz
OBSET 124.00 KHz
OBFIN 10277.00 Hz
POINT 16384
FREQU 7912.96 Hz
SCANS 8
ACQTM 2.0705 sec
PD 4.9290 sec
PW1 5.50 usec
IRNUC 1H
CTEMP 31.3 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.42 Hz
RGAIN 19
0.88
2.22
2.16
2.35
2.25
0.93
1.01
1.00
0.98
1.02
3.28
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
8.841
8.221
8.201
7.980
7.821
7.637
7.616
7.280
5.368
5.337
5.071
5.037
4.879
4.845
4.708
4.692
4.675
4.659
1.366
1.351
0.000

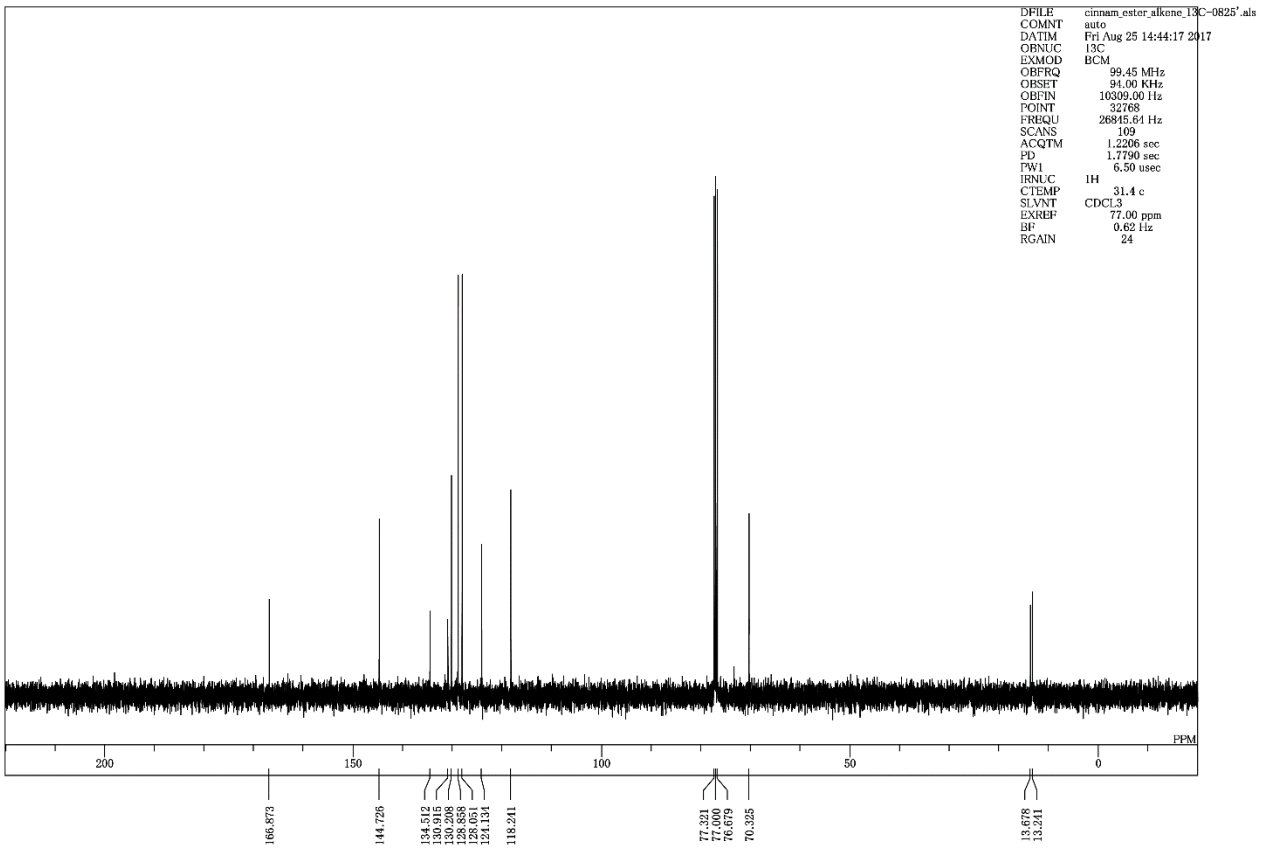
auto


DFILE NphthBz_HPO_13C-0825'.als
COMNT auto
DATIM Fri Aug 25 03:02:59 2017
OBNUC 13C
EXMOD BCM
OBFRQ 99.45 MHz
OBSET 94.00 KHz
OBFIN 10309.00 Hz
POINT 32768
FREQU 26845.64 Hz
SCANS 478
ACQTM 1.2206 sec
PD 1.7790 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 30.9 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 23
PPM
200
150
100
50
0
166.711
165.943
143.664
136.290
134.770
131.607
130.545
128.990
126.035
123.969
115.970
82.901
77.321
77.000
76.679
63.503
17.217

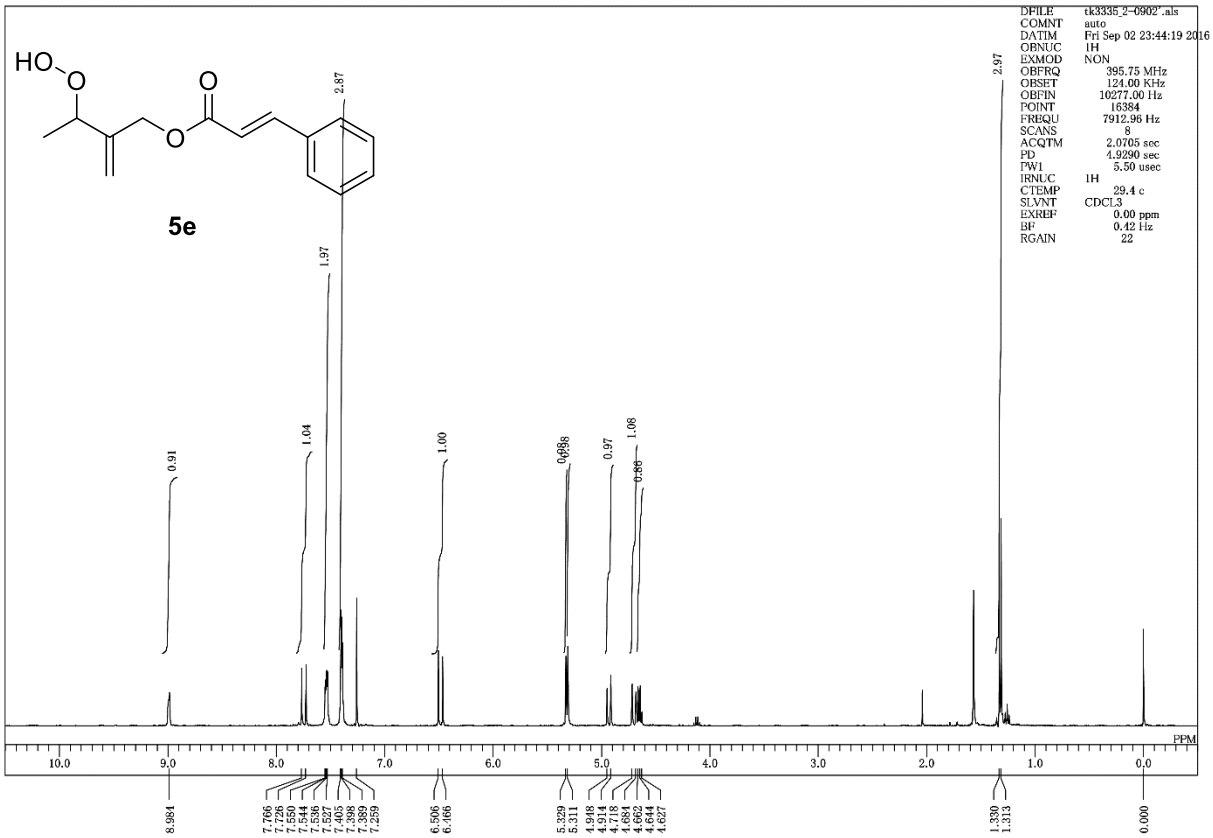
auto


1e
DFILE tk3331_1-0901'.als
COMNT auto
DATIM Thu Sep 01 22:14:17 2016
OBNUC 1H
EXMOD NON
OBFRQ 395.75 MHz
OBSET 124.00 KHz
OBFIN 10277.00 Hz
POINT 16384
FREQU 7912.96 Hz
SCANS 6
ACQTM 2.0705 sec
PD 4.9290 sec
PW1 5.50 usec
IRNUC 1H
CTEMP 30.6 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.42 Hz
RGAIN 22
1.17
2.45
3.47
1.10
1.00
2.15
2.95
3.13
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.716
7.676
7.533
7.523
7.516
7.511
7.381
7.376
7.370
7.256
6.482
6.440
5.638
5.622
5.603
5.588
4.602
1.707
1.670
1.653
0.000

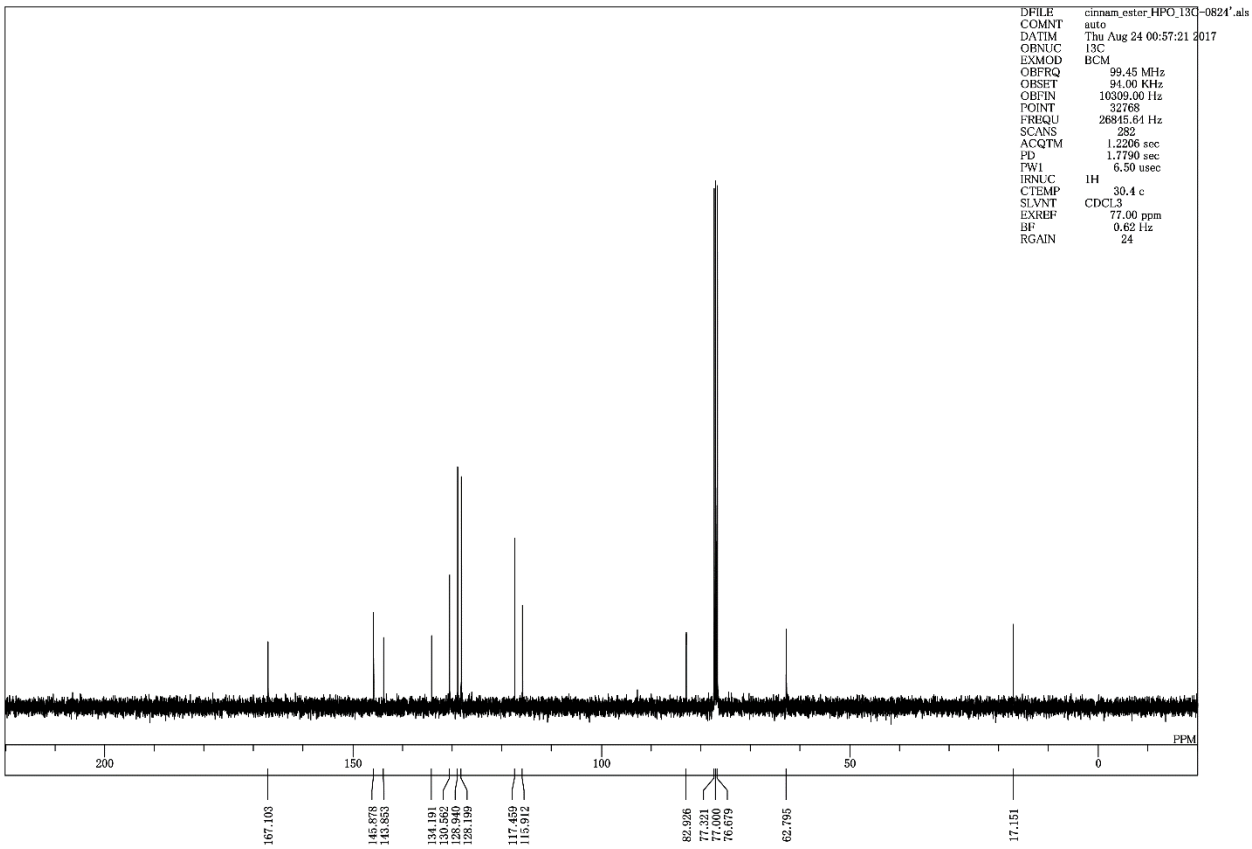
auto


DFILE cinnam_ester_alkene_13C-0825'.als
COMNT auto
DATIM Fri Aug 25 14:44:17 2017
OBNUC 13C
EXMOD BCM
OBFRQ 99.45 MHz
OBSET 94.00 KHz
OBFIN 10309.00 Hz
POINT 32768
FREQU 26845.61 Hz
SCANS 109
ACQTM 1.2206 sec
PD 1.7790 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 31.4 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.62 Hz
RGAIN 24
PPM
200
150
100
50
0
166.873
144.726
134.512
130.915
130.208
128.858
128.051
124.134
118.241
77.321
77.000
76.679
70.325
13.678
13.241

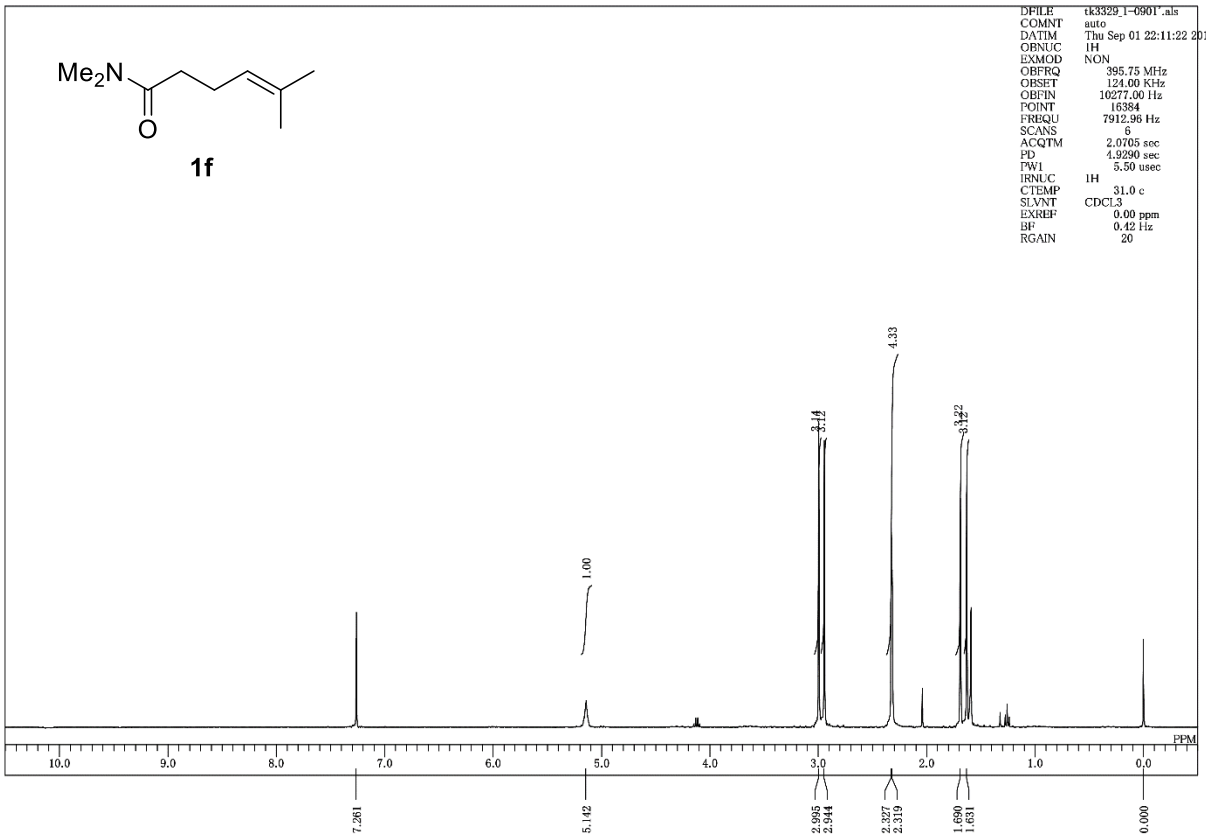
auto


HO
O
O
O
2.87
5e
DFILE tk3335_2-0902'.als
COMNT auto
DATIM Fri Sep 02 23:44:19 2016
OBNUC 1H
EXMOD NON
OBFRQ 395.75 MHz
OBSET 124.00 KHz
OBFIN 10277.00 Hz
POINT 16384
FREQU 7912.96 Hz
SCANS 8
ACQTM 2.0705 sec
PD 4.9290 sec
PW1 5.50 usec
IRNUC 1H
CTEMP 29.4 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.42 Hz
RGAIN 22
0.91
1.04
1.97
1.00
0.98
0.97
1.06
0.88
2.97
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
8.984
7.766
7.726
7.550
7.544
7.536
7.527
7.405
7.398
7.389
7.259
6.506
6.466
5.329
5.311
4.948
4.914
4.718
4.684
4.662
4.644
4.627
1.330
1.313
0.000

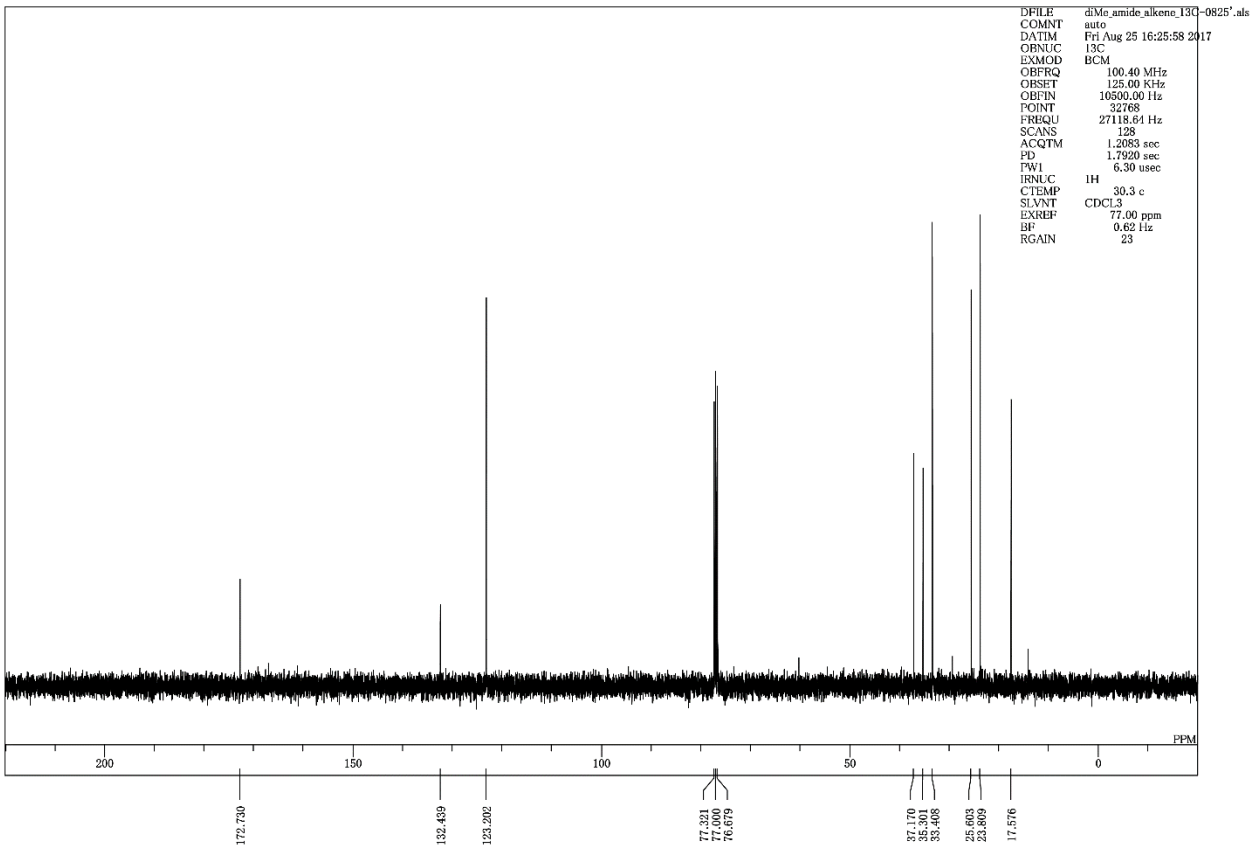
auto


DFILE cinnam_ester_HPO_13C-0824'.als
COMNT auto
DATIM Thu Aug 24 00:57:21 2017
OBNUC 13C
EXMOD BCM
OBFRQ 99.45 MHz
OBSET 94.00 KHz
OBFIN 10309.00 Hz
POINT 32768
FREQU 26845.61 Hz
SCANS 282
ACQTM 1.2206 sec
PD 1.7790 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 30.4 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.62 Hz
RGAIN 24
PPM
200
150
100
50
0
167.103
145.878
143.853
134.191
130.562
128.940
128.199
117.459
115.912
82.926
77.321
77.000
76.679
62.795
17.151

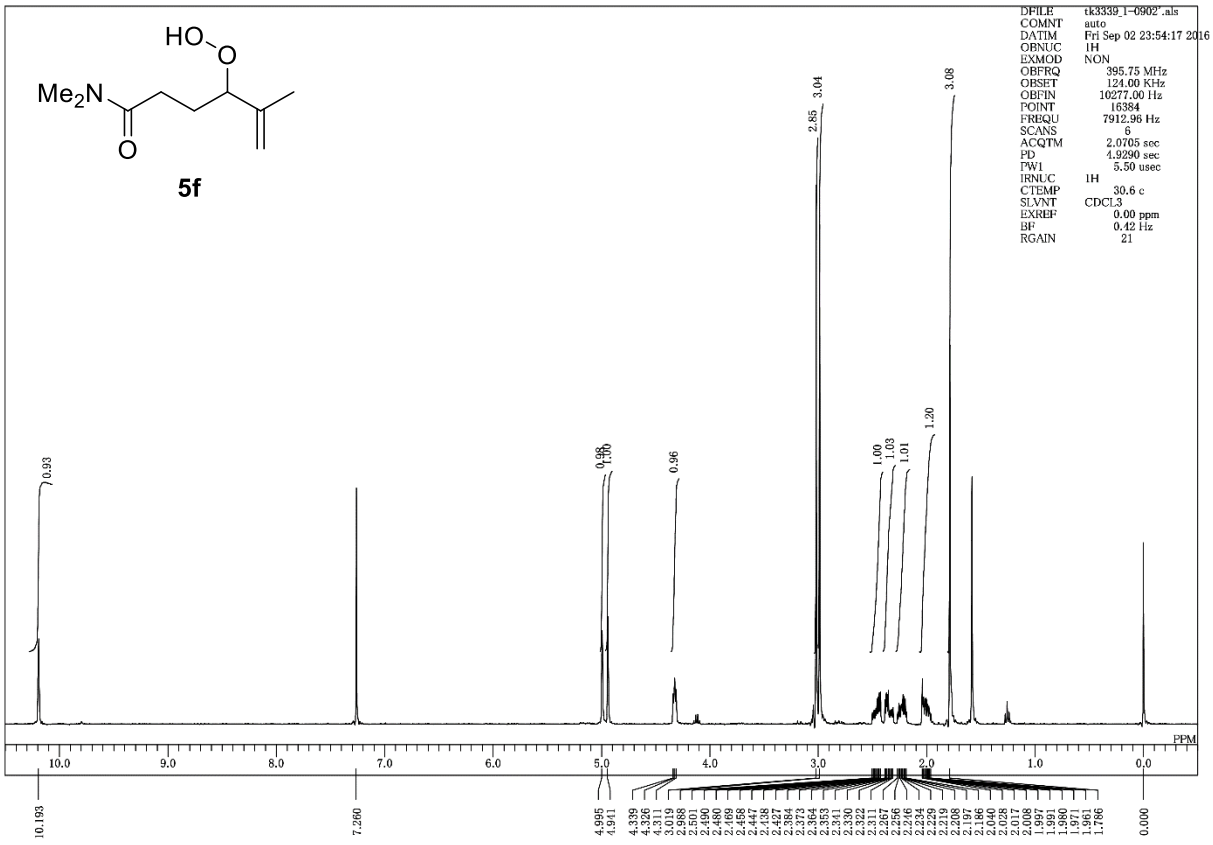
auto


Me2N
O
1f
DFILE tk3329_1-0901'.als
COMNT auto
DATIM Thu Sep 01 22:11:22 2016
OBNUC 1H
EXMOD NON
OBFRQ 395.75 MHz
OBSET 124.00 KHz
OBFIN 10277.00 Hz
POINT 16384
FREQU 7912.96 Hz
SCANS 6
ACQTM 2.0705 sec
PD 4.9290 sec
PW1 5.50 usec
IRNUC 1H
CTEMP 31.0 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.42 Hz
RGAIN 20
1.00
3.14
3.12
4.33
3.22
3.12
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.261
5.142
2.995
2.944
2.327
2.319
1.690
1.631
0.000

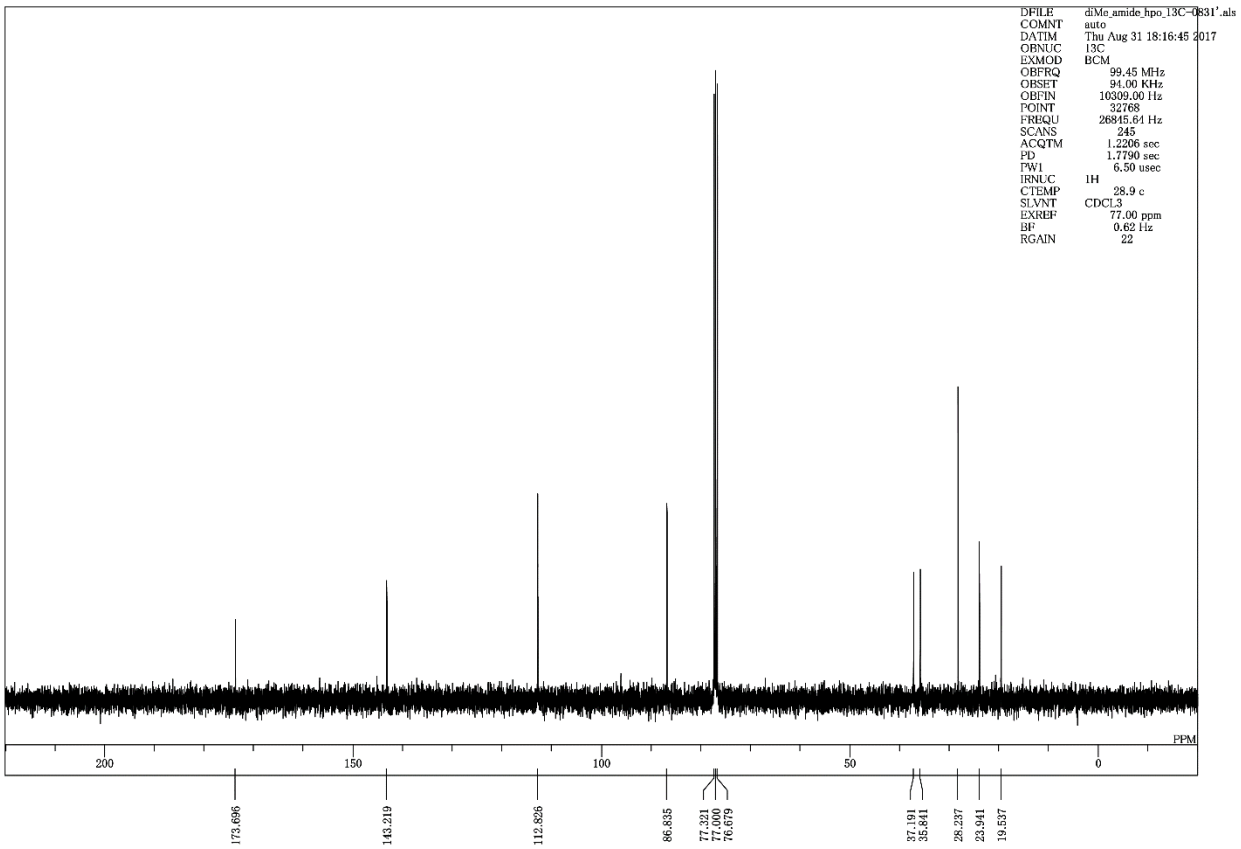
auto


DFILE diMe_amide_alkene_13C-0825'.als
COMNT auto
DATIM Fri Aug 25 16:25:58 2017
OBNUC 13C
EXMOD BCM
OBFRQ 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27118.64 Hz
SCANS 128
ACQTM 1.2083 sec
PD 1.7920 sec
PW1 6.30 usec
IRNUC 1H
CTEMP 30.3 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.62 Hz
RGAIN 23
PPM
200
150
100
50
0
172.730
132.439
123.292
77.321
77.000
76.679
37.170
35.301
33.408
25.603
23.809
17.576

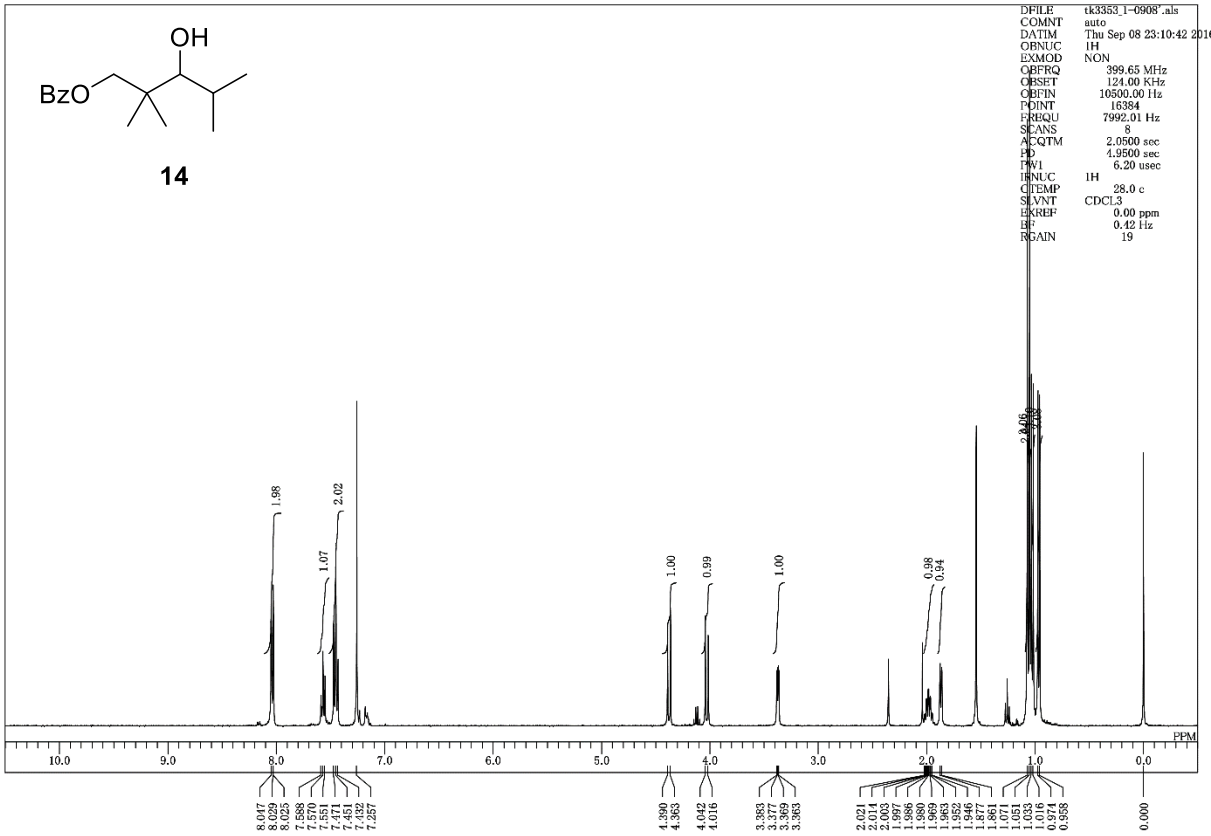
auto


HO
O
Me2N
O
5f
DFILE tk3339_1-0902'.als
COMNT auto
DATIM Fri Sep 02 23:54:17 2016
OBNUC 1H
EXMOD NON
OBFRQ 395.75 MHz
OBSET 124.00 KHz
OBFIN 10277.00 Hz
POINT 16384
FREQU 7912.96 Hz
SCANS 6
ACQTM 2.0705 sec
PD 4.9290 sec
PW1 5.50 usec
IRNUC 1H
CTEMP 30.6 c
SLVNT CDCl3
EXREF 0.00 ppm
BF 0.42 Hz
RGAIN 21
0.93
0.98
1.00
0.96
2.85
3.04
3.08
1.00
1.03
1.01
1.20
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
10.193
7.260
4.995
4.941
4.339
4.326
4.311
3.019
2.988
2.501
2.480
2.469
2.458
2.447
2.438
2.427
2.384
2.373
2.364
2.353
2.341
2.330
2.322
2.311
2.267
2.256
2.246
2.234
2.229
2.218
2.208
2.197
2.186
2.040
2.028
2.017
1.997
1.991
1.980
1.971
1.961
1.786
0.000

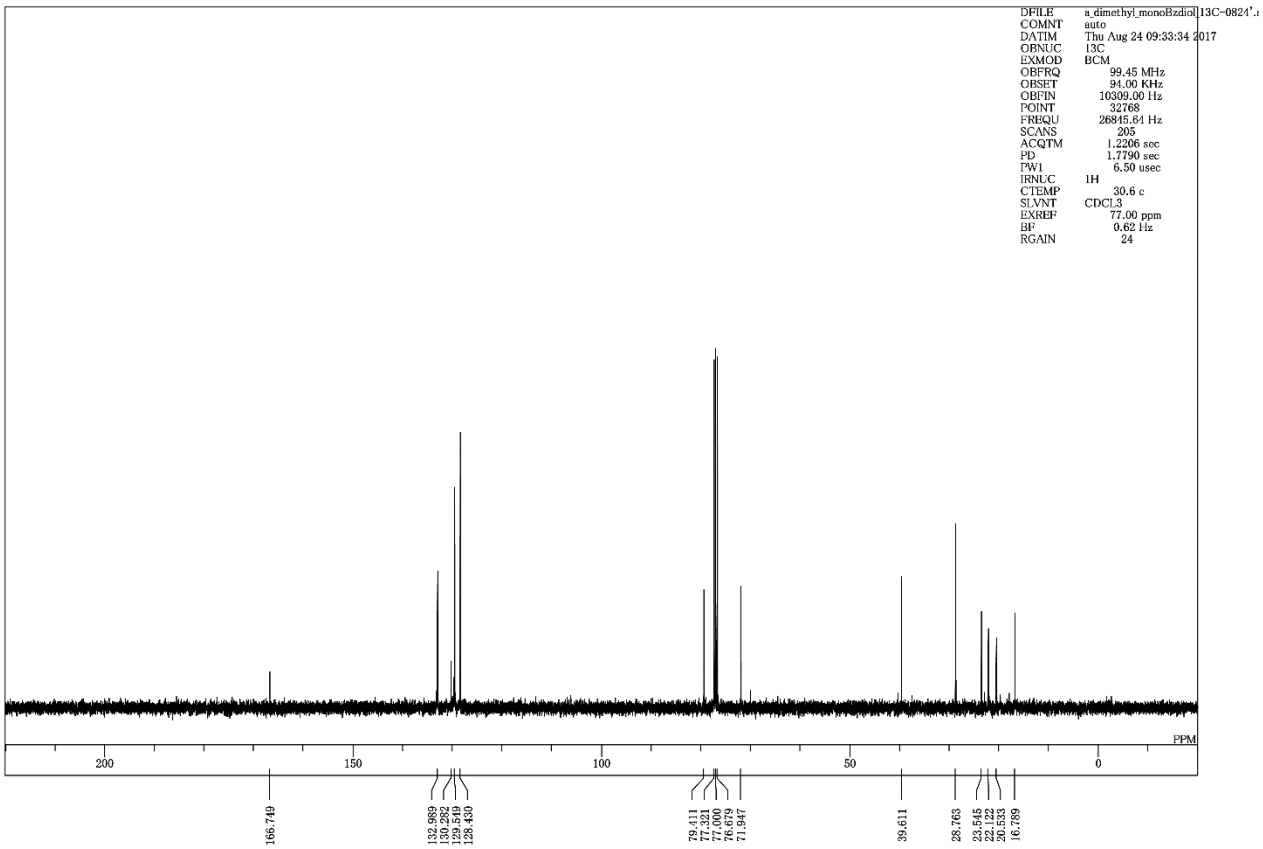
auto


DFILE diMe_amide_hpo_13C-0831'.als
COMNT auto
DATIM Thu Aug 31 18:16:45 2017
OBNUC 13C
EXMOD BCM
OBFRQ 99.45 MHz
OBSET 94.00 KHz
OBFIN 10309.00 Hz
POINT 32768
FREQU 26845.64 Hz
SCANS 245
ACQTM 1.2206 sec
PD 1.7790 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 28.9 c
SLVNT CDCl3
EXREF 77.00 ppm
BF 0.62 Hz
RGAIN 22
PPM
200
150
100
50
0
173.696
143.219
112.826
86.835
77.321
77.000
76.679
37.191
35.841
26.237
23.941
19.537

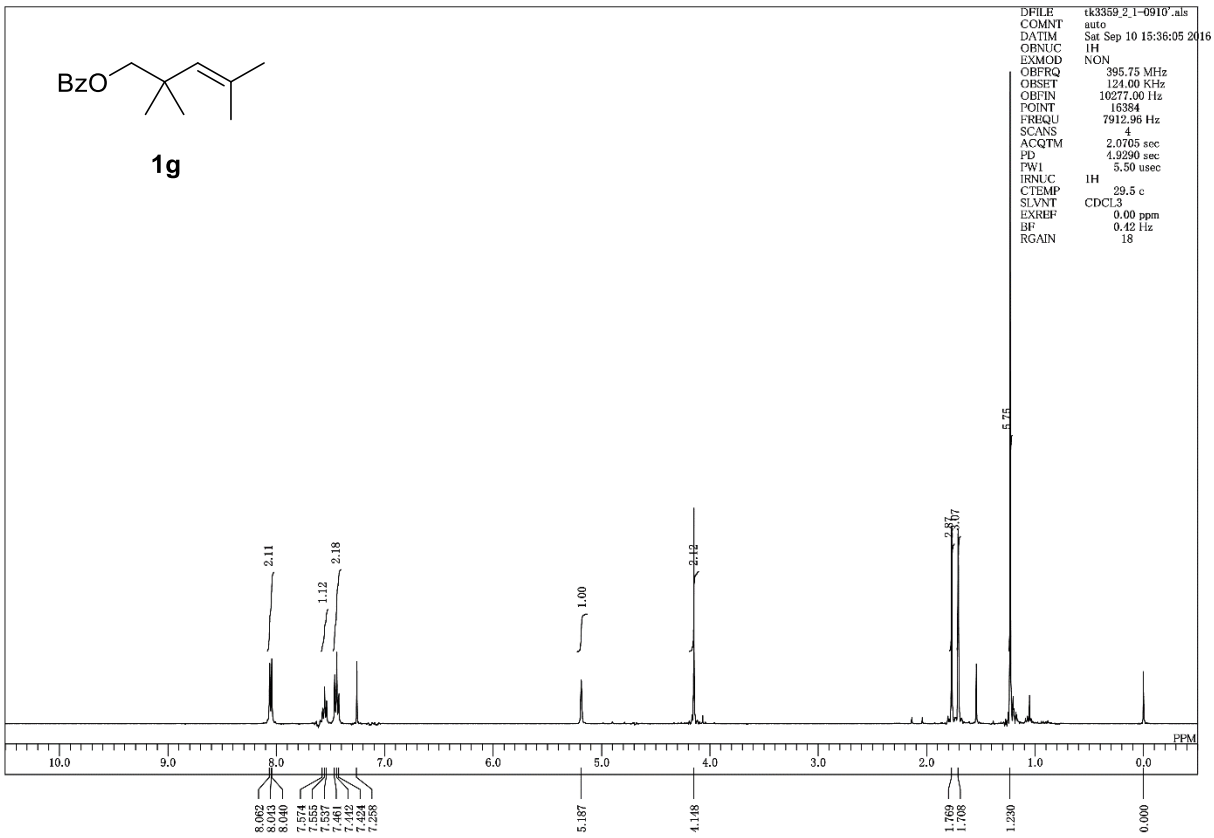
auto


OH
BzO
14
DFILE tk3353_1-0908'.als
COMNT auto
DATIM Thu Sep 08 23:10:42 2016
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 16384
FREQU 7992.01 Hz
SCANS 8
ACQTM 2.0500 sec
PD 4.9500 sec
PW1 6.20 usec
IRNUC 1H
CTEMP 28.0 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.42 Hz
RGAIN 19
1.98
2.02
1.07
1.00
0.99
1.00
0.98
0.94
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
8.047
8.029
8.023
7.588
7.570
7.551
7.471
7.451
7.432
7.257
4.390
4.383
4.042
4.016
3.383
3.377
3.369
3.363
2.021
2.011
2.003
1.997
1.986
1.980
1.963
1.953
1.946
1.877
1.861
1.071
1.051
1.038
1.025
0.974
0.958
0.000

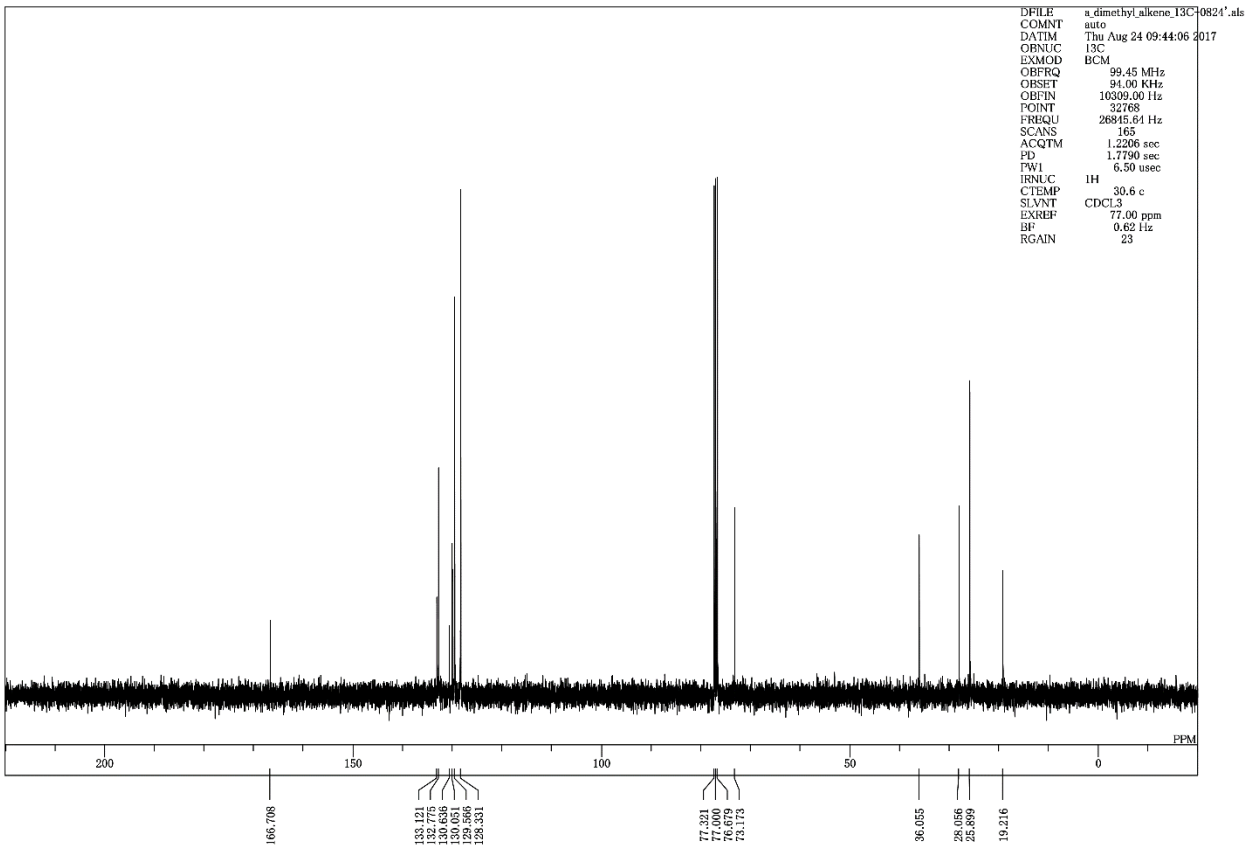
auto


DFILE a_dimethyl_monoBzdiol_13C-0824'.
COMNT auto
DATIM Thu Aug 24 09:33:34 2017
OBNUC 13C
EXMOD BCM
OBFRQ 99.45 MHz
OBSET 94.00 KHz
OBFIN 10309.00 Hz
POINT 32768
FREQU 26845.64 Hz
SCANS 205
ACQTM 1.2206 sec
PD 1.7790 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 30.6 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.62 Hz
RGAIN 24
PPM
200
150
100
50
0
166.749
132.989
130.282
129.549
128.430
79.411
77.203
77.000
76.679
71.947
39.611
28.763
23.545
22.122
20.533
16.789

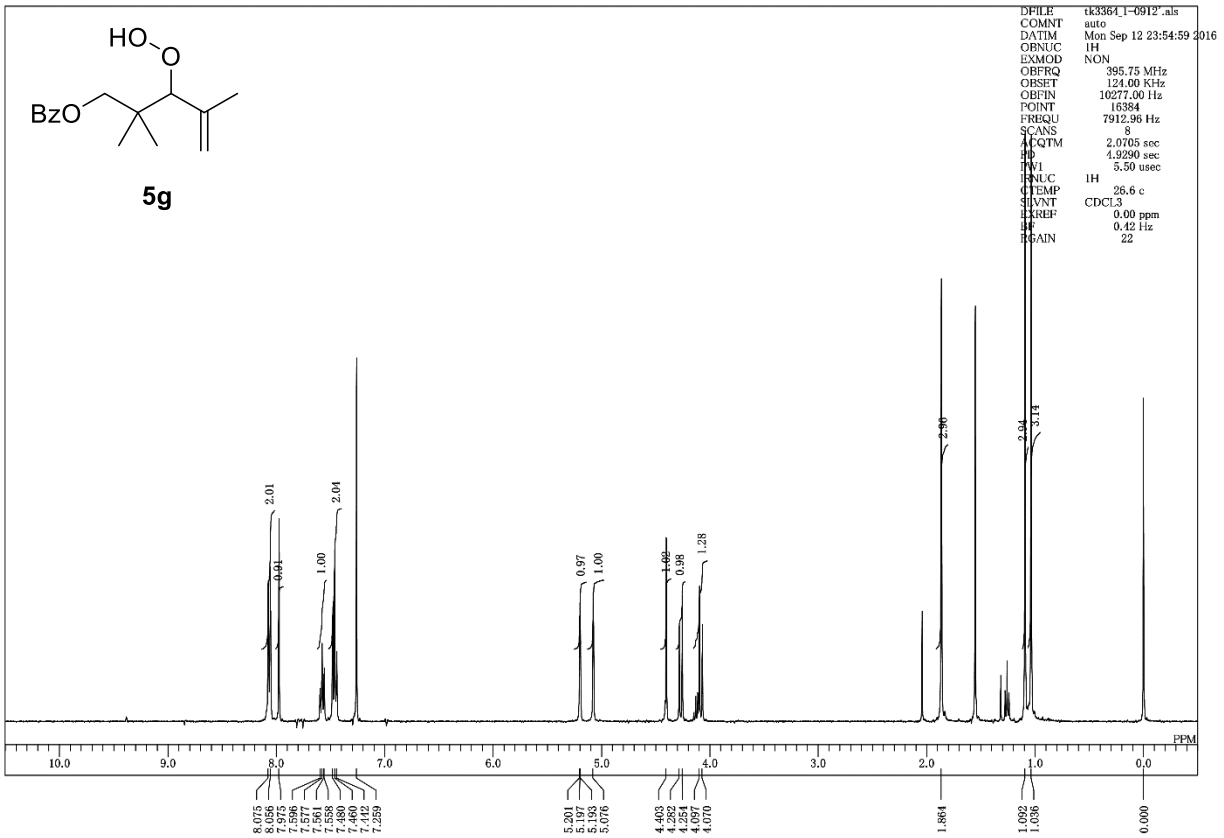
auto


BzO
1g
DFILE tk3359_2_1-0910'.als
COMNT auto
DATIM Sat Sep 10 15:36:05 2016
OBNUC 1H
EXMOD NON
OBFRQ 395.75 MHz
OBSET 124.00 KHz
OBFIN 10277.00 Hz
POINT 16384
FREQU 7912.96 Hz
SCANS 4
ACQTM 2.0705 sec
PD 4.9290 sec
PW1 5.50 usec
IRNUC 1H
CTEMP 29.5 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.42 Hz
RGAIN 18
2.11
1.12
2.18
1.00
2.12
2.87
3.07
5.75
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
8.062
8.043
8.040
7.574
7.555
7.537
7.461
7.442
7.424
7.258
5.187
4.148
1.769
1.708
1.230
0.000

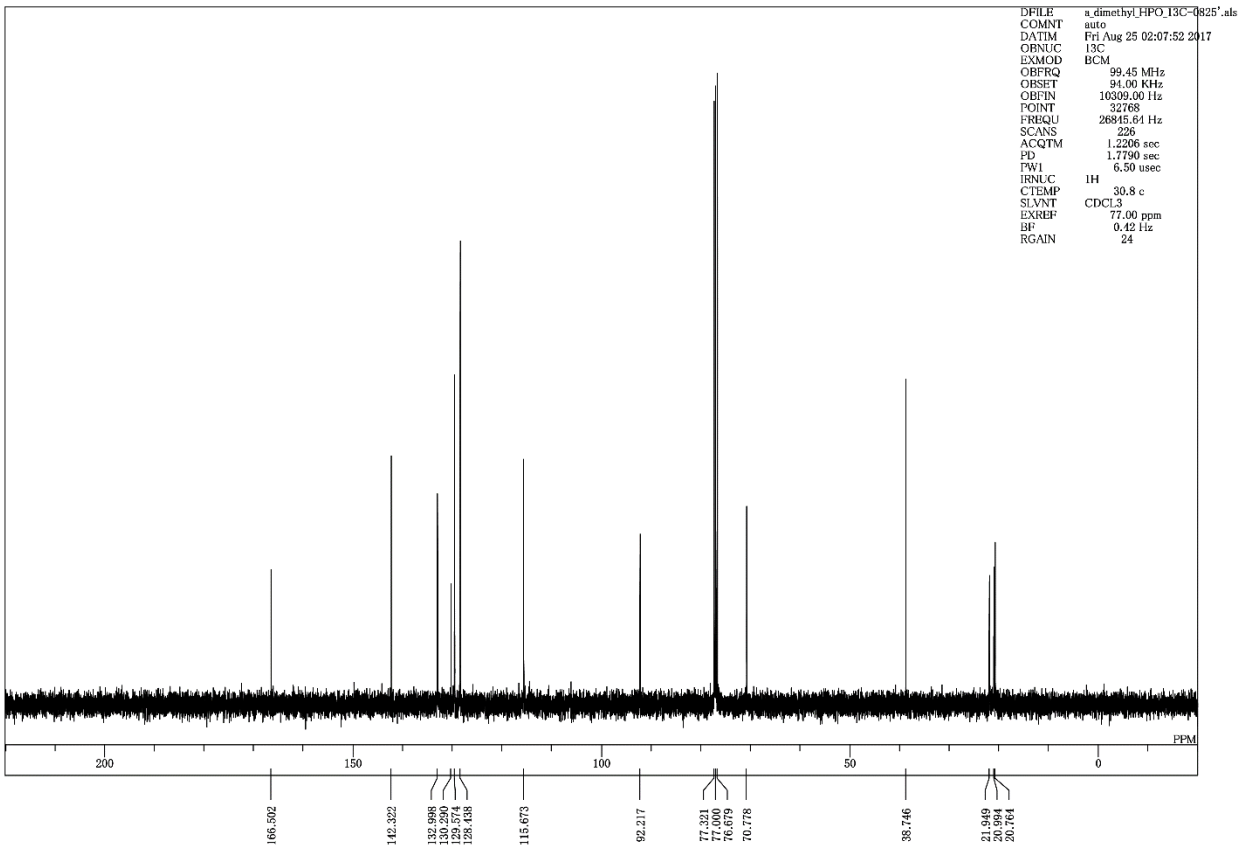
auto


DFILE a_dimethyl_alkene_13C-0824'.als
COMNT auto
DATIM Thu Aug 24 09:44:06 2017
OBNUC 13C
EXMOD BCM
OBFRQ 99.45 MHz
OBSET 94.00 KHz
OBFIN 10309.00 Hz
POINT 32768
FREQU 26845.61 Hz
SCANS 165
ACQTM 1.2206 sec
PD 1.7790 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 30.6 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.62 Hz
RGAIN 23
PPM
200
150
100
50
0
166.708
133.121
132.775
130.636
130.051
128.586
128.331
77.321
77.000
76.679
73.173
36.055
28.056
25.899
19.216

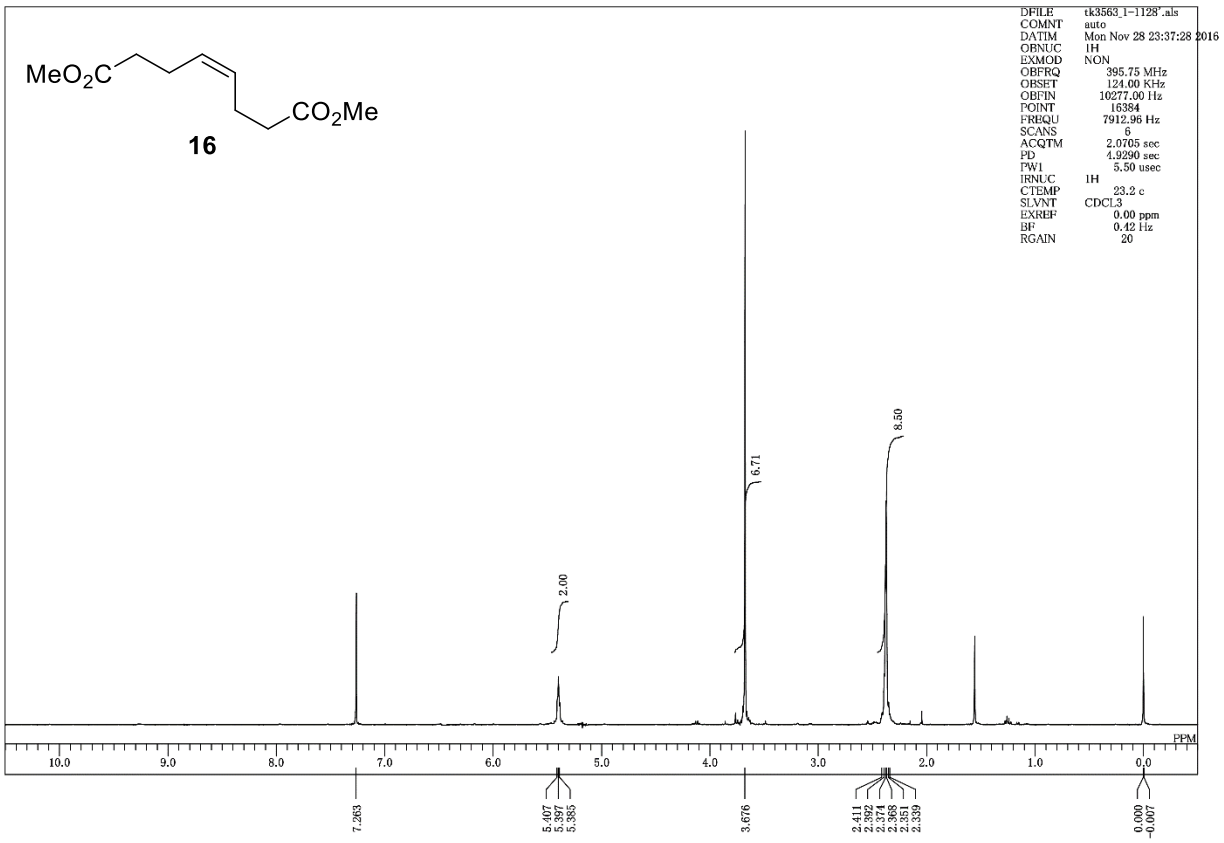
auto


HO
O
BzO
5g
DFILE tk3364_1-0912'.als
COMNT auto
DATIM Mon Sep 12 23:54:59 2016
OBNUC 1H
EXMOD NON
OBFRQ 395.75 MHz
OBSET 124.00 KHz
OBFIN 10277.00 Hz
POINT 16384
FREQU 7912.96 Hz
SCANS 8
ACQTM 2.0705 sec
PD 4.9290 sec
PW1 5.50 usec
IRNUC 1H
CTEMP 26.6 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.42 Hz
RGAIN 22
2.01
2.04
1.00
0.91
0.97
1.00
1.02
0.98
1.28
2.90
2.94
3.14
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
8.075
8.058
7.975
7.596
7.577
7.561
7.558
7.480
7.460
7.412
7.259
5.201
5.197
5.193
5.076
4.403
4.282
4.254
4.097
4.070
1.864
1.092
1.036
0.000

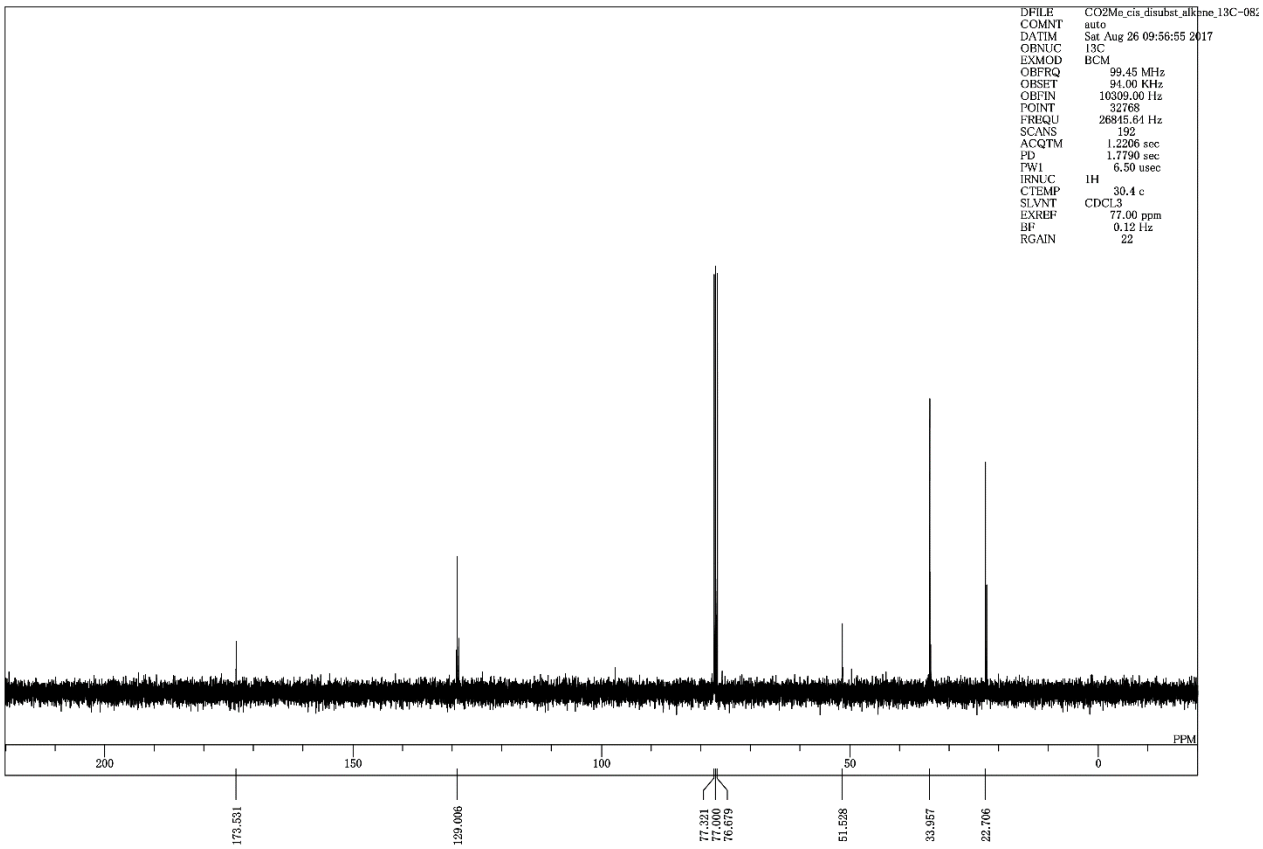
auto


DFILE a_dimethyl_HPO_13C-0825'.als
COMNT auto
DATIM Fri Aug 25 02:07:52 2017
OBNUC 13C
EXMOD BCM
OBFRQ 99.45 MHz
OBSET 94.00 KHz
OBFIN 10309.00 Hz
POINT 32768
FREQU 26845.64 Hz
SCANS 226
ACQTM 1.2206 sec
PD 1.7790 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 30.8 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.42 Hz
RGAIN 24
PPM
200
150
100
50
0
166.502
142.322
132.998
130.290
129.574
128.438
115.673
92.217
77.321
77.000
76.679
70.778
38.746
21.949
20.994
20.764

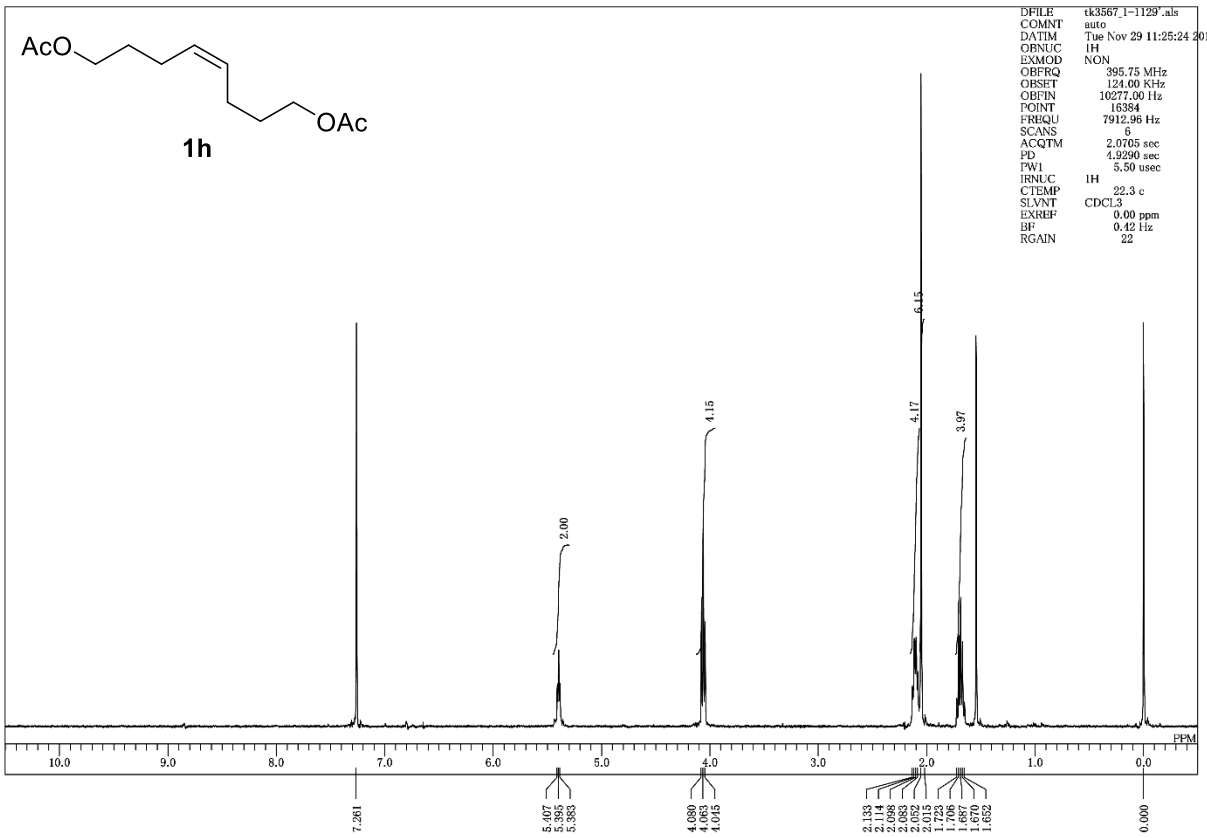
auto


MeO2C
CO2Me
16
DFILE tk3563_1-1128'.als
COMNT auto
DATIM Mon Nov 28 23:37:28 2016
OBNUC 1H
EXMOD NON
OBFRQ 395.75 MHz
OBSET 124.00 KHz
OBFIN 10277.00 Hz
POINT 16384
FREQU 7912.96 Hz
SCANS 6
ACQTM 2.0705 sec
PD 4.9290 sec
PW1 5.50 usec
IRNUC 1H
CTEMP 23.2 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.42 Hz
RGAIN 20
2.00
6.71
8.50
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.263
5.407
5.397
5.385
3.676
2.411
2.392
2.374
2.368
2.351
2.339
0.009
-0.007

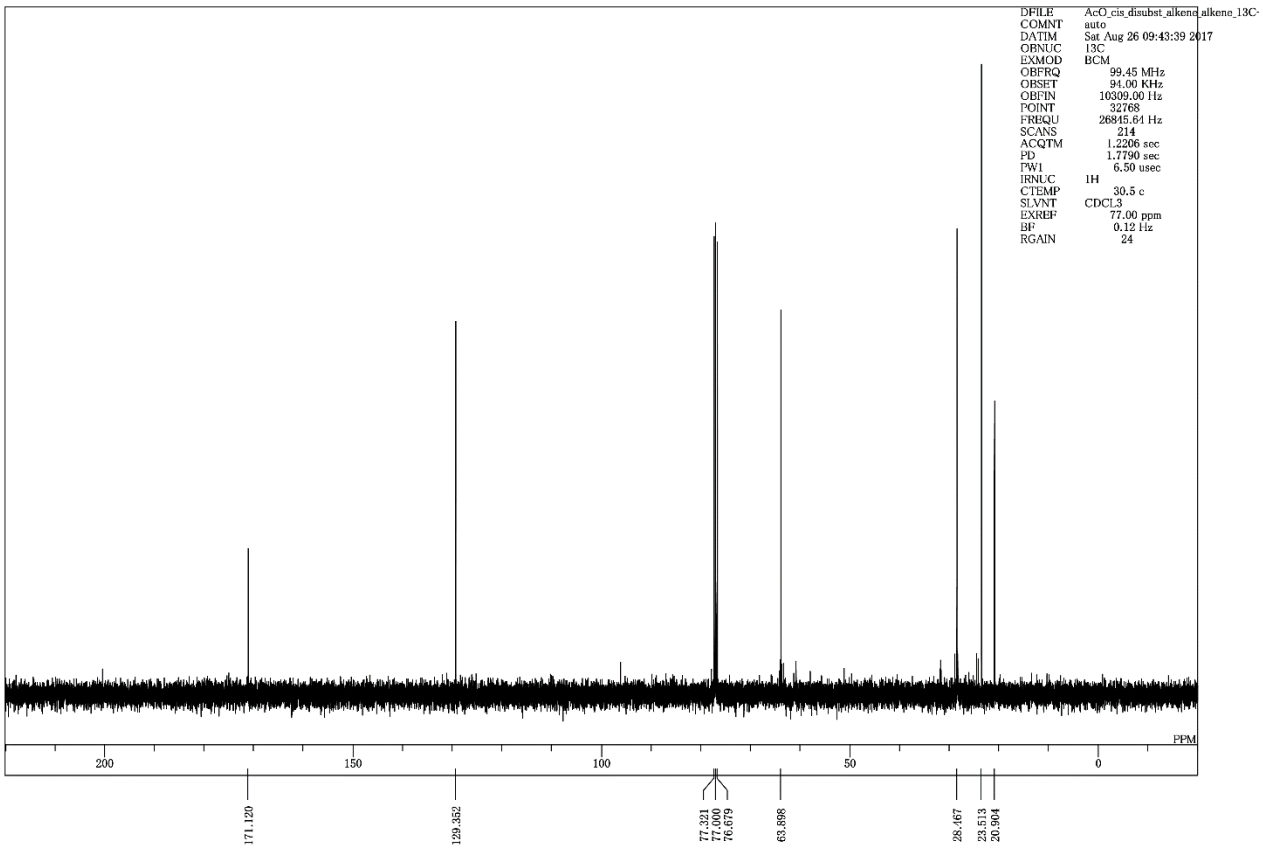
auto


DFILE CO2Me_cis_disubst_alkene_13C-082
COMNT auto
DATIM Sat Aug 26 09:56:55 2017
OBNUC 13C
EXMOD BCM
OBFRQ 99.45 MHz
OBSET 94.00 KHz
OBFIN 10309.00 Hz
POINT 32768
FREQU 26845.61 Hz
SCANS 192
ACQTM 1.2206 sec
PD 1.7790 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 30.4 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 22
PPM
200
150
100
50
0
173.531
129.006
77.321
77.000
76.679
51.528
33.957
22.706

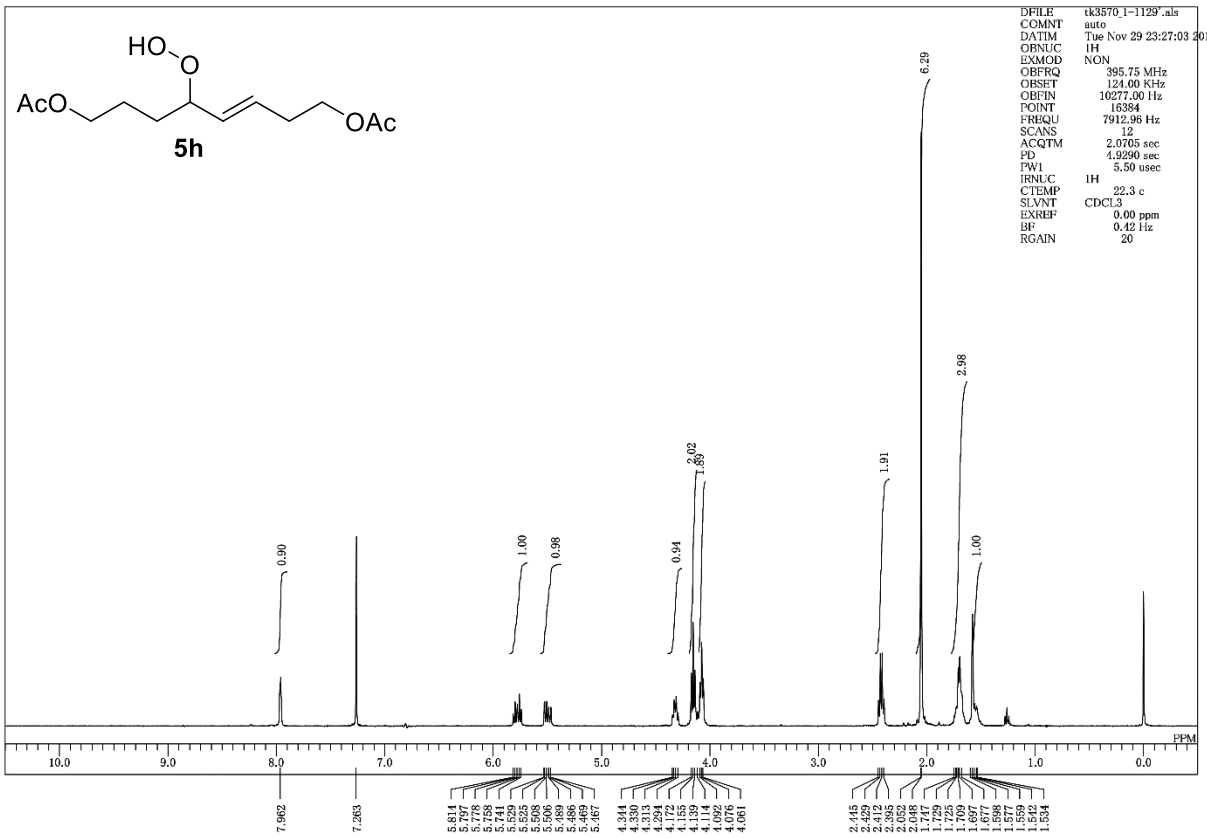
auto


AcO
OAc
1h
DFILE tk3567_1-1129'.als
COMNT auto
DATIM Tue Nov 29 11:25:24 2016
OBNUC 1H
EXMOD NON
OBFRQ 395.75 MHz
OBSET 124.00 KHz
OBFIN 10277.00 Hz
POINT 16384
FREQU 7912.96 Hz
SCANS 6
ACQTM 2.0705 sec
PD 4.9290 sec
PW1 5.50 usec
IRNUC 1H
CTEMP 22.3 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.42 Hz
RGAIN 22
2.00
4.15
4.17
6.15
3.97
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.261
5.407
5.395
5.383
4.090
4.083
4.045
2.133
2.114
2.098
2.083
2.052
2.015
1.723
1.706
1.687
1.670
1.652
0.000

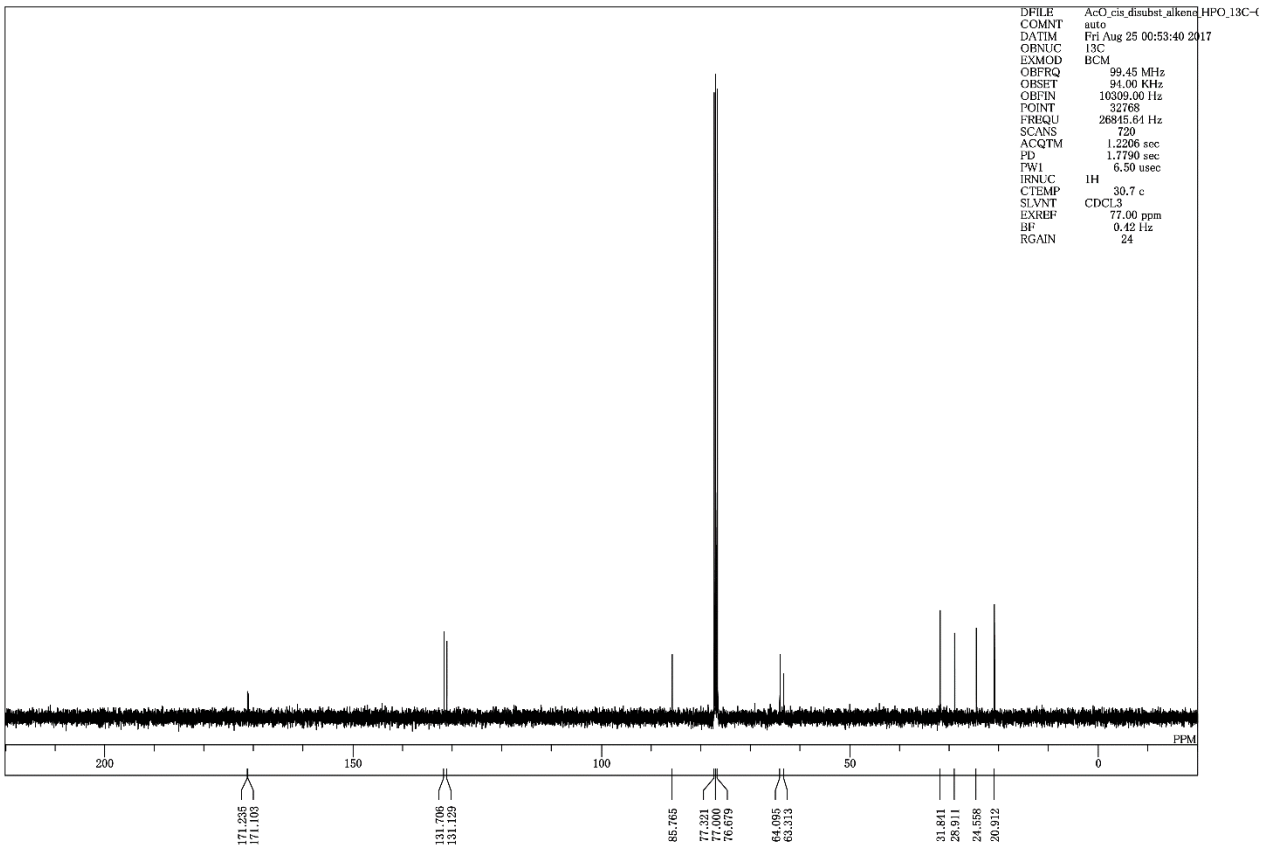
auto


DFILE AcO_cis_disubst_alkene_alkene_13C-
COMNT auto
DATIM Sat Aug 26 09:43:39 2017
OBNUC 13C
EXMOD BCM
OBFRQ 99.45 MHz
OBSET 94.00 KHz
OBFIN 10309.00 Hz
POINT 32768
FREQU 26845.61 Hz
SCANS 214
ACQTM 1.2206 sec
PD 1.7790 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 30.5 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 24
PPM
200
150
100
50
0
171.120
129.352
77.321
77.000
76.679
63.898
28.467
23.513
20.904

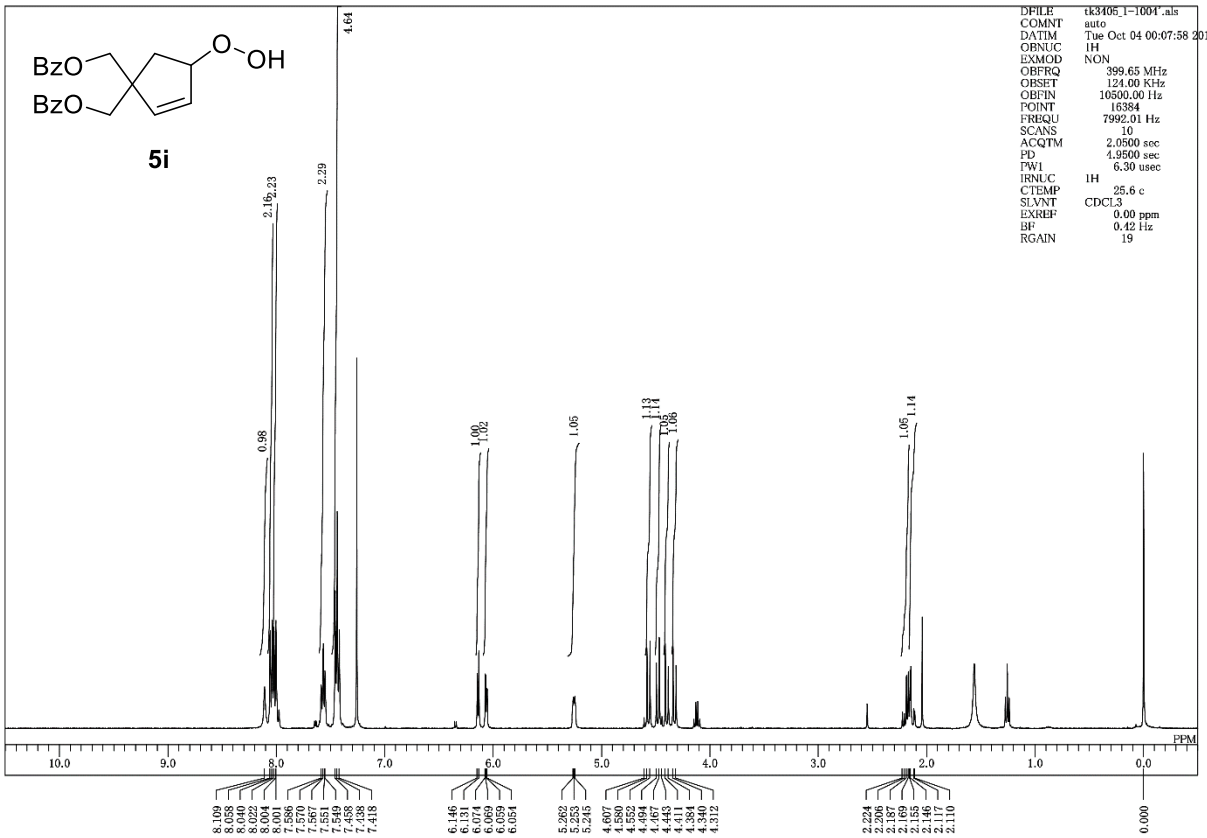
auto


HO
O
AcO
OAc
5h
DFILE tk3570_1-1129'.als
COMNT auto
DATIM Tue Nov 29 23:27:03 2016
OBNUC 1H
EXMOD NON
OBFRQ 395.75 MHz
OBSET 124.00 KHz
OBFIN 10277.00 Hz
POINT 16384
FREQU 7912.96 Hz
SCANS 12
ACQTM 2.0705 sec
PD 4.9290 sec
PW1 5.50 usec
IRNUC 1H
CTEMP 22.3 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.42 Hz
RGAIN 20
6.29
2.98
2.02
1.89
1.91
1.00
0.98
0.94
1.00
0.90
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.982
7.263
5.814
5.797
5.778
5.758
5.741
5.529
5.508
5.506
5.489
5.486
5.469
5.467
4.344
4.330
4.313
4.294
4.172
4.153
4.139
4.114
4.092
4.076
4.061
2.145
2.429
2.412
2.395
2.048
2.032
1.747
1.729
1.725
1.709
1.697
1.677
1.598
1.577
1.559
1.542
1.534

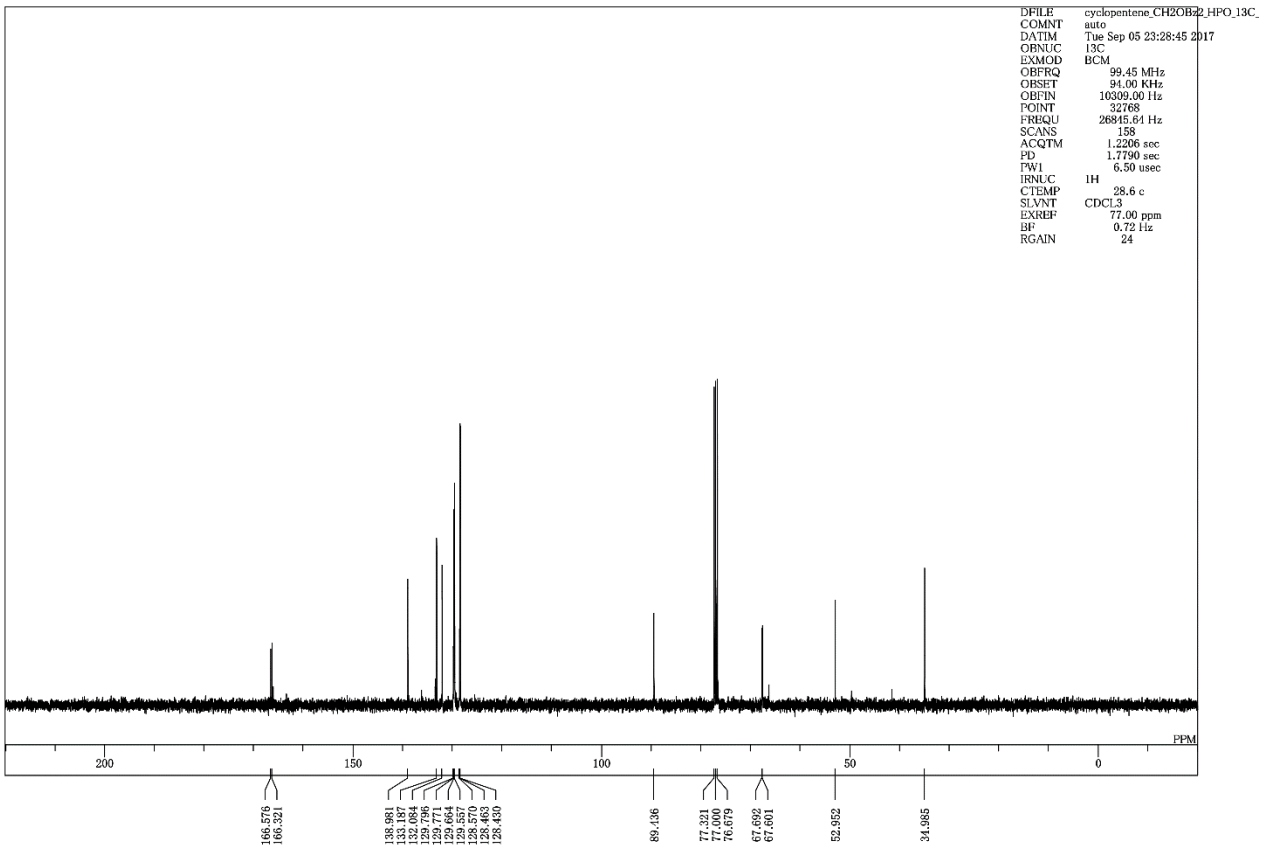
auto


DFILE AcO_cis_disubst_alkene_HPO_13C-(
COMNT auto
DATIM Fri Aug 25 00:53:40 2017
OBNUC 13C
EXMOD BCM
OBFRQ 99.45 MHz
OBSET 94.00 KHz
OBFIN 10309.00 Hz
POINT 32768
FREQU 26845.64 Hz
SCANS 720
ACQTM 1.2206 sec
PD 1.7790 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 30.7 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.42 Hz
RGAIN 24
PPM
200
150
100
50
0
171.235
171.103
131.706
131.129
85.765
77.321
77.000
76.679
64.095
63.313
31.841
28.911
24.558
20.912

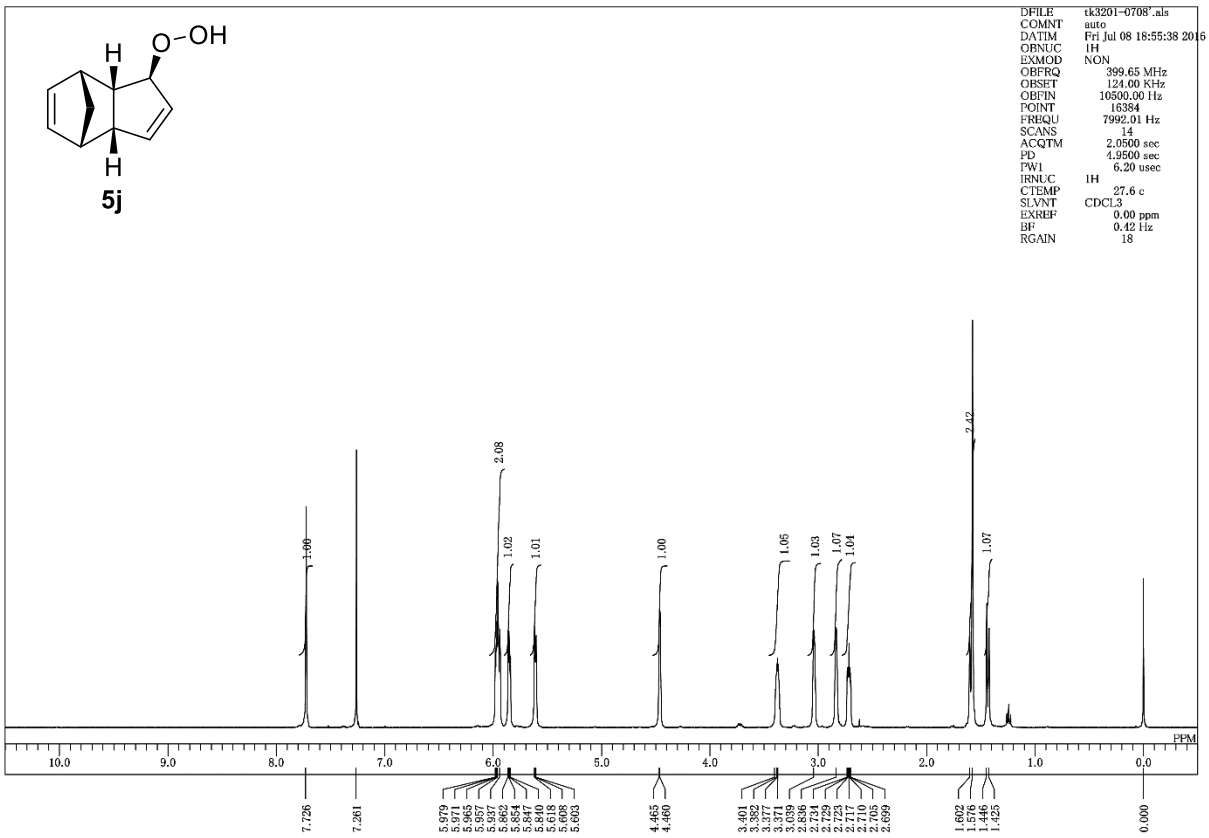
auto


BzO
BzO
O
OH
5i
DFILE tk3405_1-1004'.als
COMNT auto
DATIM Tue Oct 04 00:07:58 2016
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 16384
FREQU 7992.01 Hz
SCANS 10
ACQTM 2.0500 sec
PD 4.9500 sec
PW1 6.30 usec
IRNUC 1H
CTEMP 25.6 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.42 Hz
RGAIN 19
PPM

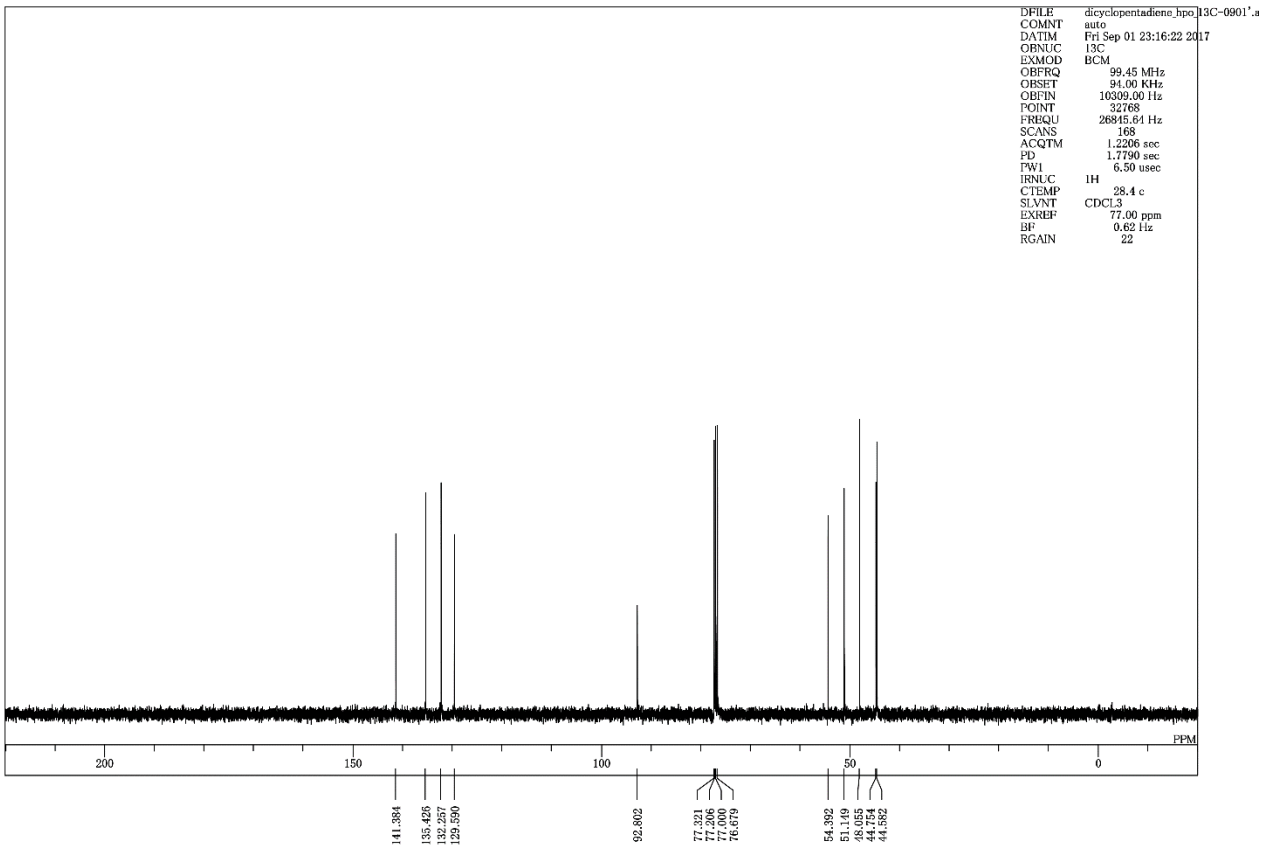
auto


DFILE cyclopentene_CH2OBz2_HPO_13C_
COMNT auto
DATIM Tue Sep 05 23:28:45 2017
OBNUC 13C
EXMOD BCM
OBFRQ 99.45 MHz
OBSET 94.00 KHz
OBFIN 10309.00 Hz
POINT 32768
FREQU 26845.61 Hz
SCANS 158
ACQTM 1.2206 sec
PD 1.7790 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 28.6 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.72 Hz
RGAIN 24
PPM

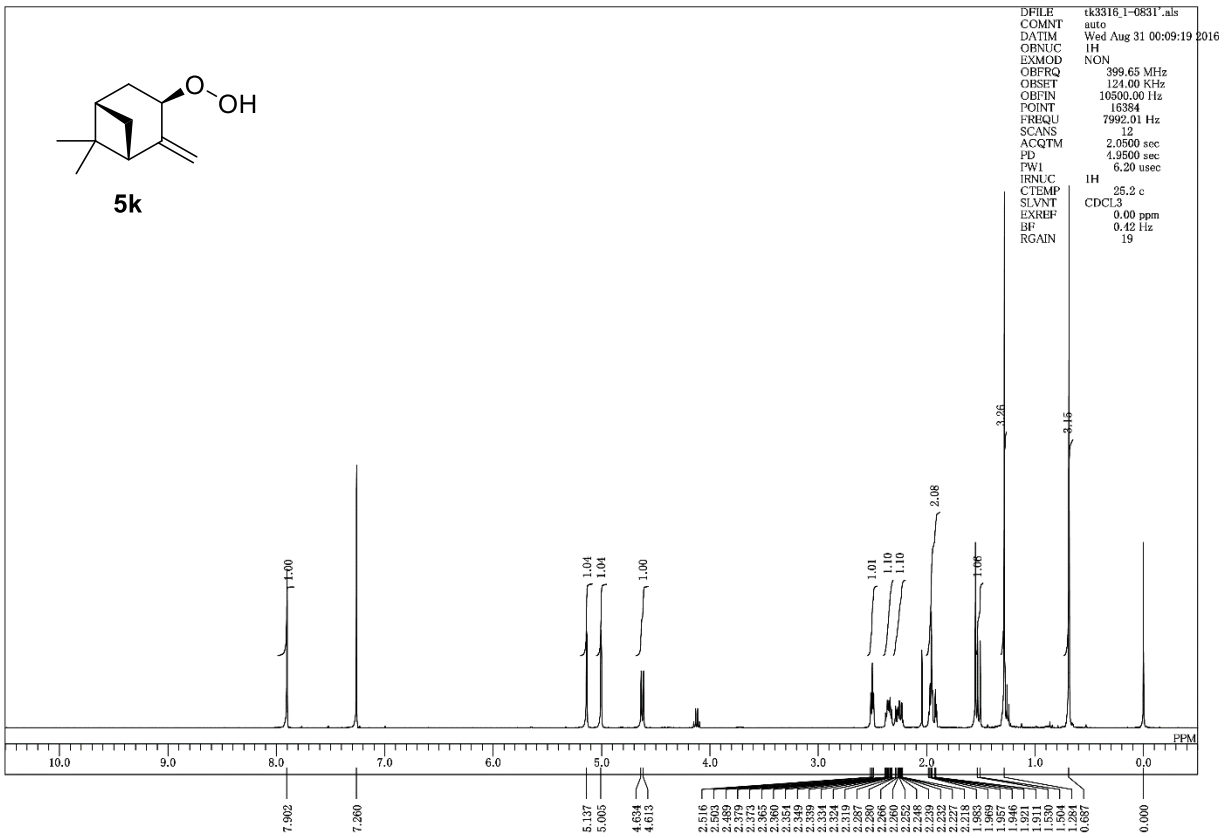
auto


H
O-OH
H
5j
DFILE tk3201-0708'.als
COMNT auto
DATIM Fri Jul 08 18:55:38 2016
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 16384
FREQU 7992.01 Hz
SCANS 14
ACQTM 2.0500 sec
PD 4.9500 sec
PW1 6.20 usec
IRNUC 1H
CTEMP 27.6 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.42 Hz
RGAIN 18
1.00
2.08
1.02
1.01
1.00
1.05
1.03
1.07
1.04
2.42
1.07
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.726
7.261
5.979
5.971
5.965
5.957
5.937
5.862
5.854
5.847
5.840
5.618
5.608
5.603
4.465
4.460
3.401
3.382
3.377
3.371
3.039
2.858
2.734
2.729
2.723
2.717
2.710
2.705
2.699
1.602
1.576
1.446
1.425
0.000

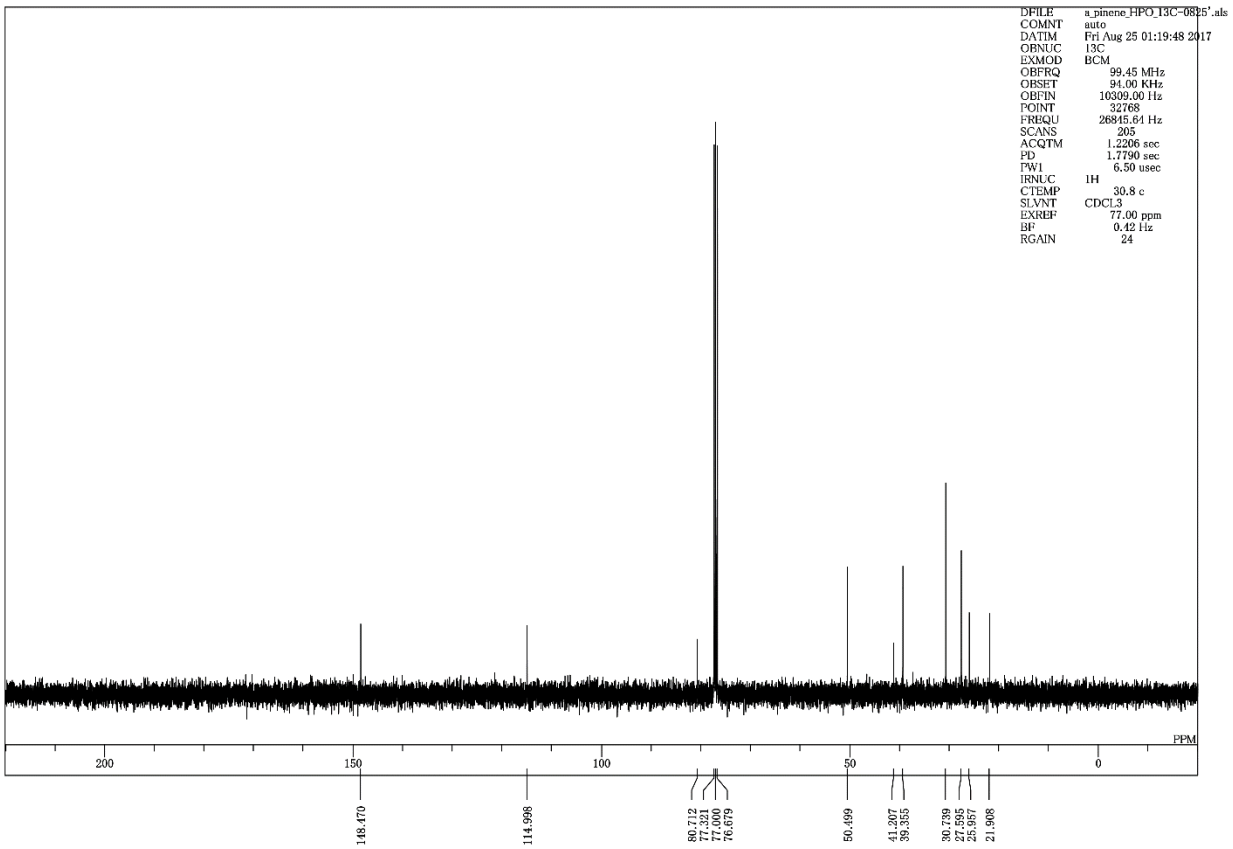
auto


DFILE dicyclopentadiene_hpo_13C-0901'.a
COMNT auto
DATIM Fri Sep 01 23:16:22 2017
OBNUC 13C
EXMOD BCM
OBFRQ 99.45 MHz
OBSET 94.00 KHz
OBFIN 10309.00 Hz
POINT 32768
FREQU 26845.61 Hz
SCANS 168
ACQTM 1.2206 sec
PD 1.7790 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 28.4 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.62 Hz
RGAIN 22
PPM
200
150
100
50
0
141.384
135.426
132.257
129.590
92.802
77.321
77.206
77.000
76.679
54.392
51.149
48.055
44.754
44.582

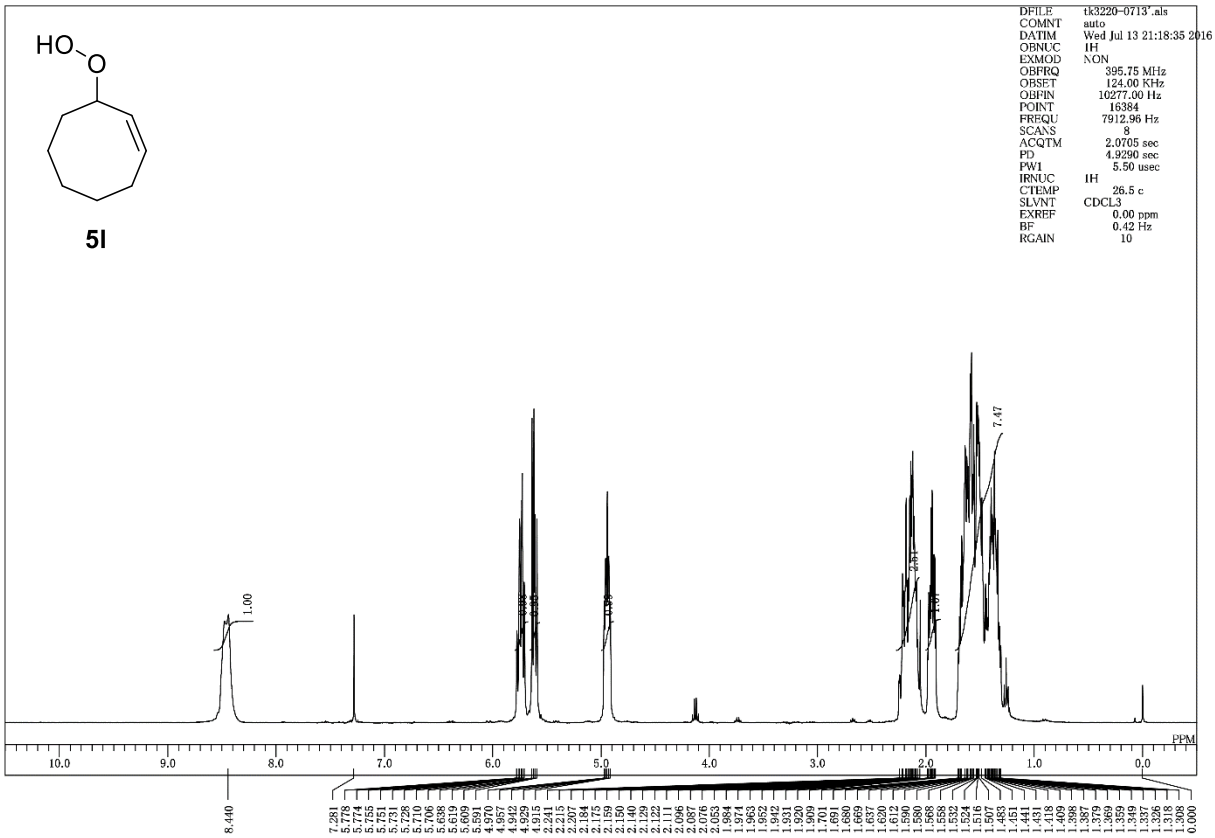
auto


5k
DFILE tk3316_1-0831'.als
COMNT auto
DATIM Wed Aug 31 00:09:19 2016
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 16384
FREQU 7992.01 Hz
SCANS 12
ACQTM 2.0500 sec
PD 4.9500 sec
PW1 6.20 usec
IRNUC 1H
CTEMP 25.2 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.42 Hz
RGAIN 19
PPM

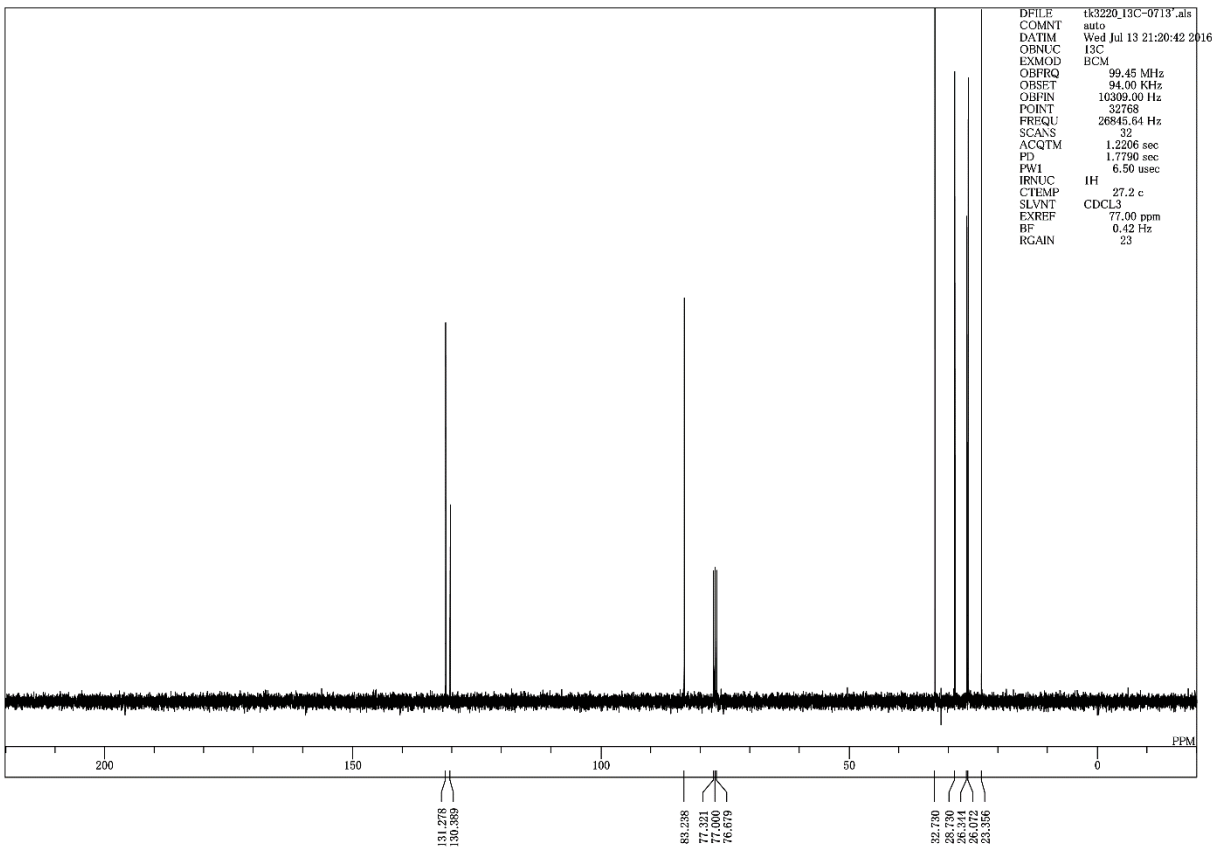
auto


DFILE a_pinene_HPO_13C-0825'.als
COMNT auto
DATIM Fri Aug 25 01:19:48 2017
OBNUC 13C
EXMOD BCM
OBFRQ 99.45 MHz
OBSET 94.00 KHz
OBFIN 10309.00 Hz
POINT 32768
FREQU 26845.61 Hz
SCANS 205
ACQTM 1.2206 sec
PD 1.7790 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 30.8 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.42 Hz
RGAIN 24
PPM

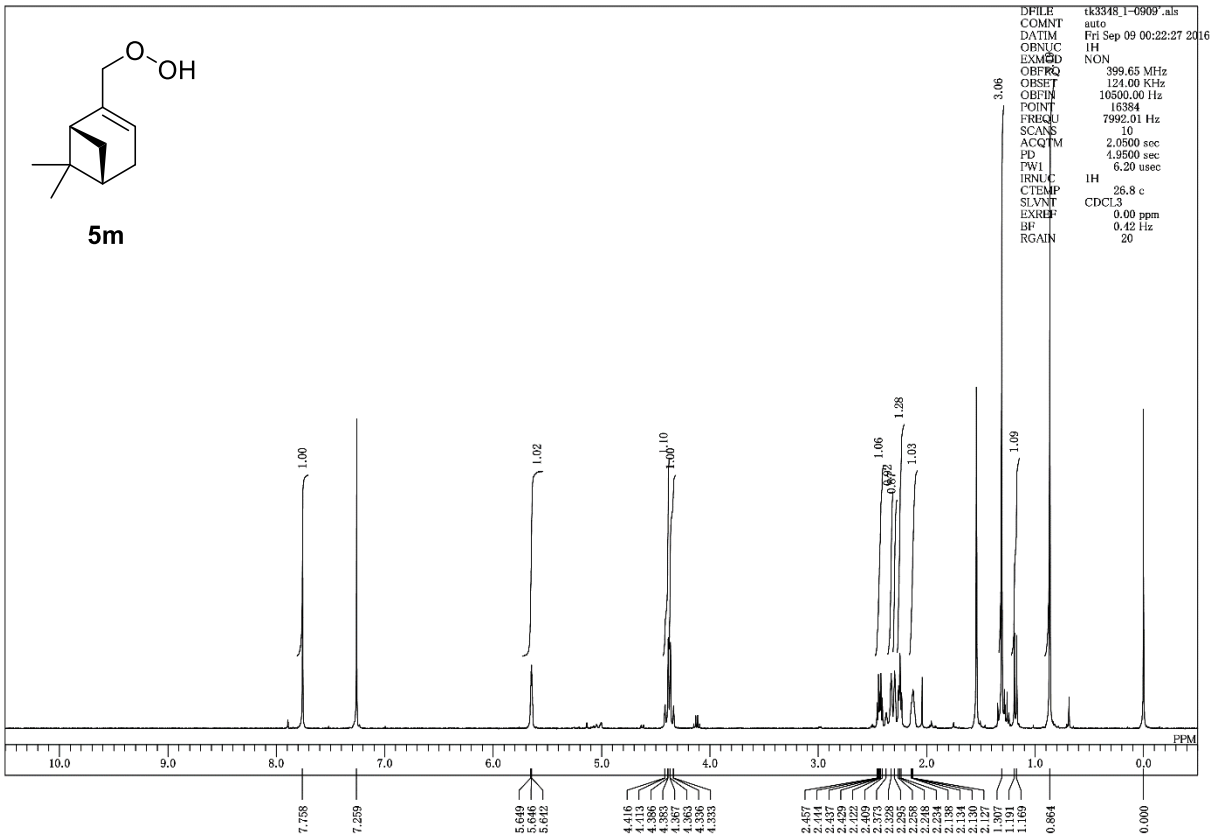
auto


HO
O
5l
DFILE tk3220-0713'.als
COMNT auto
DATIM Wed Jul 13 21:18:35 2016
OBNUC 1H
EXMOD NON
OBFRQ 395.75 MHz
OBSET 124.00 KHz
OBFIN 10277.00 Hz
POINT 16384
FREQU 7912.96 Hz
SCANS 8
ACQTM 2.0705 sec
PD 4.9290 sec
PW1 5.50 usec
IRNUC 1H
CTEMP 26.5 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.42 Hz
RGAIN 10
1.00
7.47
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
8.440
7.281
5.778
5.774
5.755
5.751
5.731
5.728
5.710
5.706
5.638
5.619
5.609
5.591
4.970
4.957
4.942
4.929
4.915
2.241
2.215
2.207
2.184
2.175
2.159
2.150
2.140
2.129
2.122
2.111
2.096
2.076
2.053
1.984
1.974
1.963
1.952
1.942
1.931
1.920
1.909
1.701
1.691
1.680
1.669
1.637
1.620
1.612
1.590
1.580
1.568
1.558
1.532
1.524
1.516
1.507
1.485
1.441
1.431
1.418
1.409
1.398
1.387
1.369
1.359
1.349
1.337
1.326
1.318
1.308
0.000

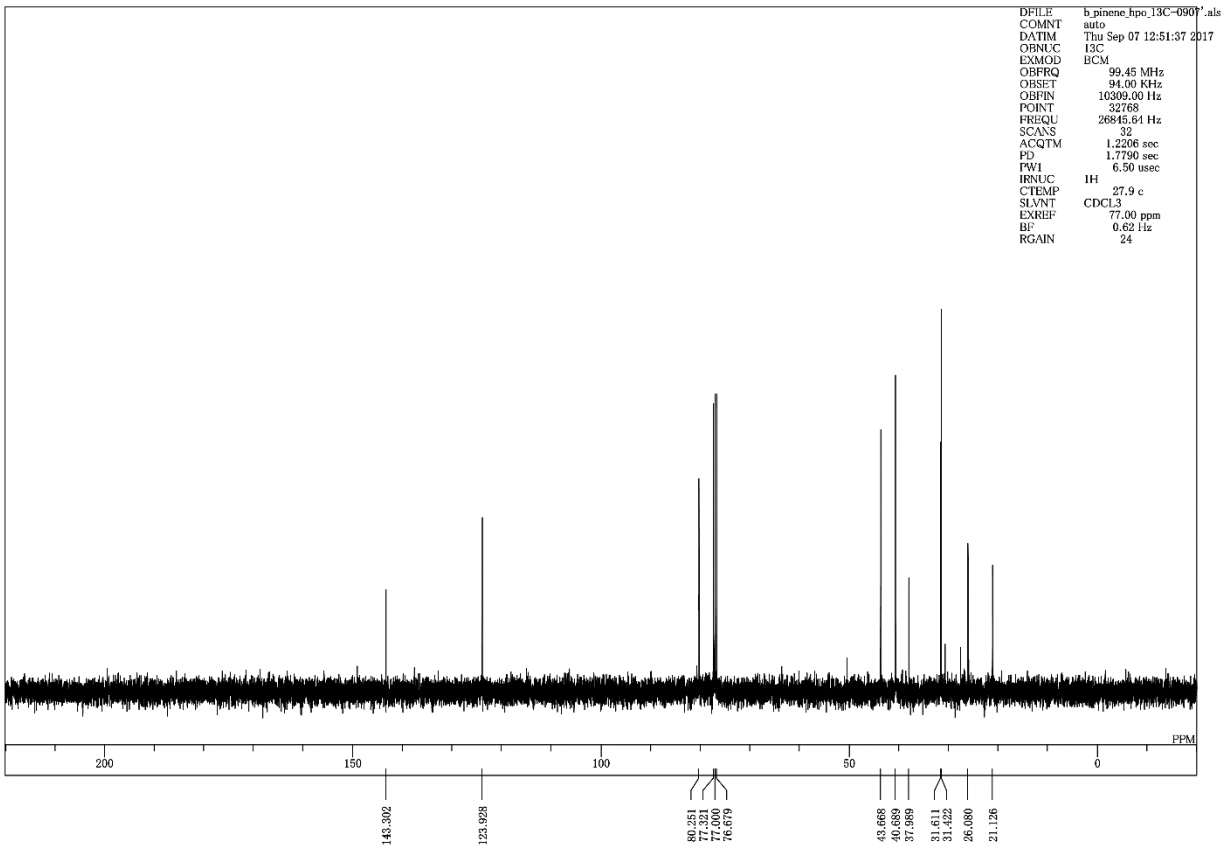
auto


DFILE tk3220_13C-0713'.als
COMNT auto
DATIM Wed Jul 13 21:20:42 2016
OBNUC 13C
EXMOD BCM
OBFRQ 99.45 MHz
OBSET 94.00 KHz
OBFIN 10309.00 Hz
POINT 32768
FREQU 26845.64 Hz
SCANS 32
ACQTM 1.2206 sec
PD 1.7790 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 27.2 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.42 Hz
RGAIN 23
PPM
200
150
100
50
0
131.278
130.389
83.238
77.321
77.000
76.679
32.730
28.730
26.344
26.072
23.356

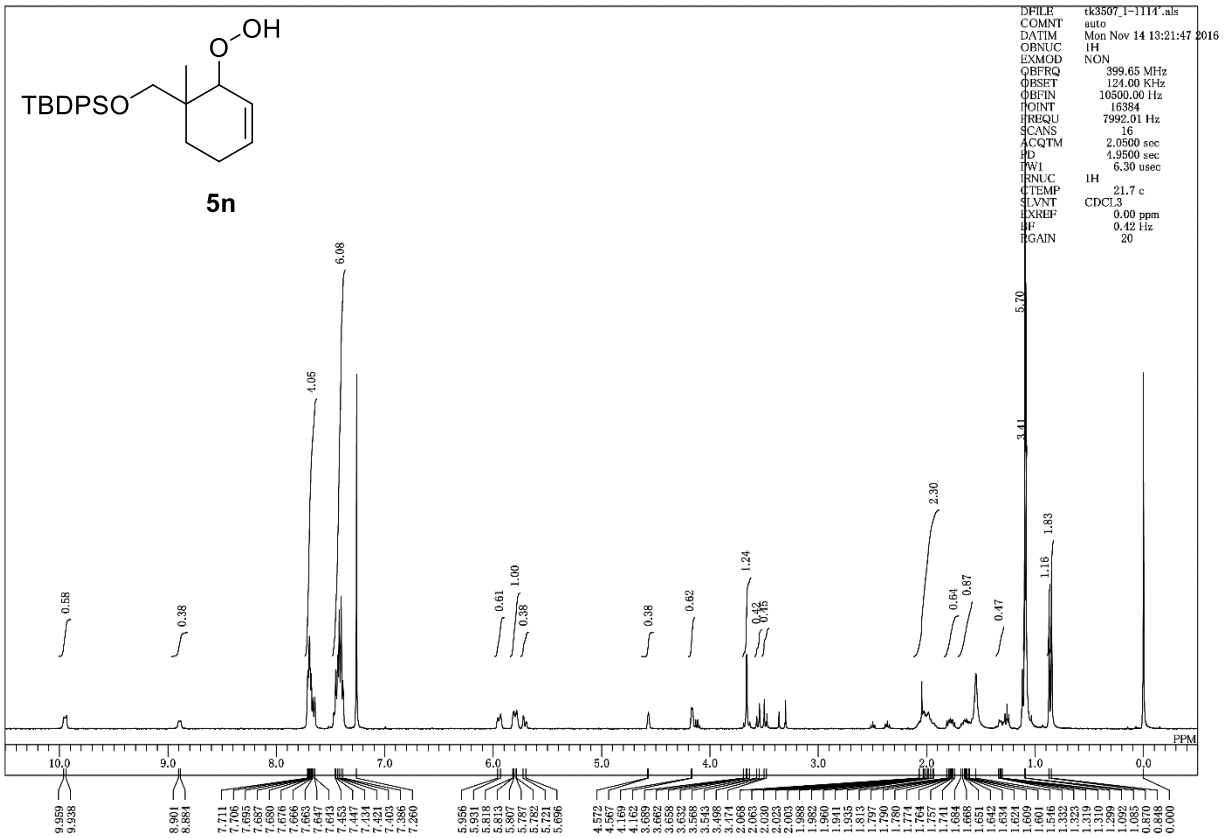
auto


5m
DFILE tk3348_1-0909'.als
COMNT auto
DATIM Fri Sep 09 00:22:27 2016
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 16384
FREQU 7992.01 Hz
SCANS 10
ACQTM 2.0500 sec
PD 4.9500 sec
PW1 6.20 usec
IRNUC 1H
CTEMP 26.8 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.42 Hz
RGAIN 20
PPM

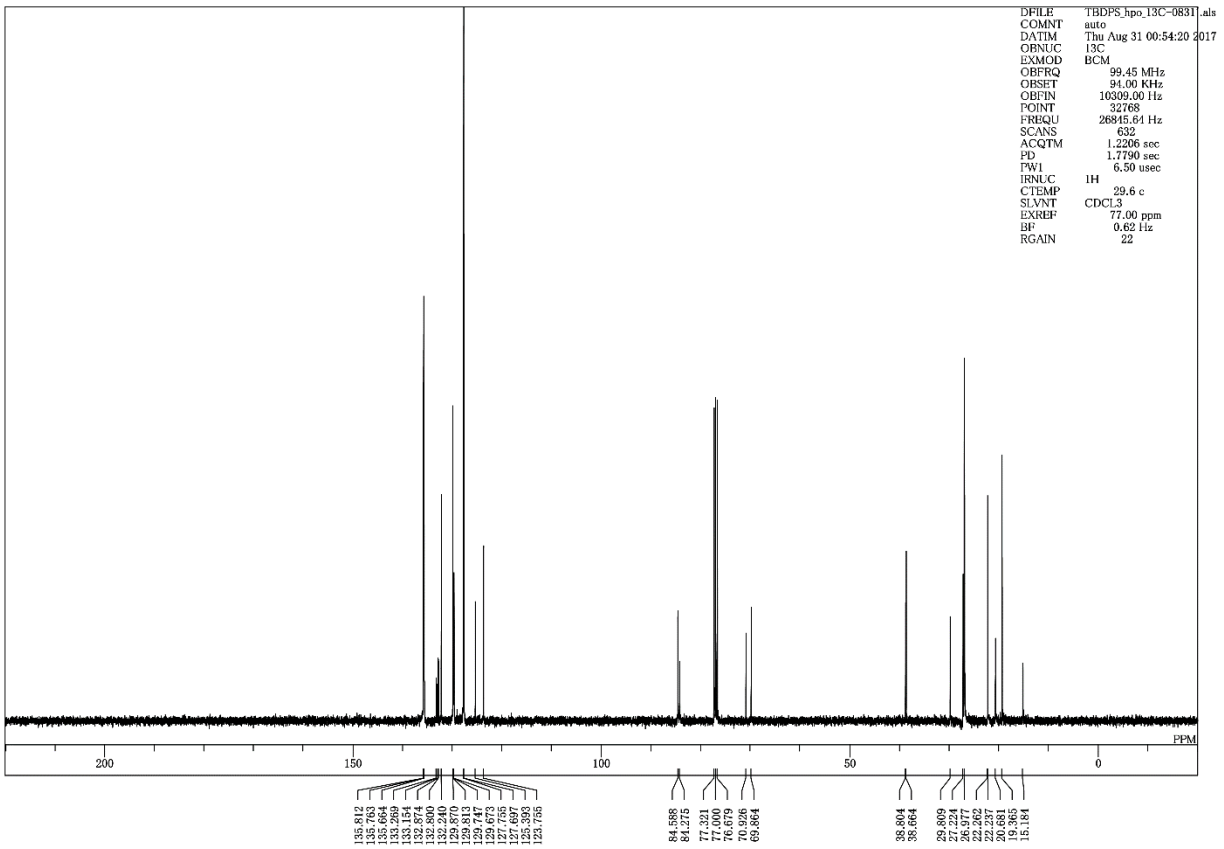
auto


DFILE b_pinene_hpo_13C-0907'.als
COMNT auto
DATIM Thu Sep 07 12:51:37 2017
OBNUC 13C
EXMOD BCM
OBFRQ 99.45 MHz
OBSET 94.00 KHz
OBFIN 10309.00 Hz
POINT 32768
FREQU 26845.64 Hz
SCANS 32
ACQTM 1.2206 sec
PD 1.7790 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 27.9 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.62 Hz
RGAIN 24
PPM

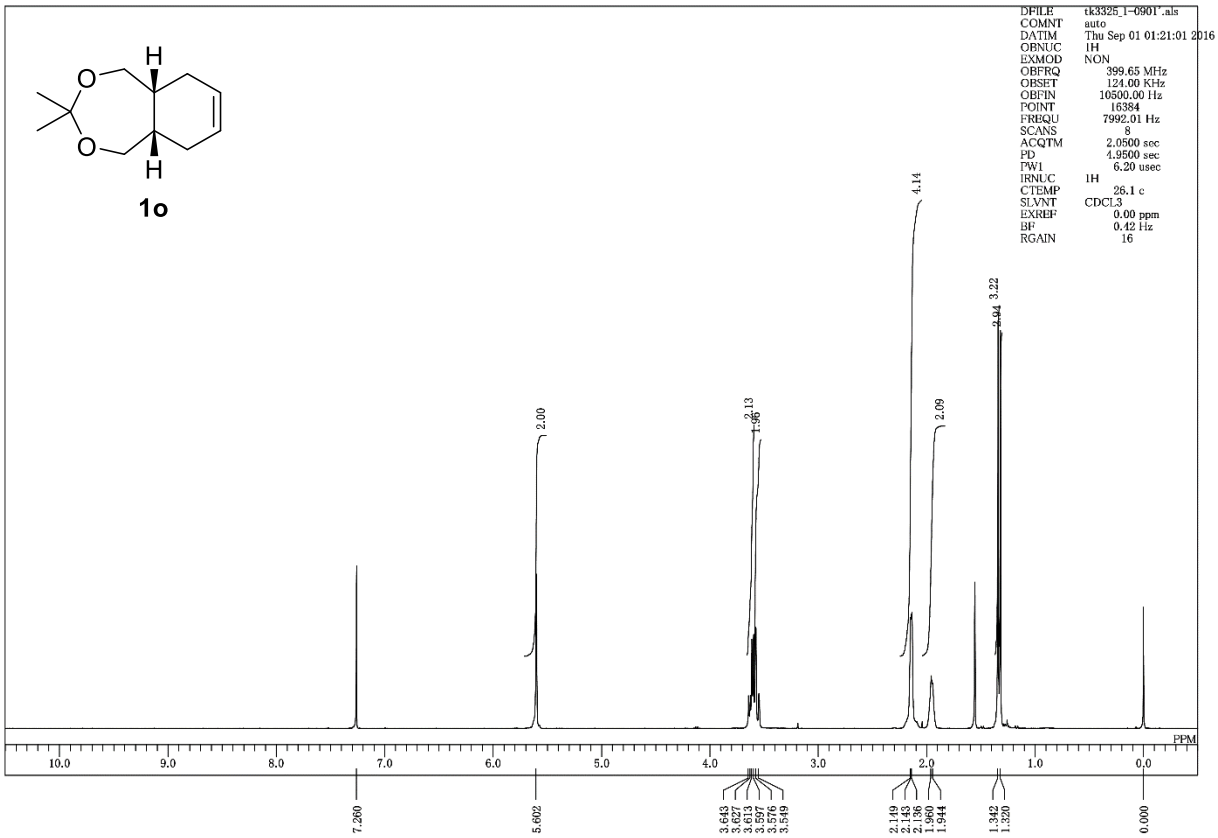
auto


TBDPSO
OH
O
5n
DFILE tk3507_1-1114'.als
COMNT auto
DATIM Mon Nov 14 13:21:47 2016
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 16384
FREQU 7992.01 Hz
SCANS 16
ACQTM 2.0500 sec
PD 4.9500 sec
PW1 6.30 usec
IRNUC 1H
CTEMP 21.7 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.42 Hz
RGAIN 20
PPM

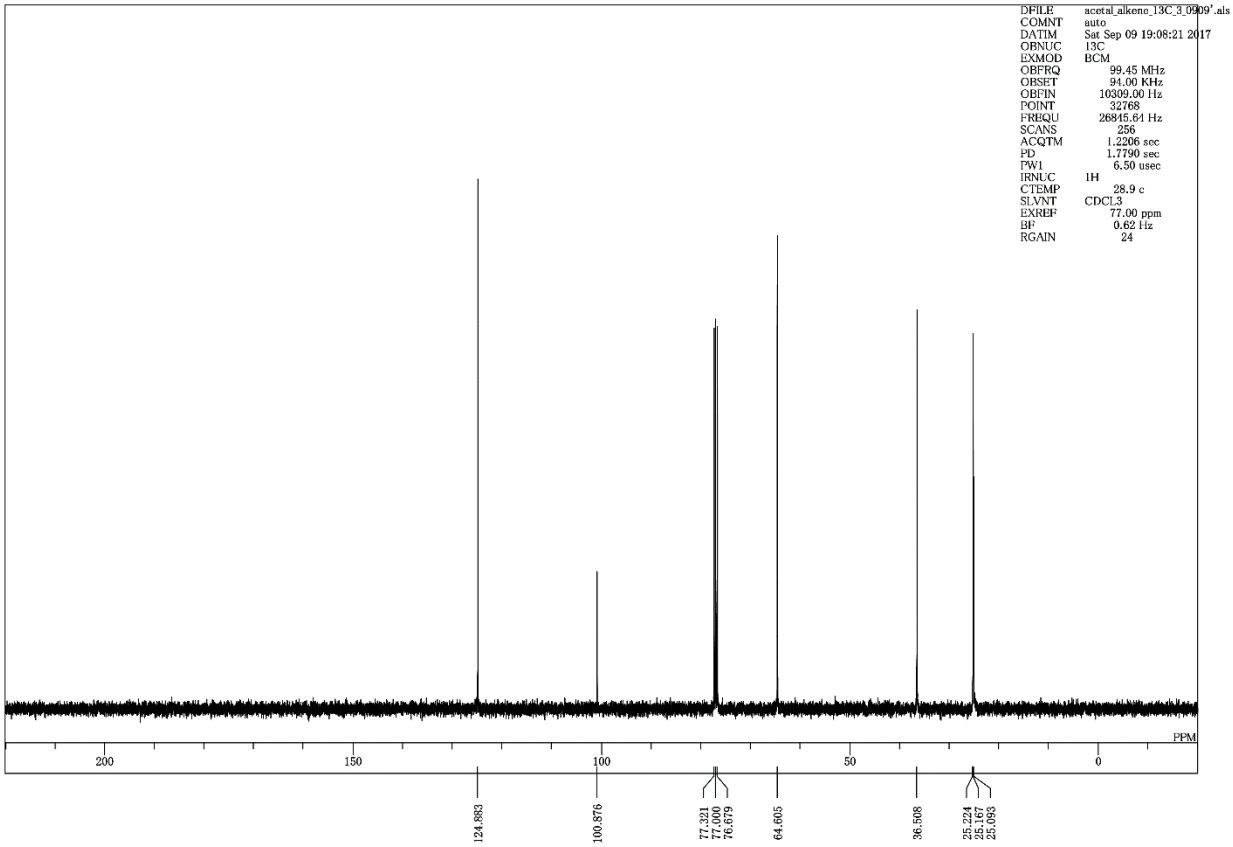
auto


DFILE TBDPS_hpo_13C-0831'.als
COMNT auto
DATIM Thu Aug 31 00:54:20 2017
OBNUC 13C
EXMOD BCM
OBFRQ 99.45 MHz
OBSET 94.00 KHz
OBFIN 10309.00 Hz
POINT 32768
FREQU 26845.64 Hz
SCANS 632
ACQTM 1.2206 sec
PD 1.7790 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 29.6 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.62 Hz
RGAIN 22
PPM

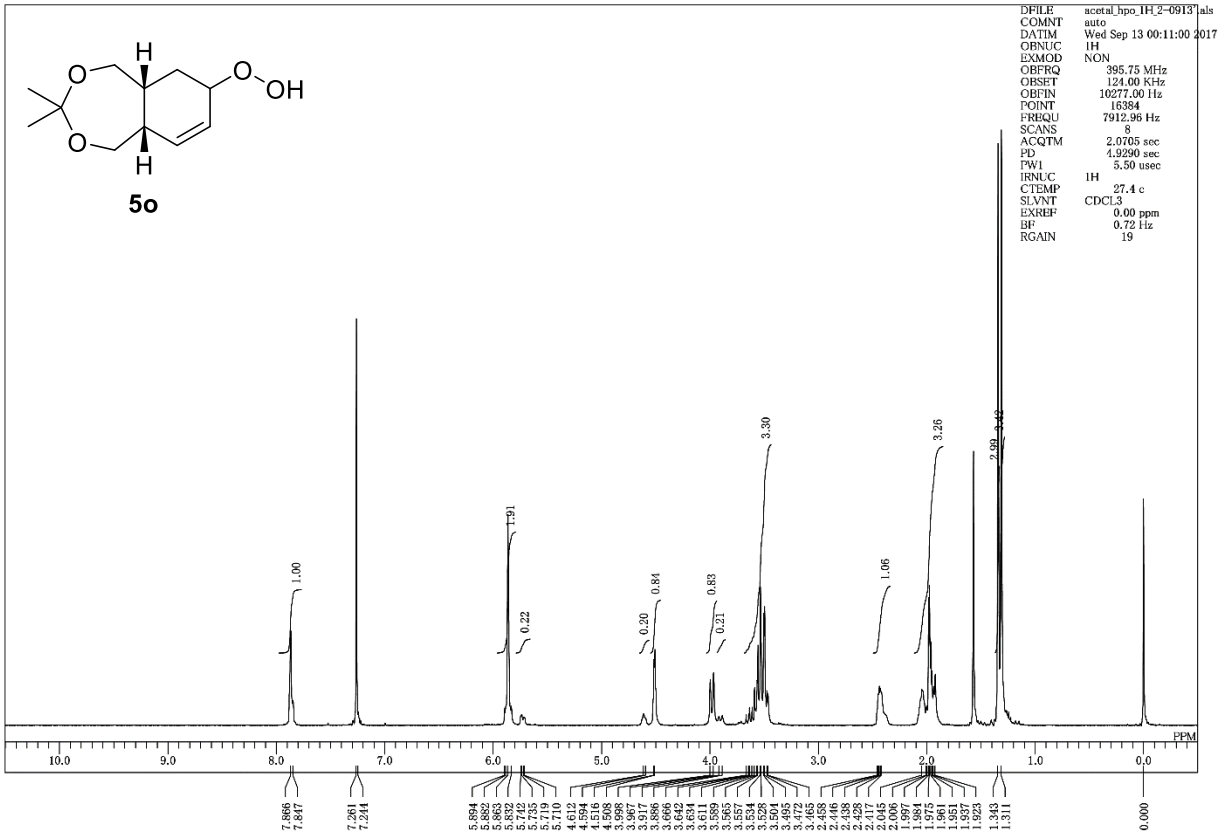
auto


1o
DFILE tk3325_1-0901'.als
COMNT auto
DATIM Thu Sep 01 01:21:01 2016
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 16384
FREQU 7992.01 Hz
SCANS 8
ACQTM 2.0500 sec
PD 4.9500 sec
PW1 6.20 usec
IRNUC 1H
CTEMP 26.1 c
SLVNT CDCl3
EXREF 0.00 ppm
BF 0.42 Hz
RGAIN 16
2.00
2.13
1.96
4.14
2.09
3.22
2.44
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.280
5.602
3.643
3.627
3.613
3.597
3.576
3.549
2.149
2.143
2.136
1.969
1.944
1.342
1.320
0.000

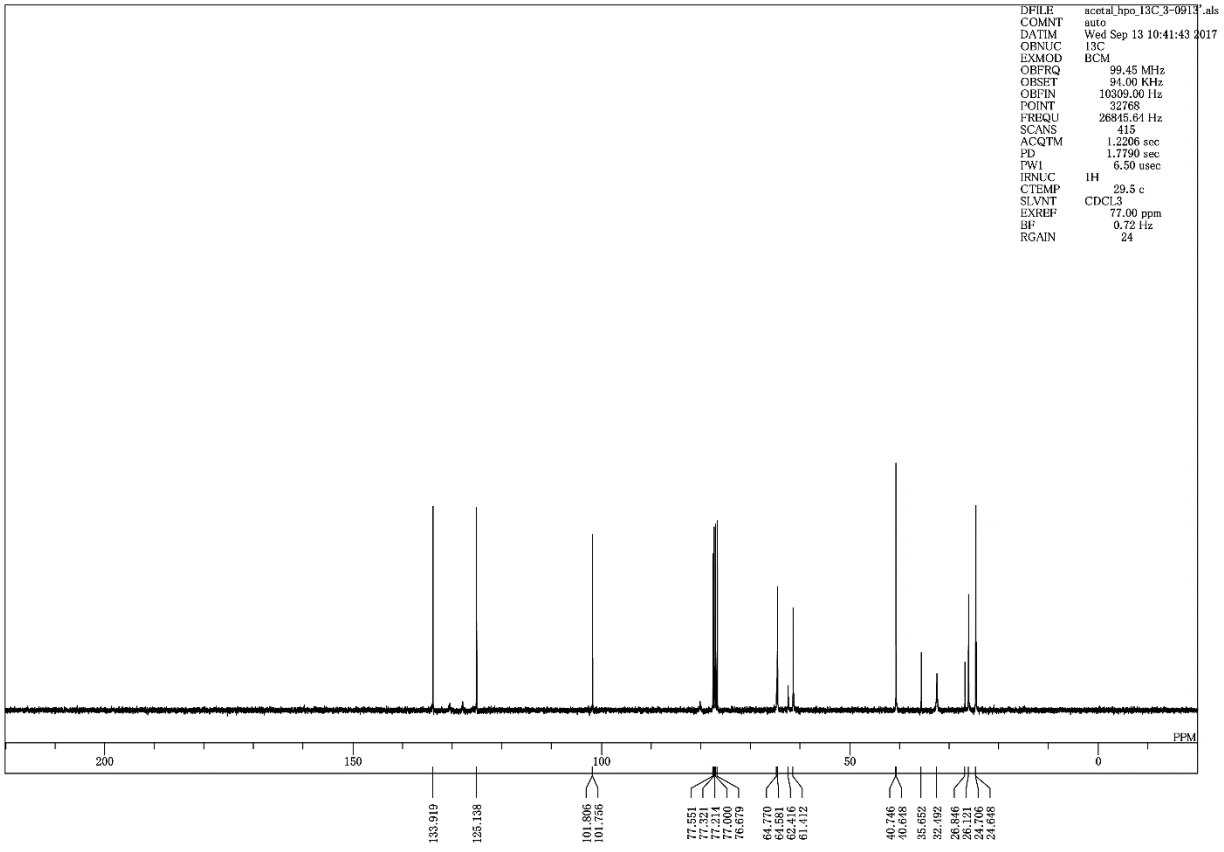
auto


DFILE acetal_alkene_13C_3-0909'.als
COMNT auto
DATIM Sat Sep 09 19:08:21 2017
OBNUC 13C
EXMOD BCM
OBFRQ 99.45 MHz
OBSET 94.00 KHz
OBFIN 10309.00 Hz
POINT 32768
FREQU 26845.64 Hz
SCANS 256
ACQTM 1.2206 sec
PD 1.7790 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 28.9 c
SLVNT CDCl3
EXREF 77.00 ppm
BF 0.62 Hz
RGAIN 24
PPM
200
150
100
50
0
124.883
100.876
77.321
77.000
76.679
64.605
36.508
25.224
25.167
25.093

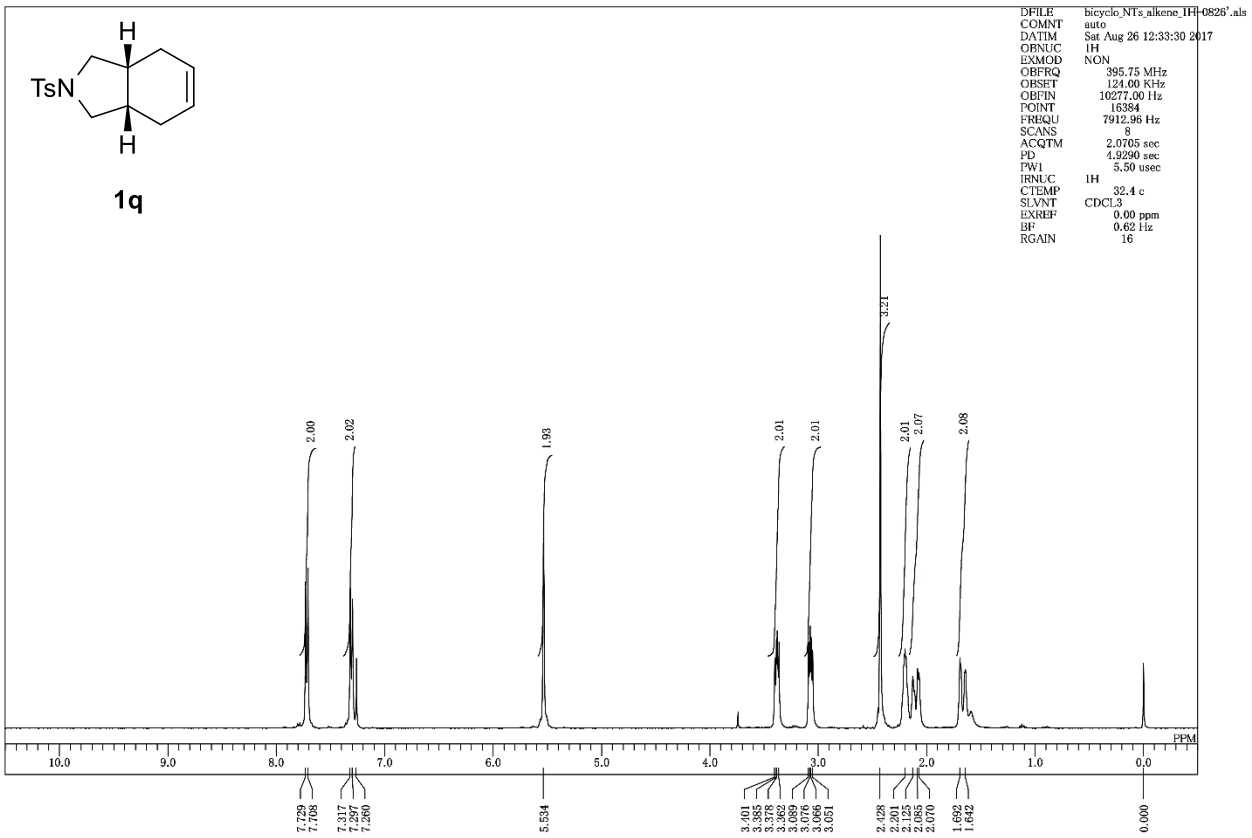
auto


5o
DFILE acetal_hpo_1H_2-0913'.als
COMNT auto
DATIM Wed Sep 13 00:11:00 2017
OBNUC 1H
EXMOD NON
OBFRQ 395.75 MHz
OBSET 124.00 KHz
OBFIN 10277.00 Hz
POINT 16384
FREQU 7912.96 Hz
SCANS 8
ACQTM 2.0705 sec
PD 4.9290 sec
PW1 5.50 usec
IRNUC 1H
CTEMP 27.4 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.72 Hz
RGAIN 19
PPM

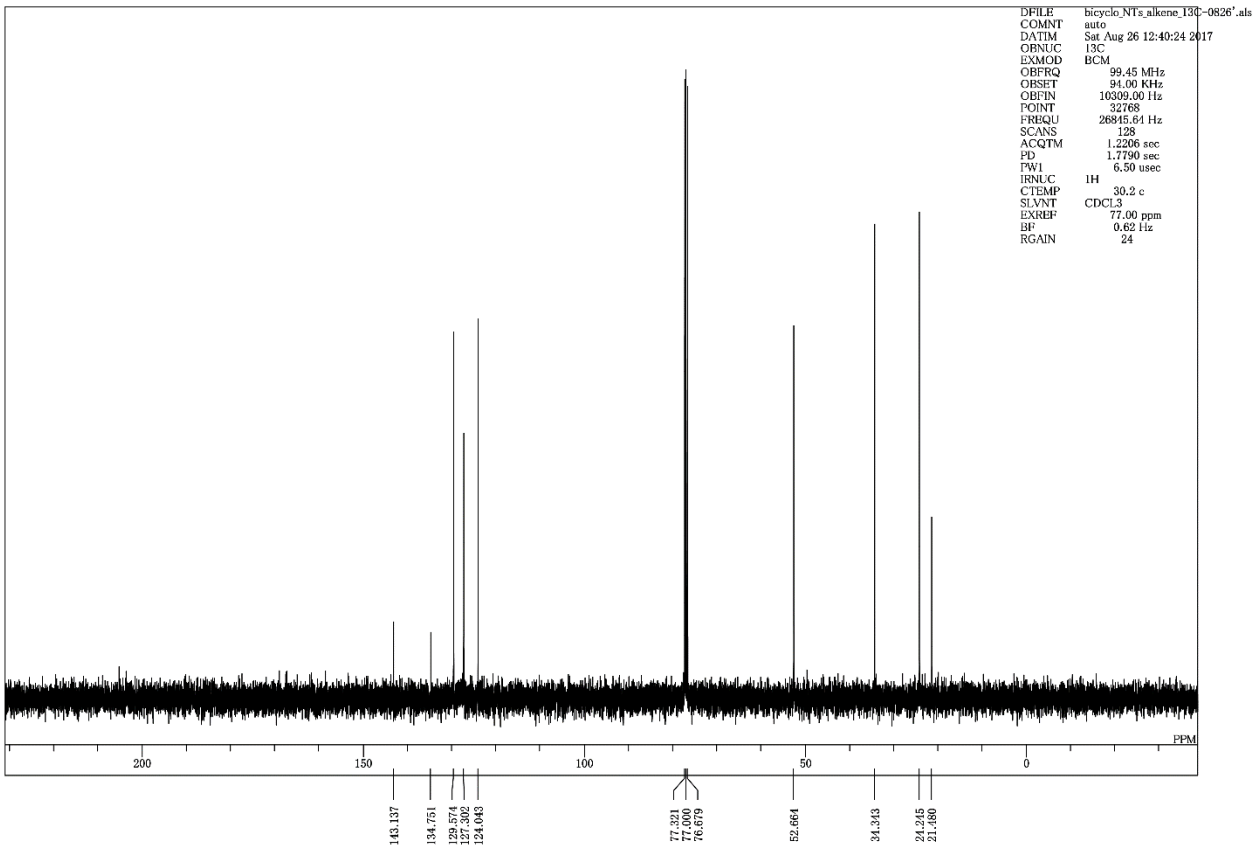
auto


DFILE acetal_hpo_13C_3-0913'.als
COMNT auto
DATIM Wed Sep 13 10:41:43 2017
OBNUC 13C
EXMOD BCM
OBFRQ 99.45 MHz
OBSET 94.00 KHz
OBFIN 10309.00 Hz
POINT 32768
FREQU 26845.61 Hz
SCANS 415
ACQTM 1.2206 sec
PD 1.7790 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 29.5 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.72 Hz
RGAIN 24
PPM

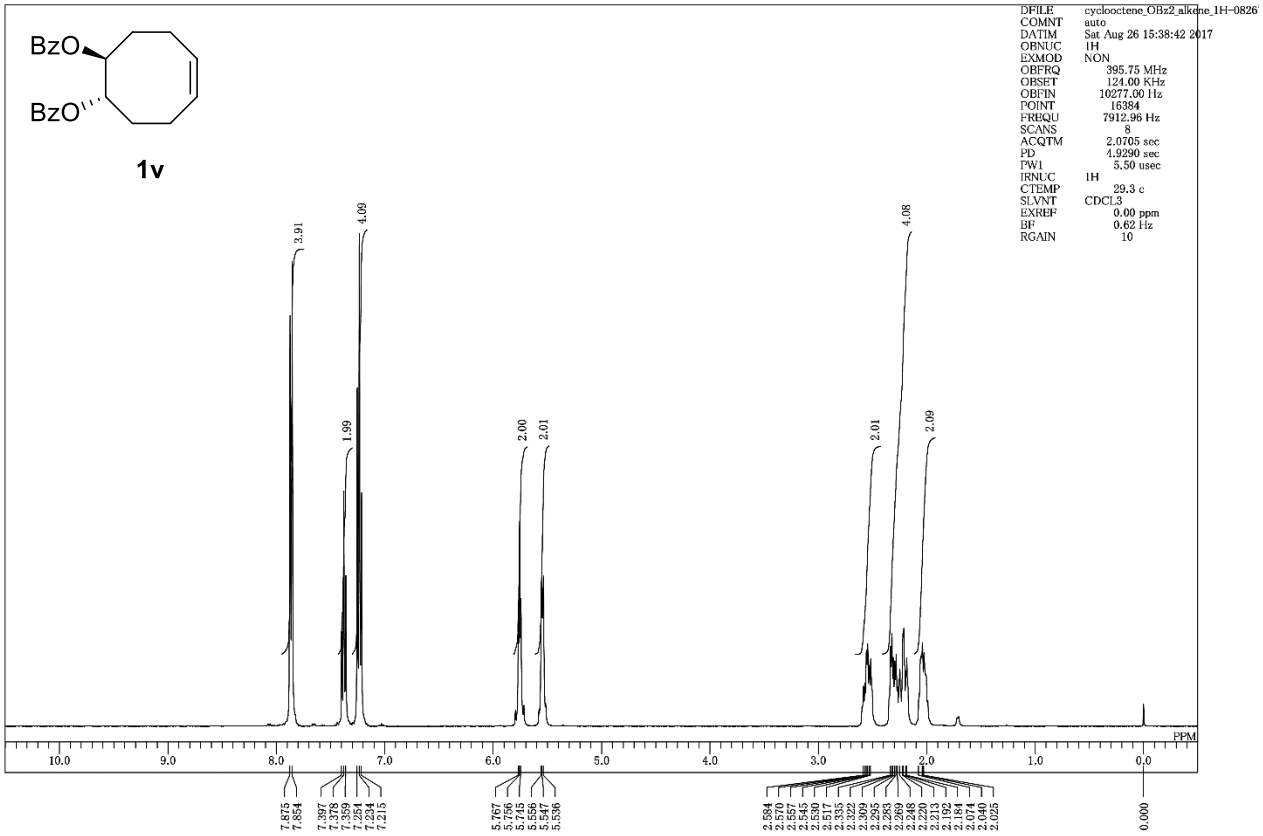
auto


TsN
H
H
1q
DFILE bicyclo_NTs_alkene_1H-0826'.als
COMNT auto
DATIM Sat Aug 26 12:33:30 2017
OBNUC 1H
EXMOD NON
OBFRQ 395.75 MHz
OBSET 124.00 KHz
OBFIN 10277.00 Hz
POINT 16384
FREQU 7912.96 Hz
SCANS 8
ACQTM 2.0705 sec
PD 4.9290 sec
PW1 5.50 usec
IRNUC 1H
CTEMP 32.4 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.62 Hz
RGAIN 16
2.00
2.02
1.93
2.01
2.01
4.21
2.01
2.07
2.08
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.729
7.708
7.317
7.297
7.280
5.534
3.401
3.385
3.378
3.362
3.089
3.076
3.066
3.051
2.428
2.201
2.125
2.085
2.070
1.692
1.642
0.000

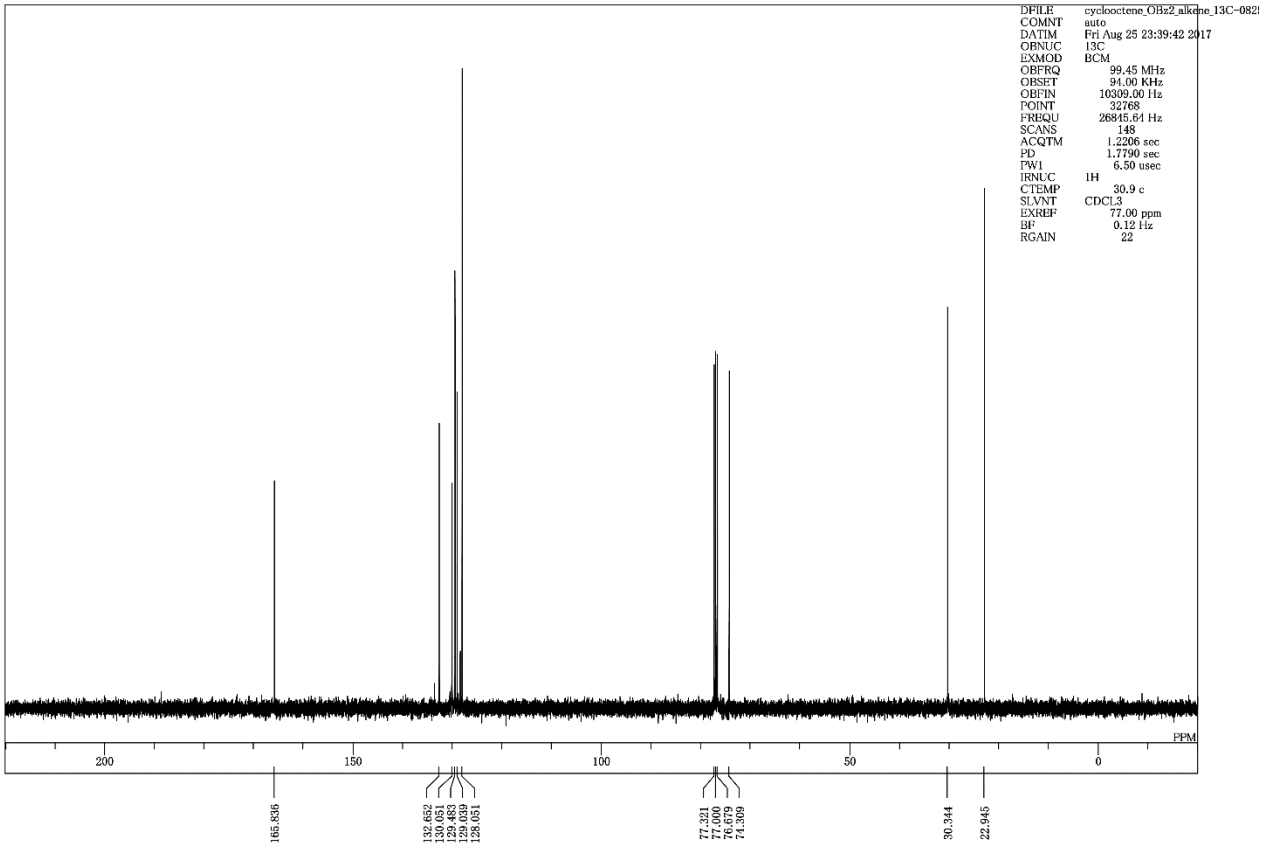
auto


DFILE bicyclo_NTs_alkene_13C-0826'.als
COMNT auto
DATIM Sat Aug 26 12:40:24 2017
OBNUC 13C
EXMOD BCM
OBFRQ 99.45 MHz
OBSET 94.00 KHz
OBFIN 10309.00 Hz
POINT 32768
FREQU 26845.61 Hz
SCANS 128
ACQTM 1.2206 sec
PD 1.7790 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 30.2 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.62 Hz
RGAIN 24
PPM
200
150
100
50
0
143.137
134.751
129.574
127.302
124.043
77.321
77.000
76.679
52.664
34.343
24.245
21.480

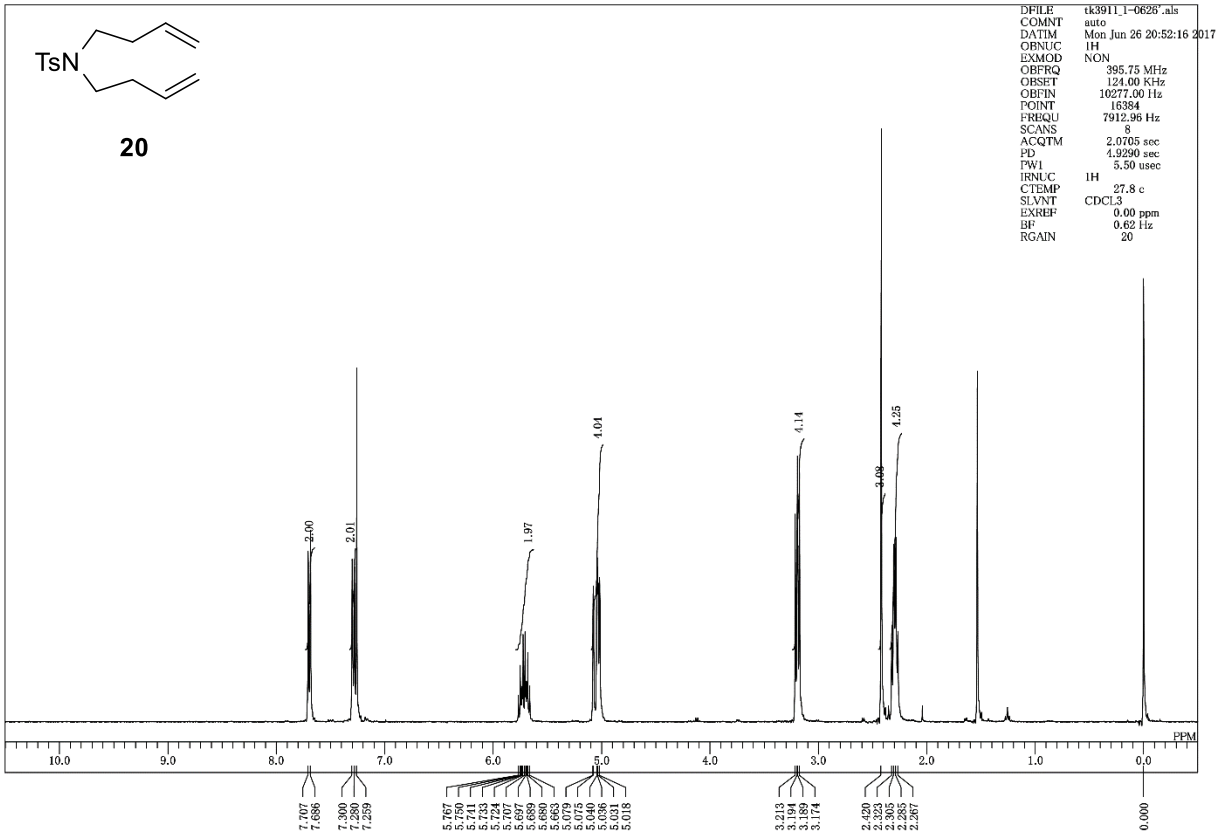
auto


BzO
BzO
1v
DFILE cyclooctene_OBz2_alkene_1H-0826
COMNT auto
DATIM Sat Aug 26 15:38:42 2017
OBNUC 1H
EXMOD NON
OBFRQ 395.75 MHz
OBSET 124.00 KHz
OBFIN 10277.00 Hz
POINT 16384
FREQU 7912.96 Hz
SCANS 8
ACQTM 2.0705 sec
PD 4.9290 sec
PW1 5.50 usec
IRNUC 1H
CTEMP 29.3 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.62 Hz
RGAIN 10
3.91
4.09
1.99
2.00
2.01
2.01
4.08
2.09
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.875
7.854
7.397
7.378
7.359
7.254
7.234
7.210
5.767
5.758
5.745
5.556
5.547
5.536
2.584
2.570
2.557
2.543
2.530
2.517
2.335
2.322
2.309
2.295
2.282
2.269
2.248
2.220
2.213
2.192
2.184
2.075
2.040
2.025
0.000

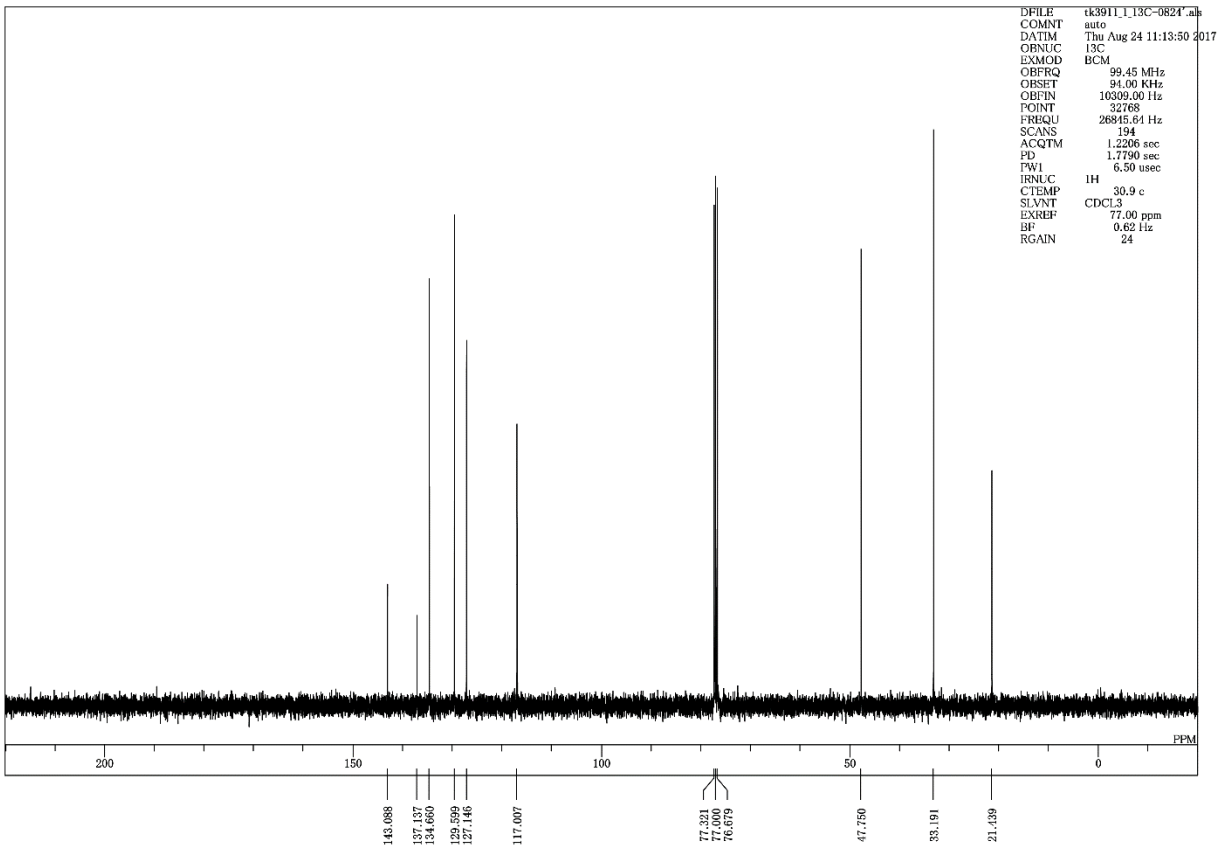
auto


DFILE cyclooctene_OBz2_alkene_13C-0825
COMNT auto
DATIM Fri Aug 25 23:39:42 2017
OBNUC 13C
EXMOD BCM
OBFRQ 99.45 MHz
OBSET 94.00 KHz
OBFIN 10309.00 Hz
POINT 32768
FREQU 26845.64 Hz
SCANS 148
ACQTM 1.2206 sec
PD 1.7790 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 30.9 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 22
PPM
200
150
100
50
0
165.836
132.652
130.051
129.483
129.039
128.051
77.321
77.000
76.679
74.309
30.344
22.945

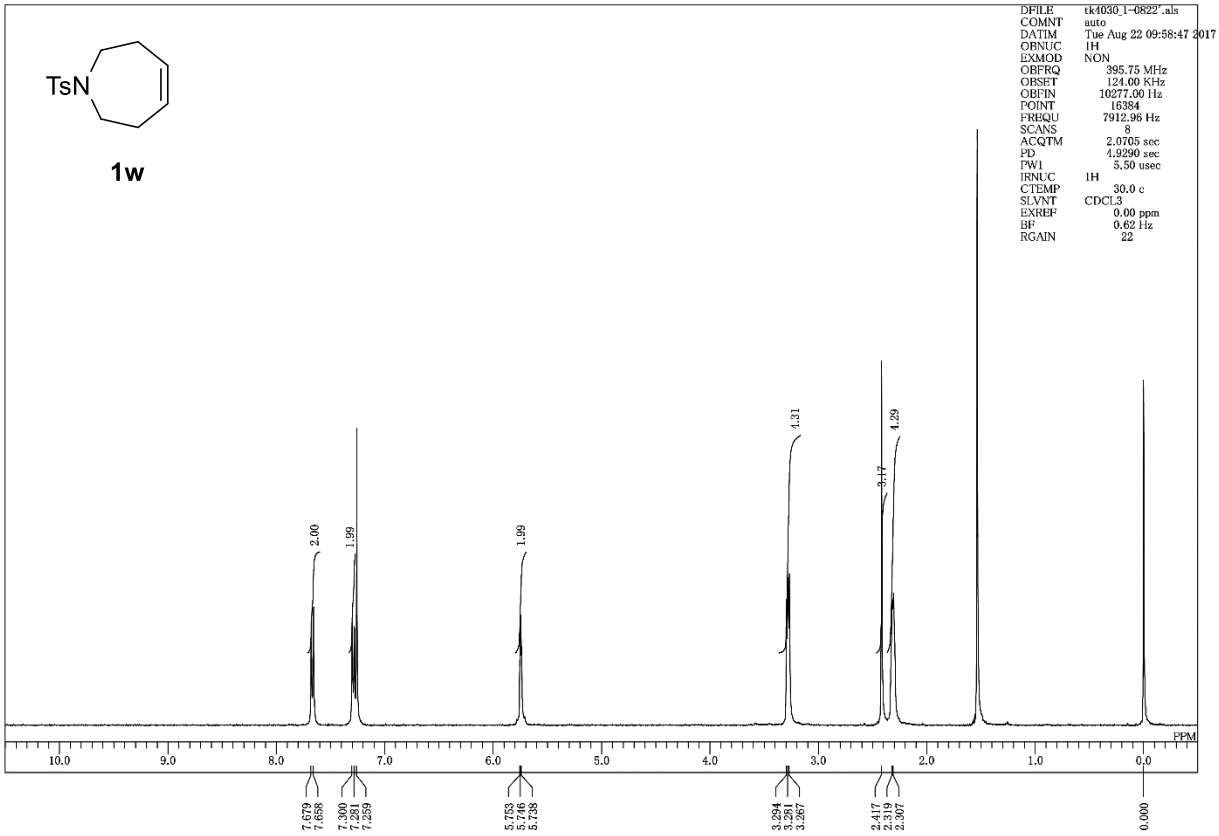
auto


TsN
20
DFILE tk3911_1-0626'.als
COMNT auto
DATIM Mon Jun 26 20:52:16 2017
OBNUC 1H
EXMOD NON
OBFRQ 395.75 MHz
OBSET 124.00 KHz
OBFIN 10277.00 Hz
POINT 16384
FREQU 7912.96 Hz
SCANS 8
ACQTM 2.0705 sec
PD 4.9290 sec
PW1 5.50 usec
IRNUC 1H
CTEMP 27.8 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.62 Hz
RGAIN 20
2.00
2.01
1.97
4.04
4.14
3.08
4.25
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.707
7.686
7.300
7.289
7.259
5.767
5.750
5.741
5.733
5.724
5.707
5.697
5.689
5.680
5.663
5.079
5.075
5.040
5.036
5.031
5.018
3.213
3.194
3.189
3.174
2.420
2.323
2.305
2.285
2.267
0.000

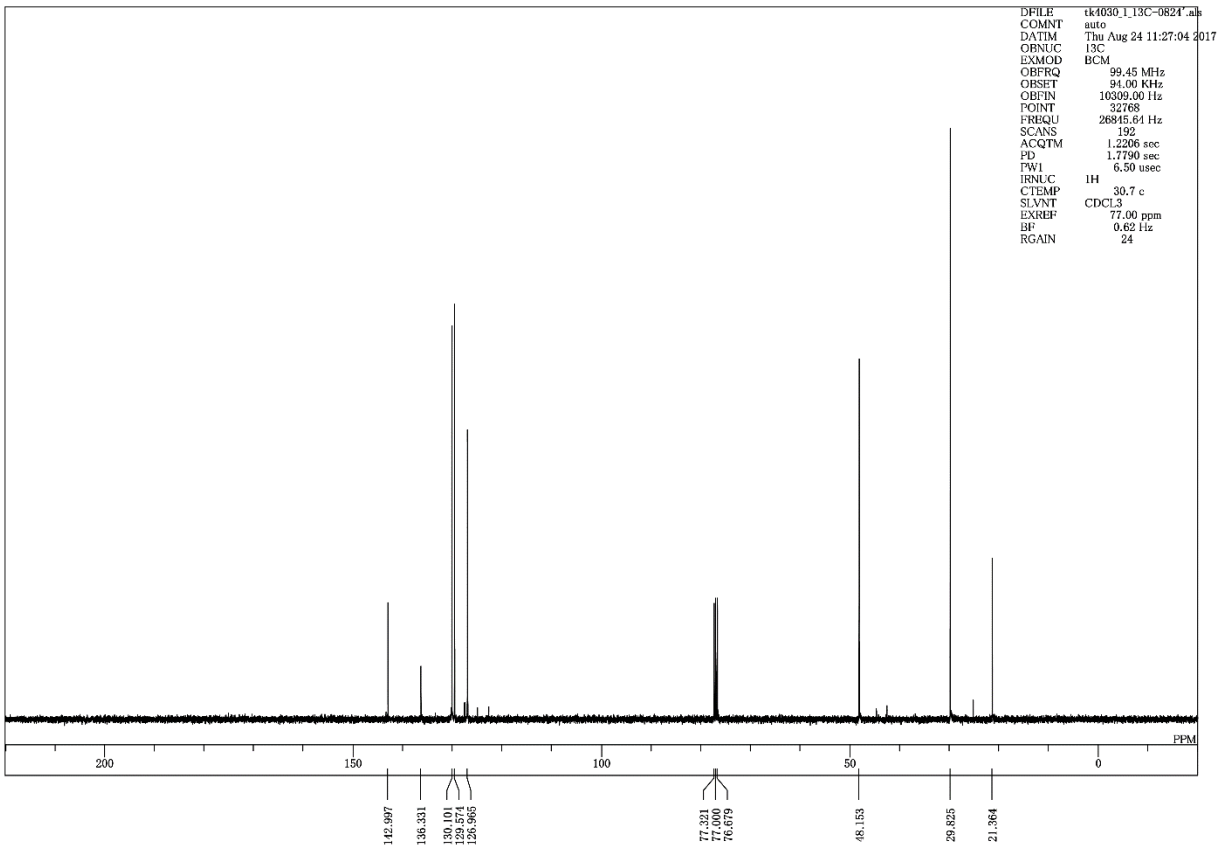
auto


DFILE tk3911_1_13C-0824'.als
COMNT auto
DATIM Thu Aug 24 11:13:50 2017
OBNUC 13C
EXMOD BCM
OBFRQ 99.45 MHz
OBSET 94.00 KHz
OBFIN 10309.00 Hz
POINT 32768
FREQU 26845.61 Hz
SCANS 194
ACQTM 1.2206 sec
PD 1.7790 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 30.9 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.62 Hz
RGAIN 24
PPM
200
150
100
50
0
143.088
137.137
134.660
129.599
127.146
117.007
77.321
77.000
76.679
47.750
33.191
21.439

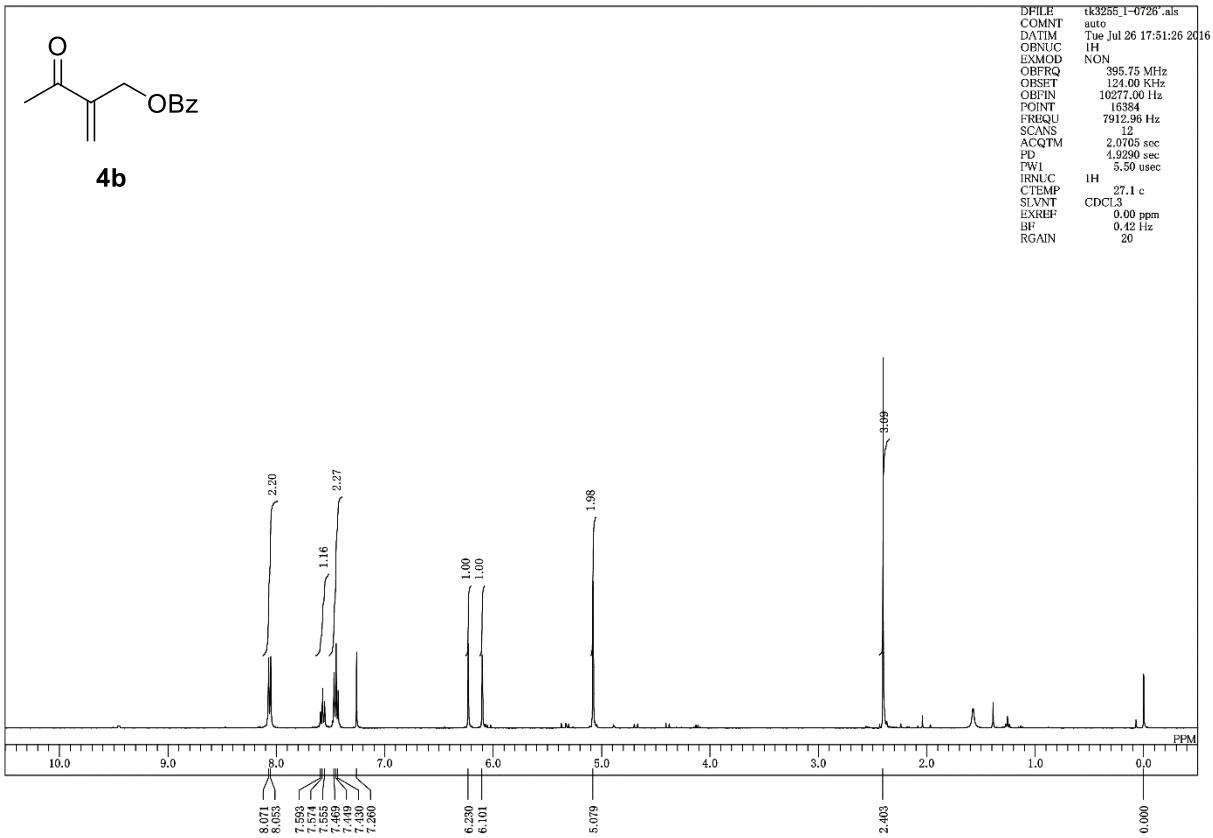
auto


TsN
1w
DFILE tk4030_1-0822'.als
COMNT auto
DATIM Tue Aug 22 09:58:47 2017
OBNUC 1H
EXMOD NON
OBFRQ 395.75 MHz
OBSET 124.00 KHz
OBFIN 10277.00 Hz
POINT 16384
FREQU 7912.96 Hz
SCANS 8
ACQTM 2.0705 sec
PD 4.9290 sec
PW1 5.50 usec
IRNUC 1H
CTEMP 30.0 c
SLVNT CDCl3
EXREF 0.00 ppm
BF 0.62 Hz
RGAIN 22
2.00
1.99
1.99
4.31
3.17
4.29
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.679
7.658
7.300
7.289
7.259
5.753
5.746
5.738
3.294
3.289
3.267
2.417
2.319
2.307
0.000

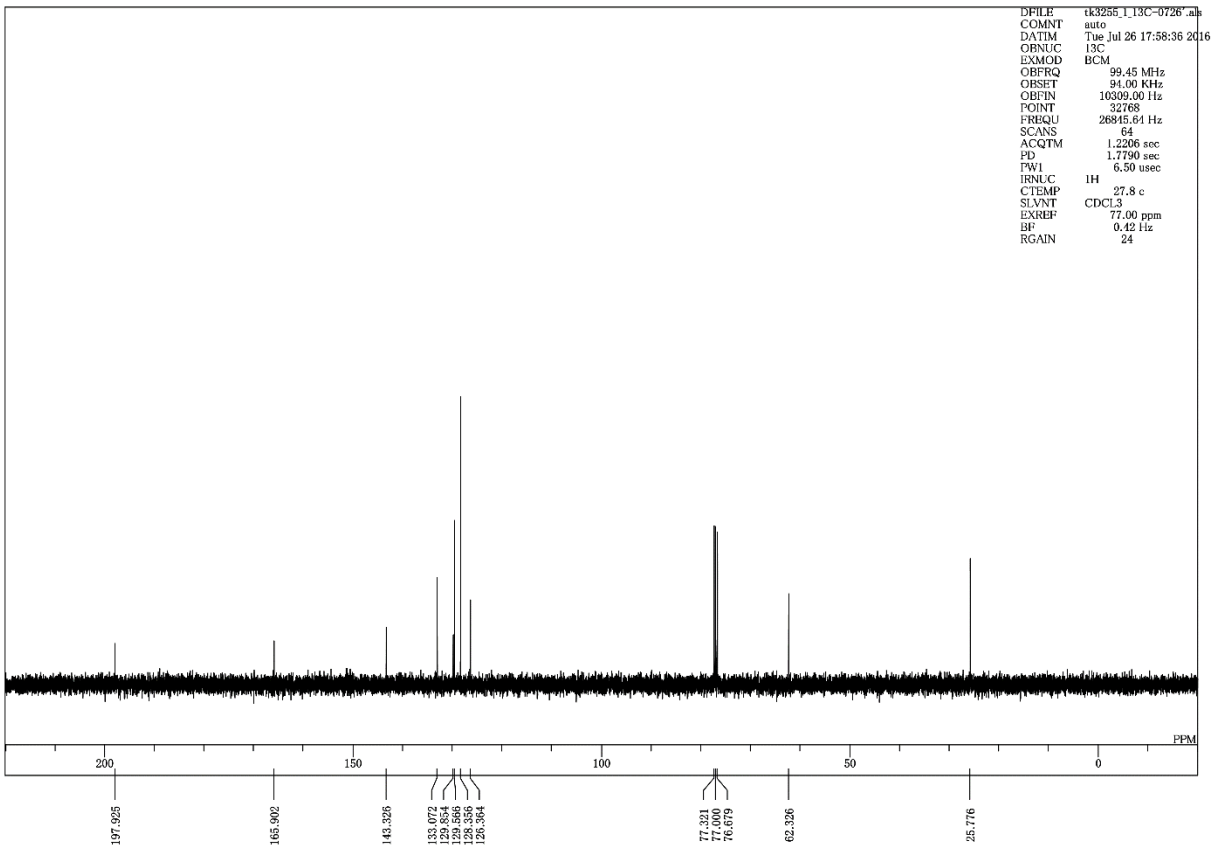
auto


DFILE tk4030_1_13C-0824'.als
COMNT auto
DATIM Thu Aug 24 11:27:04 2017
OBNUC 13C
EXMOD BCM
OBFRQ 99.45 MHz
OBSET 94.00 KHz
OBFIN 10309.00 Hz
POINT 32768
FREQU 26845.61 Hz
SCANS 192
ACQTM 1.2206 sec
PD 1.7790 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 30.7 c
SLVNT CDCl3
EXREF 77.00 ppm
BF 0.62 Hz
RGAIN 24
PPM
200
150
100
50
0
142.997
136.331
130.101
129.574
126.965
77.321
77.000
76.679
48.153
29.825
21.364

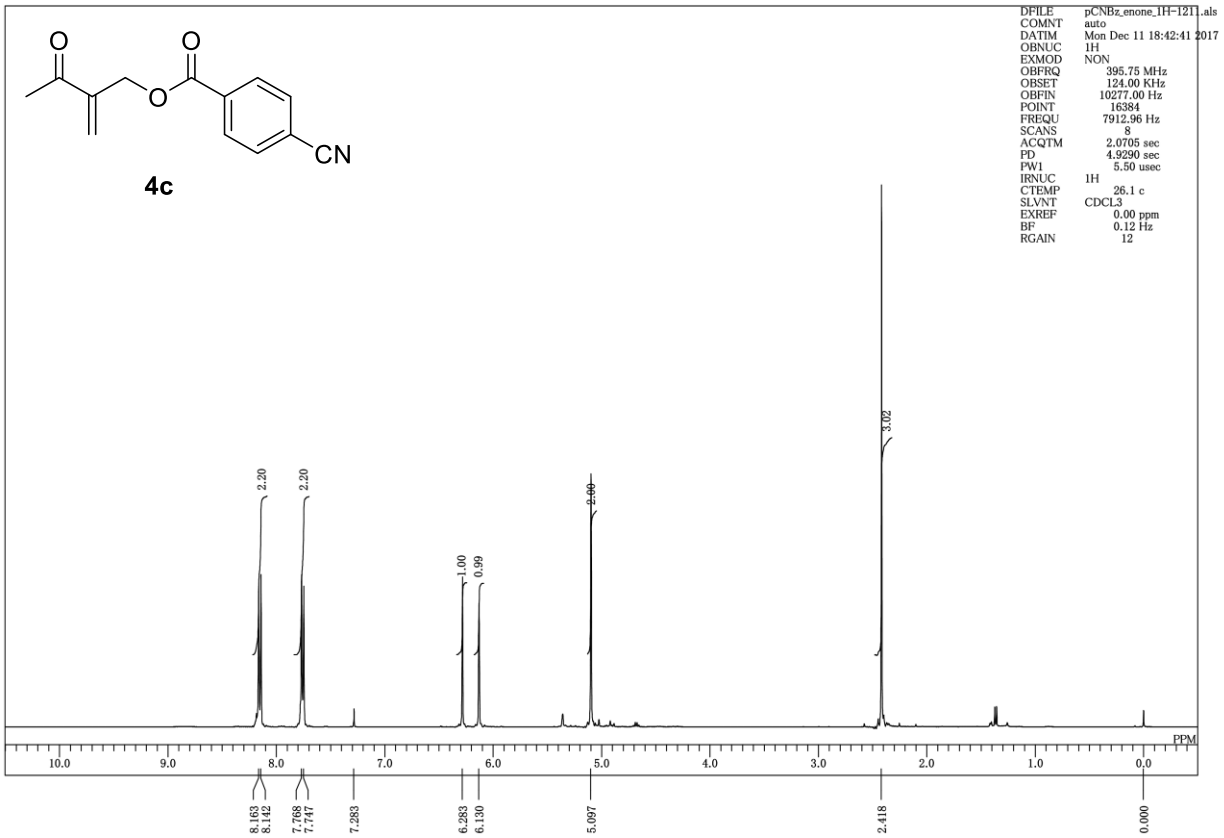
auto


O
OBz
4b
DFILE tk3255_1-0726'.als
COMNT auto
DATIM Tue Jul 26 17:51:26 2016
OBNUC 1H
EXMOD NON
OBFRQ 395.75 MHz
OBSET 124.00 KHz
OBFIN 10277.00 Hz
POINT 16384
FREQU 7912.96 Hz
SCANS 12
ACQTM 2.0705 sec
PD 4.9290 sec
PW1 5.50 usec
IRNUC 1H
CTEMP 27.1 c
SLVNT CDCl3
EXREF 0.00 ppm
BF 0.42 Hz
RGAIN 20
2.20
1.16
2.27
1.09
1.00
1.98
3.09
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
8.071
8.053
7.593
7.574
7.555
7.469
7.449
7.430
7.260
6.230
6.101
5.079
2.403
0.000

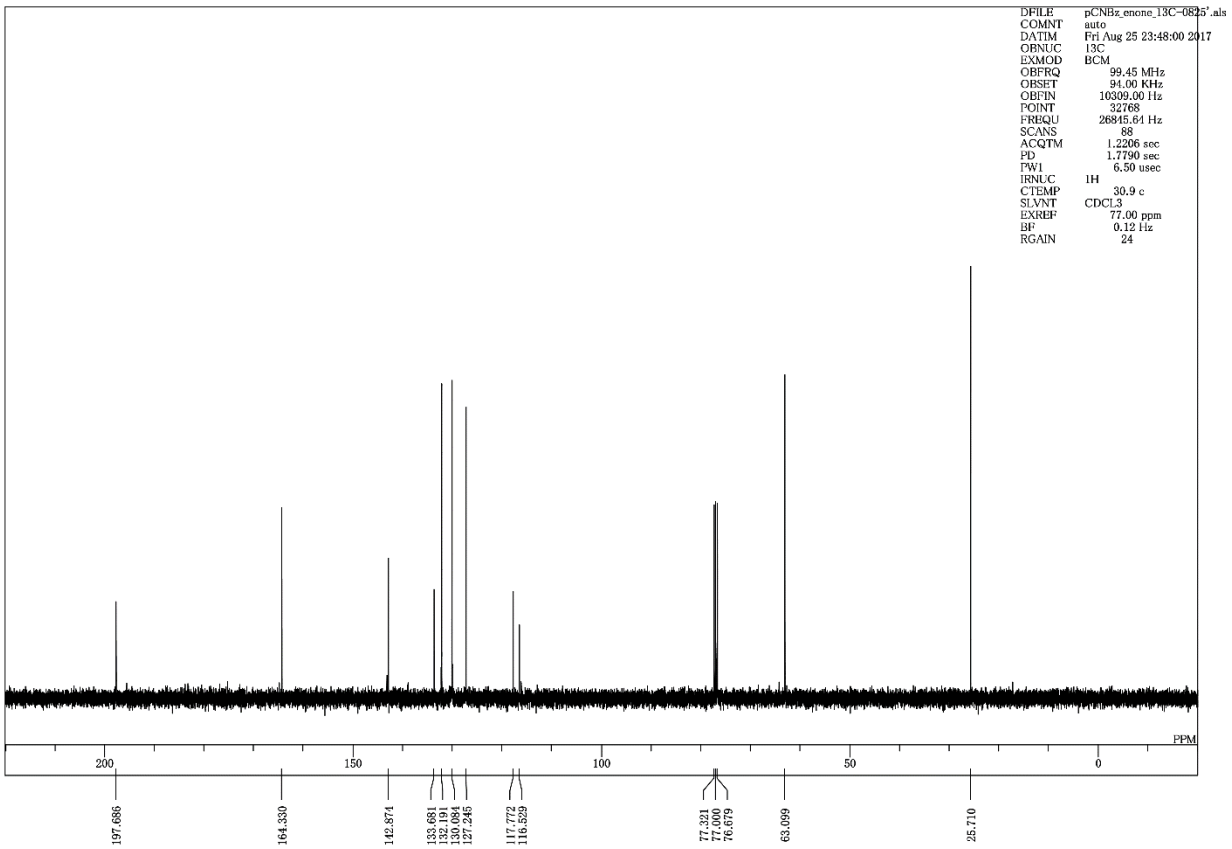
auto


DFILE tk3255_1_13C-0726'.als
COMNT auto
DATIM Tue Jul 26 17:58:36 2016
OBNUC 13C
EXMOD BCM
OBFRQ 99.45 MHz
OBSET 94.00 KHz
OBFIN 10309.00 Hz
POINT 32768
FREQU 26845.64 Hz
SCANS 64
ACQTM 1.2206 sec
PD 1.7790 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 27.8 c
SLVNT CDCl3
EXREF 77.00 ppm
BF 0.42 Hz
RGAIN 24
PPM
200
150
100
50
0
197.925
165.902
143.326
133.072
129.864
129.566
128.356
128.304
77.321
77.000
76.679
62.326
25.776

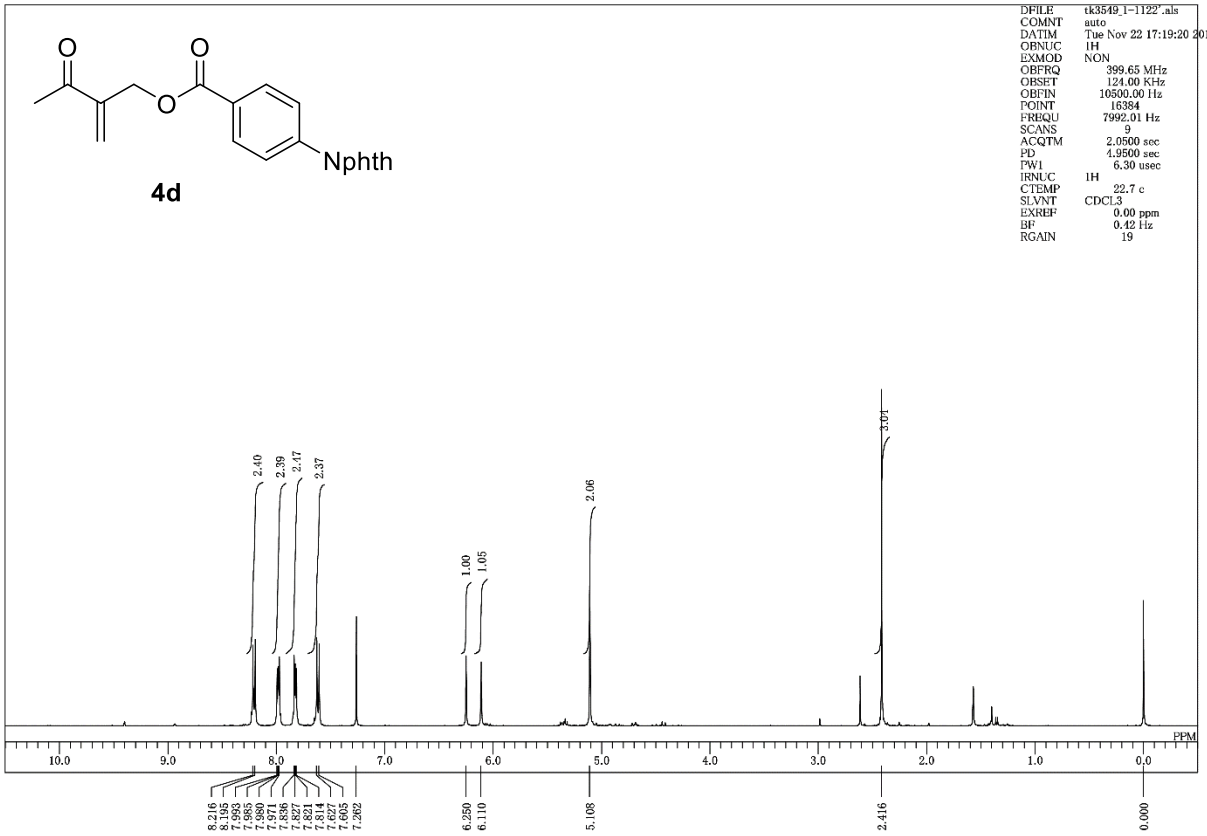
auto


4c
DFILE pCNBz_enone_1H-121..als
COMNT auto
DATIM Mon Dec 11 18:42:41 2017
OBNUC 1H
EXMOD NON
OBFRQ 395.75 MHz
OBSET 124.00 KHz
OBFIN 10277.00 Hz
POINT 16384
FREQU 7912.96 Hz
SCANS 8
ACQTM 2.0705 sec
PD 4.9290 sec
PW1 5.50 usec
IRNUC 1H
CTEMP 26.1 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 12
2.20
2.20
1.00
0.99
2.00
3.02
PPM
8.163
8.142
7.768
7.747
7.283
6.283
6.130
5.097
2.418
0.000

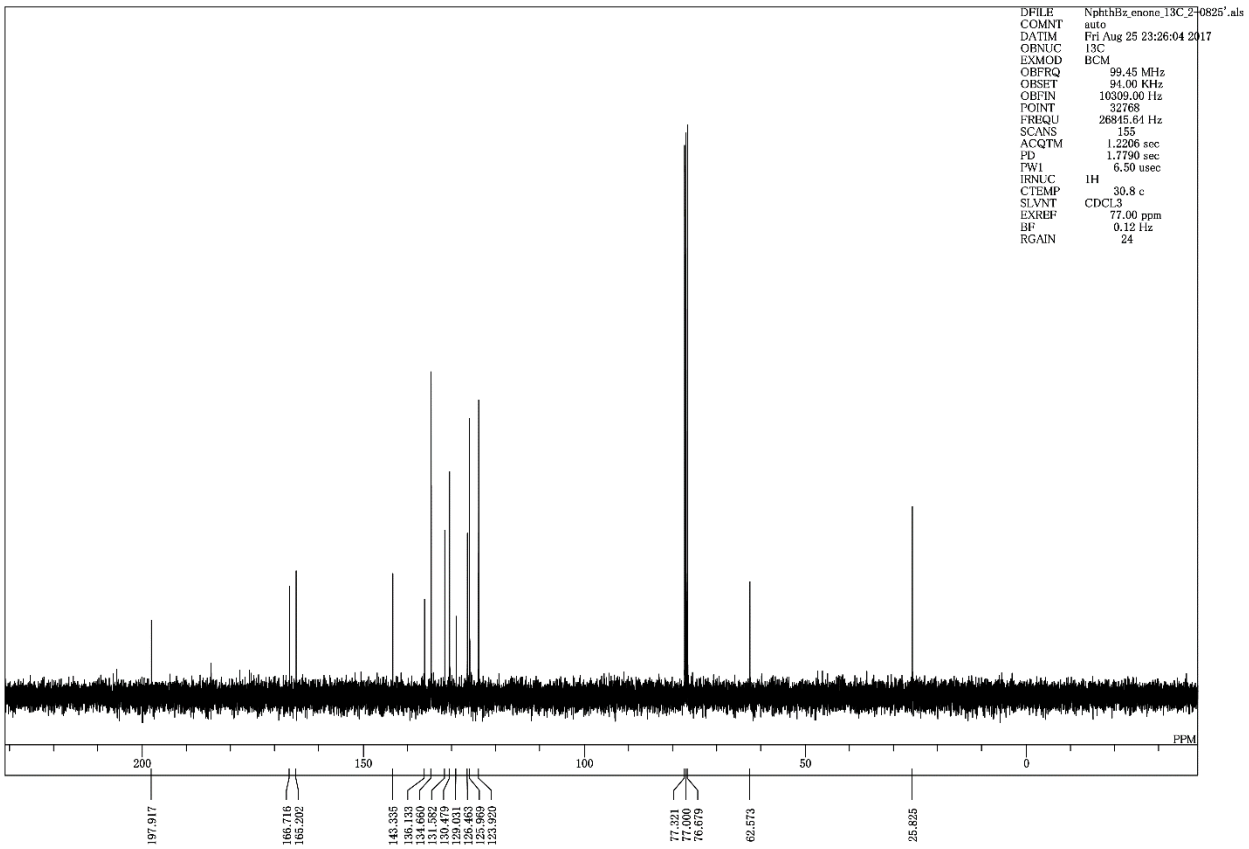
auto


DFILE pCNBz_enone_13C-0825'..als
COMNT auto
DATIM Fri Aug 25 23:48:00 2017
OBNUC 13C
EXMOD BCM
OBFRQ 99.45 MHz
OBSET 94.00 KHz
OBFIN 10309.00 Hz
POINT 32768
FREQU 26845.61 Hz
SCANS 88
ACQTM 1.2206 sec
PD 1.7790 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 30.9 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 24
PPM
197.686
164.330
142.874
133.681
132.191
130.084
127.245
117.772
116.829
77.321
77.000
76.679
63.099
25.710

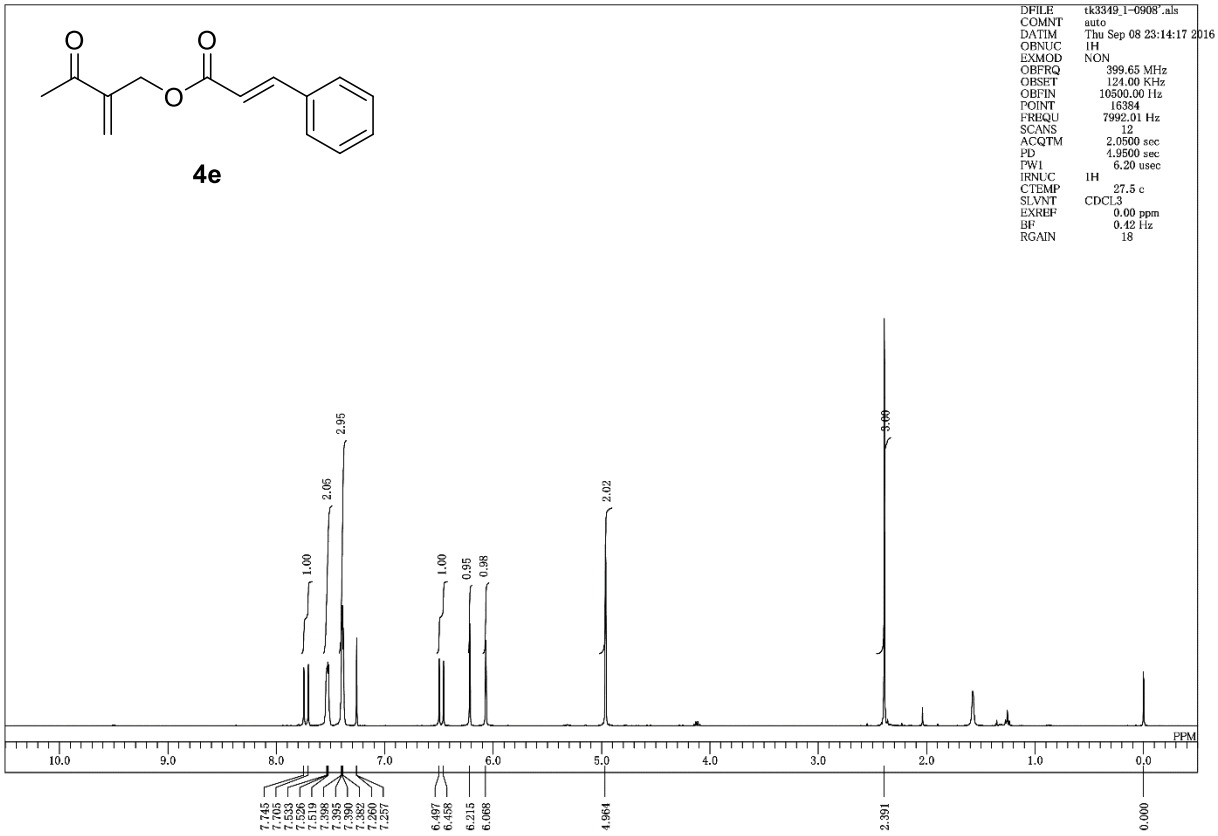
auto


4d
Nphth
DFILE tk3549_1-1122'.als
COMNT auto
DATIM Tue Nov 22 17:19:20 2016
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 16384
FREQU 7992.01 Hz
SCANS 9
ACQTM 2.0500 sec
PD 4.9500 sec
PW1 6.30 usec
IRNUC 1H
CTEMP 22.7 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.42 Hz
RGAIN 19
2.40
2.39
2.47
2.37
1.00
1.05
2.06
3.01
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
8.216
8.195
7.993
7.983
7.980
7.971
7.838
7.827
7.821
7.814
7.627
7.605
7.262
6.250
6.110
5.108
2.416
0.000

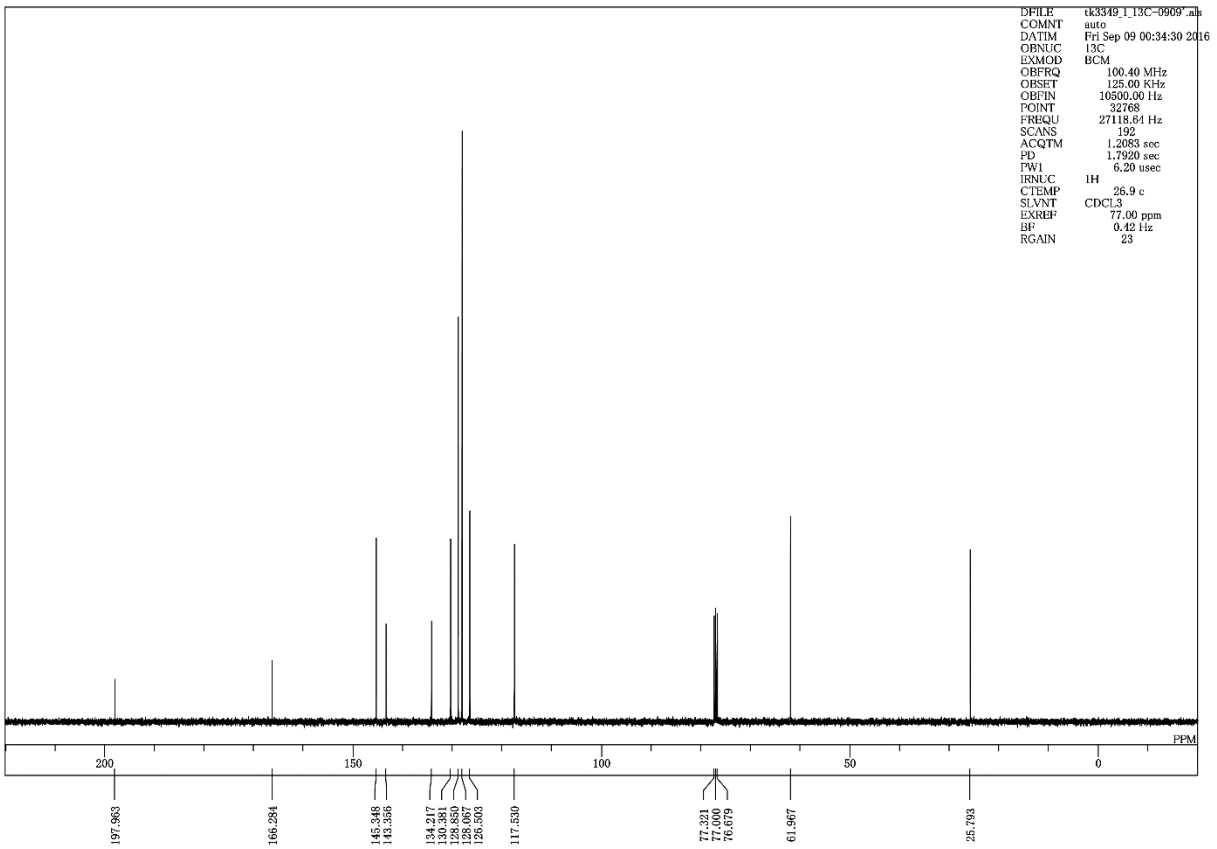
auto


DFILE NphthBz_enone_13C_2-0825'.als
COMNT auto
DATIM Fri Aug 25 23:26:04 2017
OBNUC 13C
EXMOD BCM
OBFRQ 99.45 MHz
OBSET 94.00 KHz
OBFIN 10309.00 Hz
POINT 32768
FREQU 26845.61 Hz
SCANS 155
ACQTM 1.2206 sec
PD 1.7790 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 30.8 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 24
PPM
200
150
100
50
0
197.917
165.716
165.202
143.335
136.133
134.660
131.582
130.479
129.031
128.463
125.969
123.929
77.321
77.000
76.679
62.573
25.825

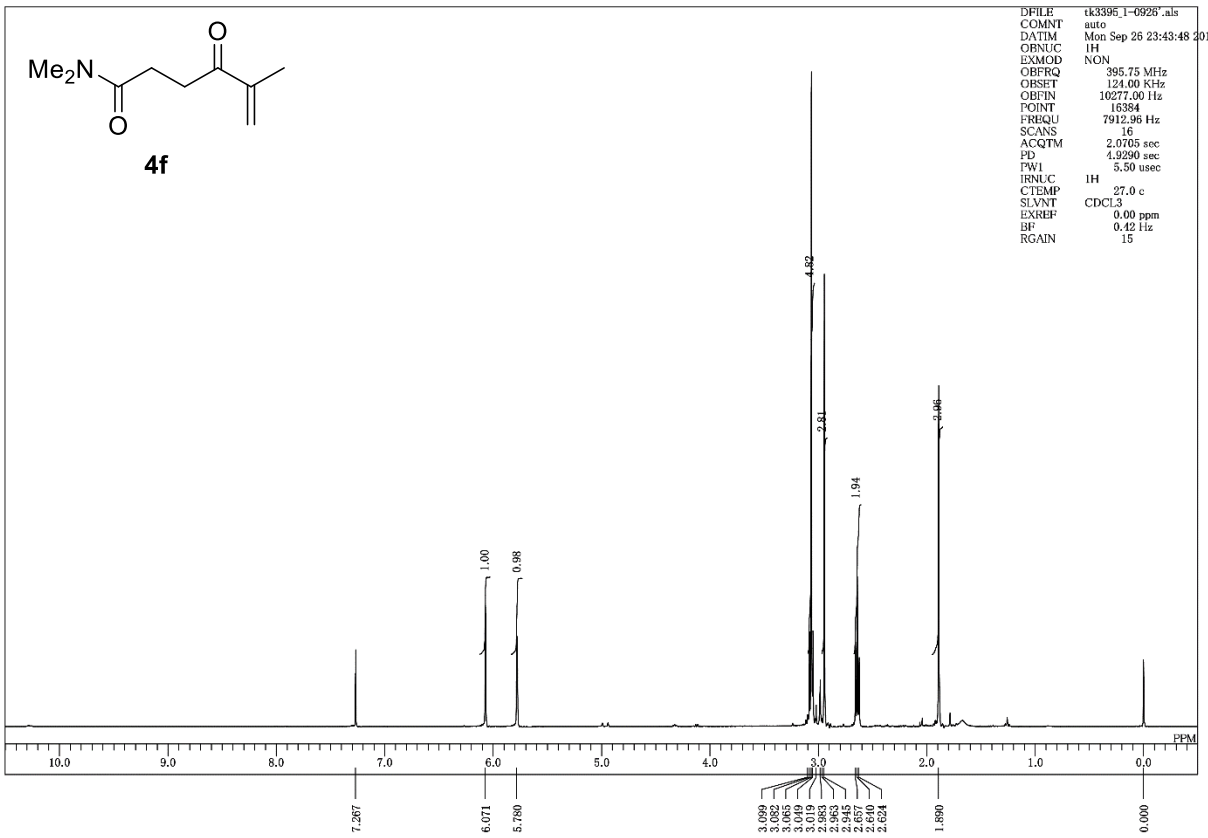
auto


4e
DFILE tk3349_1-0908'.als
COMNT auto
DATIM Thu Sep 08 23:14:17 2016
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 16384
FREQU 7992.01 Hz
SCANS 12
ACQTM 2.0500 sec
PD 4.9500 sec
PW1 6.20 usec
IRNUC 1H
CTEMP 27.5 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.42 Hz
RGAIN 18
1.00
2.05
2.95
1.00
0.95
0.98
2.02
3.00
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.745
7.705
7.533
7.526
7.519
7.398
7.395
7.390
7.382
7.260
7.257
6.497
6.458
6.215
6.068
4.964
2.391
0.000

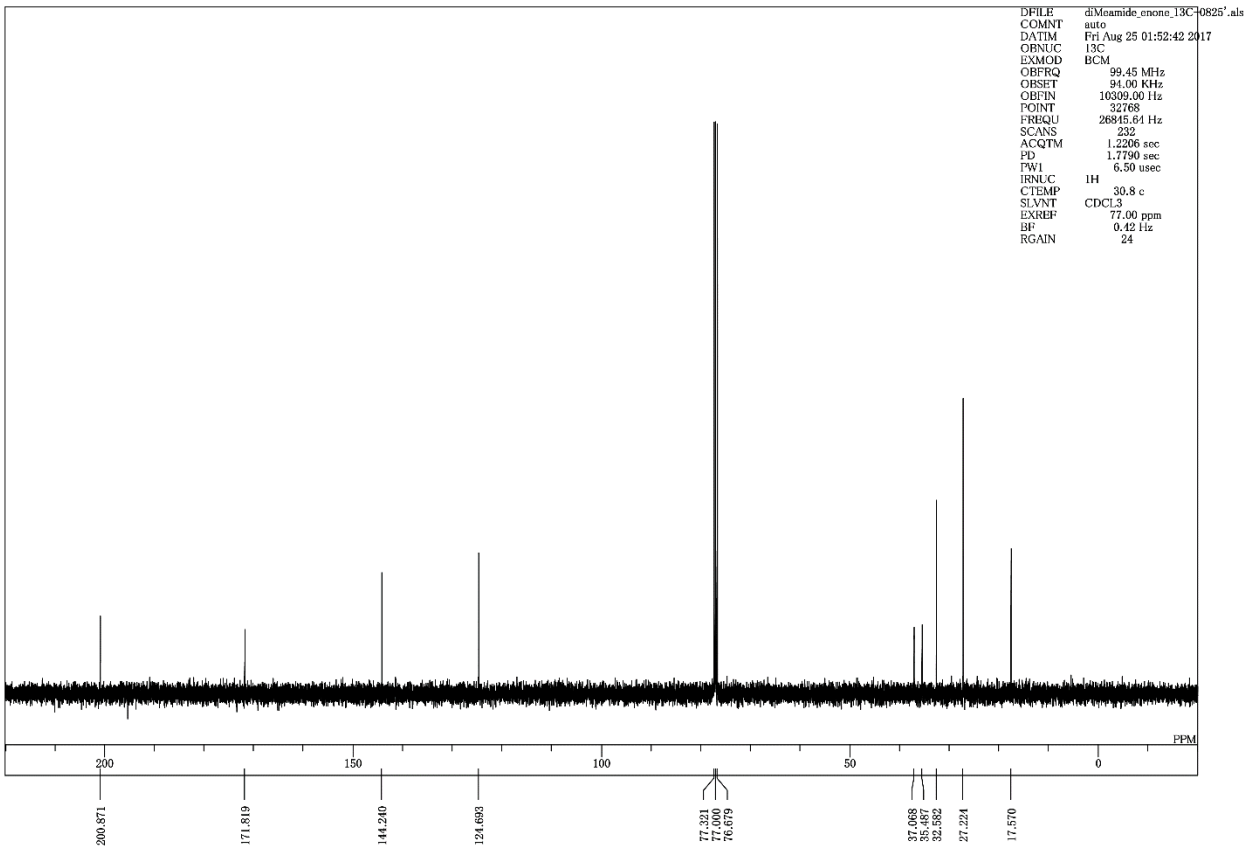
auto


DFILE tk3349_1_13C-0909'.als
COMNT auto
DATIM Fri Sep 09 00:34:30 2016
OBNUC 13C
EXMOD BCM
OBFRQ 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27118.64 Hz
SCANS 192
ACQTM 1.2083 sec
PD 1.7920 sec
PW1 6.20 usec
IRNUC 1H
CTEMP 26.9 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.42 Hz
RGAIN 23
PPM
200
150
100
50
0
197.963
166.394
145.348
143.356
134.217
130.381
128.850
128.057
126.593
117.530
77.321
77.000
76.679
61.967
25.793

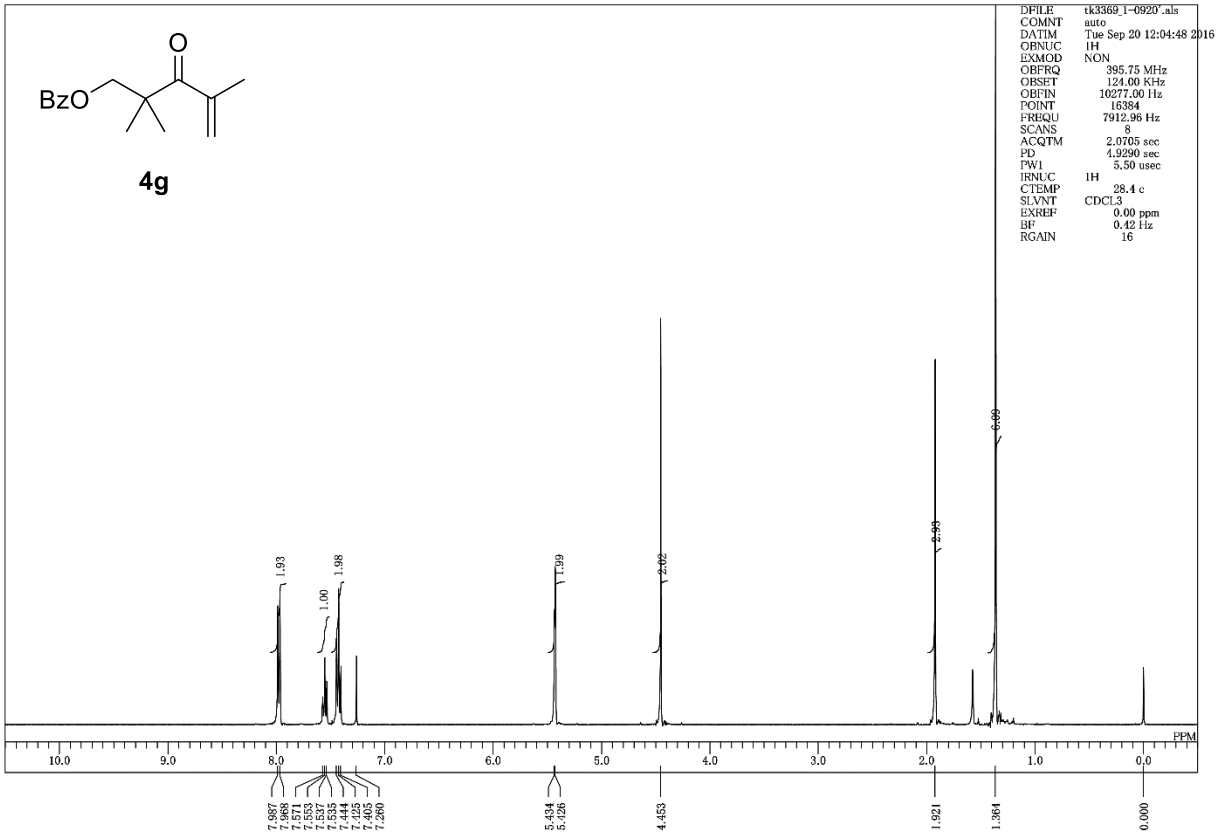
auto


Me2N
O
O
4f
DFILE tk3395_1-0926'.als
COMNT auto
DATIM Mon Sep 26 23:43:48 2016
OBNUC 1H
EXMOD NON
OBFRQ 395.75 MHz
OBSET 124.00 KHz
OBFIN 10277.00 Hz
POINT 16384
FREQU 7912.96 Hz
SCANS 16
ACQTM 2.0705 sec
PD 4.9290 sec
PW1 5.50 usec
IRNUC 1H
CTEMP 27.0 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.42 Hz
RGAIN 15
4.82
2.81
3.96
1.94
1.00
0.98
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.267
6.071
5.780
3.099
3.082
3.065
3.049
3.019
2.983
2.963
2.945
2.655
2.610
2.624
1.890
0.000

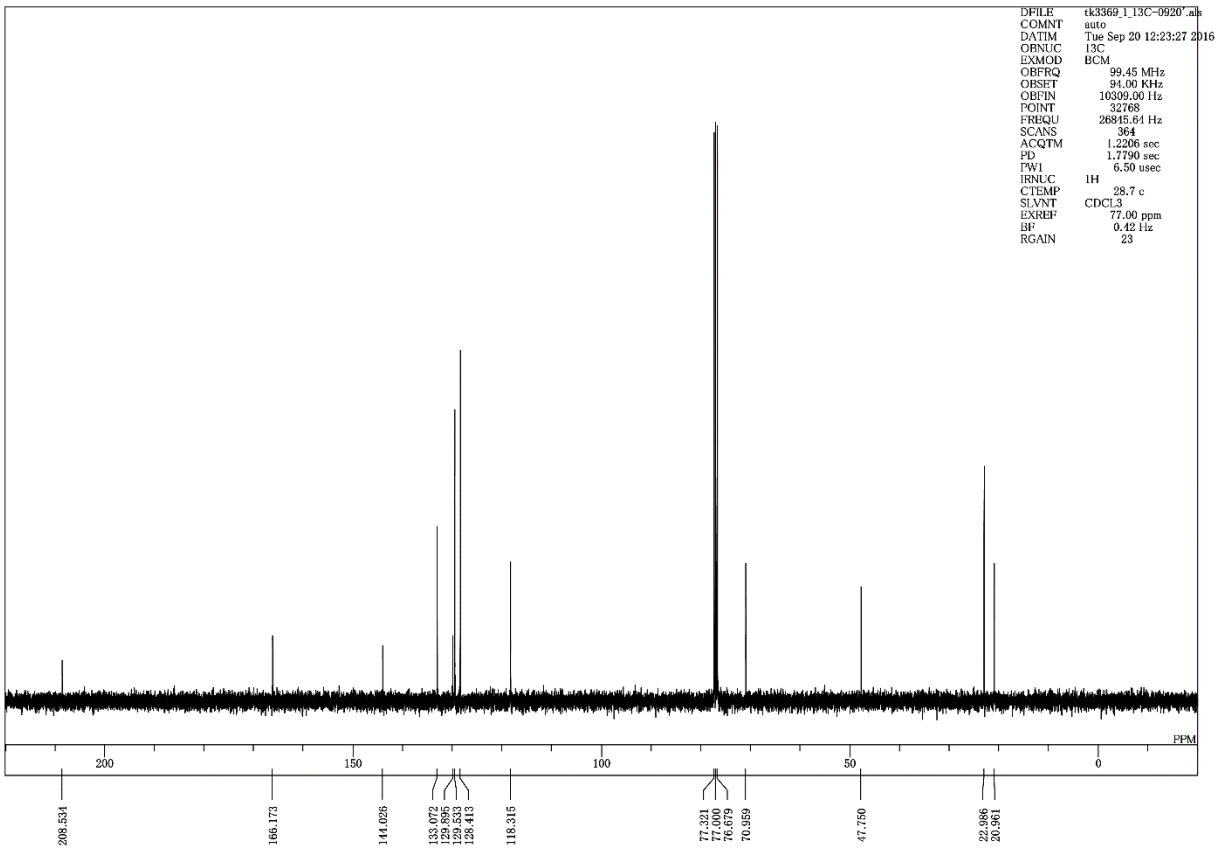
auto


DFILE diMeamide_enone_13C-0825'.als
COMNT auto
DATIM Fri Aug 25 01:52:42 2017
OBNUC 13C
EXMOD BCM
OBFRQ 99.45 MHz
OBSET 94.00 KHz
OBFIN 10309.00 Hz
POINT 32768
FREQU 26845.64 Hz
SCANS 232
ACQTM 1.2206 sec
PD 1.7790 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 30.8 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.42 Hz
RGAIN 24
PPM
200
150
100
50
0
200.871
171.819
144.240
124.693
77.321
77.000
76.679
37.068
35.487
32.582
27.224
17.570

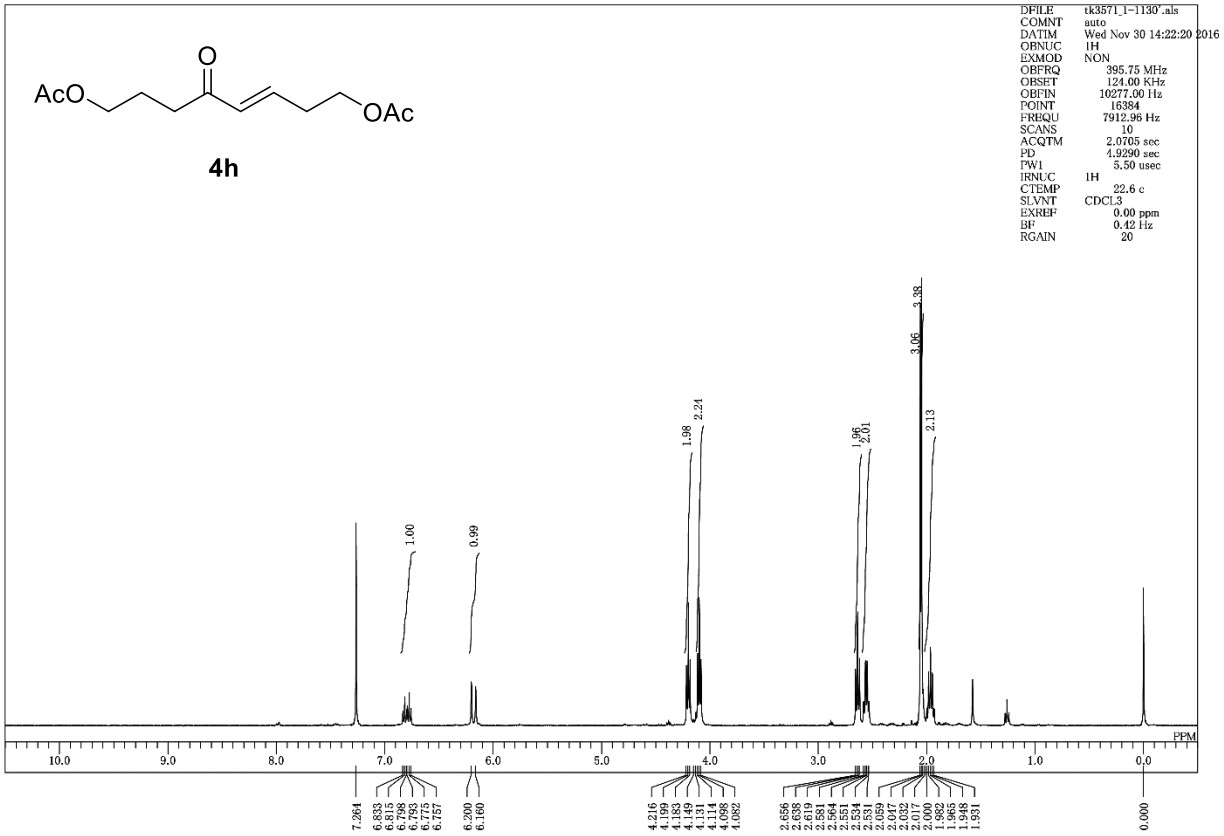
auto


O
BzO
4g
DFILE tk3369_1-0920'.als
COMNT auto
DATIM Tue Sep 20 12:04:48 2016
OBNUC 1H
EXMOD NON
OBFRQ 395.75 MHz
OBSET 124.00 KHz
OBFIN 10277.00 Hz
POINT 16384
FREQU 7912.96 Hz
SCANS 8
ACQTM 2.0705 sec
PD 4.9290 sec
PW1 5.50 usec
IRNUC 1H
CTEMP 28.4 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.42 Hz
RGAIN 16
1.93
1.00
1.98
1.99
2.02
2.93
6.09
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.987
7.968
7.571
7.553
7.537
7.535
7.444
7.425
7.405
7.280
5.434
5.426
4.453
1.921
1.364
0.000

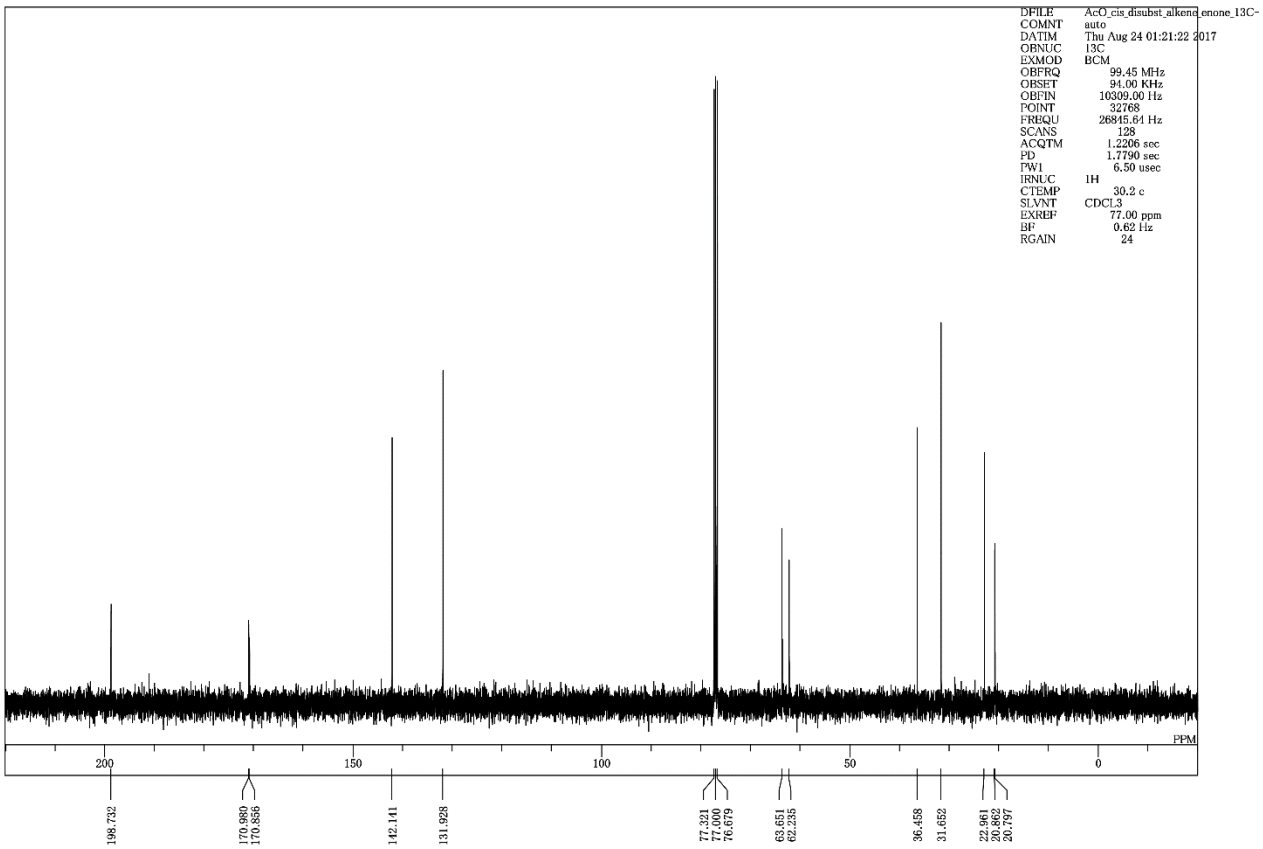
auto


DFILE tk3369_1_13C-0920'.als
COMNT auto
DATIM Tue Sep 20 12:23:27 2016
OBNUC 13C
EXMOD BCM
OBFRQ 99.45 MHz
OBSET 94.00 KHz
OBFIN 10309.00 Hz
POINT 32768
FREQU 26845.64 Hz
SCANS 364
ACQTM 1.2206 sec
PD 1.7790 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 28.7 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.42 Hz
RGAIN 23
PPM
200
150
100
50
0
208.534
166.173
144.026
133.072
129.895
129.533
128.413
118.315
77.321
77.000
76.679
70.959
47.750
22.986
20.961

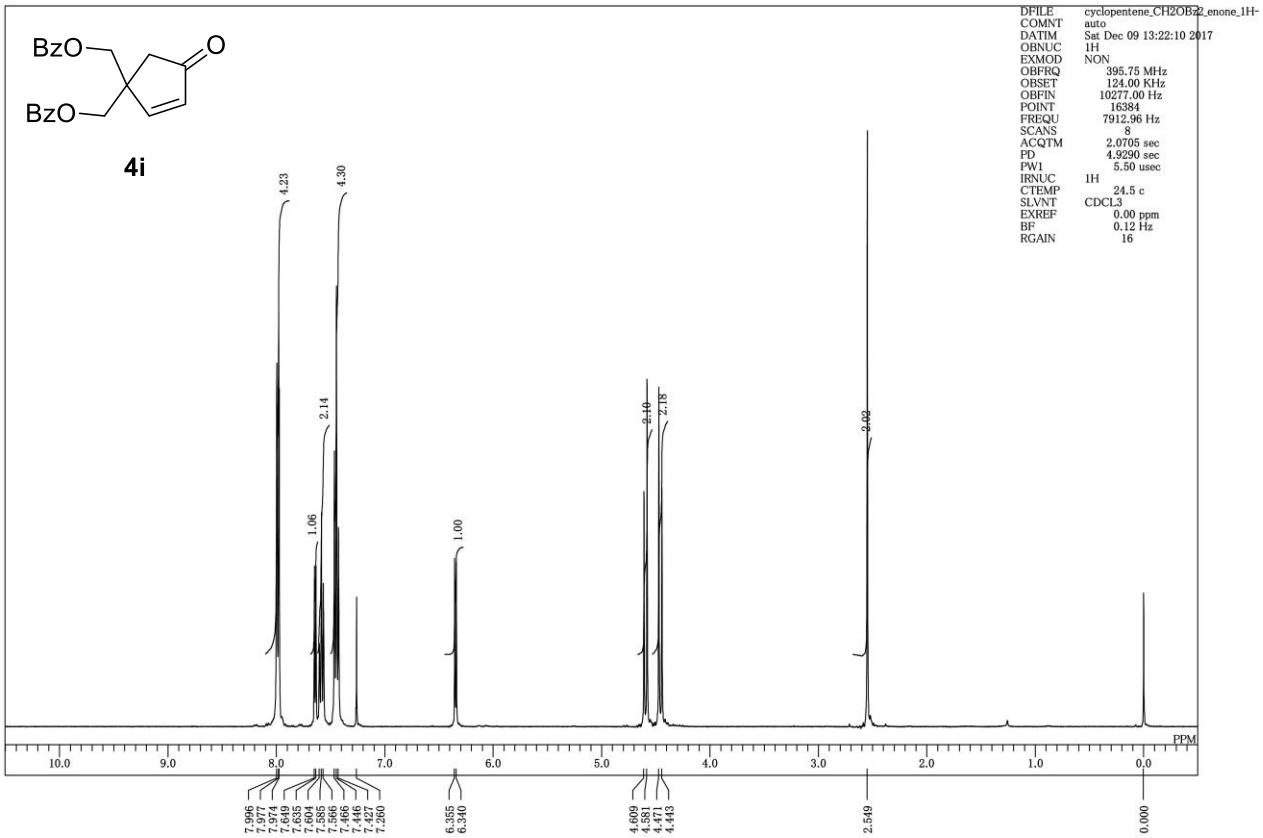
auto


AcO
O
OAc
4h
DFILE tk3571_1-1130'.als
COMNT auto
DATIM Wed Nov 30 14:22:20 2016
OBNUC 1H
EXMOD NON
OBFRQ 395.75 MHz
OBSET 124.00 KHz
OBFIN 10277.00 Hz
POINT 16384
FREQU 7912.96 Hz
SCANS 10
ACQTM 2.0705 sec
PD 4.9290 sec
PW1 5.50 usec
IRNUC 1H
CTEMP 22.6 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.42 Hz
RGAIN 20
1.00
0.99
1.98
2.24
1.96
2.01
3.06
3.38
2.13
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.264
6.833
6.815
6.798
6.793
6.777
6.757
6.200
6.180
4.216
4.199
4.182
4.149
4.131
4.114
4.098
4.082
2.656
2.638
2.619
2.581
2.564
2.555
2.534
2.531
2.059
2.047
2.032
2.017
2.000
1.982
1.965
1.948
1.931
0.000

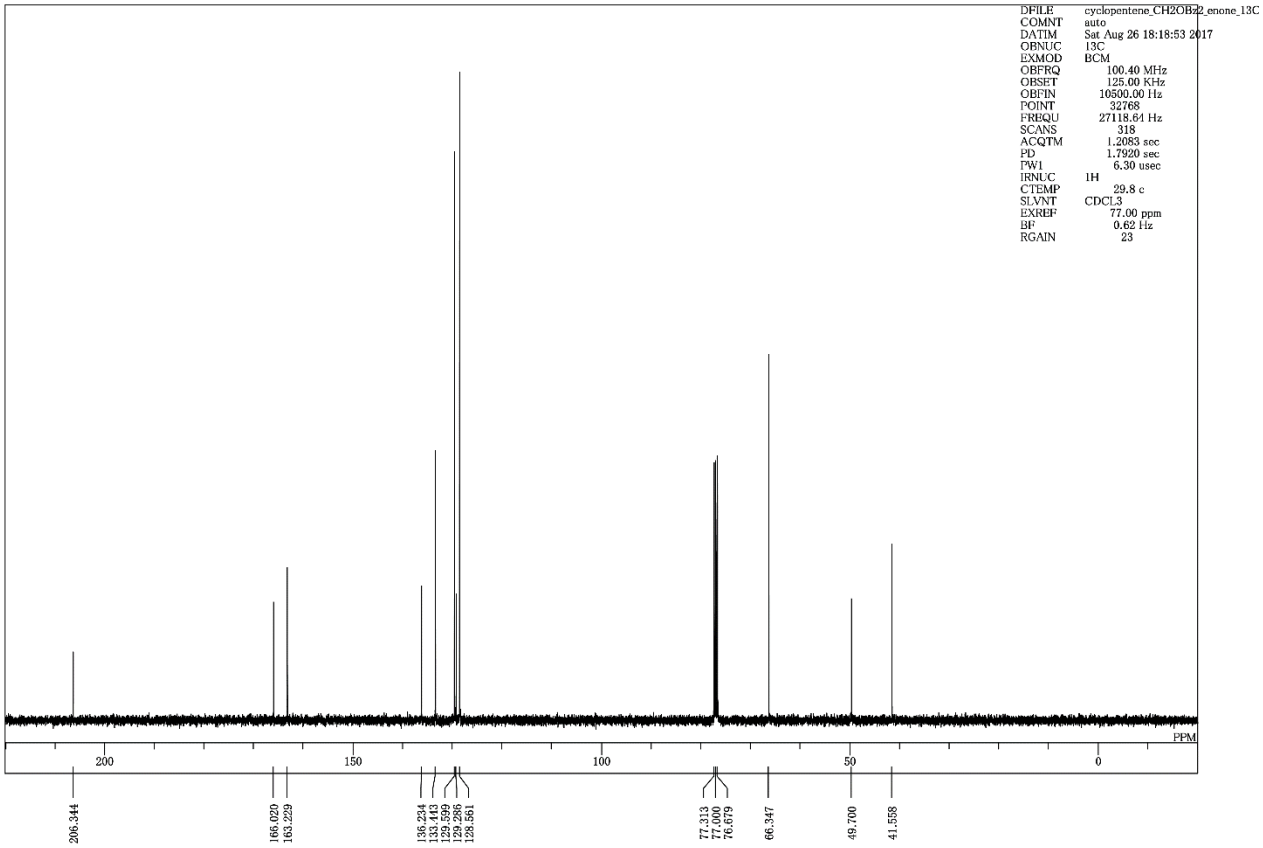
auto


DFILE AcO_cis_disubst_alkenq_enone_13C-
COMNT auto
DATIM Thu Aug 24 01:21:22 2017
OBNUC 13C
EXMOD BCM
OBFRQ 99.45 MHz
OBSET 94.00 KHz
OBFIN 10309.00 Hz
POINT 32768
FREQU 26845.61 Hz
SCANS 128
ACQTM 1.2206 sec
PD 1.7790 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 30.2 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.62 Hz
RGAIN 24
PPM
200
150
100
50
0
198.732
170.989
170.858
142.141
131.928
77.321
77.000
76.679
63.651
62.235
36.458
31.652
22.961
20.862
20.797

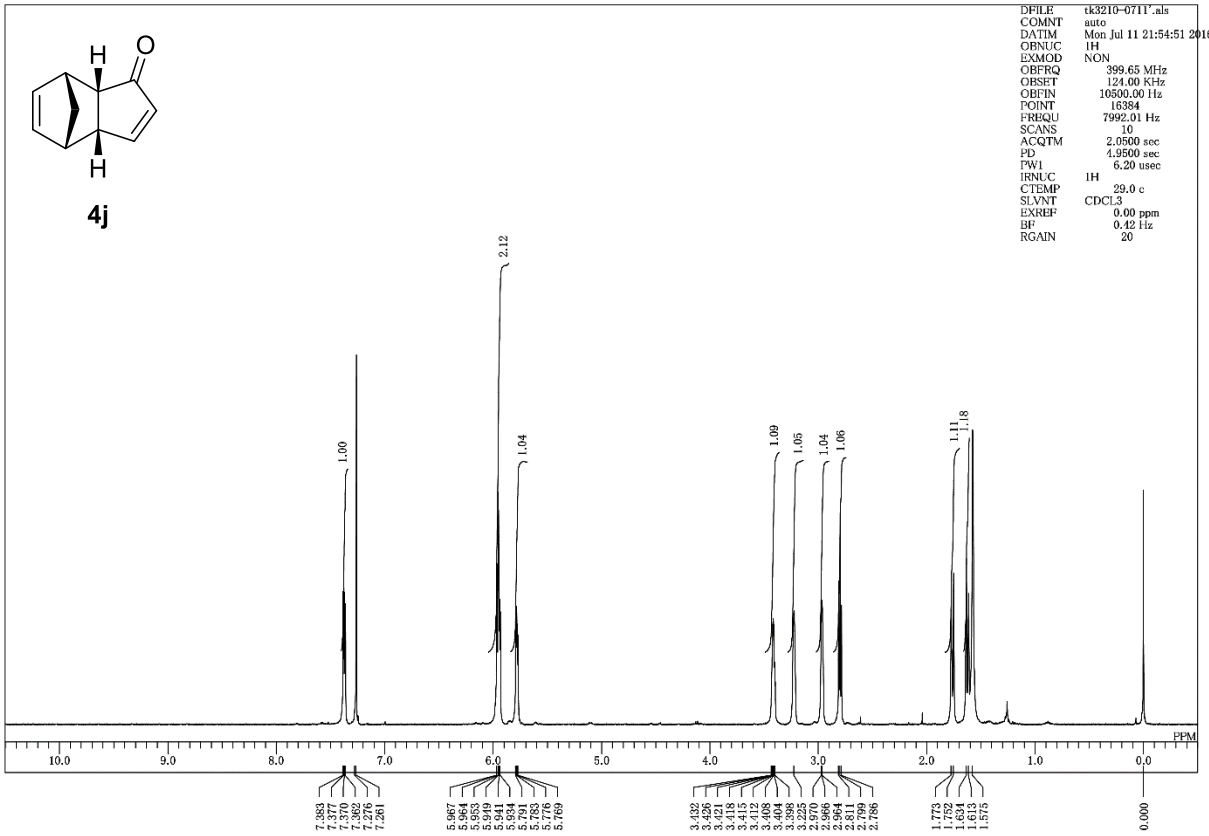
auto


BzO
O
BzO
4i
DFILE cyclopentene_CH2OBz2_enone_1H-
COMNT auto
DATIM Sat Dec 09 13:22:10 2017
OBNUC 1H
EXMOD NON
OBFRQ 395.75 MHz
OBSET 124.00 KHz
OBFIN 10277.00 Hz
POINT 16384
FREQU 7912.96 Hz
SCANS 8
ACQTM 2.0705 sec
PD 4.9290 sec
PW1 5.50 usec
IRNUC 1H
CTEMP 24.5 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 16
4.23
4.30
2.14
2.10
2.18
2.02
1.06
1.00
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.996
7.977
7.974
7.649
7.635
7.604
7.585
7.566
7.466
7.446
7.427
7.260
6.355
6.340
4.609
4.581
4.471
4.443
2.549
0.000

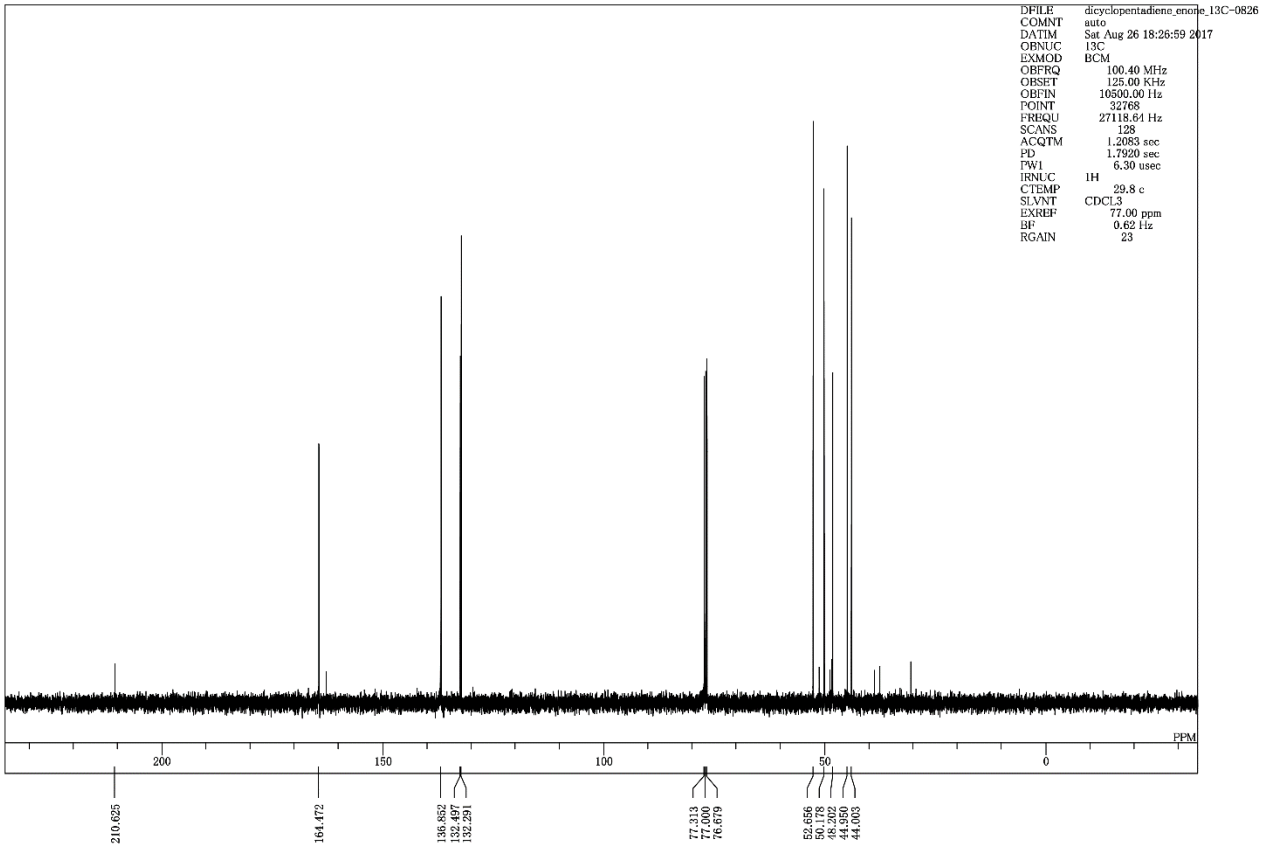
auto


DFILE cyclopentene_CH2OBz2_enone_13C
COMNT auto
DATIM Sat Aug 26 18:18:53 2017
OBNUC 13C
EXMOD BCM
OBFRQ 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27118.64 Hz
SCANS 318
ACQTM 1.2083 sec
PD 1.7920 sec
PW1 6.30 usec
IRNUC 1H
CTEMP 29.8 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.62 Hz
RGAIN 23
PPM
200
150
100
50
0
206.344
166.020
163.229
136.234
133.443
129.599
129.286
128.561
77.313
77.000
76.679
66.347
49.700
41.558

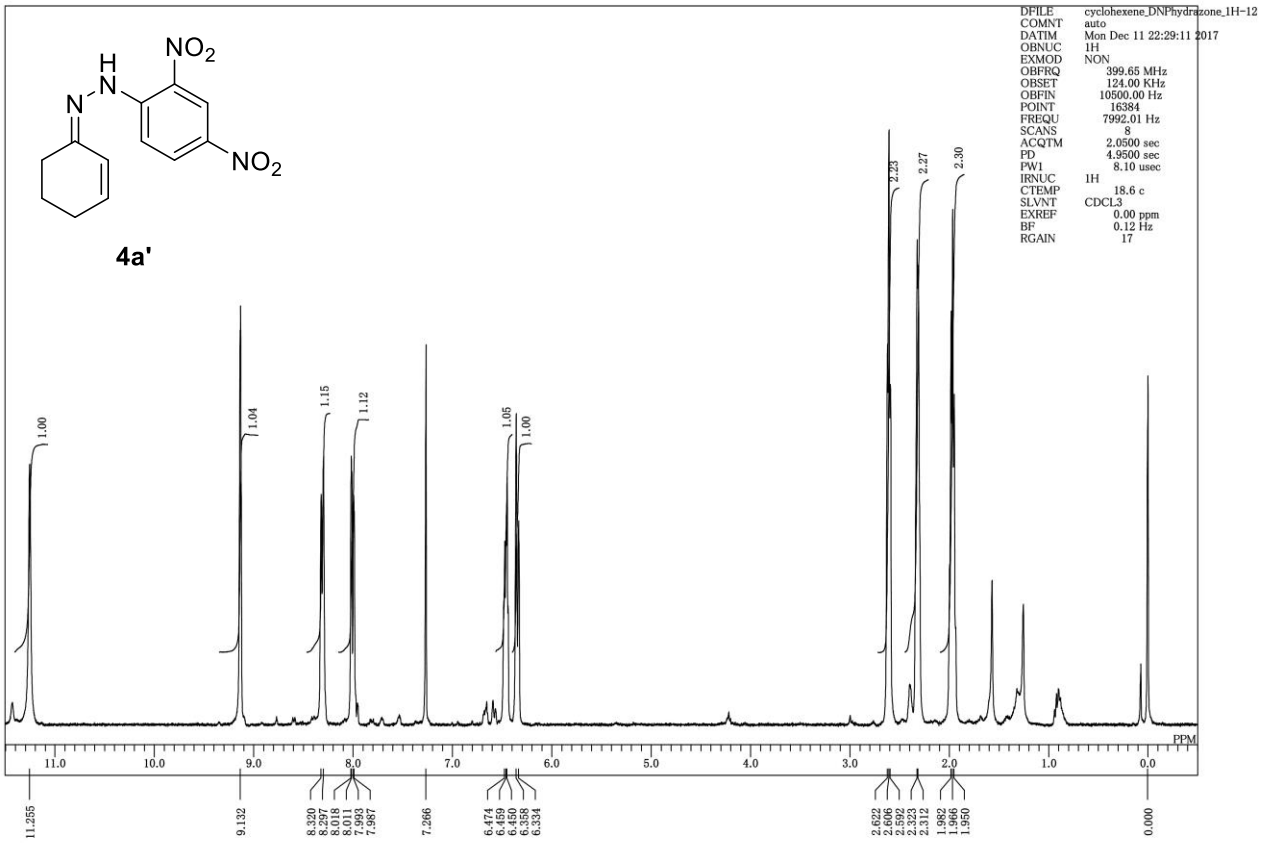
auto


4j
DFILE tk3210-0711'.als
COMNT auto
DATIM Mon Jul 11 21:54:51 2016
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 16384
FREQU 7992.01 Hz
SCANS 10
ACQTM 2.0500 sec
PD 4.9500 sec
PW1 6.20 usec
IRNUC 1H
CTEMP 29.0 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.42 Hz
RGAIN 20
2.12
1.00
1.04
1.09
1.05
1.04
1.06
1.11
1.18
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.383
7.377
7.370
7.262
7.259
7.261
5.967
5.964
5.953
5.949
5.941
5.934
5.791
5.783
5.776
5.769
3.432
3.426
3.421
3.418
3.415
3.412
3.408
3.404
3.398
3.393
2.970
2.966
2.964
2.811
2.799
2.786
1.773
1.752
1.634
1.613
1.576
0.000

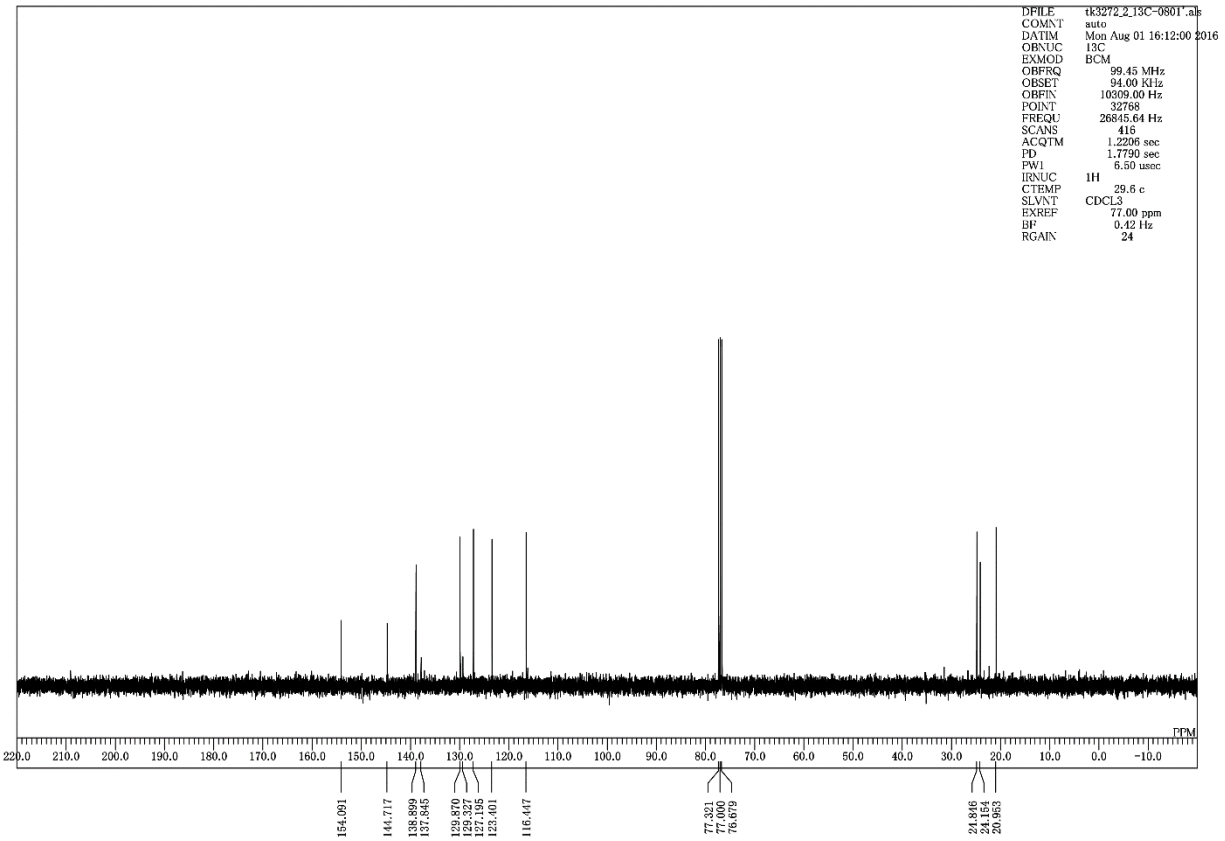
auto


DFILE dicyclopentadiene_enone_13C-0826
COMNT auto
DATIM Sat Aug 26 18:26:59 2017
OBNUC 13C
EXMOD BCM
OBFRQ 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27118.64 Hz
SCANS 128
ACQTM 1.2083 sec
PD 1.7920 sec
PW1 6.30 usec
IRNUC 1H
CTEMP 29.8 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.62 Hz
RGAIN 23
PPM
200
150
100
50
0
210.625
164.472
136.852
132.497
132.291
77.313
77.000
76.679
52.656
50.178
43.392
43.190
44.003

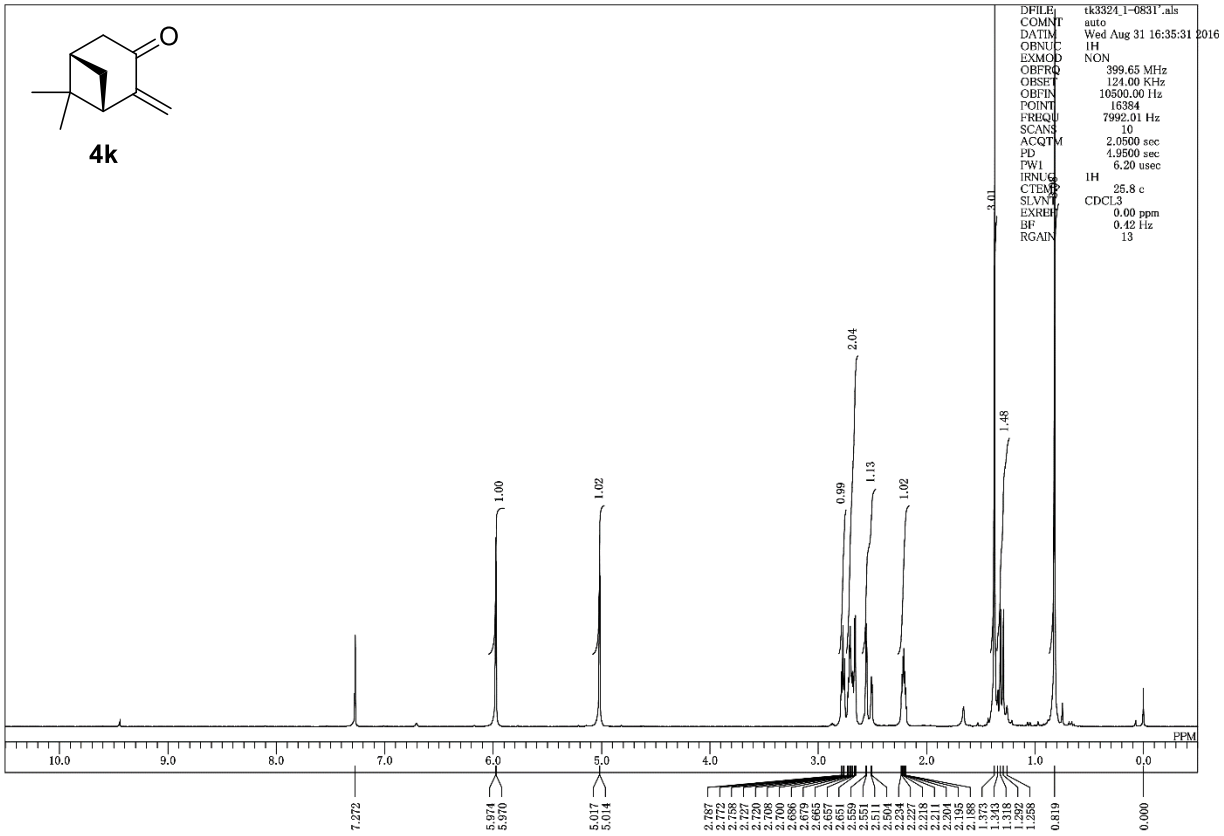
auto


4a'
DFILE cyclohexene_DNPhydrazone_1H-12
COMNT auto
DATIM Mon Dec 11 22:29:11 2017
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 16384
FREQU 7992.01 Hz
SCANS 8
ACQTM 2.0500 sec
PD 4.9500 sec
PW1 8.10 usec
IRNUC 1H
CTEMP 18.6 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 17
PPM

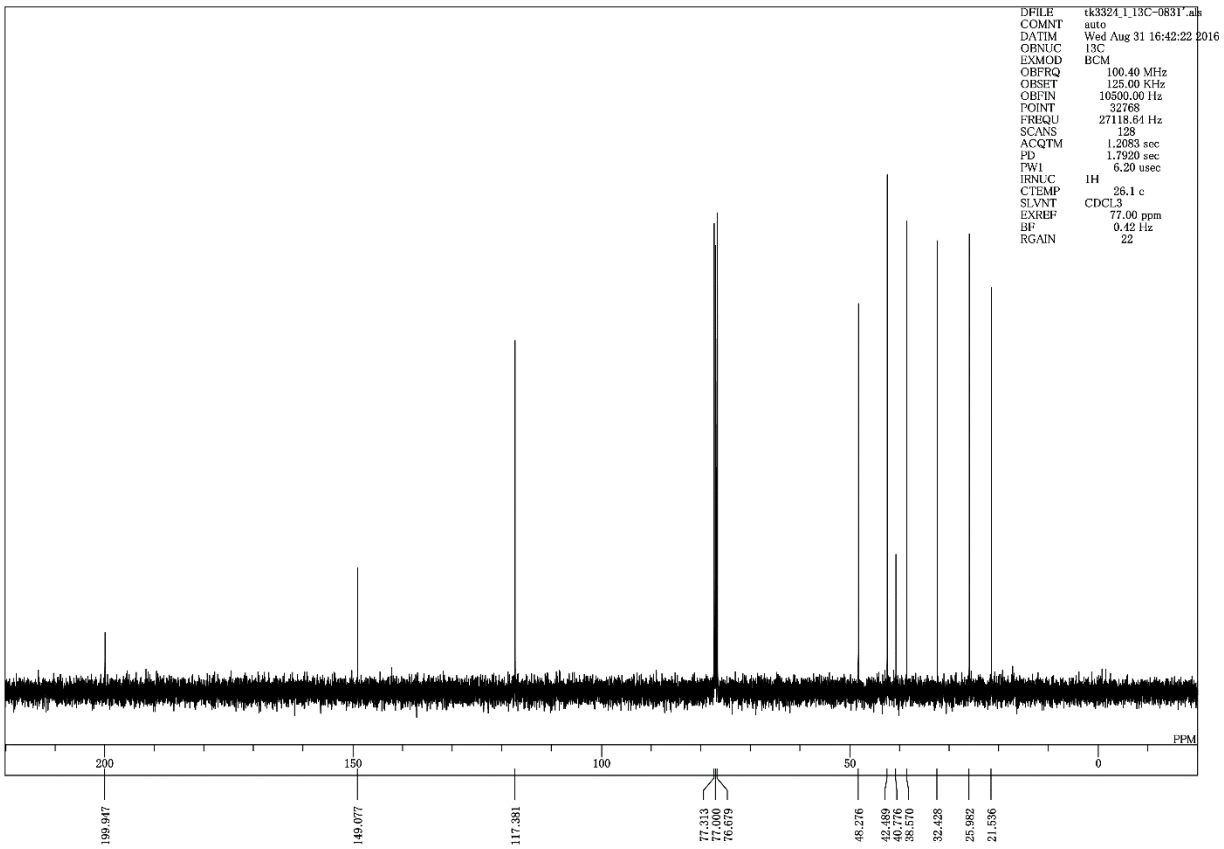
auto


DFILE tk3272_2_13C-0801.als
COMNT auto
DATIM Mon Aug 01 16:12:00 2016
OBNUC 13C
EXMOD BCM
OBFRQ 99.45 MHz
OBSET 94.00 KHz
OBFIN 10309.00 Hz
POINT 32768
FREQU 26845.64 Hz
SCANS 416
ACQTM 1.2296 sec
PD 1.7790 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 29.6 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.42 Hz
RGAIN 24
PPM

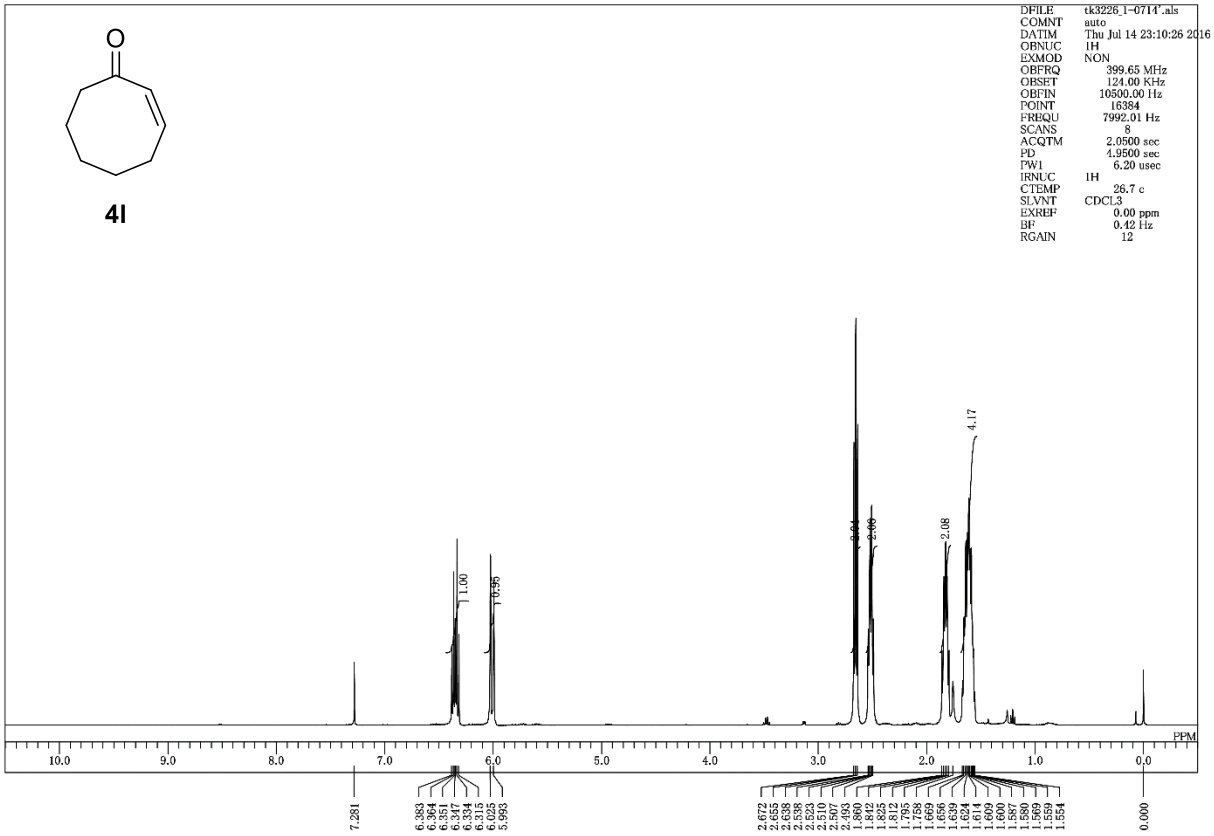
auto


4k
DFILE tk3324_1-0831'.als
COMNT auto
DATIM Wed Aug 31 16:35:31 2016
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 16384
FREQU 7992.01 Hz
SCANS 10
ACQTM 2.0500 sec
PD 4.9500 sec
PW1 6.20 usec
IRNUC 1H
CTEMP 25.8 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.42 Hz
RGAIN 13
3.01
2.04
1.48
1.13
1.02
1.02
1.00
0.99
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.272
5.974
5.970
5.017
5.014
2.787
2.772
2.759
2.727
2.720
2.708
2.700
2.686
2.679
2.665
2.657
2.651
2.559
2.551
2.511
2.504
2.494
2.227
2.218
2.211
2.204
2.156
2.148
1.373
1.343
1.318
1.292
1.258
0.819
0.000

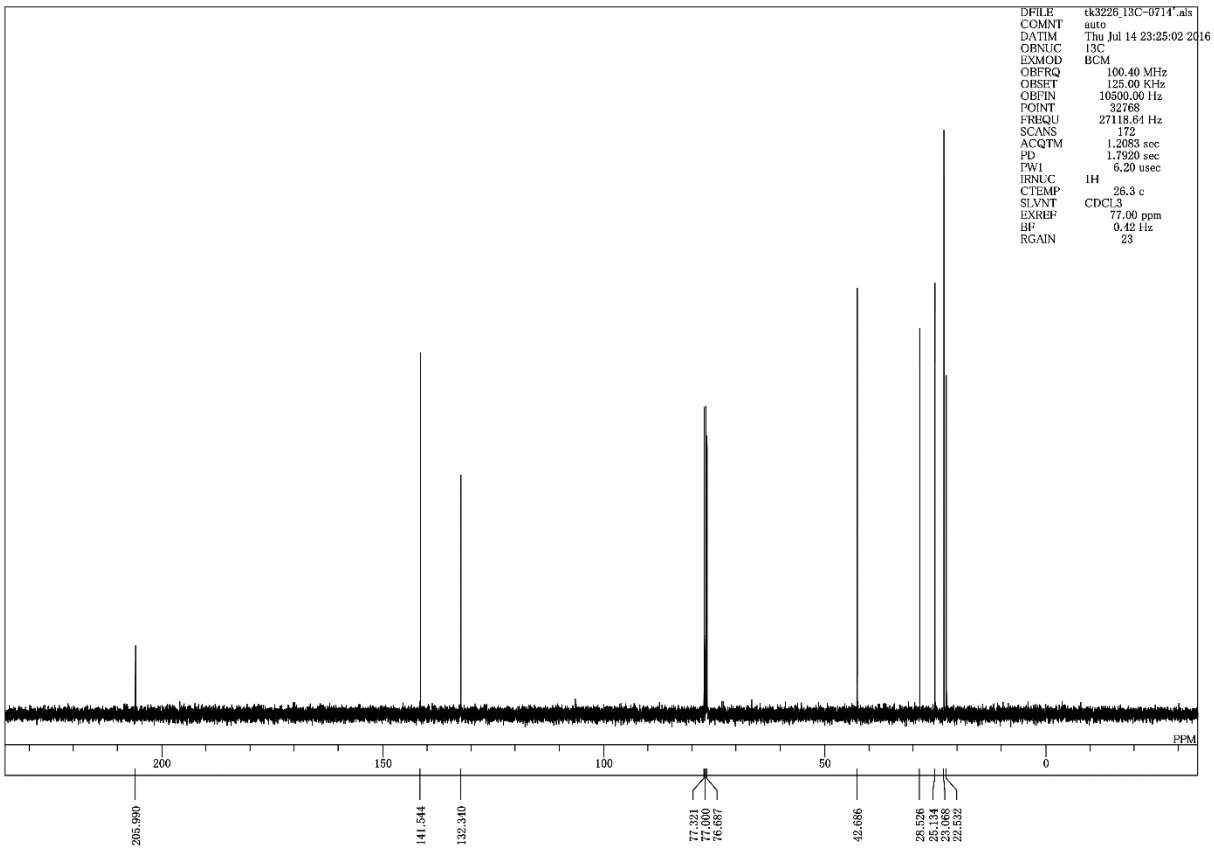
auto


DFILE tk3324_1_13C-0831'.als
COMNT auto
DATIM Wed Aug 31 16:42:22 2016
OBNUC 13C
EXMOD BCM
OBFRQ 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27118.64 Hz
SCANS 128
ACQTM 1.2083 sec
PD 1.7920 sec
PW1 6.20 usec
IRNUC 1H
CTEMP 26.1 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.42 Hz
RGAIN 22
PPM
200
150
100
50
0
199.947
149.077
117.381
77.313
77.000
76.679
48.276
42.489
40.776
38.570
32.428
25.982
21.536

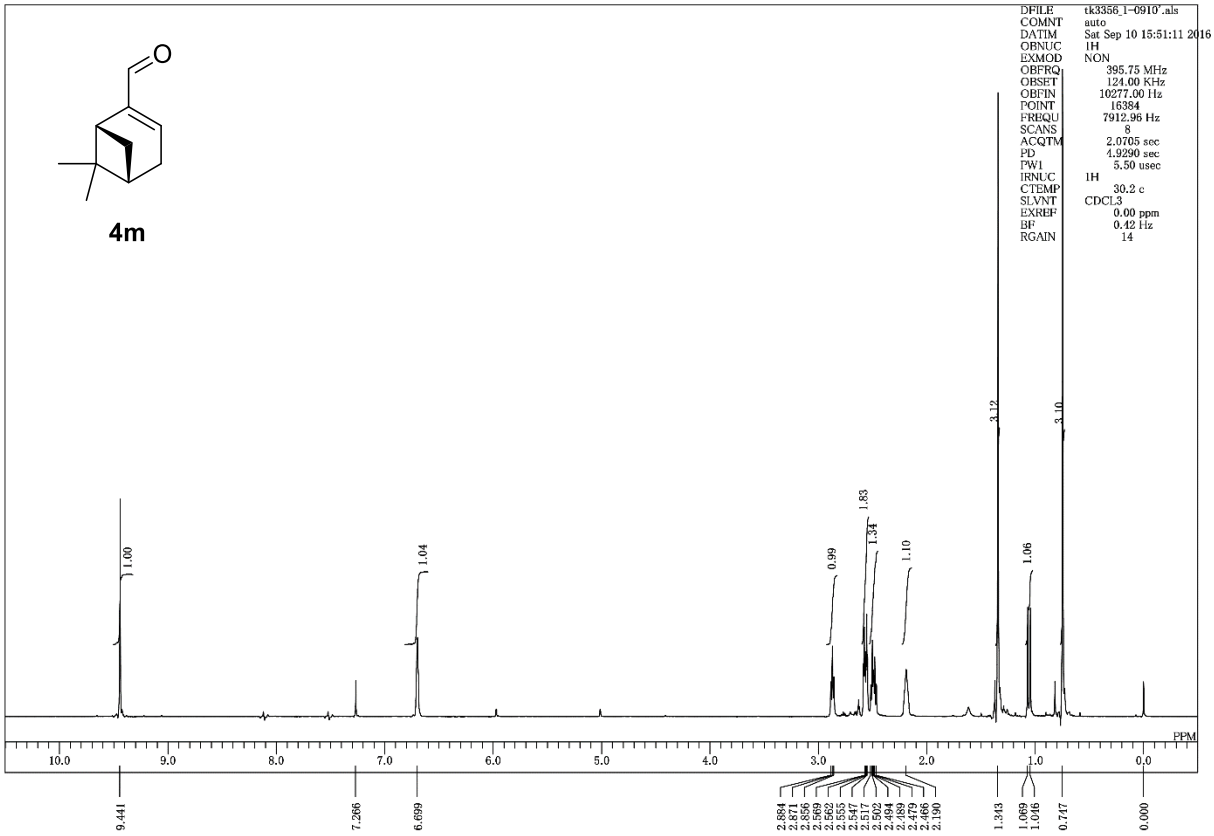
auto


4l
DFILE tk3226_1-0714'.als
COMNT auto
DATIM Thu Jul 14 23:10:26 2016
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 16384
FREQU 7992.01 Hz
SCANS 8
ACQTM 2.0500 sec
PD 4.9500 sec
PW1 6.20 usec
IRNUC 1H
CTEMP 26.7 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.42 Hz
RGAIN 12
1.00
0.95
3.04
2.00
2.08
4.17
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.281
6.383
6.364
6.351
6.347
6.334
6.315
6.025
5.993
2.672
2.655
2.638
2.538
2.523
2.510
2.507
2.490
2.482
1.842
1.825
1.812
1.795
1.758
1.695
1.676
1.639
1.624
1.614
1.609
1.600
1.587
1.580
1.569
1.559
1.554
0.000

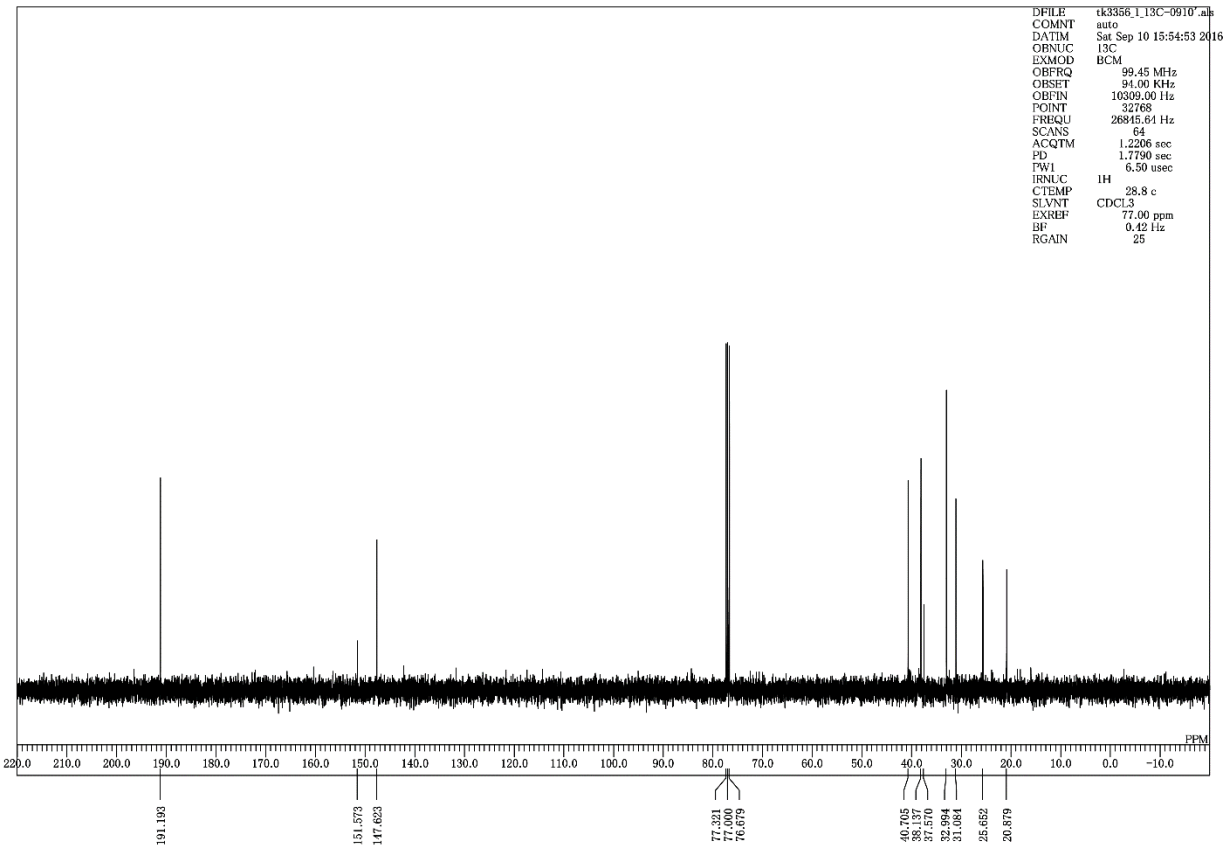
auto


DFILE tk3226_13C-0714'.als
COMNT auto
DATIM Thu Jul 14 23:25:02 2016
OBNUC 13C
EXMOD BCM
OBFRQ 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27118.64 Hz
SCANS 172
ACQTM 1.2083 sec
PD 1.7920 sec
PW1 6.20 usec
IRNUC 1H
CTEMP 26.3 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.42 Hz
RGAIN 23
PPM
200
150
100
50
0
206.990
141.544
132.340
77.321
77.000
76.687
42.686
28.526
25.134
23.068
22.532

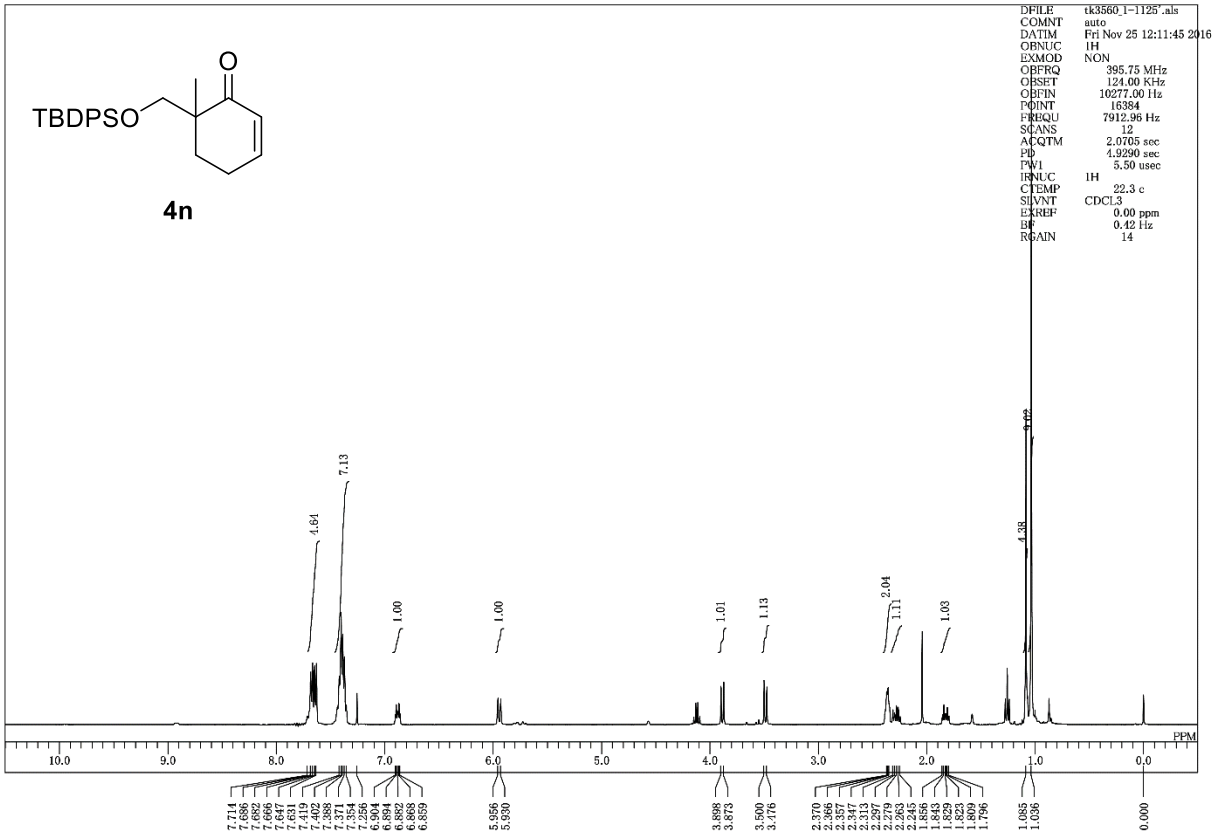
auto


4m
DFILE tk3356_1-0910'.als
COMNT auto
DATIM Sat Sep 10 15:51:11 2016
OBNUC 1H
EXMOD NON
OBFRQ 395.75 MHz
OBSET 124.00 KHz
OBFIN 10277.00 Hz
POINT 16384
FREQU 7912.96 Hz
SCANS 8
ACQTM 2.0705 sec
PD 4.9290 sec
PW1 5.50 usec
IRNUC 1H
CTEMP 30.2 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.42 Hz
RGAIN 14
1.00
1.04
0.99
1.83
1.34
1.10
3.12
3.10
1.06
PPM
9.441
7.266
6.699
2.884
2.871
2.856
2.849
2.582
2.555
2.547
2.517
2.502
2.494
2.490
2.479
2.466
2.190
1.343
1.069
1.046
0.747
0.000

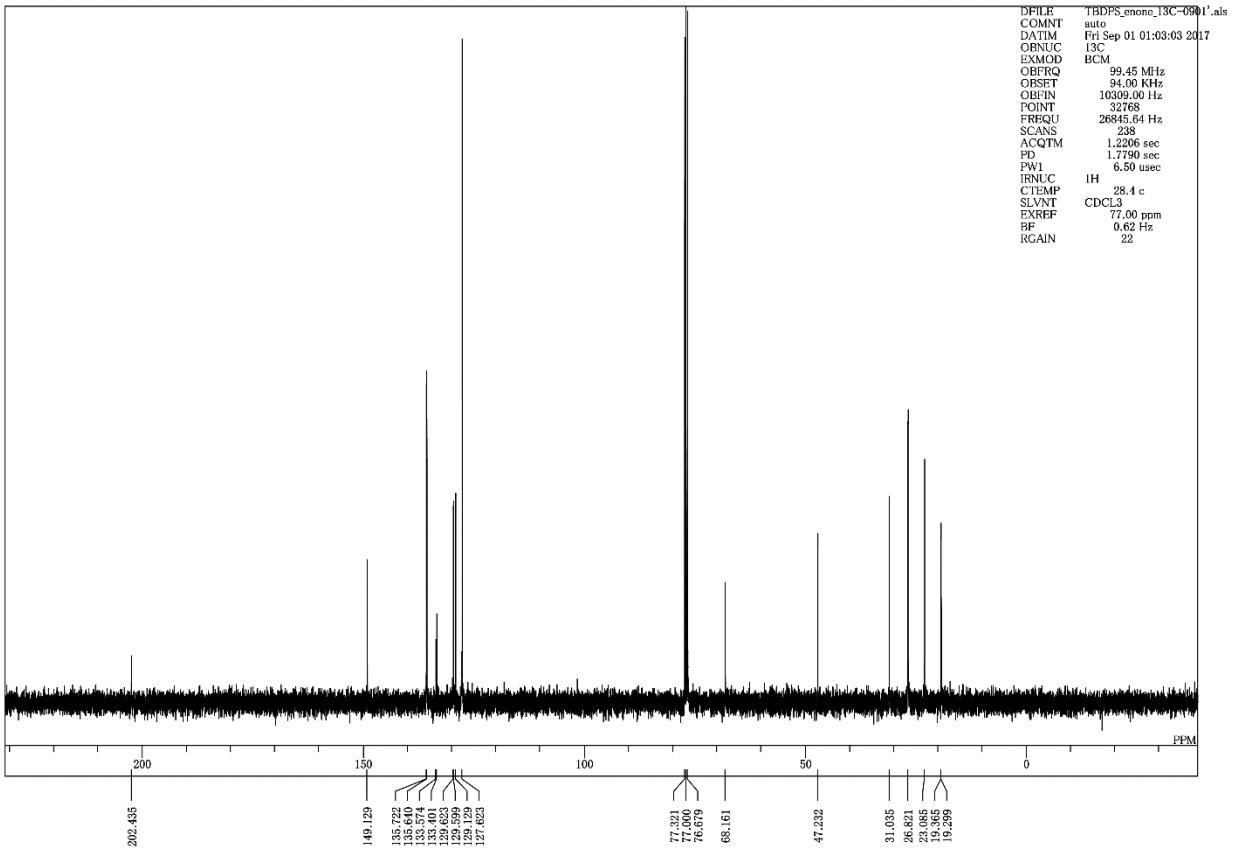
auto


DFILE tk3356_1_13C-0910'.als
COMNT auto
DATIM Sat Sep 10 15:54:53 2016
OBNUC 13C
EXMOD BCM
OBFRQ 99.45 MHz
OBSET 94.00 KHz
OBFIN 10309.00 Hz
POINT 32768
FREQU 26845.64 Hz
SCANS 64
ACQTM 1.2206 sec
PD 1.7790 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 28.8 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.42 Hz
RGAIN 25
PPM
191.193
151.573
147.623
77.321
77.000
76.679
40.705
38.137
37.570
32.994
31.084
25.652
20.879

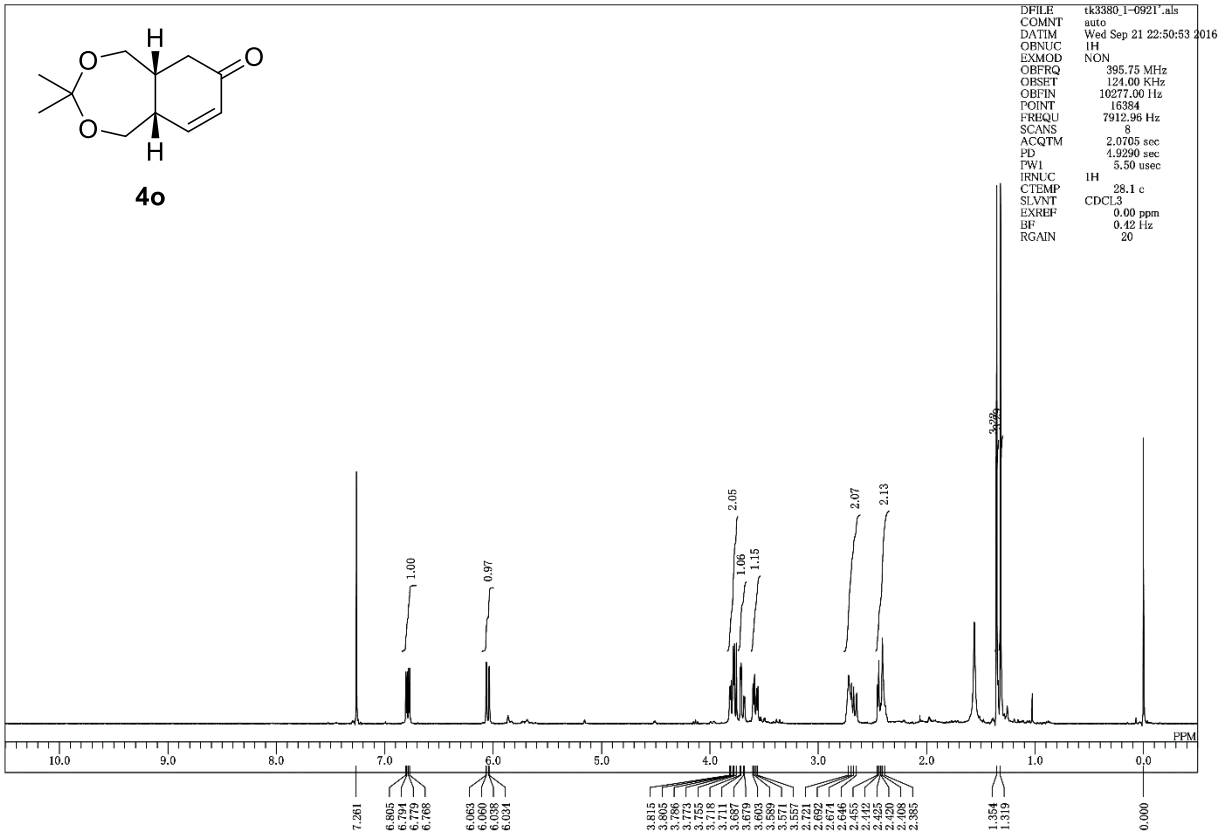
auto


TBDPSO
O
4n
DFILE tk3560_1-1125'.als
COMNT auto
DATIM Fri Nov 25 12:11:45 2016
OBNUC 1H
EXMOD NON
OBFRQ 395.75 MHz
OBSET 124.00 KHz
OBFIN 10277.00 Hz
POINT 16384
FREQU 7912.96 Hz
SCANS 12
ACQTM 2.0705 sec
PD 4.9290 sec
PW1 5.50 usec
IRNUC 1H
CTEMP 22.3 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.42 Hz
RGAIN 14
4.64
7.13
1.00
1.00
1.01
1.13
2.04
1.11
1.03
9.02
4.38
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.714
7.686
7.682
7.666
7.647
7.631
7.419
7.402
7.398
7.371
7.354
7.256
6.904
6.894
6.882
6.869
6.859
5.956
5.930
3.898
3.873
3.500
3.176
2.370
2.366
2.357
2.347
2.313
2.297
2.279
2.263
2.245
1.858
1.843
1.829
1.823
1.809
1.798
1.085
1.036
0.000

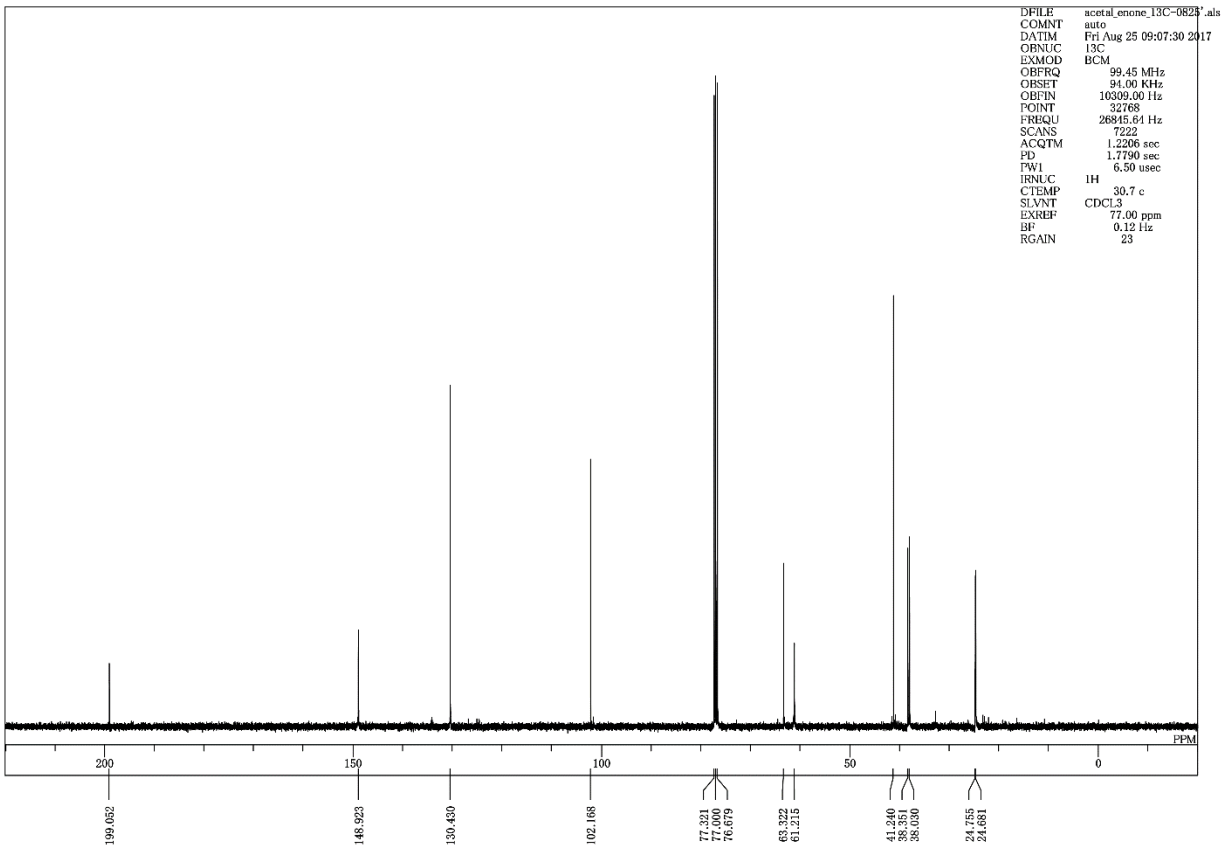
auto


DFILE TBDPS_enone_13C-0901'.als
COMNT auto
DATIM Fri Sep 01 01:03:03 2017
OBNUC 13C
EXMOD BCM
OBFRQ 99.45 MHz
OBSET 94.00 KHz
OBFIN 10309.00 Hz
POINT 32768
FREQU 26845.64 Hz
SCANS 238
ACQTM 1.2206 sec
PD 1.7790 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 28.4 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.62 Hz
RGAIN 22
PPM
200
150
100
50
0
202.435
149.129
135.722
135.640
133.574
133.401
129.623
129.599
128.129
127.623
77.321
77.000
76.679
68.161
47.232
31.035
26.821
23.085
19.365
19.299

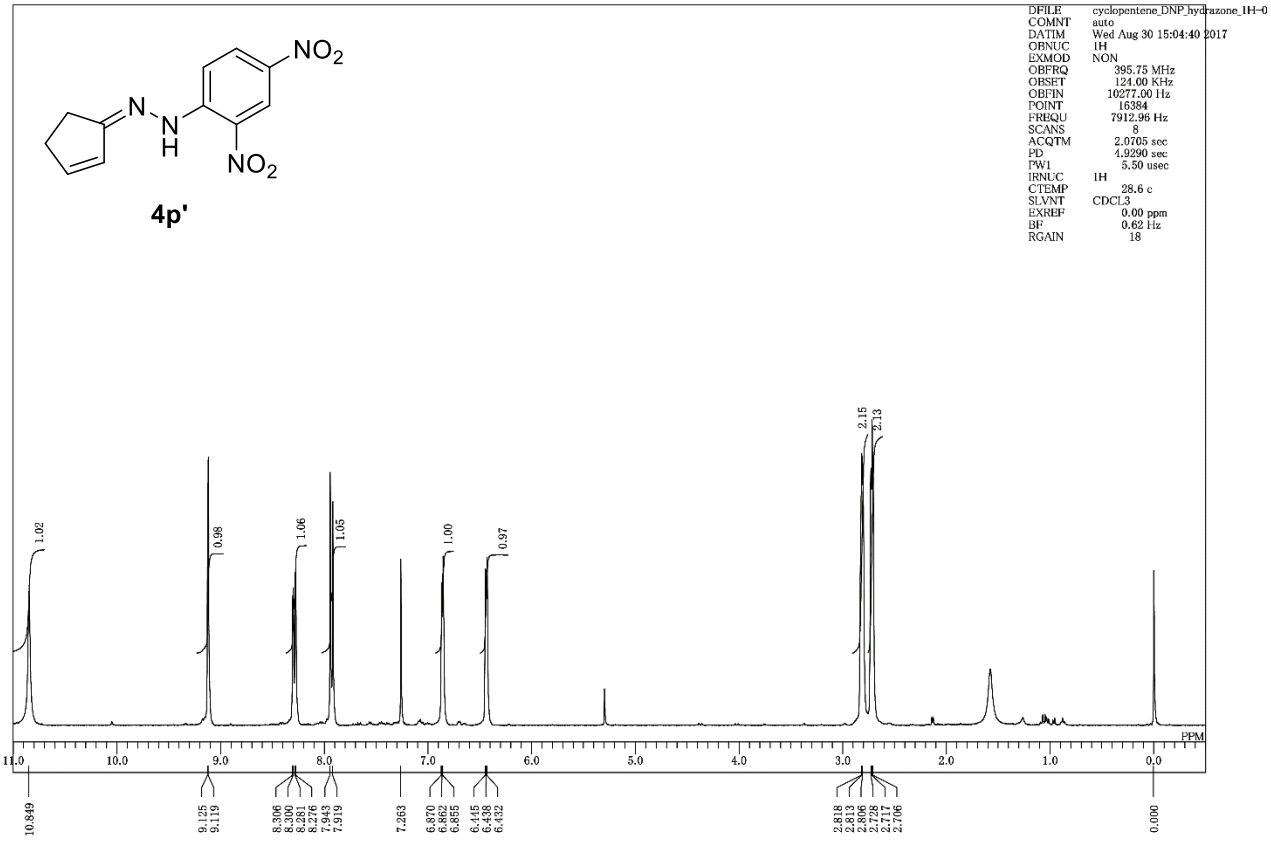
auto


4o
DFILE tk3380_1-0921'.als
COMNT auto
DATIM Wed Sep 21 22:50:53 2016
OBNUC 1H
EXMOD NON
OBFRQ 395.75 MHz
OBSET 124.00 KHz
OBFIN 10277.00 Hz
POINT 16384
FREQU 7912.96 Hz
SCANS 8
ACQTM 2.0705 sec
PD 4.9290 sec
PW1 5.50 usec
IRNUC 1H
CTEMP 28.1 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.42 Hz
RGAIN 20
1.00
0.97
2.05
1.06
1.15
2.07
2.13
3.979
3.969
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.261
6.805
6.794
6.779
6.768
6.063
6.060
6.038
6.034
3.815
3.805
3.788
3.773
3.755
3.718
3.711
3.687
3.670
3.603
3.589
3.571
3.557
2.721
2.692
2.672
2.646
2.455
2.442
2.425
2.420
2.408
2.393
1.354
1.319
0.000

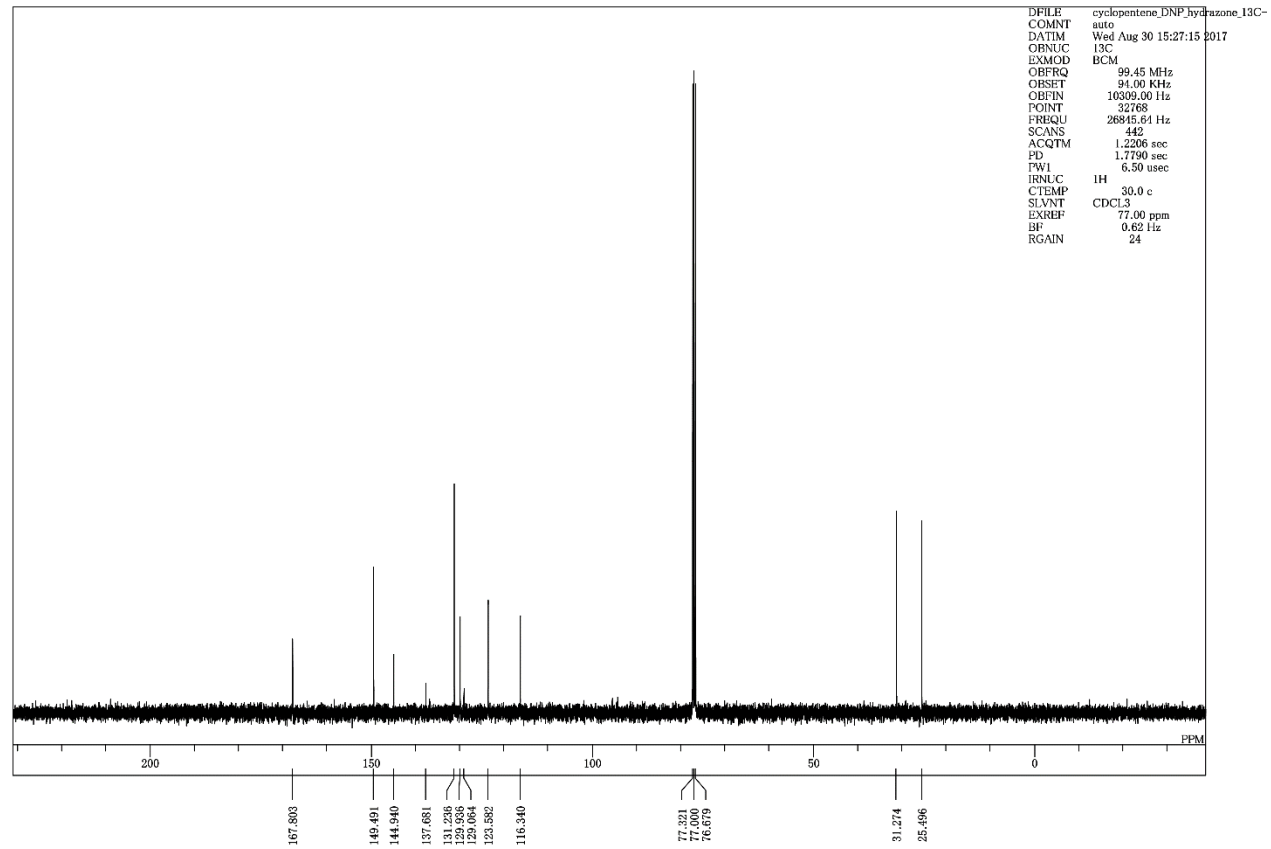
auto


DFILE acetal_enone_13C-0825'.als
COMNT auto
DATIM Fri Aug 25 09:07:30 2017
OBNUC 13C
EXMOD BCM
OBFRQ 99.45 MHz
OBSET 94.00 KHz
OBFIN 10309.00 Hz
POINT 32768
FREQU 26845.64 Hz
SCANS 7222
ACQTM 1.2206 sec
PD 1.7790 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 30.7 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 23
PPM
200
150
100
50
0
199.052
148.923
130.430
102.168
77.321
77.000
76.679
63.322
61.215
41.240
38.351
38.030
24.755
24.681

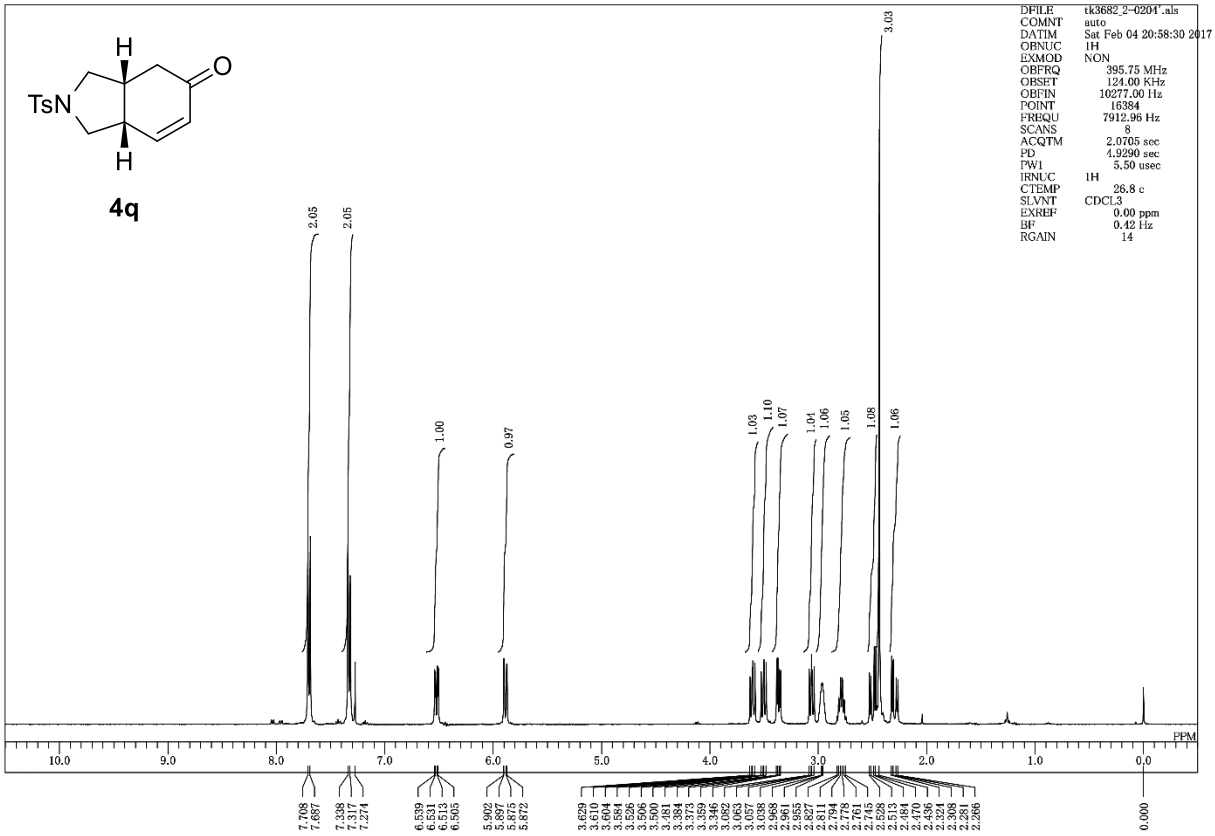
auto


4p'
DFILE cyclopentene_DNP_hydrazone_1H-0
COMNT auto
DATIM Wed Aug 30 15:04:40 2017
OBNUC 1H
EXMOD NON
OBFRQ 395.75 MHz
OBSET 124.00 KHz
OBFIN 10277.00 Hz
POINT 16384
FREQU 7912.96 Hz
SCANS 8
ACQTM 2.0705 sec
PD 4.9290 sec
PW1 5.50 usec
IRNUC 1H
CTEMP 28.6 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.62 Hz
RGAIN 18
1.02
0.98
1.06
1.05
1.00
0.97
2.15
2.13
PPM
10.849
9.125
9.119
8.306
8.300
8.281
8.276
7.943
7.919
7.263
6.870
6.862
6.855
6.445
6.438
6.432
2.818
2.813
2.806
2.728
2.717
2.706
0.000

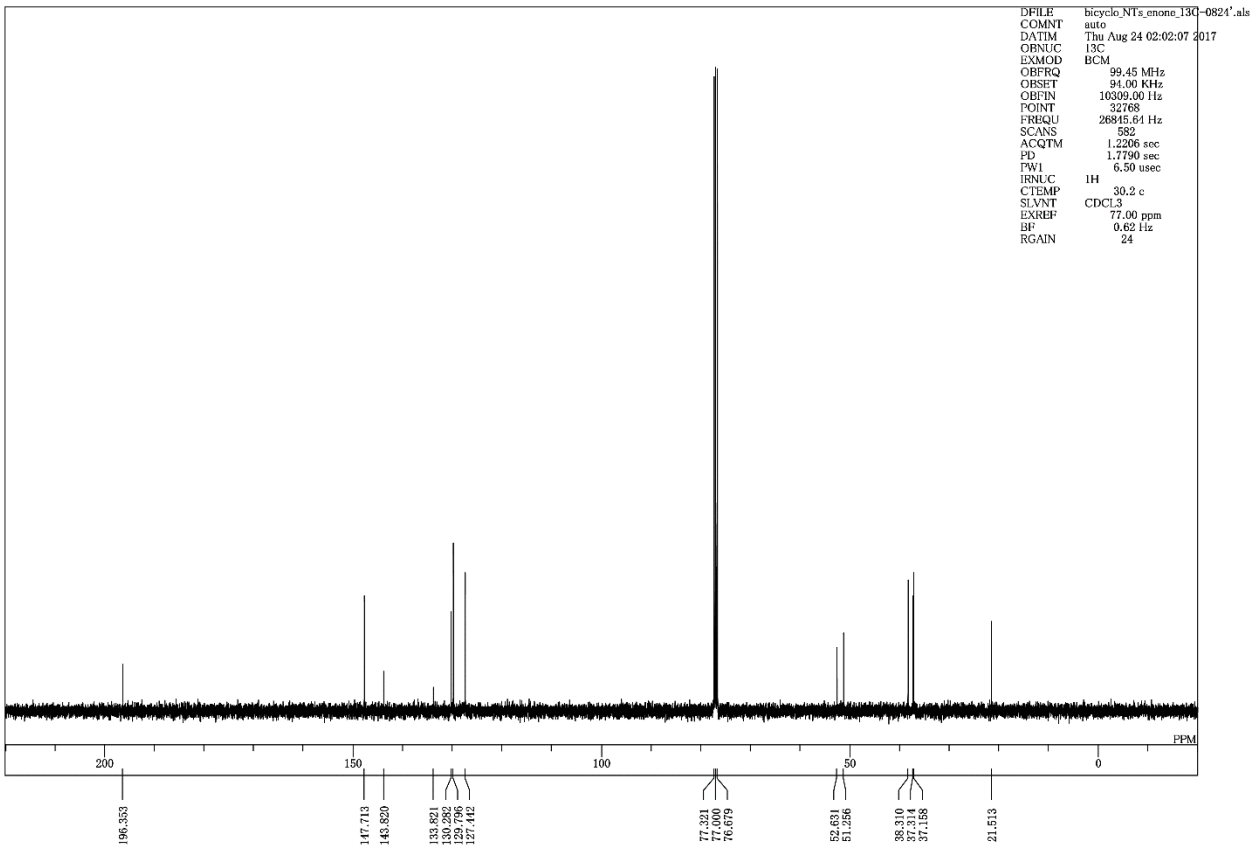
auto


DFILE cyclopentene_DNP_hydrazone_13C-
COMNT auto
DATIM Wed Aug 30 15:27:15 2017
OBNUC 13C
EXMOD BCM
OBFRQ 99.45 MHz
OBSET 94.00 KHz
OBFIN 10309.00 Hz
POINT 32768
FREQU 26845.64 Hz
SCANS 442
ACQTM 1.2206 sec
PD 1.7790 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 30.0 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.62 Hz
RGAIN 24
PPM
167.803
149.491
144.940
137.681
131.238
129.936
129.064
123.582
116.340
77.321
77.000
76.679
31.274
25.496

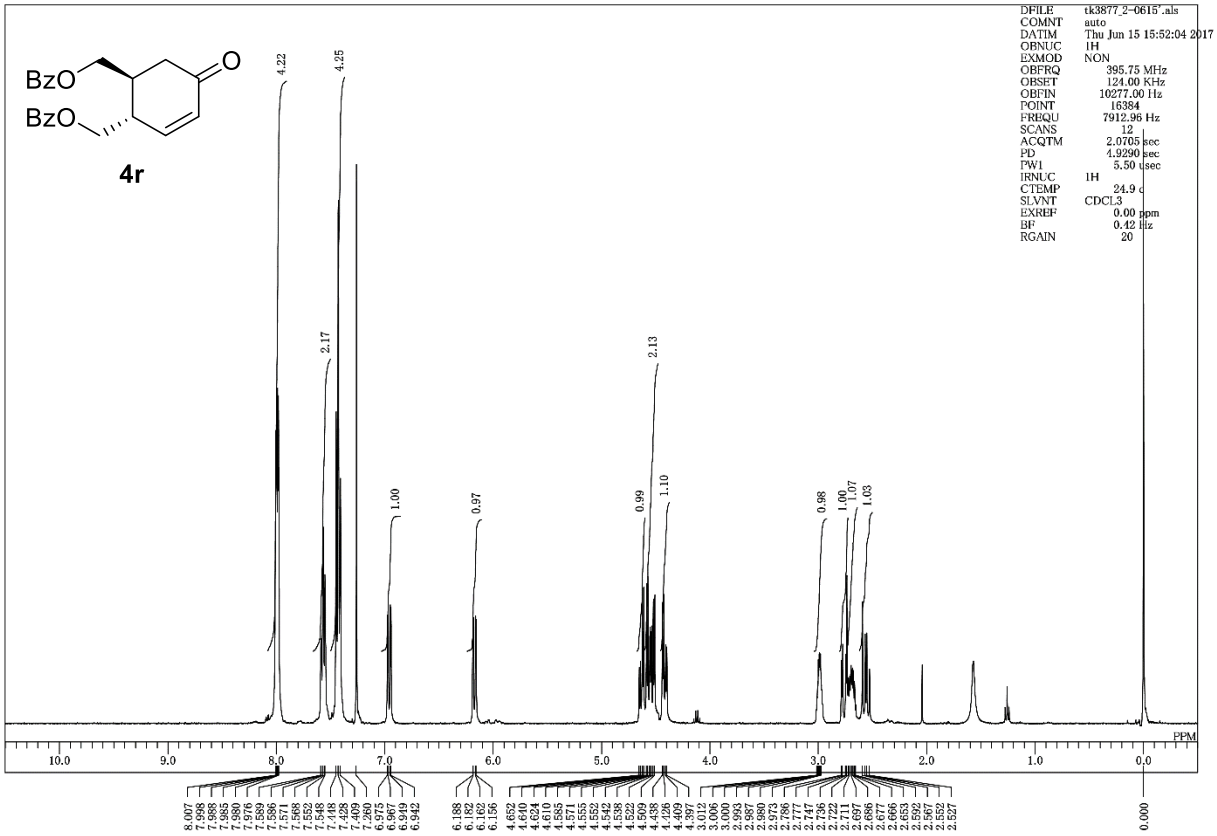
auto


TsN
H
H
O
4q
DFILE tk3682_2-0204'.als
COMNT auto
DATIM Sat Feb 04 20:58:30 2017
OBNUC 1H
EXMOD NON
OBFRQ 395.75 MHz
OBSET 124.00 KHz
OBFIN 10277.00 Hz
POINT 16384
FREQU 7912.96 Hz
SCANS 8
ACQTM 2.0705 sec
PD 4.9290 sec
PW1 5.50 usec
IRNUC 1H
CTEMP 26.8 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.42 Hz
RGAIN 14
PPM

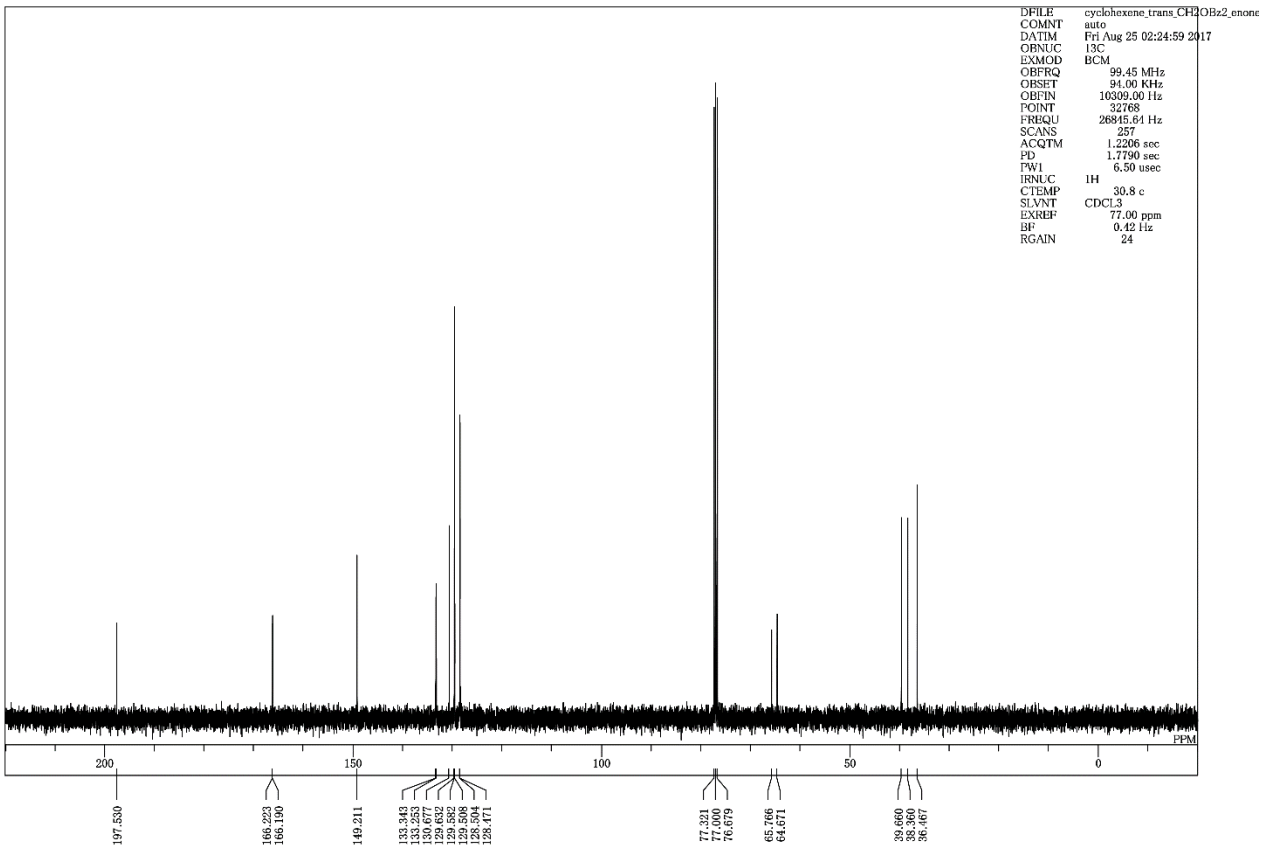
auto


DFILE bicyclo_NTs_enone_13C-0824'.als
COMNT auto
DATIM Thu Aug 24 02:02:07 2017
OBNUC 13C
EXMOD BCM
OBFRQ 99.45 MHz
OBSET 94.00 KHz
OBFIN 10309.00 Hz
POINT 32768
FREQU 26845.61 Hz
SCANS 582
ACQTM 1.2206 sec
PD 1.7790 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 30.2 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.62 Hz
RGAIN 24
PPM

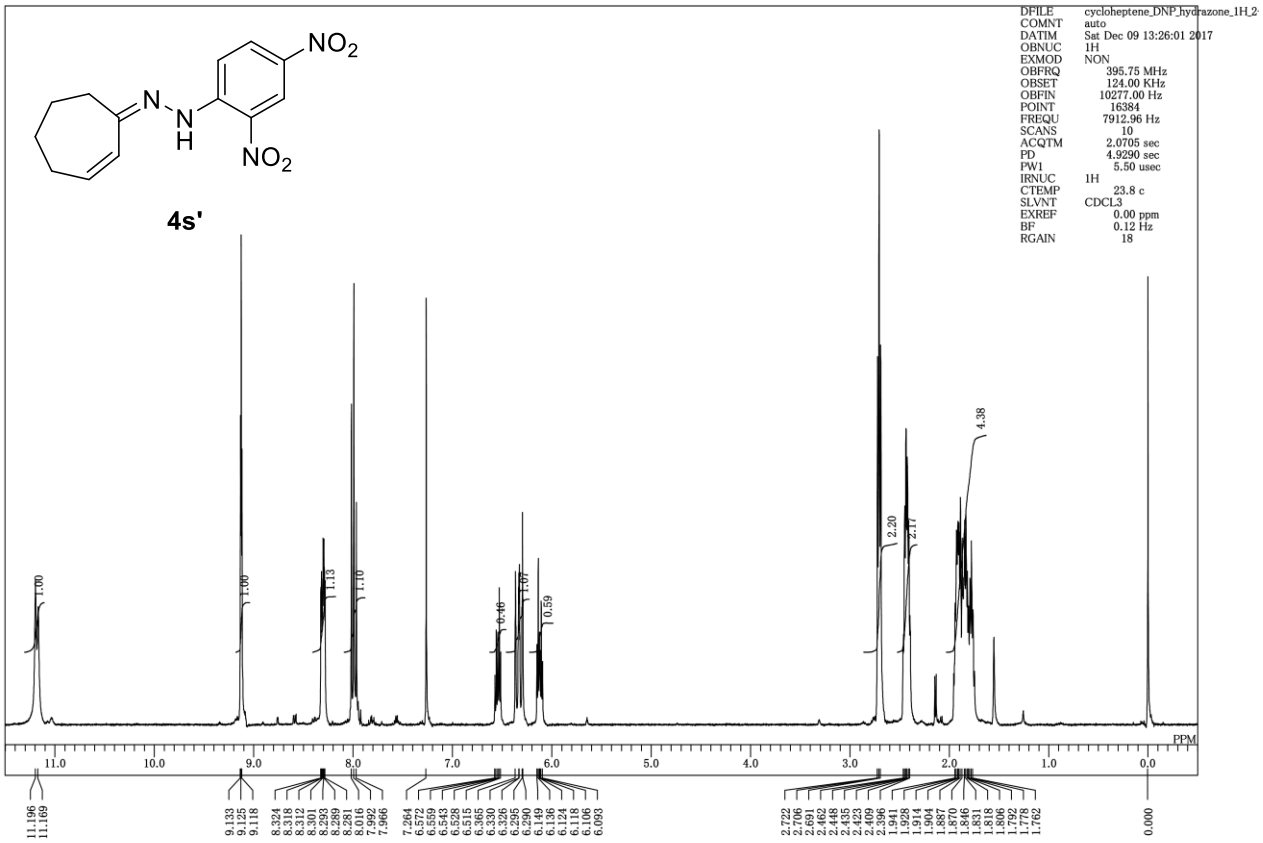
auto


BzO
BzO
O
4r
4.22
4.25
2.17
2.13
1.00
0.97
0.99
1.10
0.98
1.00
1.07
1.03
DFILE tk3877_2-0615'.als
COMNT auto
DATIM Thu Jun 15 15:52:04 2017
OBNUC 1H
EXMOD NON
OBFRQ 395.75 MHz
OBSET 124.00 KHz
OBFIN 10277.00 Hz
POINT 16384
FREQU 7912.96 Hz
SCANS 12
ACQTM 2.0705 sec
PD 4.9290 sec
PW1 5.50 usec
IRNUC 1H
CTEMP 24.9 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.42 Hz
RGAIN 20
PPM

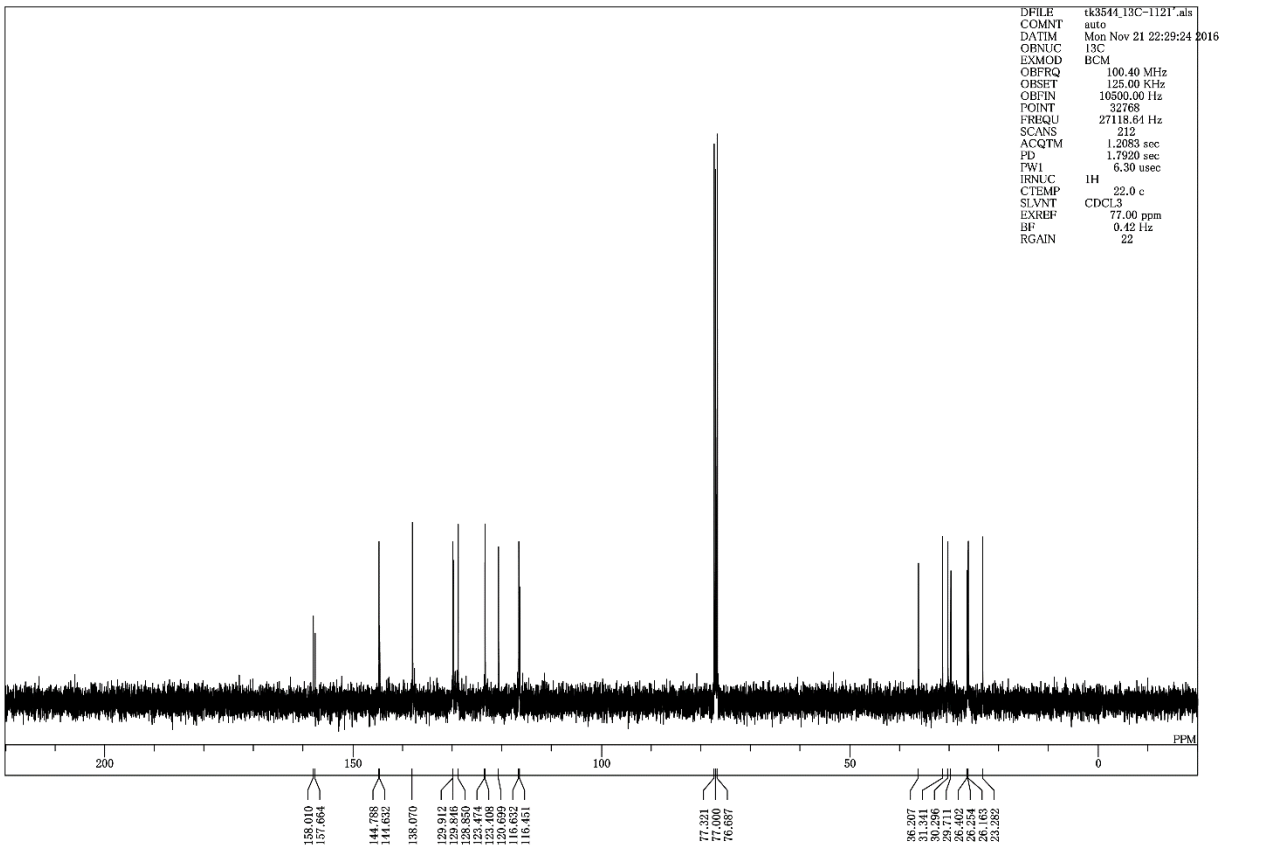
auto


DFILE cyclohexene_trans_CH2OBz2_enone
COMNT auto
DATIM Fri Aug 25 02:24:59 2017
OBNUC 13C
EXMOD BCM
OBFRQ 99.45 MHz
OBSET 94.00 KHz
OBFIN 10309.00 Hz
POINT 32768
FREQU 26845.61 Hz
SCANS 257
ACQTM 1.2206 sec
PD 1.7790 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 30.8 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.42 Hz
RGAIN 24
PPM

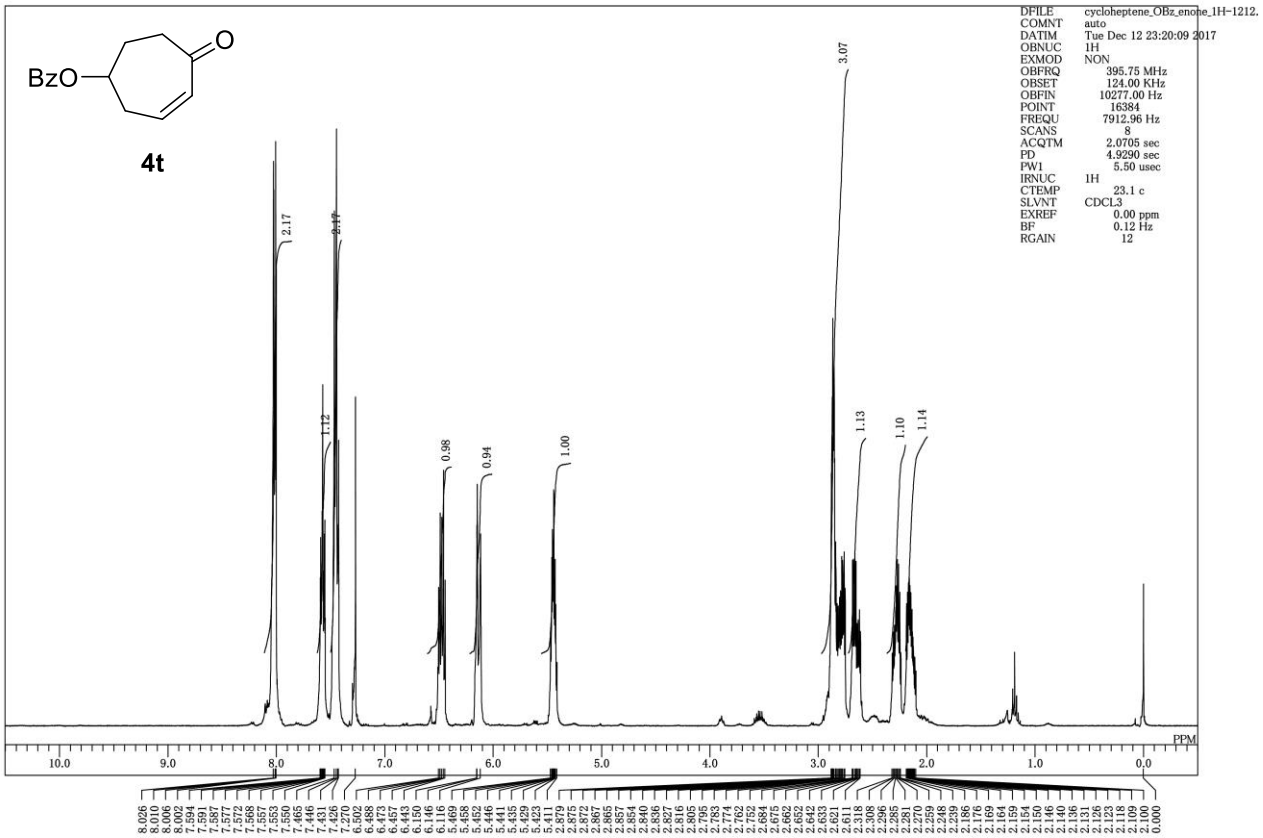
auto


4s'
DFILE cycloheptene_DNP_hydrazone_1H_2
COMNT auto
DATIM Sat Dec 09 13:26:01 2017
OBNUC 1H
EXMOD NON
OBFRQ 395.75 MHz
OBSET 124.00 KHz
OBFIN 10277.00 Hz
POINT 16384
FREQU 7912.96 Hz
SCANS 10
ACQTM 2.0705 sec
PD 4.9290 sec
PW1 5.50 usec
IRNUC 1H
CTEMP 23.8 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 18
PPM

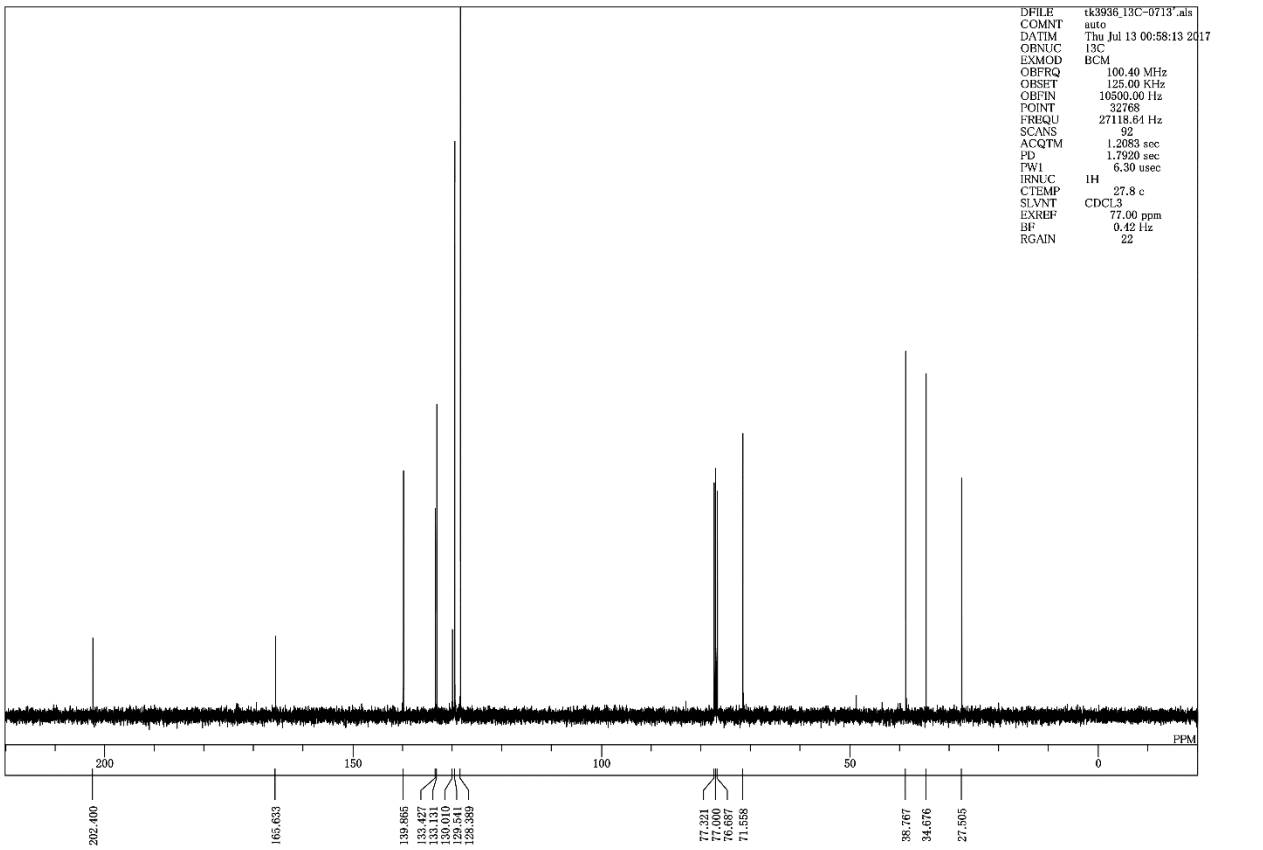
auto


DFILE tk3544_13C-11217.als
COMNT auto
DATIM Mon Nov 21 22:29:24 2016
OBNUC 13C
EXMOD BCM
OBFRQ 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27118.64 Hz
SCANS 212
ACQTM 1.2083 sec
PD 1.7920 sec
PW1 6.30 usec
IRNUC 1H
CTEMP 22.0 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.42 Hz
RGAIN 22
PPM

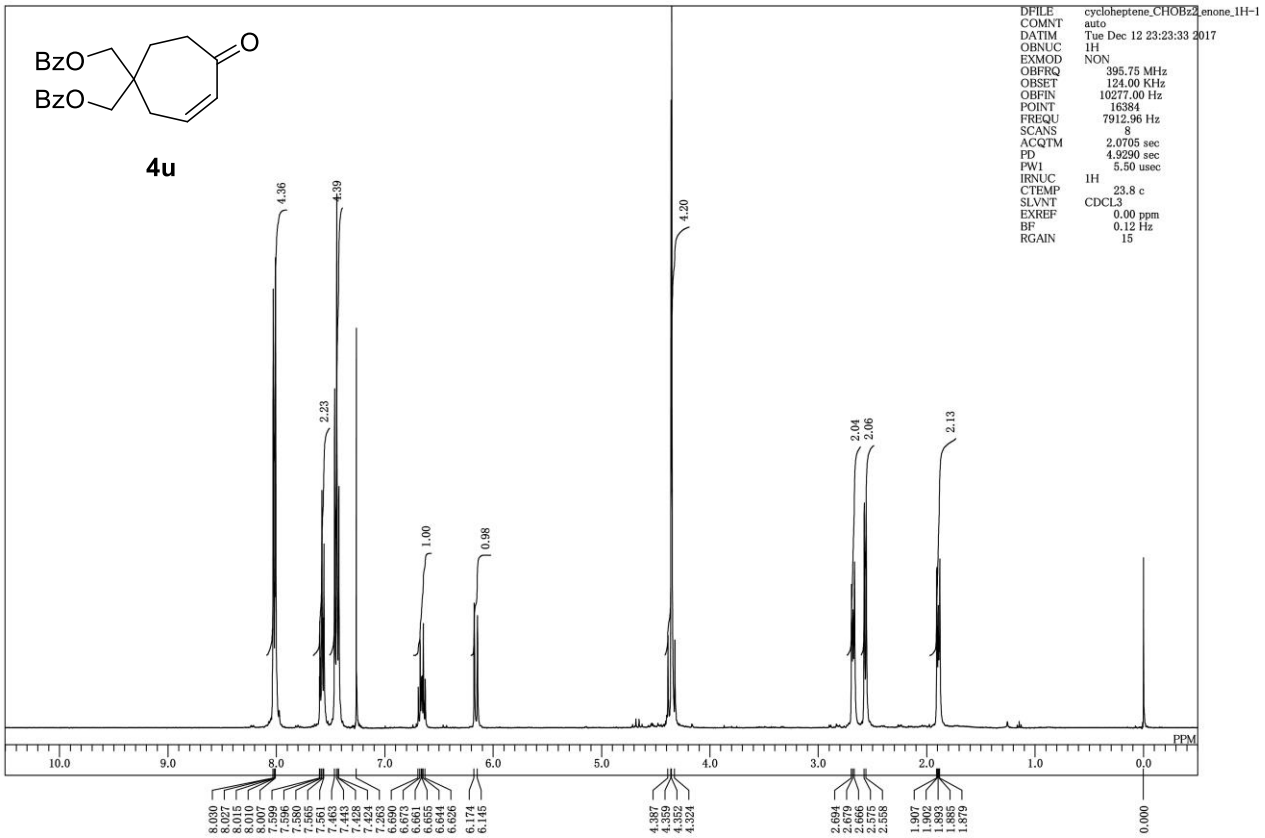
auto


BzO
O
4t
DFILE cycloheptene_OBz_enone_1H-1212.
COMNT auto
DATIM Tue Dec 12 23:20:09 2017
OBNUC 1H
EXMOD NON
OBFRQ 395.75 MHz
OBSET 124.00 KHz
OBFIN 10277.00 Hz
POINT 16384
FREQU 7912.96 Hz
SCANS 8
ACQTM 2.0705 sec
PD 4.9290 sec
PW1 5.50 usec
IRNUC 1H
CTEMP 23.1 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 12
2.17
2.17
1.12
0.98
0.94
1.00
3.07
1.13
1.10
1.14
PPM

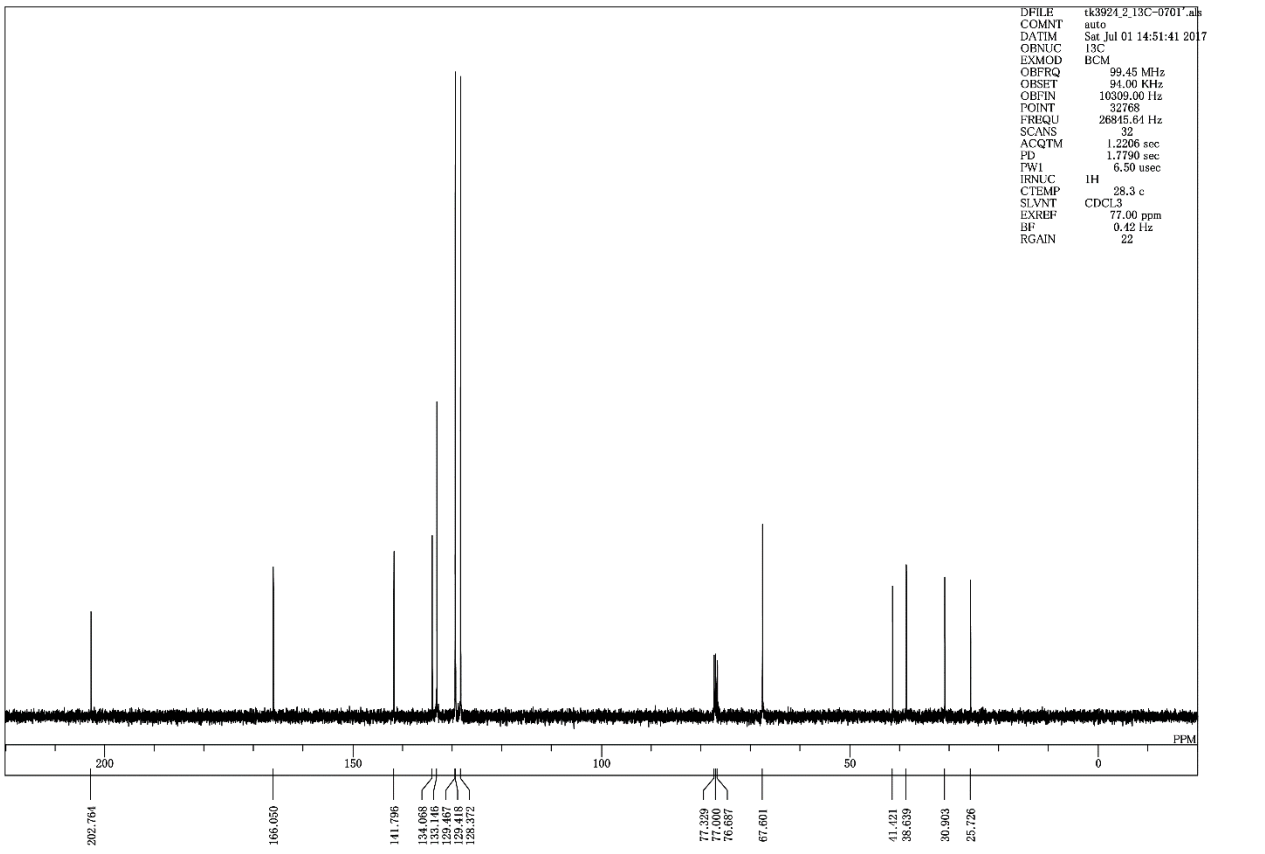
auto


DFILE tk3936_13C-0713'.als
COMNT auto
DATIM Thu Jul 13 00:58:13 2017
OBNUC 13C
EXMOD BCM
OBFRQ 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQU 27118.64 Hz
SCANS 92
ACQTM 1.2083 sec
PD 1.7920 sec
PW1 6.30 usec
IRNUC 1H
CTEMP 27.8 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.42 Hz
RGAIN 22
PPM

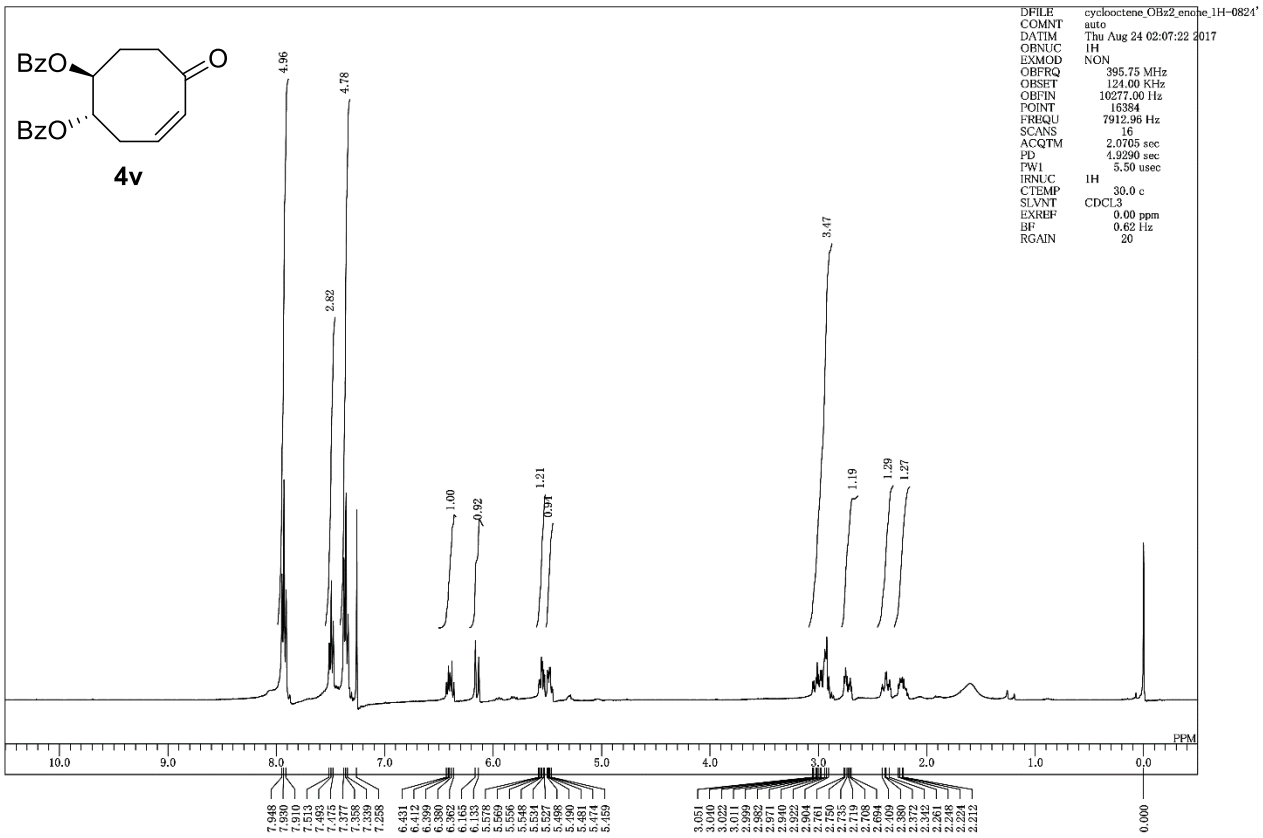
auto


BzO
BzO
O
4u
DFILE cycloheptene_CHOBz2_enone_1H-1
COMNT auto
DATIM Tue Dec 12 23:23:33 2017
OBNUC 1H
EXMOD NON
OBFRQ 395.75 MHz
OBSET 124.00 KHz
OBFIN 10277.00 Hz
POINT 16384
FREQU 7912.96 Hz
SCANS 8
ACQTM 2.0705 sec
PD 4.9290 sec
PW1 5.50 usec
IRNUC 1H
CTEMP 23.8 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 15
4.36
4.39
4.20
2.23
2.04
2.06
2.13
1.00
0.98
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
8.030
8.027
8.015
8.010
8.007
7.599
7.596
7.580
7.565
7.561
7.463
7.443
7.428
7.424
7.263
6.690
6.673
6.661
6.655
6.644
6.626
6.174
6.145
4.387
4.359
4.352
4.324
2.694
2.679
2.666
2.575
2.558
1.907
1.902
1.893
1.885
1.879
0.000

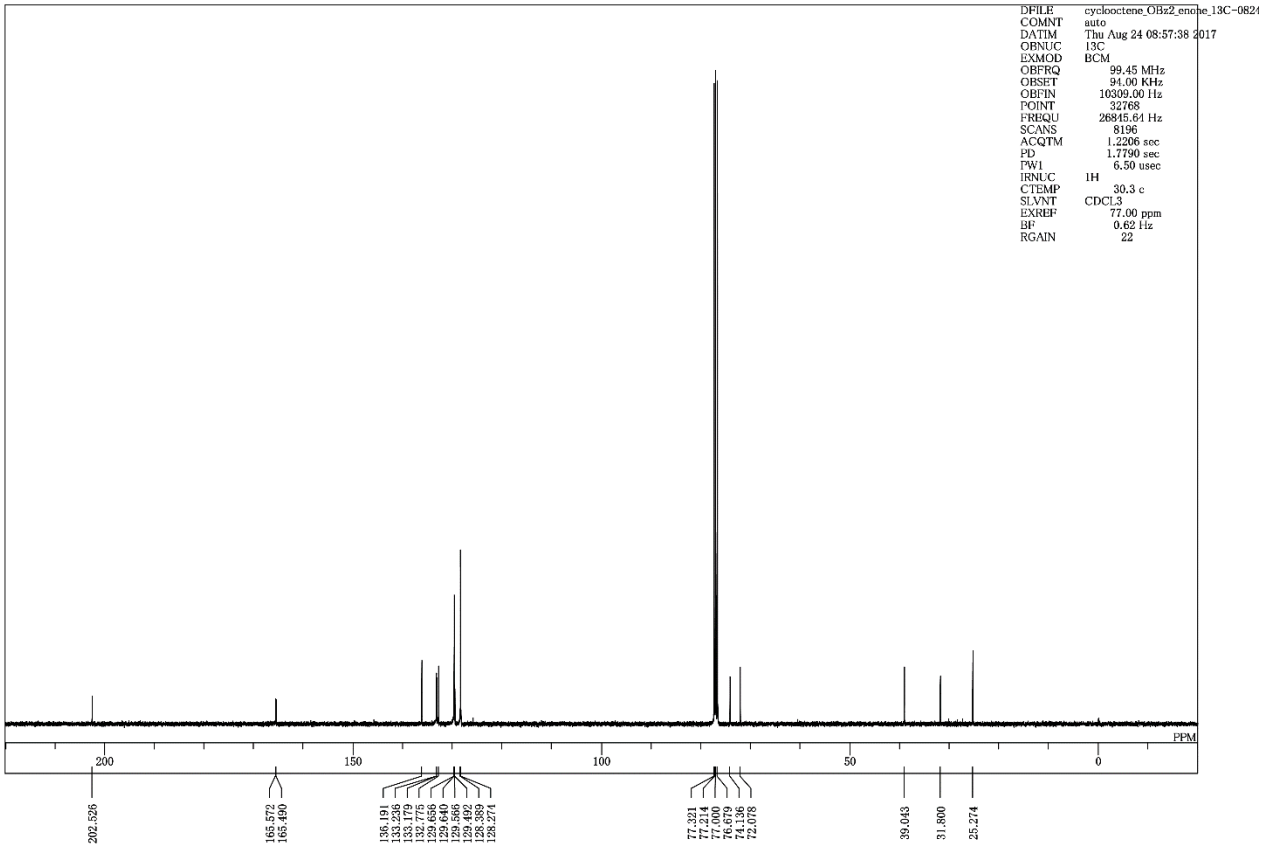
auto


DFILE tk3924_2_13C-0701*.als
COMNT auto
DATIM Sat Jul 01 14:51:41 2017
OBNUC 13C
EXMOD BCM
OBFRQ 99.45 MHz
OBSET 94.00 KHz
OBFIN 10309.00 Hz
POINT 32768
FREQU 26845.64 Hz
SCANS 32
ACQTM 1.2206 sec
PD 1.7790 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 28.3 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.42 Hz
RGAIN 22
PPM
200
150
100
50
0
202.764
166.650
141.796
134.068
133.146
129.467
129.418
128.372
77.329
77.000
76.687
67.601
41.421
38.639
30.903
25.726

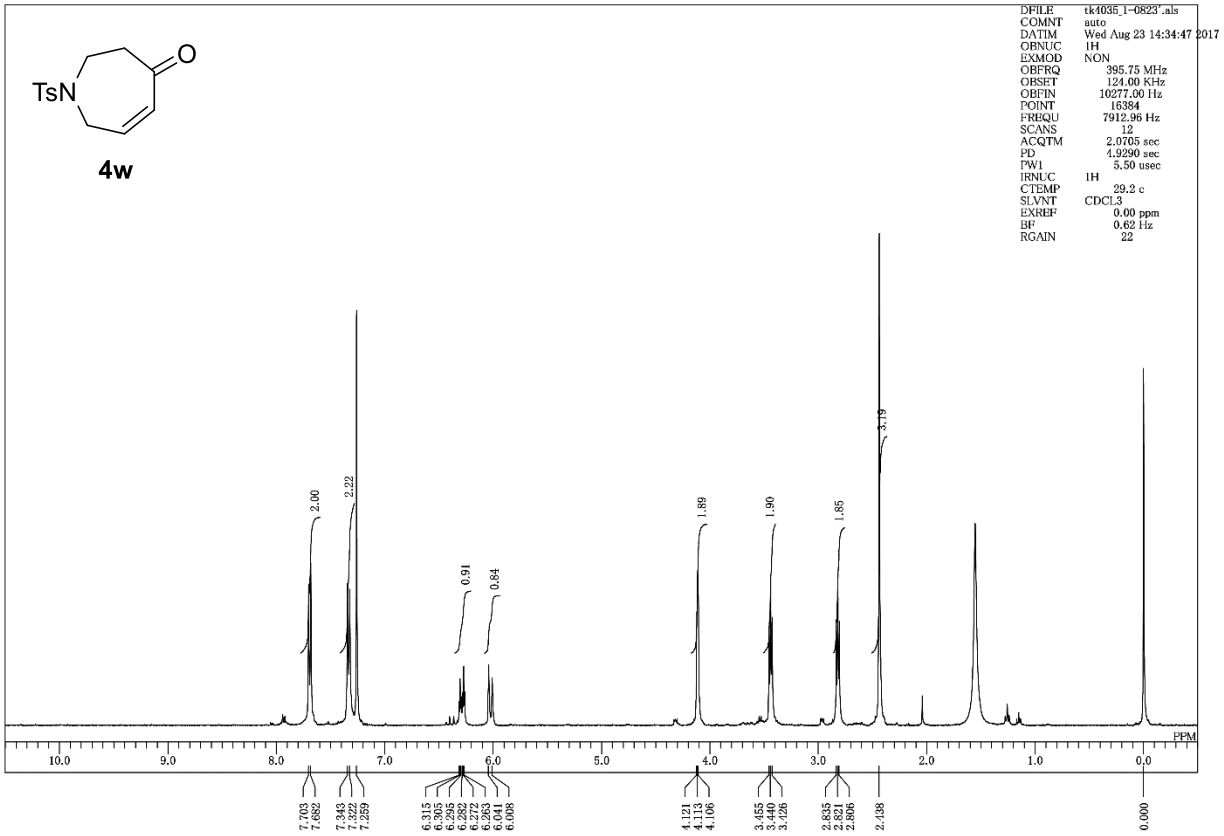
auto


BzO
BzO
O
4v
4.96
4.78
2.82
3.47
1.00
0.92
1.21
0.91
1.19
1.29
1.27
DFILE cyclooctene_OBz2_enone_1H-0824'
COMNT auto
DATIM Thu Aug 24 02:07:22 2017
OBNUC 1H
EXMOD NON
OBFRQ 395.75 MHz
OBSET 124.00 KHz
OBFIN 10277.00 Hz
POINT 16384
FREQU 7912.96 Hz
SCANS 16
ACQTM 2.0705 sec
PD 4.9290 sec
PW1 5.50 usec
IRNUC 1H
CTEMP 30.0 c
SLVNT CDCl3
EXREF 0.00 ppm
BF 0.62 Hz
RGAIN 20
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.948
7.930
7.910
7.513
7.493
7.475
7.377
7.358
7.338
7.258
6.431
6.412
6.389
6.369
6.982
6.165
6.133
5.578
5.569
5.556
5.544
5.534
5.527
5.498
5.490
5.481
5.474
5.469
3.051
3.040
3.022
3.011
2.999
2.982
2.971
2.940
2.922
2.904
2.781
2.769
2.735
2.719
2.708
2.694
2.409
2.389
2.372
2.342
2.261
2.248
2.224
2.212
0.000

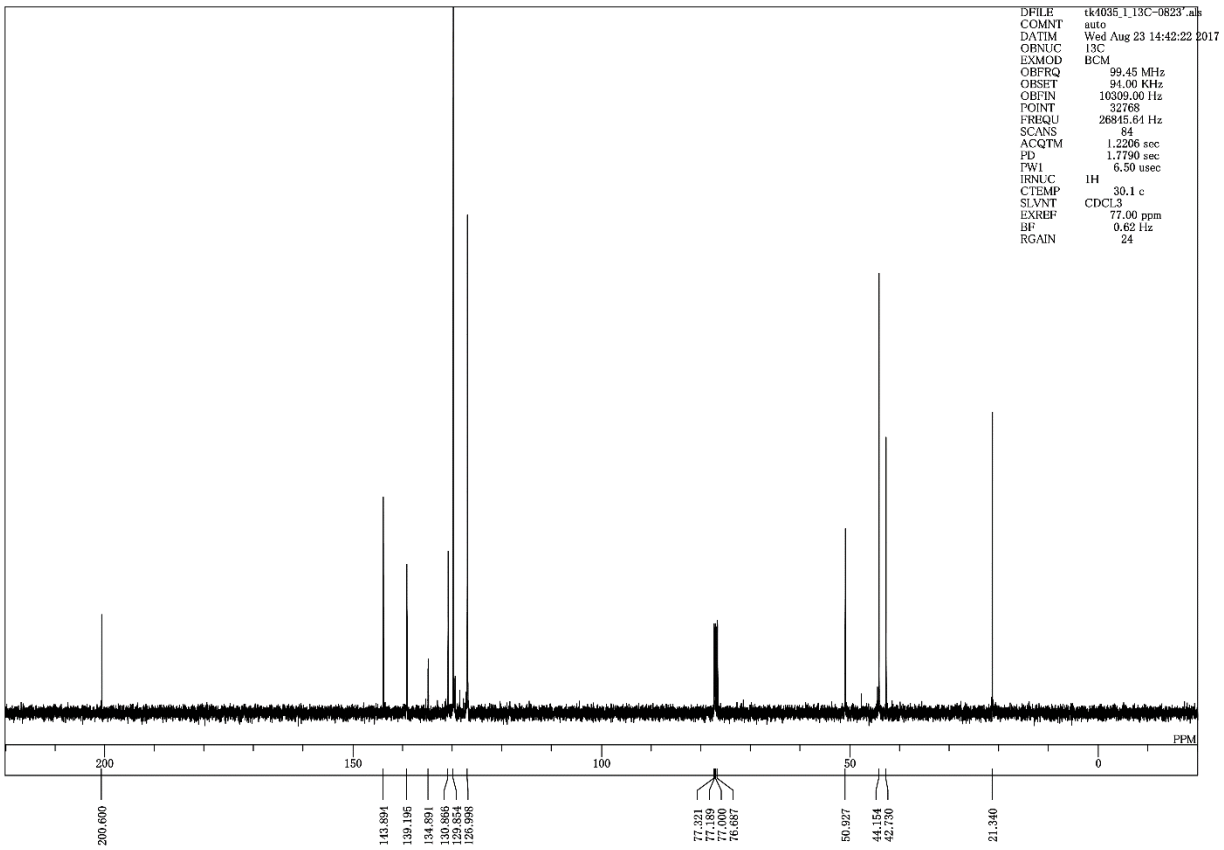
auto


DFILE cyclooctene_OBz2_enone_13C-0824
COMNT auto
DATIM Thu Aug 24 08:57:38 2017
OBNUC 13C
EXMOD BCM
OBFRQ 99.45 MHz
OBSET 94.00 KHz
OBFIN 10309.00 Hz
POINT 32768
FREQU 26845.64 Hz
SCANS 8196
ACQTM 1.2206 sec
PD 1.7790 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 30.3 c
SLVNT CDCl3
EXREF 77.00 ppm
BF 0.62 Hz
RGAIN 22
PPM
200
150
100
50
0
202.526
165.572
165.490
136.191
133.238
133.179
132.775
129.656
129.640
129.595
129.490
128.382
128.271
77.321
77.224
77.000
76.679
74.136
72.078
39.043
31.800
25.274

auto


TsN
O
4w
DFILE tk4035_1-0823'.als
COMNT auto
DATIM Wed Aug 23 14:34:47 2017
OBNUC 1H
EXMOD NON
OBFRQ 395.75 MHz
OBSET 124.00 KHz
OBFIN 10277.00 Hz
POINT 16384
FREQU 7912.96 Hz
SCANS 12
ACQTM 2.0705 sec
PD 4.9290 sec
PW1 5.50 usec
IRNUC 1H
CTEMP 29.2 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.62 Hz
RGAIN 22
2.00
2.22
0.91
0.84
1.89
1.90
1.85
3.19
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.703
7.682
7.343
7.322
7.259
6.315
6.295
6.282
6.272
6.263
6.041
6.008
4.121
4.113
4.106
3.455
3.440
3.426
2.835
2.821
2.806
2.438
0.000

auto


DFILE tk4035_1_13C-0823'.als
COMNT auto
DATIM Wed Aug 23 14:42:22 2017
OBNUC 13C
EXMOD BCM
OBFRQ 99.45 MHz
OBSET 94.00 KHz
OBFIN 10309.00 Hz
POINT 32768
FREQU 26845.64 Hz
SCANS 84
ACQTM 1.2206 sec
PD 1.7790 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 30.1 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.62 Hz
RGAIN 24
PPM
200
150
100
50
0
200.600
143.894
139.195
134.891
130.866
129.854
126.998
77.321
77.189
77.000
76.687
50.927
44.154
42.730
21.340