Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Catalytic Radical Cascade Cyclization of Alkene-Tethered Enones to Fused Bicyclic Cyclopropanols

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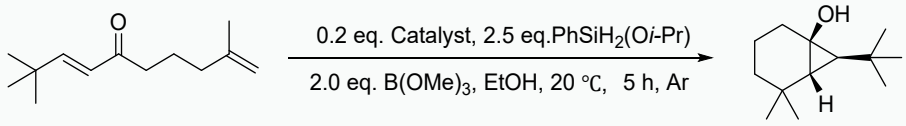
Table of Contents

1. General information

All reactions are carried out in flame-dried sealed tubes with magnetic stirring. Unless otherwise noted, all experiments are performed under argon atmosphere. All chemicals were purchased commercially and used without further purification, unless otherwise stated. Solvents are treated with CaH_2 or sodium and distilled prior to use. Purifications of reaction products are carried out by flash chromatography using Qingdao Haiyang Chemical Co. Ltd silica gel (200-300 mm) or Keshi Co. Ltd Aluminum oxide active (200-300). Infrared spectra (IR) are recorded on a Nexus 670FT-IR spectrophotometer and are reported as wavelength numbers (cm^{-1}). ^{1}H NMR and ^{13}C NMR spectra are recorded with tetramethylsilane (TMS) as internal standard at ambient temperature unless otherwise indicated on a Bruker Avance DPX 400 Fourier Transform spectrometer operating at 400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR. Chemical shifts are reported in parts per million (ppm) and coupling constants are reported as Hertz (Hz). Splitting patterns are designated as singlet (s), broad singlet (bs), doublet (d), triplet (t). Splitting patterns that could not be interpreted or easily visualized are designated as multiple (m). High resolution mass spectra (HRMS) are recorded on an IF-TOF spectrometer (Micromass). Oil bath was used for reactions that require heating. Low temperature reactor (ethanol bath) was used for reactions that require cooling. In $^{1}H/^{13}C$ NMR spectrum, nomenclature for compounds **3a**-**3t** only refers to the depicted enantiomer.

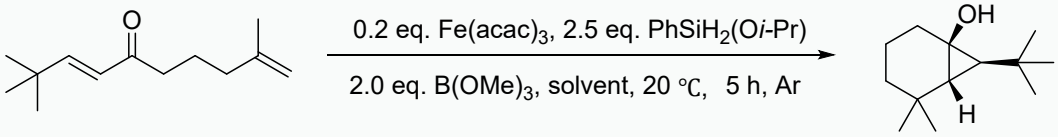
2. Screening of Reaction Conditions

2.1 Table 1. The effect of the catalyst for the catalytic radical cascade cyclization of alkene-tethered enones.



Catalyst	Yield%
$Fe(acac)_3$	69%
$Fe(dpm)_3$	45%
Co(salen)	mess
$Co(acac)_2$	mess
$Fe(TPP)_3$	mess
$Mn(acac)_3$	no reaction
$Fe(OTf)_3$	no reaction
$Fe_2(SO_4)_3$	no reaction
$FeCl_3$	trace

2.2 Table 2. The effect of the solvent for the catalytic radical cascade cyclization of alkene-tethered enones.

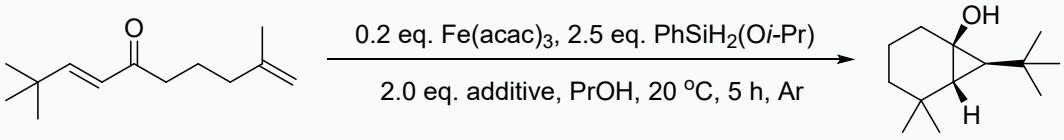


Solvent	Yield (%) [a]
MeOH	33%
EtOH	69%
i-PrOH	78%
n-PrOH	90%
n-BuOH	trace
CF_3CH_2OH	79%

$C_3H_2F_6O$	58%
CH_3CN	65%
EA	42%
Hexane	2%
1,4-dioxane	61%
THF	69%
DCE	25%
Toluene	13%
1,4-dioxane: *n*-PrOH (5:1)	53%
THF: *n*-PrOH (5:1)	49%
methyl borate (1.5 ml)	84%

[a] isolated yield.

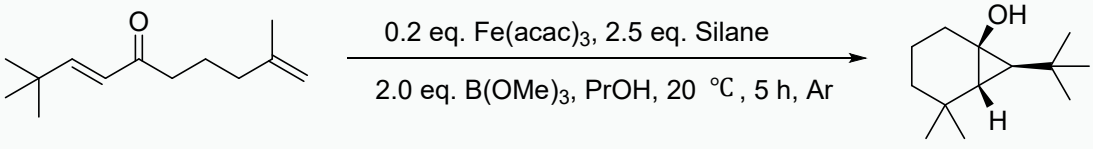
2.3 Table 3. The effect of the additive for the catalytic radical cascade cyclization of alkene-tethered enones.



Additive	Yield (%) [a]
$B(OMe)_3$	90
$B(O$*i*$-Pr)_3$	57
$(BPin)_2$	43
$BF_3 \cdot Et_2O$	mess
-	68

[a] isolated yield.

2.4 Table 4. The effect of the silane for the catalytic radical cascade cyclization of alkene-tethered enones.



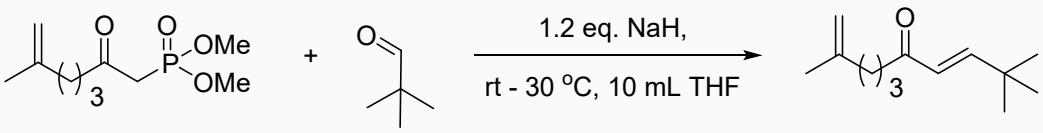
Silanes	Yield (%) [a]
$PhSiH_2(O$*i*$-Pr)$	90
$PhSiH_3$	32

Et_3SiH_2	no reaction
$^{i}PrSiH_2$	no reaction
Ph_2SiH_2	26
$(EtO)_2CH_3SiH$	no reaction

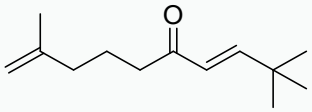
[a] isolated yield.

3. Experimental Procedures

3.1 General procedure for the synthesis of substrate (1a – 1t)



To the solution of the phosphonate [1] (524 mg, 2.0 mmol) in the 10 mL dry THF was added NaH (96 mg, 2.4 mmol) under Ar at rt. The reaction was stirred at rt for 30 min. Then aldehyde (1.2 eq.) was added. The mixture was stirred at 30 ℃ for another 24 h and quenched with saturated NH_4Cl (10 mL). The organic layer was separated and water layer was extracted with EA and dried over Na_2SO_4. The combined organic layers were evaporated and the residue was purified via column chromatography to give desired product. [2] The other substrates could also be prepared using the similar methods.



2a

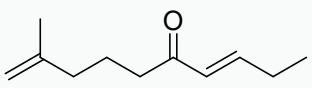
Physical state: colorless oil
Rf = 0.5 (PE/EtOAc = 5:1; UV) 349.2 mg, 90% yield

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.79 (d, *J* = 16.1 Hz, 1H), 5.99 (d, *J* = 16.1 Hz, 1H), 4.70 (s, 1H), 4.66 (s, 1H), 2.54 – 2.49 (m, 2H), 2.10 – 1.99 (m, 2H), 1.80 – 1.70 (m, 2H), 1.69 (s, 3H), 1.06 (s, 9H).

^{13}C NMR (100MHz, $CDCl_3$) δ 201.15, 156.84, 145.11, 125.41, 110.48, 39.51, 37.15, 33.68, 28.70, 22.19, 21.92.

HRMS(ESI^{+}) m/z Calculated for $C_{13}H_{23}O$ $[M+H]^{+}$:195.1749, found: 195.1749.

IR (thin film) ν $_{max}$ (cm^{-1}): 2962, 1720, 1620, 1364, 988.



2b

Physical state: colorless oil

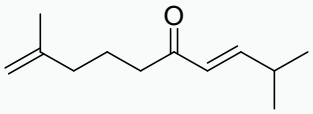
Rf = 0.5 (PE/EtOAc = 5:1; UV) 252.32 mg, 76% yield

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.87 (dt, *J* = 15.9, 6.4 Hz, 1H), 6.08 (dt, *J* = 15.9, 1.7 Hz, 1H), δ 4.72 (s, 1H), 4.67 (s, 1H), 2.52 (t, *J* = 7.6 Hz, 2H), 2.23 (qdd, *J* = 7.5, 6.3, 1.7 Hz, 2H), 2.03 (t, *J* = 7.4 Hz, 2H), 1.75(q, *J* = 7.6 Hz, 2H) 1.70 (s, 3H), 1.07 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 200.77, 148.61, 145.16, 129.45, 110.48, 39.29, 37.16, 25.52, 22.22, 21.92, 12.26.

HRMS(ESI$^+$) m/z Calculated for $C_{11}H_{19}O$ $[M+H]^+$: 167.1430, found: 167.1431.

IR (thin film) ν $_{max}$ (cm^{-1}): 2934, 1688, 1625, 1446, 1115.



2c

Physical state: colorless oil

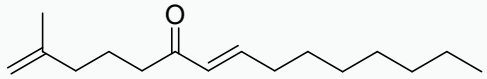
Rf = 0.5 (PE/EtOAc = 5:1; UV) 338.4 mg, 94% yield

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.79 (dd, *J* = 16.0, 6.7 Hz, 1H), 6.04 (dd, *J* = 16.0, 1.5 Hz, 1H), 4.73 (s, 1H), 4.69 (s, 1H), 2.53 (t, *J* = 7.4 Hz, 2H), 2.46 (qd, *J* = 6.7, 1.5 Hz, 1H), 2.04 (t, *J* = 7.5 Hz, 2H), 1.85 – 1.74 (q, *J* = 7.2 Hz, 2H), 1.72 (s, 3H), 1.07 (d, *J* = 6.8 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 201.06, 153.37, 145.19, 127.55, 110.49, 39.38, 37.17, 31.11, 29.71, 22.22, 21.95, 21.34.

HRMS(ESI$^+$) m/z Calculated for $C_{12}H_{21}O$ $[M+H]^+$: 181.1587, found: 181.1589.

IR (thin film) ν $_{max}$ (cm^{-1}): 2923, 2851, 1460, 1377.



2d

Physical state: colorless oil

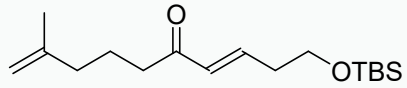
Rf = 0.5 (PE/EtOAc = 5:1; UV) 424.8 mg, 90% yield

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.82 (dt, *J* = 15.9, 6.9 Hz, 1H), 6.09 (d, *J* = 15.9 Hz, 1H), 4.73 (s, 1H), 4.68 (s, 1H), 2.52 (t, *J* = 7.4 Hz, 2H), 2.20 (qd, *J* = 7.1 Hz, *J* = 1.6 Hz, 2H), 2.04 (t, *J* = 7.5 Hz, 2H), 1.77 (q, *J* = 7.5 Hz, 2H), 1.71 (s, 3H), 1.46 (t, *J* = 7.3 Hz, 2H), 1.40 – 1.15 (m, 8H), 0.88 (t, *J* = 6.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 200.74, 147.48, 145.18, 130.35, 110.48, 39.31, 37.18, 32.47, 31.74, 29.16, 29.06, 28.13, 22.63, 22.22, 21.97, 14.08.

HRMS(ESI$^+$) m/z Calculated for $C_{16}H_{29}O$ $[M+H]^+$: 237.2213, found: 237.2213.

IR (thin film) ν $_{max}$ (cm^{-1}): 2962, 1678, 1625, 1364, 984.



2e

Physical state: colorless oil

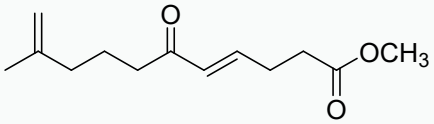
Rf = 0.5 (PE/EtOAc = 5:1; UV) 544.6 mg, 92% yield

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.78 (dt, *J* = 16.0, 7.0 Hz, 1H), 6.08 (dt, *J* = 16.0, 1.5 Hz, 1H), 4.67 (s, 1H), 4.62 (s, 1H), 3.68 (t, *J* = 6.4 Hz, 2H), 2.47 (t, *J* = 7.6 Hz, 2H), 2.37 (qd, *J* = 6.5, 1.5 Hz, 2H), 1.98 (t, *J* = 7.6 Hz, 2H), 1.75 – 1.67 (m, 2H), 1.66 (s, 3H), 0.84 (s, 9H), 0.00 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 200.50, 145.10, 143.94, 131.93, 110.52, 61.60, 39.15, 37.16, 35.92, 25.87, 22.21, 21.89, 18.29, -5.33.

HRMS(ESI$^+$) m/z Calculated for $C_{17}H_{33}O_2Si$ $[M+H]^+$: 297.2244, found: 297.2241.

IR (thin film) ν $_{max}$ (cm^{-1}): 2925, 2856, 1254, 1099, 836.



2f

Physical state: colorless oil

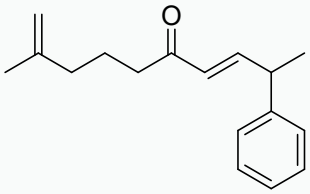
Rf = 0.4 (PE/EtOAc = 5:1; UV) 259.8 mg, 58% yield

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.81 (dt, *J* = 16.0, 6.2 Hz, 1H), 6.12 (d, *J* = 15.9 Hz, 1H), 4.73 (s, 1H), 4.67 (s, 1H), 3.69 (s, 3H), 2.62 – 2.44 (m, 6H), 2.03 (t, *J* = 7.5 Hz, 2H), 1.80 - 1.74 (m, 2H), 1.71 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 200.29, 172.73, 145.08, 144.33, 130.92, 110.54, 51.80, 39.52, 37.10, 32.32, 27.39, 22.20, 21.78.

HRMS(ESI$^+$) m/z Calculated for $C_{13}H_{21}O_3$ $[M+H]^+$: 225.1485, found: 225.1469.

IR (thin film) ν $_{max}$ (cm^{-1}): 2932, 1676, 1456, 1118, 885.



2g

Physical state: colorless oil

Rf = 0.5 (PE/EtOAc = 5:1; UV) 242 mg, 50% yield

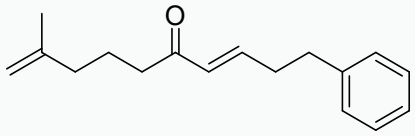
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (t, *J* =7.4 Hz, 2H), 7.24 (d, *J* = 7.9 Hz, 1H), 7.21 – 7.15 (m, 2H), 6.95 (dd, *J* = 15.9, 6.7 Hz, 1H), 6.08 (dd, *J* = 16.0, 1.6 Hz, 1H), 4.71 (s, 1H), 4.66 (s,

1H), 3.62 (td, *J* = 6.9, 1.5 Hz, 1H), 2.52 (t, *J* = 7.4 Hz, 2H), 2.02 (t, *J* = 7.5 Hz, 2H), 1.77 – 1.73 (m, 2H), 1.69 (s, 3H), 1.43 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 200.78, 150.45, 145.10, 143.41, 128.81, 128.75, 127.35, 126.81, 110.54, 42.22, 39.43, 37.13, 22.21, 21.84, 20.27.

HRMS(ESI$^+$) m/z Calculated for $C_{17}H_{23}O$ $[M+H]^+$: 243.1743, found: 243.1741.

IR (thin film) ν $_{max}$ (cm^{-1}):2967, 1672, 1625, 1451, 887, 699.



2h

Physical state: colorless oil

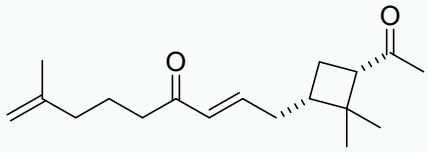
Rf = 0.5 (PE/EtOAc = 5:1; UV) 338.8 mg, 70% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29(t, *J* = 7.2 Hz, 2H), 7.22-7.16(m, 3H) 6.84 (dt, *J* = 15.9, 6.8 Hz, 1H), 6.10 (dt, *J* = 15.9, 1.5 Hz, 1H), 4.72 (s, 1H), 4.67 (s, 1H), 2.79 (t, *J* = 7.7 Hz, 2H), 2.56 – 2.48 (m, 4H), 2.02 (t, *J* = 7.6 Hz, 2H), 1.79 – 1.72 (m, 2H), 1.71 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 200.54, 145.89, 145.13, 140.75, 130.80, 128.51, 128.35, 126.22, 110.52, 39.40, 37.15, 34.47, 34.14, 22.22, 21.92.

HRMS(ESI$^+$) m/z Calculated for $C_{17}H_{23}O$ $[M+H]^+$: 243.1743, found: 243.1739.

IR (thin film) ν $_{max}$ (cm^{-1}):2932, 1670, 1453, 886, 746, 698.



2i

Physical state: colorless oil

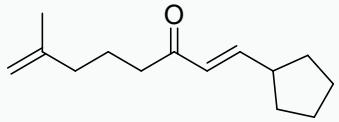
Rf = 0.4 (PE/EtOAc = 5:1; UV) 342.2 mg, 62% yield. (dr = 5.2:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.71 (dt, *J* = 15.8, 6.9 Hz, 1H), 6.10 (dt, *J* = 15.7, 1.5 Hz, 1H), 4.73 (s, 1H), 4.67 (s, 1H), 2.85 (dd, *J* = 9.9, 7.5 Hz, 1H), 2.50 (t, *J* = 7.4 Hz, 2H), 2.34 – 2.18 (m, 1H), 2.17 – 2.09 (m, 1H), 2.04 (s, 3H), 2.03 (s, 2H), 1.98 – 1.90 (m, 1H), 1.83 – 1.73 (m, 2H), 1.71 (s, 3H), 1.58 (s, 2H), 1.30 (s, 3H), 0.88 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 207.55, 200.35, 145.11, 144.81, 130.92, 110.53, 54.09, 43.48, 40.79, 39.55, 37.14, 33.29, 30.54, 30.21, 23.03, 22.21, 21.91, 17.32.

HRMS(ESI$^+$) m/z Calculated for $C_{18}H_{29}O_2$ $[M+H]^+$: 277.2162, found: 277.2161

IR (thin film) ν $_{max}$ (cm^{-1}): 2902, 2848, 1676, 1456, 885.



2j

Physical state: colorless oil

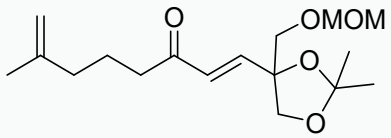
Rf = 0.5 (PE/EtOAc = 5:1; UV) 210.2 mg, 51% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.80 (dd, *J* = 15.8, 7.9 Hz, 1H), 6.09 (d, *J* = 1.2 Hz, 1H), 4.73 (s, 1H), 4.68 (s, 1H), 2.59 (q, *J* = 8.1 Hz, 1H), 2.52 (t, *J* = 7.4 Hz, 2H), 2.02 (t, *J* = 7.5 Hz, 2H), 1.84 (tdd, *J* = 7.3, 5.5, 3.5 Hz, 2H), 1.77 (q, *J* = 7.5 Hz, 2H), 1.71 (s, 3H), 1.69 – 1.59 (m, 4H), 1.44 – 1.35 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 200.87, 151.50, 145.17, 128.41, 110.47, 43.06, 39.38, 37.18, 32.54, 25.31, 22.22, 21.97.

HRMS(ESI$^+$) m/z Calculated for $C_{14}H_{23}O$ $[M+H]^+$: 207.1743, found: 207.1743.

IR (thin film) ν $_{max}$ (cm^{-1}): 2950, 2868, 1669, 1625, 1451, 1371, 885.



2k

Physical state: colorless oil

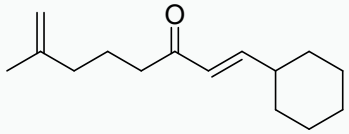
Rf = 0.4 (PE/EtOAc = 5:1; UV) 386.9 mg, 62% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.91 (d, *J* = 15.8 Hz, 1H), 6.47 (d, *J* = 15.8 Hz, 1H), 4.73 (s, 1H), 4.68 (s, 1H), 4.64 (s, 2H), 4.14 (d, *J* = 8.8 Hz, 1H), 3.85 (dd, *J* = 8.8 Hz, *J* = 0.6 Hz, 1H), 3.60 (d, *J* = 9.6 Hz, 1H), 3.51 (d, *J* = 9.6 Hz, 1H), 3.36 (s, 3H), 2.56 (t, *J* = 7.4 Hz, 2H), 2.04 (t, *J* = 7.5 Hz, 2H), 1.79 – 1.71 (m, 2H), 1.71 (s, 3H), 1.46 (s, 3H), 1.42 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 200.13, 145.02, 144.85, 128.84, 110.84, 110.59, 96.72, 82.04, 71.01, 70.77, 67.99, 55.51, 40.36, 37.08, 26.86, 26.11, 25.62, 22.20, 21.68.

HRMS(ESI$^+$) m/z Calculated for $C_{17}H_{29}O_5$ $[M+H]^+$: 313.2010, found: 313.2008.

IR (thin film) ν $_{max}$ (cm^{-1}): 2936, 1677, 1371, 1110, 1044.



2l

Physical state: colorless oil

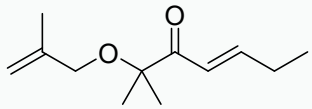
Rf = 0.5 (PE/EtOAc = 5:1; UV) 286 mg, 65% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.76 (dd, *J* = 16.0, 6.8 Hz, 1H), 6.04 (dd, *J* = 16.0, 1.4 Hz, 1H), 4.73 (s, 1H), 4.68 (s, 1H), 2.53 (t, *J* = 7.4 Hz, 2H), 2.13 (tdtd, *J* = 7.9, 6.6, 3.3, 1.6 Hz, 1H), 2.04 (t, *J* = 7.5 Hz, 2H), 1.78 – 1.73 (m, 6H), 1.71 (s, 3H), 1.29 (qt, *J* =13.6, 2.7 Hz, 2H), 1.24 – 1.08 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 201.09, 152.21, 145.16, 127.85, 110.47, 40.60, 39.34, 37.17, 31.80, 25.93, 25.72, 22.21, 21.98.

HRMS(ESI$^+$) m/z Calculated for $C_{15}H_{25}O$ $[M+H]^+$: 221.1900, found: 221.1893.

IR (thin film) ν $_{max}$ (cm^{-1}): 2925, 2832, 1672, 1449, 980.



2m

Physical state: colorless oil

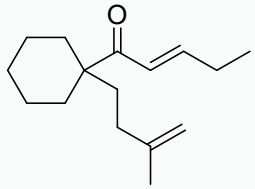
Rf = 0.5 (PE/EtOAc = 5:1; UV) 356.7 mg, 91% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (dt, *J* = 15.6, 6.3 Hz, 1H), 6.74 (dt, *J* = 15.6, 1.7 Hz, 1H), 5.03 (s, 1H), 4.89 (s, 1H), 3.70 (s, 2H), 2.29 – 2.22 (m, 2H), 1.75 (s, 3H), 1.35 (s, 6H), 1.08 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 202.99, 150.25, 142.32, 122.85, 111.54, 81.40, 68.36, 25.69, 23.15, 19.78, 12.23.

HRMS(ESI$^+$) m/z Calculated for $C_{12}H_{21}O$ $[M+H]^+$:197.1536, found: 197.1536

IR (thin film) ν $_{max}$ (cm^{-1}): 2973, 1697, 1625, 1170, 1071.



2n

Physical state: colorless oil

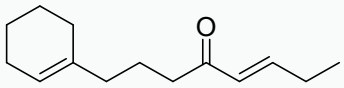
Rf = 0.5 (PE/EtOAc = 5:1; UV) 365 mg, 78% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 (dt, *J* = 15.2, 6.5 Hz, 1H), 6.51 (dt, *J* = 15.2, 1.6 Hz, 1H), 4.66 (s, 1H), 4.62 (s, 1H), 2.27 – 2.19 (m, 2H), 2.06 – 2.02 (m, 2H), 1.80 – 1.76 (m, 2H), 1.67 (s, 3H), 1.64 – 1.56 (m, 5H), 1.36 – 1.26 (m, 5H), 1.07 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 203.95, 148.88, 146.05, 123.59, 109.50, 50.31, 36.96, 33.25, 31.74, 26.20, 25.61, 22.89, 22.62, 12.52.

HRMS(ESI$^+$) m/z Calculated for $C_{16}H_{27}O$ $[M+H]^+$:235.2056, found: 235.2055.

IR (thin film) ν $_{max}$ (cm^{-1}): 2967, 2935, 1672, 1628, 977.



2o

Physical state: colorless oil

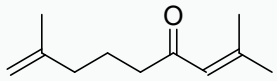
Rf = 0.5 (PE/EtOAc = 5:1; UV) 300.7 mg, 73% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.87 (dt, *J* = 15.9, 6.3 Hz, 1H), 6.09 (dt, *J* = 15.8, 1.7 Hz, 1H), 5.39 (s, 1H), 2.50 (t, *J* = 7.4 Hz, 2H), 2.29 – 2.18 (m, 2H), 2.01 – 1.86 (m, 6H), 1.72 (ddd, *J* = 7.4, 6.8 Hz, 2H), 1.66 – 1.48 (m, 4H), 1.08 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 200.98, 148.45, 137.02, 129.46, 121.60, 39.51, 37.48, 28.08, 25.50, 25.22, 22.96, 22.53, 22.21, 12.27.

HRMS(ESI$^+$) m/z Calculated for $C_{14}H_{23}O$ $[M+H]^+$: 207.1743, found: 207.1747.

IR (thin film) ν $_{max}$ (cm^{-1}): 2960, 1674, 1625, 1364, 984, 889.



2p

Physical state: colorless oil

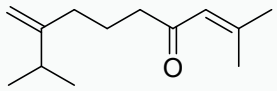
Rf = 0.5 (PE/EtOAc = 5:1; UV) 365.6 mg, 80 % yield

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.07 (p, *J* = 1.3 Hz, 1H), 4.72 (s, 1H), 4.67 (s, 1H), 2.40 (t, *J* = 7.4 Hz, 2H), 2.14 (d, *J* = 1.3 Hz, 3H), 2.02 (t, *J* = 7.9 Hz, 2H), 1.88 (d, *J* = 1.4 Hz, 3H), 1.80 – 1.64 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 201.00, 154.82, 145.27, 123.81, 110.33, 43.56, 37.17, 27.63, 22.21, 21.95, 20.66.

HRMS(ESI$^+$) m/z Calculated for $C_{11}H_{19}O$ $[M+H]^+$:167.1430, found: 167.1439.

IR (thin film) ν $_{max}$ (cm^{-1}): 2934, 1688, 1620, 1446, 1110.



2q

Physical state: colorless oil

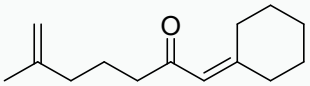
Rf = 0.5 (PE/EtOAc = 5:1; UV) 232.8 mg, 60% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.00 (s, 1H), 4.69 (s, 1H), 4.61(d, *J* = 1.6 Hz ,1H), 2.34 (t, *J* = 7.4 Hz, 2H), 2.15 (qd, *J* = 6.8, 1.1 Hz, 1H), 2.07 (s, 3H), 1.96 (t, *J* = 7.7 Hz ,2H), 1.81 (s, 3H), 1.71 - 1.67 (m, 2H), 0.95 (d, *J* = 6.9 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 200.13, 154.32, 153.84, 122.80, 105.73, 42.84, 32.82, 32.56, 26.63, 21.53, 20.81, 19.67.

HRMS(ESI$^+$) m/z Calculated for $C_{13}H_{23}O$ $[M+H]^+$: 195.1743, found: 195.1743.

IR (thin film) ν $_{max}$ (cm^{-1}): 2959, 2925, 1687, 1621, 1446.



2r

Physical state: colorless oil

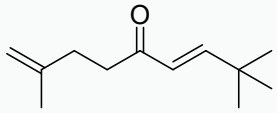
Rf = 0.5 (PE/EtOAc = 5:1; UV) 313.2 mg, 76% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.96 (s, 1H), 4.71 (s, 1H), 4.67 (s, 1H), 2.79 (s, 2H), 2.40 (t, *J* = 7.2 Hz, 2H), 2.15 (t, *J* = 6.1 Hz, 2H), 2.02 (t, *J* = 7.7 Hz, 3H), 1.83 – 1.61 (m, 10H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 201.84, 161.69, 145.34, 121.04, 110.36, 43.77, 38.11, 37.19, 31.23, 29.97, 28.82, 27.93, 26.28, 25.00, 22.24, 22.02, 21.90.

HRMS(ESI^{+}) m/z Calculated for $C_{14}H_{23}O$ $[M+H]^{+}$: 207.1743, found: 207.1746

IR (thin film) ν $_{max}$ (cm^{-1}): 2929, 2856, 1712, 1620, 1447, 1095.



2s

Physical state: colorless oil

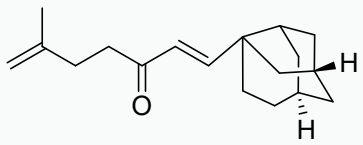
Rf = 0.5 (PE/EtOAc = 5:1; UV) 262.8 mg, 73% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.84 (d, *J* = 16.1 Hz, 1H), 6.03 (d, *J* = 16.1 Hz, 1H), 4.74 (s, 1H), 4.68 (s, 1H), 2.78 – 2.56 (m, 2H), 2.37 – 2.26 (m, 2H), 1.75 (s, 3H), 1.09 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 200.58, 157.06, 144.75, 125.29, 110.07, 38.49, 33.74, 31.86, 28.71, 22.68.

HRMS(ESI^{+}) m/z Calculated for $C_{12}H_{21}O$ $[M+H]^{+}$: 181.1587, found: 181.1598.

IR (thin film) ν $_{max}$ (cm^{-1}): 2962, 1672, 1625, 1364, 984.



2t

Physical state: colorless oil

Rf = 0.5 (PE/EtOAc = 5:1; UV) 103.2 mg, 20% yield.

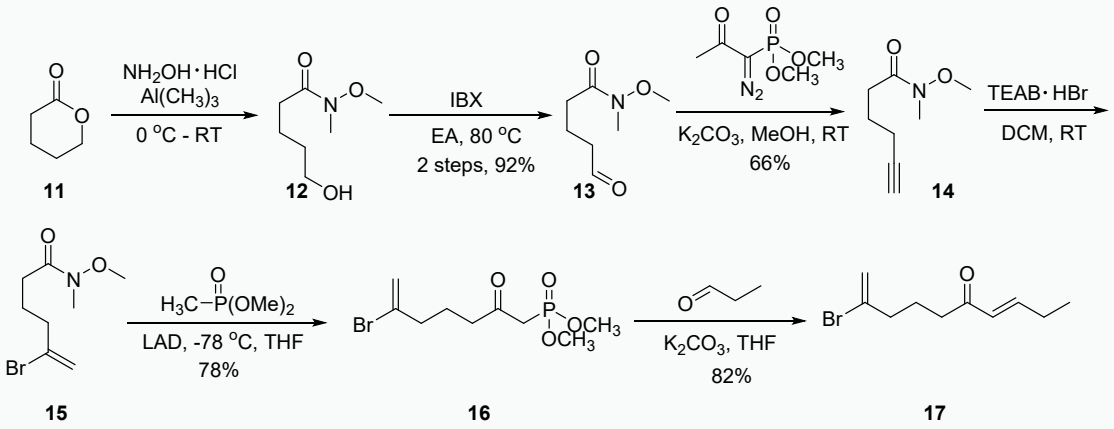
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.67 (d, *J* = 16.2 Hz, 1H), 5.97 (d, *J* = 16.2 Hz, 1H), 4.73 (s, 1H), 4.68 (s, 1H), 2.71 – 2.67 (m, 2H), 2.32 (t, *J* = 8 Hz, 2H), 2.03 (s, 3H), 1.74 (m, 5H), 1.71 – 1.54 (m, 10H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 200.81, 156.89, 144.82, 125.14, 110.06, 41.18, 38.43, 36.61, 35.70, 31.94, 28.07, 22.70.

HRMS(ESI^{+}) m/z Calculated for $C_{18}H_{27}O$ $[M+H]^{+}$: 259.2056, found: 259.2059.

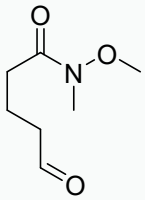
IR (thin film) ν $_{max}$ (cm^{-1}): 2902, 2848, 1672, 1451, 885.

3.2 General procedure for the synthesis of **2u** and **2v**.



To solution of *N, O*-dimethylhydroxyl-amine hydrochloride (11.7 g, 120 mmol) in dry CH_2Cl_2 (50 mL) at 0℃ was added the $AlMe_3$ (60 mL, 120 mmol, 2.0 M in hexane). The reaction was stirred at 0℃ for 20 min and tetrahydro-2H-pyran-2-one (8.0 g, 80 mmol) was added slowly. Then the reaction was stirred at 0℃ for 1 h. The DCM (30 mL) was added to the above reaction and quenched with aq. HCl (15 mL, 0.1 N). The residue was extracted with DCM (4×10 mL). The organic layer was separated, dried, filtered and concentrated under reduced pressure. The residue was used for the next step without further purified.[3]

To a suspension of IBX (44.8 g, 160 mmol) in EA (250 mL) was added above residue and the resulting mixture was stirred at 80℃ for 24 h. Then, the reaction was filtrated and concentrated under reduced pressure. The crude product was purified on SiO_2 to give the *N*-methoxy-*N*-methyl-5-oxopentanamide. The ^{1}H and ^{13}C NMR spectral data for the rest of *N*-methoxy-*N*-methyl-5-oxopentanamide showed good agreement with literature data [4]



13

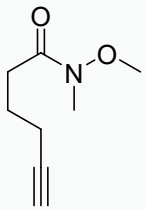
Physical state: colorless oil

Rf = 0.5 (PE/EtOAc = 1:1; anisaldehyde) 11.7 g, 92% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.75 (s, 1H), 3.66 (s, 3H), 3.16 (s, 3H), 2.52 (td, *J* = 7.1, 1.5 Hz, 2H), 2.44 (dt, *J* = 21.9, 7.1 Hz, 2H), 1.95 (p, *J* = 7.2 Hz, 1H).[4]

^{13}C NMR (100 MHz, $CDCl_3$) δ 202.14, 176.44, 61.23, 43.13, 32.17, 30.73, 17.03.

To the suspension of *N*-methoxy-*N*-methyl-5-oxopentanamide (11.2 g, 70 mmol) anddimethyl (1-diazo-2-oxopropyl)phosphonate (20.16 g, 105 mmol) in MeOH (200 mL) was added K_2CO_3 (19.3 g, 140 mmol). The mixture was stirred at rt for 24 h and the resulting mixture was concentrated under reduced pressure. Then, the water (50 mL) was added and aqueous phase was extracted with EA (4×50 mL). The organic layer was dried and filtrated and concentrated. The crude product was purified on SiO_2 to give the compound *N*-methoxy-*N*-methylhex-5-ynamide (7.16 g, 66%) . The ^{1}H and ^{13}C NMR spectral data for the rest of *N*-methoxy-*N*-methylhex-5-ynamide showed good agreement with literature data [5]



14

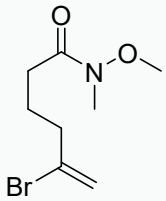
Physical state: colorless oil

Rf = 0.6 (PE/EtOAc = 1:1; $KMnO_4$) 7.16 g, 66% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.70 (s,3 H), 3.18 (s, 3H), 2.58 (t, *J* = 7.4 Hz, 2H), 2.29 (td, *J* = 6.9, 2.6 Hz, 2H), 1.98 (t, *J* = 2.6 Hz, 1H), 1.86 (p, *J* = 7.1 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.81, 83.77, 68.88, 61.20, 32.15, 30.39, 23.16, 17.93.[5]

HBr gas was prepared by adding the PBr_3 (3.8 mL, 40 mmol) to water (1.5 mL). The HBr was led into the solution of Et_4NBr (16.8 g, 12 mmol) in DCM (40 mL). *N*-methoxy-*N*-methylhex-5-ynamide (6.2 g, 40 mmol) was added to the above solution and the reaction was heated at 40 ℃ for 5 h. After the reaction was completed (monitored by TLC), water (50 mL) was added into reaction mixture and aqueous phase was extracted with EA (3×15 mL), dried over Na_2SO_4, filtered and concentrated. The crude product was purified on SiO_2 to give the 5-bromo-*N*-methoxy-*N*-methylhex-5-enamide.



15

Physical state: colorless oil

Rf = 0.6 (PE/EtOAc = 1:1; $KMnO_4$) 7.4 g, 76% yield.

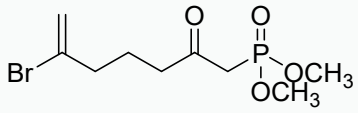
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.60 (d, *J* = 1.5 Hz, 1H), 5.42 (d, *J* = 1.7 Hz, 1H), 3.68 (s, 3H), 3.18 (s, 3H), 2.57 – 2.47 (m, 2H), 2.44 (t, *J* = 7.3 Hz, 2H), 1.91 (p, *J* = 7.3 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.96, 133.85, 117.15, 61.25, 52.23, 40.69, 30.19, 22.64.

HRMS(ESI$^+$) m/z Calculated for $C_8H_{15}BrNO_2$ $[M+H]^+$: 236.0286, found:236.0286

IR (thin film) ν_{max} (cm^{-1}): 2937, 1659, 1415, 1385, 1177, 993, 889.

To the solution of dimethyl methylphosphonate (7.45 g, 60 mmol) in dry THF (150 mL) at -78℃ was added LDA (60 mmol) under Ar. The reaction was stirred at -78℃ for 30 min. Then 5-bromo-N-methoxy-N-methylhex-5-enamide (7.05 g, 30 mmol) was added to the above solution. The mixture was stirred at -78℃ for another 2 h and quenched with saturated NH_4Cl (30 mL). The organic layer was separated and aqueous phase was extracted with EA and dried over Na_2SO_4. The combined organic layers were evaporated and the residue was purified via column chromatography to give dimethyl (6-bromo-2-oxohept-6-en-1-yl)phosphonate.



16

Physical state: colorless oil

Rf = 0.3 (PE/EtOAc = 2:1; anisaldehyde) 6.95 g, 78% yield.

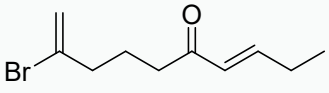
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.58 (d, *J* = 1.5 Hz, 1H), 5.42 (d, *J* = 1.6 Hz, 1H), 3.79 (s, 3H), 3.77 (s, 3H), 3.11 (s, 1H), 3.05 (s, 1H), 2.64 (t, *J* = 7.1 Hz, 2H), 2.44 (td, *J* = 7.2, 1.1 Hz, 2H), 1.85 (p, *J* = 7.1 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 201.24, 201.17, 133.49, 117.42, 53.11, 53.04, 42.23, 42.03, 40.76, 40.12, 21.45.

HRMS(ESI$^+$) m/z Calculated for $C_9H_{17}BrO_4P$ $[M+H]^+$: 299.0048, found:299.0049

IR (thin film) ν_{max} (cm^{-1}): 2939, 1712, 1250, 1022, 885, 808.

To the solution of the phosphonate (594 mg, 2.0 mmol) in the 10 mL dry THF was added NaH (96 mg, 2.4 mmol) under Ar at rt. The reaction was stirred at rt for 30 min. Then aldehyde (1.2 eq.) was added. The mixture was stirred at 30 ℃ for another 24 h and quenched with saturated NH_4Cl (10 mL). The organic layer was separated and water layer was extracted with EA and dried over Na_2SO_4. The combined organic layers were evaporated and the residue was purified via column chromatography to give desired product (377 mg, 82%)



17

Physical state: colorless oil

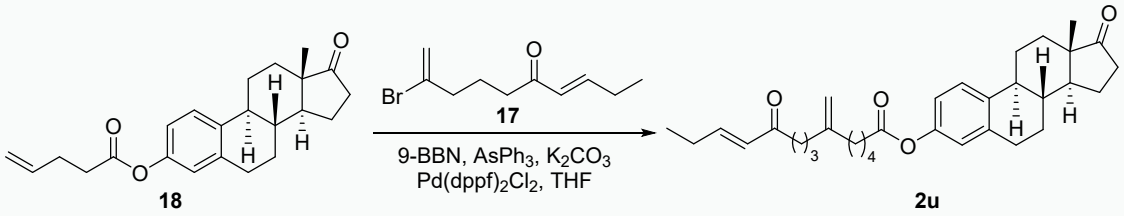
Rf = 0.3 (PE/EtOAc = 2:1; anisaldehyde) 377 mg, 82% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.89 (dt, *J* = 15.9, 6.4 Hz, 1H), 6.09 (dt, *J* = 15.9, 1.7 Hz, 1H), 5.58 (d, *J* = 1.4 Hz, 1H), 5.43 (d, *J* = 1.6 Hz, 1H), 2.56 (t, *J* = 7.3 Hz, 2H), 2.47 (td, *J* = 7.2, 1.2 Hz, 2H), 2.29 – 2.18 (m, 2H), 1.89 (p, *J* = 7.2 Hz, 2H), 1.08 (t, *J* = 7.4 Hz, 3H).

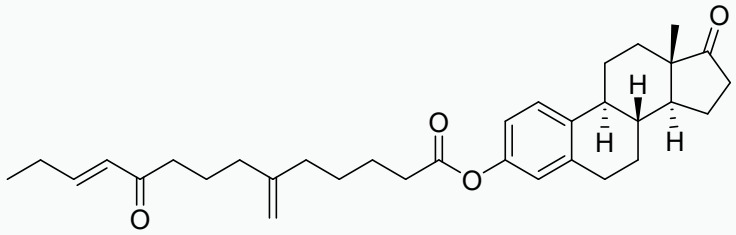
^{13}C NMR (101 MHz, $CDCl_3$) δ 199.98, 148.93, 133.83, 129.33, 117.27, 40.53, 38.06, 25.54, 22.16, 12.25.

HRMS(ESI$^+$) m/z Calculated for $C_{10}H_{16}BrO$ $[M+H]^+$: 231.0385, found:231.0389

IR (thin film) ν $_{max}$ (cm^{-1}): 2925, 1461, 1250, 835, 774.



Compound **18** was synthesized according to known reports.[6] To the solution of the compound **18** (176 mg, 0.5 mmol) in dry THF (5 mL) was added 9-BBN (1.2 mL, 0.6 mmol, 0.5 M) under Ar at rt. The reaction was stirred at 40 ℃ for 4 h. Then $Pd(dppf)_2Cl_2$ (14.7 mg, 5 mol%), K_2CO_3 (109 mg, 0.8 mmol), $AsPh_3$(12.2 mg, 10 mol%) was added sequentially to solution of compound **17** (140.8 mg, 0.4 mmol) in 5 mL dry THF under Ar. Finally, the pre-synthesized boron reagent and water (0.1 mL) was added to the above solution. The reaction was stirred at 60 ℃ for 12 h. The reaction was quenched with water and extracted with EA. The organic layer was dried over Na_2SO_4 and filtered and concentrated. The residue was purified via column chromatography to give desired product.



2u

Physical state: white solid, m.p 193.4 – 194.9 ℃

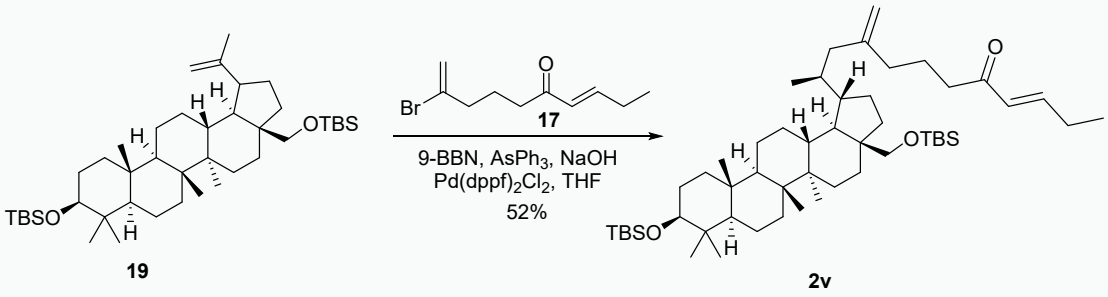
Rf = 0.4 (PE/EtOAc = 5:1; UV) 81.2 mg, 50% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (s, 1H), 6.89 – 6.75 (m, 3H), 6.06 (dt, *J* = 15.9, 1.7 Hz, 1H), 4.74 (s, 1H), 4.73 (s, 1H), 3.70 (t, *J* = 8.5 Hz, 1H), 2.90 – 2.75 (m, 2H), 2.52 (td, *J* = 7.4, 3.3 Hz, 4H), 2.38 – 2.15 (m, 4H), 2.12 – 1.98 (m, 4H), 1.96 – 1.89 (m, 1H), 1.85 (ddt, *J* = 11.4, 5.8, 2.8 Hz, 1H), 1.78 – 1.62 (m, 4H), 1.60 – 1.38 (m, 6H), 1.37 – 1.24 (m, 3H), 1.22 – 1.09 (m, 1H), 1.05 (t, *J* = 7.4 Hz, 3H), 0.75 (s, 3H).

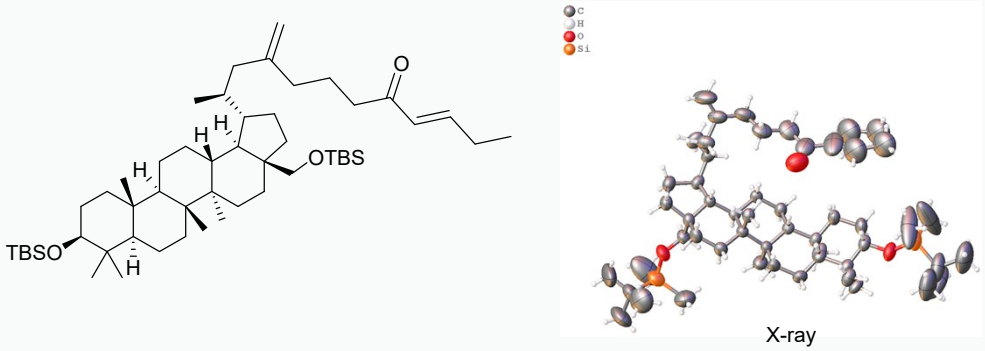
^{13}C NMR (100 MHz, $CDCl_3$) δ 200.72, 172.49, 148.66, 148.45, 148.42, 138.22, 137.90, 129.45, 126.37, 121.50, 118.58, 109.85, 81.87, 50.09, 44.15, 43.22, 39.39, 38.50, 36.69, 35.44, 35.33, 34.27, 30.58, 29.54, 27.10, 27.06, 26.17, 25.53, 24.66, 23.14, 22.07, 12.28, 11.06.

HRMS(ESI$^+$) m/z Calculated for $C_{33}H_{45}O_4[M+H]^+$: 505.3312, found: 505.3319

IR (thin film) ν $_{max}$ (cm^{-1}): 2927, 2868, 1755, 1133, 1055.



Compound **19** was synthesized according to the known procedure.[7] To the solution of the compound **19** (335 mg, 0.5 mmol) in the 5 mL dry THF was added 9-BBN (1.2 mL, 0.6 mmol, 0.5 M) under Ar at rt. The reaction was stirred at 40 ℃ for 4 h. Then $Pd(dppf)_2Cl_2$ (14.7 mg, 5%), NaOH (32 mg, 0.8 mmol), $AsPh_3$(12.2 mg, 10%) was added sequentially to the solution of compound **17** (140.8 mg, 0.4 mmol) in 5 mL dry THF under Ar. Finally, the pre-synthesized boron reagent and water (0.1 mL) was added to above solution. The reaction was stirred at 60 ℃ for 12 h. The reaction was quenched with water and extracted with EA. The organic layer was dried over Na_2SO_4 and filtered and concentrated. The residue was purified via column chromatography to give desired product.



2v

Physical state: white solid, m.p. 182.2 – 182.9 ℃

Rf = 0.5 (PE/EtOAc = 5:1; UV) 170.9 mg, 52% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.88 (dt, *J* = 15.9, 6.4 Hz, 1H), 6.10 (dt, *J* = 15.8, 1.7 Hz, 1H), 4.74 (s, 2H), 3.66 (d, *J* = 9.7 Hz, 1H), 3.30 – 3.09 (m, 2H), 2.54 (ddd, *J* = 8.0, 6.9, 1.4 Hz, 2H), 2.31 – 2.19 (m, 2H), 2.17 (d, *J* = 13.1 Hz, 1H), 2.01 (t, *J* = 7.4 Hz, 2H), 1.96 – 1.58 (m, 12H), 1.55 (s, 6H), 1.55 – 1.41 (m, 4H), 1.44 – 1.25 (m, 6H), 1.09 (t, *J* = 7.4 Hz, 3H), 1.02 (s,

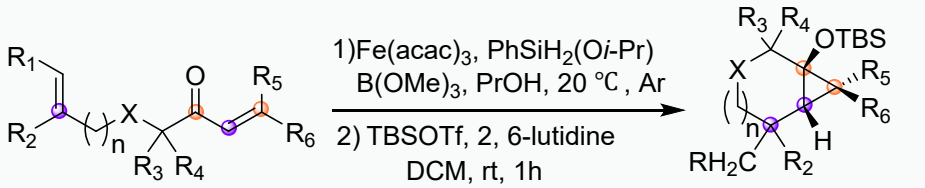
3H), 0.93 (s, 3H), 0.89 (d, *J* = 1.3 Hz, 21H), 0.83 (s, 3H), 0.79 (d, *J* = 6.5 Hz, 3H), 0.73 (s, 3H), 0.68 (d, *J* = 10.6 Hz, 1H), 0.03 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 200.64, 148.48, 148.24, 129.51, 111.08, 79.46, 60.34, 55.35, 50.19, 48.13, 47.52, 44.95, 42.86, 41.02, 39.44, 39.38, 38.73, 37.05, 36.96, 35.99, 35.10, 34.44, 34.38, 33.15, 29.56, 28.42, 27.83, 27.30, 26.93, 25.98, 25.94, 25.56, 22.50, 22.16, 20.99, 19.97, 18.50, 18.33, 18.14, 16.14, 15.91, 15.89, 14.65, 12.33, 0.01, -3.76, -4.90, -5.44.

HRMS(ESI$^+$) m/z Calculated for $C_{52}H_{95}O_3Si_2[M+H]^+$: 823.6814, found: 823.6819

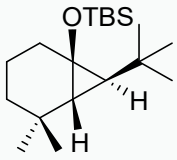
IR (thin film) ν $_{max}$ (cm^{-1}): 2918, 2849, 2360, 1630, 1020.

3.2. General procedures for the radical cascade reaction



X = CH_2, O; n = 0, 1

$Fe(acac)_3$ (0.2 eq.) was added to the solution of α, β-unsaturated compound (0.1 mmol) in 1.5 mL *n*-PrOH at 20 ℃ under Ar atmosphere. Then $PhSiH_2$(O*i*-Pr) (2.5 eq.) and $B(OMe)_3$ (2.0 eq) was added to the above solution and the reaction was stirred at 20 ℃ until the starting material was consumed. Then, the reaction mixture was direct purified by neutral alumina column chromatography. After that 2,6-lutidine (6 eq) was added to the received cyclopropanols in dry DCM (5 mL) and the solution was stirred at 0 ℃ for 30 min, then slow addition of TBSOTf (3 eq.). The reaction mixture was stirred at 0 ℃ for another 1h. Then, the reaction was quenched with saturated $NaHCO_3$ (5 mL) and extracted with EA, the organic layer was dried over Na_2SO_4, filtrated and concentrated under reduced pressure. The crude product was purified on SiO_2.[8]



3a

Physical state: colorless oil

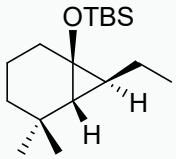
Rf = 0.9 (PE; anisaldehyde) 28.8 mg, 93%

^{1}H NMR (400 MHz, Acetone-d_6) δ 1.94 – 1.80 (m, 2H), 1.52 – 1.45 (m, 1H), 1.23 – 1.18 (m, 1H), 1.17 (s, 3H), 1.12 – 1.00 (m, 2H), 0.99 (s, 9H), 0.92 (d, *J* = 1.6 Hz, 1H), 0.89 (s, 9H), 0.86 (s, 3H), 0.24 (d, *J* = 7.4 Hz, 1H), 0.22 (s, 3H), 0.11 (s, 3H).

^{13}C NMR (100 MHz, Acetone-d_6) δ 60.50, 36.98, 35.59, 34.02, 33.60, 30.53, 30.10, 29.42, 28.10, 25.39, 18.56, 17.52, -3.73, -3.81.

HRMS(APCI-TOF) m/z Calculated for $C_{19}H_{39}OSi[M+H]^+$: 311.2765, found: 311.2761.

IR (thin film) ν $_{max}$ (cm^{-1}): 2954, 2922, 2360, 2337,1462.



3b

Physical state: colorless oil

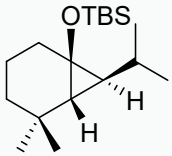
Rf = 0.9 (PE; anisaldehyde) 20.6 mg ,73%

^{1}H NMR (400 MHz, Acetone-d_6) δ 1.94 – 1.82 (m, 2H), 1.50 – 1.40 (m, 2H), 1.32 (dd, *J* = 14.4, 7.0 Hz, 1H), 1.23 – 1.14 (m, 1H), 1.14 (s, 3H), 1.03 (ddd, *J* = 15.9, 8.6, 3.1 Hz, 2H), 0.96 (t, *J* = 7.4 Hz, 3H), 0.87 (s, 9H), 0.86 (s, 3H), 0.47 (d, *J* = 6.1 Hz, 1H), 0.40 – 0.34 (m, 1H), 0.17 (s, 3H), 0.11 (s, 3H).

^{13}C NMR (100 MHz, Acetone-d_6) δ 60.34, 38.04, 36.17, 33.06, 31.06, 28.05, 27.73, 25.25, 25.22, 21.61, 18.49, 17.60, 13.49, -3.87, -3.97.

HRMS(APCI-TOF) m/z Calculated for $C_{17}H_{35}OSi[M+H]^+$: 283.2452, found: 283.2457.

IR (thin film) ν $_{max}$ (cm^{-1}): 2925, 2853, 1462, 1250, 1200, 833.



3c

Physical state: colorless oil

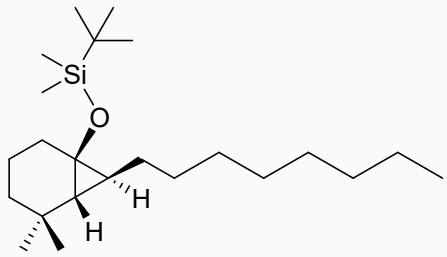
Rf = 0.9 (PE; anisaldehyde) 25.5 mg, 86%

^{1}H NMR (400 MHz, Acetone-d_6) δ 1.94 – 1.82 (m, 2H), 1.52 – 1.43 (m, 1H), 1.34 (ddd, *J* = 13.4, 9.7, 6.7 Hz, 1H), 1.22 – 1.16 (m, 1H), 1.15 (s, 3H), 1.10 – 1.04 (m, 2H), 0.98 (t, *J* = 6.5 Hz, 6H), 0.87 (s, 9H), 0.86 (s, 3H), 0.52 (d, *J* = 6.0 Hz, 1H), 0.18 (s, 3H), 0.14 (dd, *J* = 9.8, 6.1 Hz, 1H), 0.11 (s, 3H).

^{13}C NMR (100 MHz, Acetone-d_6) δ 60.29, 37.76, 36.14, 34.16, 33.26, 30.97, 28.19, 25.21, 21.99, 21.91, 18.46, 17.54, -3.84, -4.04.

HRMS(APCI-TOF) m/z Calculated for $C_{18}H_{37}OSi[M+H]^+$: 297.2608, found: 297.2605.

IR (thin film) ν $_{max}$ (cm^{-1}): 2954, 2928, 2361, 1464, 1253, 1200.



3d

Physical state: colorless oil

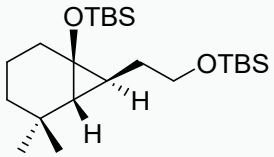
Rf = 0.9 (PE; anisaldehyde) 30.7 mg, 84%

^{1}H NMR (400 MHz, Acetone-d_6) δ 1.94 – 1.82 (m, 2H), 1.51 – 1.44 (m, 1H), 1.39 – 1.28 (m, 14H), 1.22 – 1.16 (m, 1H), 1.14 (s, 3H), 1.10 – 0.97 (m, 3H), 0.93 – 0.89 (m, 2H), 0.88 (s, 9H), 0.86 (s, 3H), 0.48 (d, J = 6.1 Hz, 1H), 0.41 – 0.39 (m, 1H), 0.18 (s, 3H), 0.12 (s, 3H).

^{13}C NMR (100 MHz, Acetone-d_6) δ 60.25, 38.01, 36.21, 33.04, 31.77, 31.10, 29.64, 29.55, 29.24, 28.81, 28.47, 28.02, 25.94, 25.28, 22.44, 18.49, 17.61, 13.45, -3.86, -3.93.

HRMS(APCI-TOF) m/z Calculated for $C_{23}H_{47}OSi[M+H]^+$: 367.3391, found: 367.3390.

IR (thin film) ν $_{max}$ (cm^{-1}): 2925, 2853, 1462, 1250, 1200, 859.



3e

Physical state: colorless oil

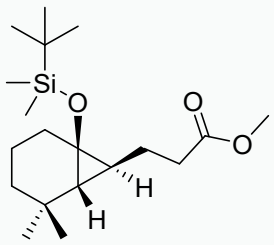
Rf = 0.9 (PE; anisaldehyde) 33.8 mg, 82%

^{1}H NMR (400 MHz, Acetone-d_6) δ 3.72 – 3.67 (m, 2H), 1.97 – 1.81 (m, 2H), 1.76 – 1.60 (m, 1H), 1.59 – 1.40 (m, 3H), 1.15 (s, 3H), 1.11 – 0.99 (m, 2H), 0.90 (s, 9H), 0.88 (d, J = 3.4 Hz, 12H), 0.62 – 0.47 (m, 2H), 0.18 (s, 3H), 0.12 (s, 3H), 0.06 (d, J = 2.1 Hz, 6H).

^{13}C NMR (100 MHz, Acetone-d_6) δ 62.94, 59.97, 37.90, 36.15, 32.89, 32.11, 31.03, 27.99, 25.42, 25.29, 22.35, 18.46, 17.92, 17.60, -3.89, -3.94, -5.94, -5.97.

HRMS(APCI-TOF) m/z Calculated for $C_{23}H_{49}O_2Si_2$ $[M+H]^+$: 413.3266, found: 413.3269

IR (thin film) ν $_{max}$ (cm^{-1}): 2954, 2929, 1462, 1252, 1097, 834.



3f

Physical state: colorless oil

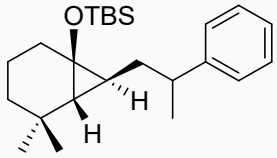
Rf = 0.8 (PE; anisaldehyde) 15 mg, 44%

^{1}H NMR (400 MHz, Acetone-d_6) δ 3.62 (s, 3H), 2.39 (td, J = 7.5, 5.4 Hz, 2H), 1.96 – 1.82 (m, 2H), 1.68 (q, J = 7.3 Hz, 2H), 1.56 – 1.42 (m, 1H), 1.27 – 1.16 (m, 1H), 1.15 (s, 3H), 1.13 – 0.95 (m, 2H), 0.89 (s, 9H), 0.86 (s, 3H), 0.56 (d, J = 6.0 Hz, 1H), 0.53 – 0.46 (m, 1H), 0.19 (s, 3H), 0.14 (s, 3H).

^{13}C NMR (100 MHz, Acetone-d_6) δ 173.25, 60.22, 50.49, 37.98, 36.10, 33.55, 32.79, 30.98, 27.89, 25.25, 24.96, 24.06, 18.41, 17.58, -3.88, -4.00.

HRMS(APCI-TOF) m/z Calculated for $C_{19}H_{37}O_3Si[M+H]^+$:341.2506, found: 341.2509

IR (thin film) ν $_{max}$ (cm^{-1}): 2952, 2930, 2355, 1744, 1251, 836.



3g

Physical state: colorless oil

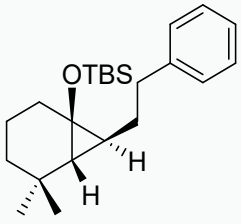
Rf = 0.9 (PE; anisaldehyde) 25.3 mg, 1.5:1 dr, 68%

^{1}H NMR (400 MHz, Acetone-d_6) δ 7.45 – 7.32 (m, 0.73H), 7.32 – 7.21 (m, 3.25H), 7.19 – 7.08 (m, 1H), 2.61 (dq, J = 9.8, 7.2 Hz, 0.43H), 2.46 (dq, J = 9.5, 6.9 Hz, 0.63H), 2.03 – 1.96 (m, 0.71H), 1.95 – 1.80 (m, 1.47H), 1.55 – 1.42 (m, 1H), 1.35 (d, J = 7.2 Hz, 1.19H), 1.32 (d, J = 6.9 Hz, 1.85H), 1.30 – 1.22 (m, 1H), 1.21 (s, 1.26H), 1.20 – 1.12 (m, 1H), 1.12 – 1.03 (m, 1H), 1.01 (s, 1.84H), 0.97 (dd, J = 5.5, 3.4 Hz, 1H), 0.95 (s, 6.89H), 0.93 – 0.87 (m, 1H), 0.84 (s, 3.53H), 0.75 – 0.57 (m, 2H), 0.34 (s, 1.81H), 0.21 (d, J = 9.4 Hz, 3.57H), 0.17 (d, J = 9.4 Hz, 2.36H).

^{13}C NMR (100 MHz, Acetone-d_6) δ 147.74, 147.56, 128.03, 127.83, 127.14, 126.92, 125.63, 125.30, 60.97, 60.83, 40.15, 37.83, 37.64, 37.56, 36.17, 36.07, 33.91, 33.80, 33.14, 32.92, 31.02, 30.97, 28.38, 28.26, 27.60, 25.29, 25.27, 21.03, 20.76, 18.42, 17.64, 17.57, -3.92.

HRMS(APCI-TOF) m/z Calculated for $C_{24}H_{41}OSi[M+H]^+$: 373.2927, found: 373.2931.

IR (thin film) ν $_{max}$ (cm^{-1}): 2954, 2928, 1250, 1199, 832, 773.



3h

Physical state: colorless oil

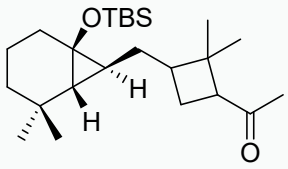
Rf = 0.9 (PE; anisaldehyde) 18.6 mg, 52%

^{1}H NMR (400 MHz, Acetone-d_6) δ 7.17 – 7.05 (m, 4H), 7.03 – 6.97 (m, 1H), 2.64 – 2.48 (m, 2H), 1.85 – 1.65 (m, 2H), 1.64 – 1.48 (m, 2H), 1.42 – 1.20 (m, 1H), 1.01 (s, 3H), 0.98 – 0.79 (m, 3H), 0.76 (s, 9H), 0.72 (s, 3H), 0.44 (d, *J* = 6.1 Hz, 1H), 0.39 – 0.29 (m, 1H), 0.06 (s, 3H), -0.00 (s, 3H).

^{13}C NMR (100 MHz, Acetone-d_6) δ 142.91, 128.28, 128.15, 125.47, 60.30, 38.14, 36.18, 35.86, 32.99, 31.07, 30.97, 28.85, 28.05, 25.53, 25.33, 18.47, 17.63, -3.87.

HRMS(APCI-TOF) m/z Calculated for $C_{23}H_{39}O$ Si$[M+H]^+$: 359.2765, found: 359.2763.

IR (thin film) ν $_{max}$ (cm^{-1}): 2925, 2854, 1461, 1250, 835, 774.



3i

Physical state: colorless oil

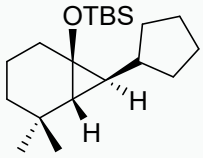
Rf = 0.8 (PE; anisaldehyde) 31.7 mg, 1.23:1 dr, 84%

^{1}H NMR (400 MHz, Acetone-d_6) δ 2.92 – 2.84 (m, 1H), 1.98 (d, *J* = 1.7 Hz, 3H), 1.94 – 1.85 (m, 3.4H), 1.79 (dt, *J* = 10.8, 7.7 Hz, 0.63H), 1.51 – 1.36 (m, 2H), 1.30 (d, *J* = 1.7 Hz, 4H), 1.26 – 1.16 (m, 1H), 1.14 (s, 3H), 1.03 (dtd, *J* = 20.9, 12.8, 2.7 Hz, 3H), 0.89 (d, *J* = 3.3 Hz, 10.47H), 0.85 (d, *J* = 4.6 Hz, 3H), 0.82 (s, 1.57H), 0.51 (d, *J* = 6.0 Hz, 0.53H), 0.44 (d, *J* = 6.1 Hz, 0.43H), 0.32 (dt, *J* = 7.0, 6.1 Hz, 1 H), 0.18 (d, *J* = 2.1 Hz, 3H), 0.12 (d, *J* = 2.1 Hz, 3H).

^{13}C NMR (100 MHz, Acetone-d_6) δ 206.20, 206.17, 60.29, 59.56, 53.72, 53.56, 42.72, 42.50, 42.03, 41.89, 37.85, 37.78, 36.22, 32.89, 32.82, 31.15, 31.13, 29.89, 29.85, 27.97, 27.91, 25.31, 23.75, 23.54, 23.45, 23.04, 18.45, 17.64, 16.73, 16.54, -3.86, -3.92.

HRMS(APCI-TOF) m/z Calculated for $C_{24}H_{46}O_2Si$ $[M+H]^+$: 393.3819, found: 393.3813.

IR (thin film) ν $_{max}$ (cm^{-1}): 2928, 2855, 1707, 1462, 1359, 1201, 835.



3j

Physical state: colorless oil

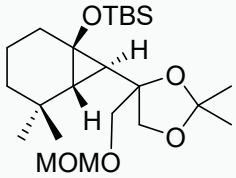
Rf = 0.9 (PE; anisaldehyde) 27 mg, 84%

^{1}H NMR (400 MHz, Acetone-d_6) δ 1.90 – 1.80 (m, 3H), 1.78– 1.73 (m, 1H), 1.65 – 1.56 (m, 2H), 1.51 – 1.45 (m, 3H), 1.36 – 1.14 (m, 3H), 1.14 (s, 3H), 1.07 – 0.95 (m, 3H), 0.87 (s, 9H), 0.86 (s, 3H), 0.57 (d, *J* = 6.0 Hz, 1H), 0.28 (dd, *J* = 9.5, 6.0 Hz, 1H), 0.18 (s, 3H), 0.11 (s, 3H).

^{13}C NMR (100 MHz, Acetone-d_6) δ 60.12, 40.41, 38.23, 36.14, 33.16, 32.43, 32.28, 31.80, 30.97, 28.23, 25.23, 25.01, 24.60, 18.50, 17.55, -3.79, -4.01.

HRMS(APCI-TOF) m/z Calculated for $C_{20}H_{39}OSi$ $[M+H]^+$: 323.2765 found: 323.2763.

IR (thin film) ν $_{max}$ (cm^{-1}): 2952, 2929, 1360, 1251, 1201, 884.



3k

Physical state: colorless oil

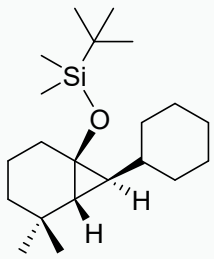
Rf = 0.7 (PE; anisaldehyde) 37.2 mg, 1.9:1 dr, 87%

^{1}H NMR (400 MHz, Acetone-d_6) δ 4.65 (s, 1.30H), 4.63 (s, 0.69H), 4.15 (d, *J* = 8.3 Hz, 0.31H), 3.80 – 3.65 (m, 2H), 3.58 – 3.49 (m, 1.34H), 3.42 (d, *J* = 8.8 Hz, 0.28H), 3.32 (d, *J* = 3.0 Hz, 3H), 1.98 – 1.78 (m, 2H), 1.63 – 1.48 (m, 2H), 1.44 (d, *J* = 6.7 Hz, 0.43H), 1.34 (d, *J* = 5.7 Hz, 6H), 1.20 (s, 3H), 1.13 (d, *J* = 6.9 Hz, 1H), 1.07 – 1.01 (m, 1H), 0.94 (d, *J* = 7.3 Hz, 1H), 0.89 (d, *J* = 1.8 Hz, 9H), 0.72 (d, *J* = 6.7 Hz, 0.45H), 0.24 (s, 2.24H), 0.18 (s, 1.66H), 0.15 (d, *J* = 4.3 Hz, 3H).

^{13}C NMR (100 MHz, Acetone-d_6) δ 107.39, 96.56, 96.53, 82.44, 80.57, 72.59, 71.97, 70.72, 66.77, 59.62, 59.51, 54.25, 54.20, 36.04, 35.41, 33.69, 33.25, 32.74, 32.37, 30.97, 30.87, 30.59, 28.43, 27.21, 26.72, 26.16, 25.35, 25.30, 18.35, 17.53, -3.89.

HRMS(APCI-TOF) m/z Calculated for $C_{23}H_{45}O_5Si$$[M+H]^+$: 429.3031, found: 429.3029.

IR (thin film) ν $_{max}$ (cm^{-1}): 2925, 1462, 1259, 1047, 799.



3l

Physical state: colorless oil

Rf = 0.9 (PE; anisaldehyde) 27.9 mg, 83%

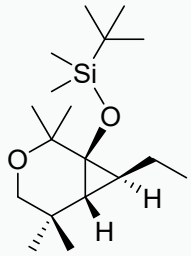
^{1}H NMR (400 MHz, Acetone-d_6) δ 1.89 (ddd, *J* = 7.0, 5.8, 3.9 Hz, 3H), 1.80 – 1.60 (m, 4H), 1.49 (ddtd, *J* = 13.2, 7.1, 5.9, 2.8 Hz, 1H), 1.23 – 1.17 (m, 3H), 1.16 (s, 3H), 1.12 – 0.96 (m,

6H), 0.90 (d, *J* = 2.8 Hz, 1H), 0.89 (s, 9H), 0.86 (s, 1H), 0.54 (d, *J* = 6.0 Hz, 1H), 0.18 (s, 3H), 0.13 (s, 3H).

^{13}C NMR (100 MHz, Acetone-d_6) δ 60.05, 38.22, 37.48, 36.17, 33.35, 33.23, 32.75, 32.33, 30.97, 28.62, 28.34, 26.56, 26.41, 26.12, 25.22, 18.49, 17.58, -3.75, -4.04.

HRMS(APCI-TOF) m/z Calculated for $C_{21}H_{41}OSi$ $[M+H]^+$: 337.2921, found: 337.2928.

IR (thin film) ν $_{max}$ (cm^{-1}): 2924, 2852, 1462, 1250, 1065, 833.



3m

Physical state: colorless oil

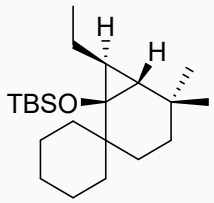
Rf = 0.8 (PE; anisaldehyde) 25 mg, 80%

^{1}H NMR (400 MHz, Acetone-d_6) δ 3.29 (d, *J* = 12.0 Hz, 1H), 2.98 (d, *J* = 12.1 Hz, 1H), 1.58 – 1.39 (m, 1H), 1.34 (s, 3H), 1.30 (dd, *J* = 5.7, 2.1 Hz, 1H), 1.16 (s, 3H), 1.08 (s, 3H), 0.98 (t, *J* = 7.4 Hz, 3H), 0.92 (s, 12H), 0.87 (d, *J* = 6.2 Hz, 1H), 0.77 (dt, *J* = 8.3, 6.3 Hz, 1H), 0.23 (s, 3H), 0.11 (s, 3H).

^{13}C NMR (100 MHz, Acetone-d_6) δ 71.62, 69.84, 65.22, 36.01, 28.22, 26.35, 25.92, 25.53, 25.14, 21.88, 20.41, 18.05, 13.55, -1.90, -3.91.

HRMS(APCI-TOF) m/z Calculated for $C_{18}H_{37}O_2Si$$[M+H]^+$: 313.2557 found: 313.2557.

IR (thin film) ν $_{max}$ (cm^{-1}): 2925, 2854, 1250, 1001, 832.



3n

Physical state: colorless oil

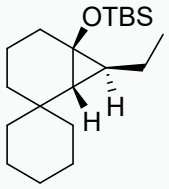
Rf = 0.9 (PE; anisaldehyde) 21.7 mg, 62%

^{1}H NMR (400 MHz, Acetone-d_6) δ 1.84 – 1.68 (m, 4H), 1.63 – 1.50 (m, 5H), 1.47 – 1.36 (m, 4H), 1.27 – 1.17 (m, 3H), 1.15 (s, 3H), 0.95 (m, 12H), 0.85 (s, 3H), 0.73 (d, *J* = 6.1 Hz, 1H), 0.52 (dt, *J* = 8.2, 6.1 Hz, 1H), 0.19 (s, 3H), 0.08 (s, 3H).

^{13}C NMR (100 MHz, Acetone-d_6) δ 68.39, 37.63, 35.73, 34.66, 33.52, 32.48, 29.78, 28.10, 27.40, 26.42, 25.84, 24.63, 24.46, 21.63, 20.84, 18.42, 13.74, -1.55, -3.92.

HRMS(APCI-TOF) m/z Calculated for $C_{22}H_{43}OSi$$[M+H]^+$: 351.3078, found: 351.3074.

IR (thin film) ν $_{max}$ (cm^{-1}): 2925, 2855, 1461, 1250, 1197, 875.



3o

Physical state: colorless oil

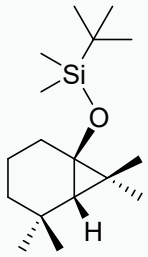
Rf = 0.9 (PE; anisaldehyde) 20.9 mg, 65%

^{1}H NMR (400 MHz, Acetone-d_6) δ 2.01 – 1.93 (m, 1H), 1.90 – 1.80 (m, 1H), 1.65 – 1.39 (m, 12H), 1.18 – 1.02 (m, 3H), 1.03 – 0.94 (m, 4H), 0.89 (s, 9H), 0.67 (d, *J* = 6.1 Hz, 1H), 0.40 (dt, *J* = 7.5, 6.2 Hz, 1H), 0.18 (s, 3H), 0.13 (s, 3H).

^{13}C NMR (100 MHz, Acetone-d_6) δ60.22, 39.78, 36.54, 33.50, 31.59, 26.29, 25.24, 22.06, 21.96, 17.73, 17.60, 13.70, -3.81, -4.04.

HRMS(APCI-TOF) m/z Calculated for $C_{20}H_{39}OSi[M+H]^+$: 323.2765, found:323.2769

IR (thin film) ν $_{max}$ (cm^{-1}): 2928, 2855, 1250, 1197, 879.



3p

Physical state: colorless oil

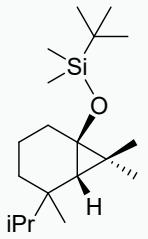
Rf = 0.9 (PE; anisaldehyde) 19.7 mg, 70%

^{1}H NMR (400 MHz, Acetone-d_6) δ 1.98 – 1.74 (m, 2H), 1.58 (ddq, *J* = 16.7, 9.7, 3.5 Hz, 1H), 1.49 – 1.38 (m, 1H), 1.19 (dt, *J* = 13.7, 3.7 Hz, 1H), 1.12 (s, 3H), 1.11 (s, 3H), 1.10 (s, 3H), 1.08 (d, *J* = 3.7 Hz, 1H), 0.97 (s, 3H), 0.89 (s, 9H), 0.46 (s, 1H), 0.19 (s, 3H), 0.13 (s, 3H).;

^{13}C NMR (100 MHz, Acetone-d_6) δ 61.46, 39.22, 35.43, 31.98, 28.41, 25.36, 24.13, 24.05, 19.45, 17.74, 17.58, -3.87.

HRMS(APCI-TOF) m/z Calculated for $C_{17}H_{35}OSi[M+H]^+$: 283.2452, found: 283.2459.

IR (thin film) ν $_{max}$ (cm^{-1}): 2952, 2923, 2364, 1457, 1376.



3q

Physical state: colorless oil

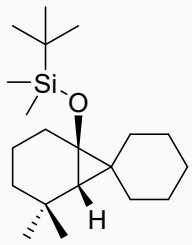
Rf = 0.9 (PE; anisaldehyde) 21.1 mg, 1.5:1 dr, 68%

^{1}H NMR (400 MHz, Acetone-d_6) δ 1.97 – 1.86 (m, 1.8H), 1.84 – 1.71 (m, 1.2H), 1.61 – 1.30 (m, 4H), 1.18 – 1.12 (m, 4H), 1.07 (s, 1.8H), 0.95 (s, 3H), 0.94 – 0.91 (m, 2H), 0.88 (d, *J* = 1.6 Hz, 9H), 0.86 (d, *J* = 6.9 Hz, 1H), 0.79 (d, *J* = 6.9 Hz, 2H), 0.76 (s, 1.2H), 0.71 (s, 0.4H), 0.45 (s, 0.6H), 0.18 (s, 1.8H), 0.14 (s, 1.16H), 0.12 (d, *J* = 1.8 Hz, 3H).

^{13}C NMR (100 MHz, Acetone-d_6) δ 61.57, 38.14, 37.46, 36.27, 36.12, 34.77, 34.63, 34.40, 31.32, 28.49, 25.40, 25.30, 25.22, 25.17, 25.15, 24.34, 24.10, 23.73, 21.07, 19.82, 19.32, 19.04, 18.17, 17.81, 17.79, 17.68, 17.64, 16.98, 16.75, 16.02, -3.78, -3.83, -3.86.

HRMS(APCI-TOF) m/z Calculated for $C_{19}H_{39}OSi[M+H]^+$: 311.2765, found: 311.2765.

IR (thin film) ν $_{max}$ (cm^{-1}): 2928, 2361, 1464, 1253, 884, 835.



3r

Physical state: colorless oil

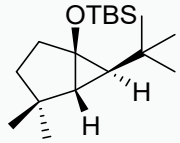
Rf = 0.9 (PE; anisaldehyde) 26.4 mg, 82%

^{1}H NMR (400 MHz, Acetone-d_6) δ 1.99 – 1.89 (m, 1H), 1.81 (ddd, *J* = 15.2, 13.3, 5.1 Hz, 1H), 1.68 – 1.42 (m, 10H), 1.36 – 1.17 (m, 3H), 1.12 (s, 3H), 1.04 (td, *J* = 13.9, 3.4 Hz, 1H), 0.96 (s, 3H), 0.89 (s, 9H), 0.42 (s, 1H), 0.21 (s, 3H), 0.12 (s, 3H).

^{13}C NMR (100 MHz, Acetone-d_6) δ 61.90, 40.48, 36.21, 34.93, 31.99, 30.69, 28.80, 28.29, 26.37, 26.20, 25.47, 25.28, 19.59, 17.64, -3.75, -3.93.

HRMS(APCI-TOF) m/z Calculated for $C_{20}H_{39}OSi$ $[M+H]^+$: 323.2765, found: 323.2757.

IR (thin film) ν $_{max}$ (cm^{-1}): 2925, 2854, 1250, 1001, 832.



3s

Physical state: colorless oil

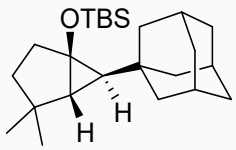
Rf = 0.9 (PE; anisaldehyde) 19.8 mg, 67%

^{1}H NMR (400 MHz, Acetone-d_6) δ 2.13 (ddd, J = 12.2, 11.2, 8.7 Hz, 1H), 1.89 (ddd, J = 12.2, 8.2, 0.8 Hz, 1H), 1.25 (ddt, J = 13.3, 8.7, 1.1 Hz, 2H), 1.12 (s, 3H), 1.10 (d, J = 4.6 Hz, 1H), 1.01 (s, 9H), 0.91 (s, 9H), 0.90 (s, 3H), 0.44 (d, J = 4.6 Hz, 1H), 0.22 (s, 3H), 0.15 (s, 3H).;

^{13}C NMR (100 MHz, Acetone-d_6) δ 68.88, 38.38, 36.71, 35.84, 34.45, 34.09, 29.43, 28.16, 25.58, 25.54, 17.73, -2.90, -3.83.

HRMS(APCI-TOF) m/z Calculated for $C_{18}H_{37}OSi[M+H]^+$: 297.2608 found:297.2601

IR (thin film) ν $_{max}$ (cm^{-1}): 2956, 2922, 2360, 2327, 1460.



3t

Physical state: colorless oil

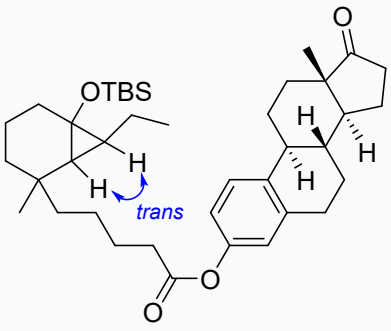
Rf = 0.9 (PE; anisaldehyde) 17.2 mg, 46%

^{1}H NMR (400 MHz, Acetone-d_6) δ 2.27 – 2.08 (m, 1H), 1.95 – 1.89 (m, 3H), 1.87 (ddd, J = 12.2, 8.3, 0.8 Hz, 1H), 1.80 – 1.73 (m, 3H), 1.69 (s, 5H), 1.63 (d, J = 12.0 Hz, 3H), 1.27 – 1.19 (m, 1H), 1.16 (dd, J = 4.7, 1.0 Hz, 1H), 1.14 – 1.06 (s, 3H), 0.99 – 0.94 (m, 1H), 0.92 (s, 9H), 0.90 (d, J = 3.7 Hz, 1H), 0.87 (s, 3H), 0.22 (d, J = 3.0 Hz, 4H), 0.14 (s, 3H).

^{13}C NMR (100 MHz, Acetone-d_6) δ 68.76, 42.20, 38.33, 37.03, 35.86, 35.26, 35.05, 34.63, 31.83, 28.87, 28.19, 25.70, 25.61, 17.81, -2.84, -3.81.

HRMS(APCI-TOF) m/z Calculated for $C_{24}H_{43}OSi$ $[M+H]^+$: 375.3078 found:.375.3083

IR (thin film) ν $_{max}$ (cm^{-1}): 2955, 2354, 1545, 1118.



3u

Physical state: white solid, m.p 284.2 – 284.9 ℃

Rf = 0.7 (PE; anisaldehyde) 29.1 mg ,1.5:1 dr, 47%

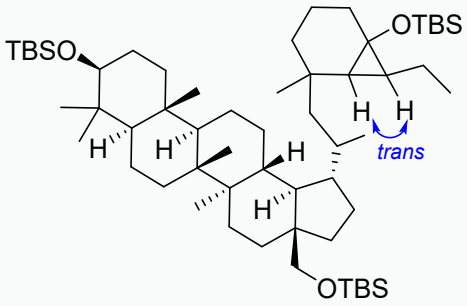
^{1}H NMR (400 MHz, Acetone-d_6) δ 7.30 (d, J = 8.5 Hz, 1H), 6.98 – 6.82 (m, 1H), 6.78 (d, J = 2.4 Hz, 1H), 3.74 (dd, J = 8.7, 7.7 Hz, 1H), 2.85 (dd, J = 9.4, 6.0 Hz, 2H), 2.64 – 2.50 (m,

2H), 2.35 (dt, *J* = 13.3, 3.7 Hz, 1H), 2.22 (td, *J* = 10.9, 10.4, 4.0 Hz, 1H), 2.03 – 1.94 (m, 1H), 1.94 – 1.86 (m, 3H), 1.77 – 1.64 (m, 3H), 1.56 – 1.43 (m, 6H), 1.42 – 1.29 (m, 4H), 1.28 – 1.17 (m, 2H), 1.10 – 1.01 (m, 1H), 0.97 (t, *J* = 7.4 Hz, 3H), 0.92 (s, 9H), 0.88 (d, *J* = 4.1 Hz, 6H), 0.84 (s, 1H), 0.79 (s, 3H), 0.55 (d, *J* = 6.1 Hz, 0.35H), 0.51 (d, *J* = 6.1 Hz, 0.53H), 0.45 (q, *J* = 6.7 Hz, 0.37H), 0.39 (dt, *J* = 8.0, 5.9 Hz, 0.58H), 0.08 (s, 3H), 0.07 (s, 3H).

^{13}C NMR (100 MHz, Acetone-d_6) δ 171.67, 171.60, 148.89, 137.89, 137.60, 126.16, 121.56, 118.78, 81.67, 60.48, 60.11, 49.50, 44.18, 44.11, 43.45, 41.06, 38.72, 37.06, 36.91, 36.74, 35.41, 35.06, 33.88, 33.83, 33.53, 32.87, 31.59, 31.49, 30.83, 27.48, 27.43, 26.94, 26.90, 26.18, 25.77, 25.75, 25.37, 25.28, 25.26, 24.33, 23.49, 23.20, 23.00, 22.11, 21.70, 18.14, 18.12, 17.77, 17.60, 13.70, 13.52, 10.93.

HRMS(ESI$^+$) m/z Calculated for $C_{39}H_{61}O_4Si$ $[M+H]^+$: 621.4334, found:621.4337

IR (thin film) ν $_{max}$ (cm^{-1}): 2929, 1463, 1250, 1166, 1110, 833.



3v

Physical state: white solid, m.p. 202.6 – 203.4 ℃

Rf = 0.9 (PE; anisaldehyde) 58 mg, 2.3:1 dr, 62%

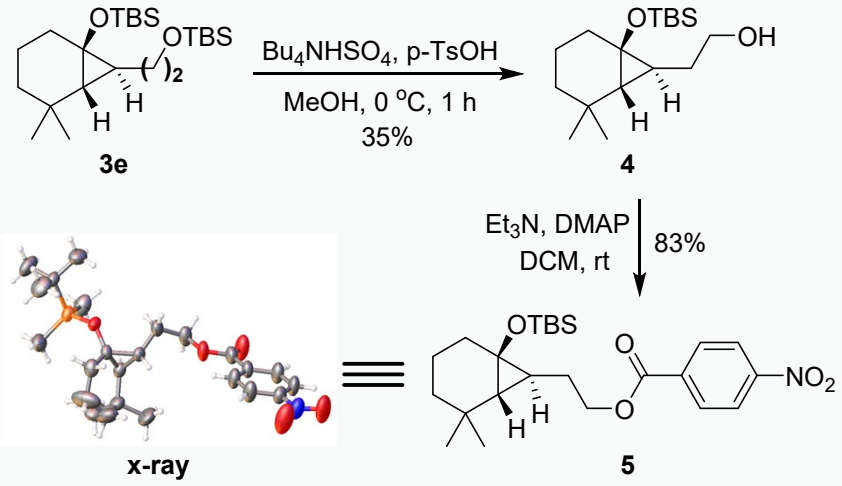
^{1}H NMR (400 MHz, Acetone-d_6) δ 3.76 – 3.67 (m, 1H), 3.21 (td, *J* = 7.6, 3.8 Hz, 2H), 1.92 – 1.78 (m, 3H), 1.74 – 1.17 (m, 27H), 1.16 – 0.99 (m, 10H), 0.99 – 0.89 (m, 9H), 0.88 – 0.78 (m, 34H), 0.69 (s, 3H), 0.48 (d, *J* = 6.1 Hz, 0.28H), 0.42 (d, *J* = 6.1 Hz, 0.65H), 0.38 – 0.24 (m, 0.94H), 0.12 (s, 2.59H), 0.06 (s, 2.45H), 0.00 (s, 10.53H), -0.08 (s, 2.59H).

^{13}C NMR (100 MHz, Acetone-d_6) δ 79.32, 60.14, 55.15, 50.34, 48.07, 47.92, 46.61, 42.87, 41.42, 41.02, 39.74, 39.24, 38.48, 37.15, 36.90, 34.61, 34.33, 33.55, 31.97, 31.57, 30.50, 28.00, 27.71, 27.27, 26.94, 25.46, 25.28, 23.39, 22.79, 21.69, 20.95, 18.32, 18.00, 17.79, 17.62, 15.75, 15.59, 15.50, 14.48, 13.68, -0.90, -4.45, -5.59, -6.13.

HRMS(APCI-TOF) m/z Calculated for $C_{58}H_{111}O_3Si_3$ $[M+H]^+$: 939.7836, found: 939.7833.

IR (thin film) ν $_{max}$ (cm^{-1}): 2928, 1462, 1252, 1097, 834.

4. Synthesis of compound 5 was confirmed by single-crystal X-ray diffraction analysis



Compound **3e** (0.1 mmol, 41.2 mg) dissolved in 5 mL of methanol was stirred at 0 ℃ for 30 min. Then Bu_4NHSO_4 (3.5 mg. 0.01 mmol) and p-TsOH (1 mg, 0.006 mmol) was added to above the mixture which was stirred at 0 ℃ for 1 h. The reaction was quenched with water (5 mL) and extracted with EA. the organic layer was dried over Na_2SO_4, filtrated and concentrated under reduced pressure. The residue was purified via column chromatography to give desired product **4** (14.4 mg, 35%)

To a solution of compound **4** (14.4 mg, 0.05 mmol) in DCM (5 mL) at rt was added DMAP (0.1 eq) and 4-Nitrobenzoyl chloride (9 mg, 0.05 mmol). the reaction mixture was stirred at rt for 12 h before being concentrated in vacuo to give the crude reaction mixture. The residue was purified via column chromatography to give desired product **4**.

Physical state: yellow solid, m.p.106.6 – 107.4 ℃

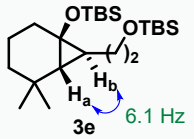
Rf = 0.5 (PE: EA = 5:1; UV) 18.5 mg, 83%

^{1}H NMR (400 MHz, Acetone-d_6) δ 8.38 (d, J = 9.0 Hz, 2H), 8.30 (d, J = 9.0 Hz, 2H), 4.46 (qdd, J = 10.6, 7.0, 6.2 Hz, 2H), 2.02 – 1.82 (m, 4H), 1.59 – 1.47 (m, 1H), 1.16 (s, 3H), 1.12 – 0.98 (m, 2H), 0.88 (d, J = 2.8 Hz, 13H), 0.68 – 0.61 (m, 2H), 0.18 (s, 3H), 0.16 (s, 3H).

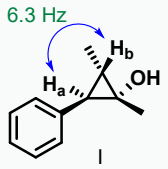
^{13}C NMR (100 MHz, Acetone-d_6e) δ 166.19, 137.82, 132.46, 125.42, 67.69, 61.86, 39.57, 37.85, 34.44, 32.76, 29.67, 29.31, 27.06, 24.26, 20.20, 19.40, -2.08, -2.20.

HRMS(APCI-TOF) m/z Calculated for $C_{24}H_{38}NO_5Si$ $[M+H]^+$:448.2519, found:44.2514

IR (thin film) ν $_{max}$ (cm^{-1}): 2954, 2929, 1727, 1530, 1277, 836.

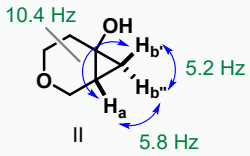


trans H_a and H_b, J = 6.1 Hz



trans H_a and H_b, J = 6.3 Hz

Tetrahedron. Lett., **2015**, 56, 3982.



trans H_a and $H_{b''}$, J = 5.8 Hz

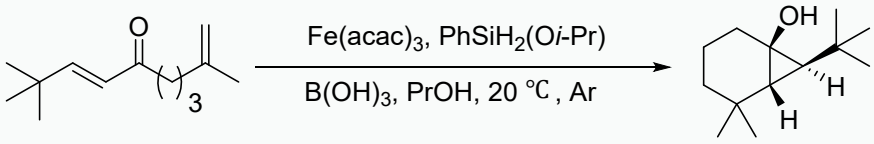
cis H_a and $H_{b'}$, J = 10.4 Hz

Org. Biomol. Chem., **2003**, 3600.

The relative configuration of the compound **3e** is confirmed by single-crystal X-ray diffraction analysis where the hydrogen coupling constant between H_a and H_b is 6.1 Hz with *trans*-configuration. Moreover, the hydrogen coupling constant of H_a and H_b for the other fused bicyclic cyclopropanols in this work is between 3.0-7.6 Hz. Wang & Lv report the coupling constant between H_a with H_b in *trans* cyclopropanols **I** equal to 6.3 Hz. [9a] Ollivier and co-workers reveal the coupling constant between H_a with $H_{b''}$ in compound **II** is 5.8 Hz with *trans*-configuration while the coupling constant between H_a with $H_{b'}$ is 10.4 Hz with *cis*-configuration. [9b] In above cases, the value of coupling constant in *cis*-configuration is much higher than the value in *trans*-configuration. Based on the above information, we determine the relative configurations of other fused bicyclic cyclopropanols in our work are consistent with compound **3e**.

5. Preliminary mechanistic studies

5.1 Synthesis of compound **3a′**



$Fe(acac)_3$ (7 mg, 0.02 mmol) was added to the solution of a, β-unsaturated compound (19.8 mg, 0.1 mmol) in 1.5 mL *n*-PrOH at 20 ℃ under Ar atmosphere. Then $PhSiH_2(Oi\text{-}Pr)$ (2.5 eq.) and $B(OMe)_3$ (2.0 eq.) was added to the above solution and the reaction was stirred at 20 ℃ until the starting material was consumed. Then, the reaction mixture was direct purified by neutral alumina column chromatography.

Physical state: oil,

Rf = 0.4 (PE: EA = 5:1; anisaldehyde) 17.6 mg, 90%

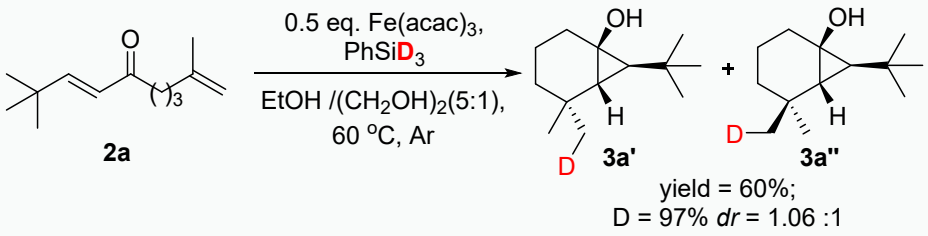
^{1}H NMR (400 MHz, Acetone-d_6) δ 3.88 (s, 1H), 1.92 – 1.78(m, 2H), 1.48 – 1.43 (m, 1H), 1.14 (ddddd, J = 13.4, 8.2, 6.6, 5.4, 2.9 Hz, 1H), 1.08 (s, 3H), 1.04 – 1.01 (m, 1H), 0.99 (s, 9H), 0.98 – 0.92 (m, 1H), 0.84 (s, 3H), 0.80 (d, J = 7.4 Hz, 1H), 0.26 (d, J = 7.4 Hz, 1H).

^{13}C NMR (100 MHz, Acetone-d_6) δ 58.64, 37.75, 35.96, 34.50, 33.46, 30.84, 30.18, 29.53, 28.66, 27.81, 18.49.

HRMS(APCI-TOF) m/z Calculated for $C_{13}H_{24}DO[M+H]^+$:197.1095, found: 197.1099.

IR (thin film) ν $_{max}$ (cm^{-1}): 2925, 1705, 1461, 1365.

5.2 Deuteration study with $PhSiD_3$



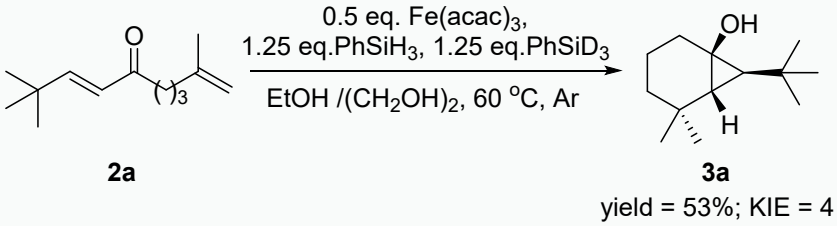
$Fe(acac)_3$ (0.5 eq.) was added to the solution of a, β-unsaturated compound (0.1 mmol) in 1.5 mL EtOH and 0.3 mL $(CH_2OH)_2$ under Ar atmosphere. Then $PhSiD_3$ (2.5 eq.) was added to the above solution and the reaction was stirred at 60 ℃ for 12 h. Then, the reaction mixture was direct purified by neutral alumina column chromatography to give the desired compound (11.8 mg, 60%) (D = 97%; dr = 1.06:1 or 1:1.06)

^{1}H NMR (400 MHz, Acetone-d_6) δ 3.85 (s, 1H), 1.99 – 1.71 (m, 2H), 1.57 – 1.38 (m, 1H), 1.16 (ddddd, *J* = 13.4, 8.2, 6.6, 5.4, 2.9 Hz, 1H), 1.09 (s, 1.41H), 1.08 – 1.06 (m, 1.09H), 1.04 (dd, *J* = 8.2, 3.2 Hz, 1H), 1.01 (s, 9H), 0.97 (dd, *J* = 9.6, 3.1 Hz, 1H), 0.85 (s, 1.50H), 0.83 (t, *J* = 1.8 Hz, 1.03H), 0.81 (d, *J* = 7.4 Hz, 1H), 0.27 (d, *J* = 7.3 Hz, 1H).; **^{13}C NMR** (100 MHz, Acetone-d_6) δ 59.41, 38.53, 36.68, 35.24, 34.23, 31.55, 30.91, 30.27, 29.37, 28.48, 19.23.

HRMS(APCI-TOF) m/z Calculated for $C_{13}H_{24}DO[M+H]^+$:198.1963, found: 198.1962.

IR (thin film) ν $_{max}$ (cm^{-1}): 2925, 1705, 1461, 1365.

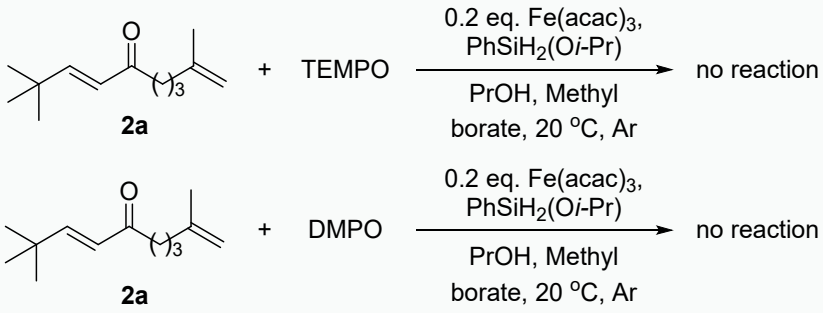
5.3 Competitive experimental study



To solution of **2a** (20.1 mg, 0.1 mmol) and $Fe(acac)_3$ (0.5 eq.) in 1.5 mL EtOH and 0.3 mL $(CH_2OH)_2$ was added $PhSiD_3$ (1.25 eq) and $PhSiH_3$ (1.25 eq.) under Ar atmosphere. Then the reaction was stirred at 60 ℃ for 12 h. Then, the reaction mixture was direct purified by neutral alumina column chromatography to give the desired compound (10.3 mg, 53%).

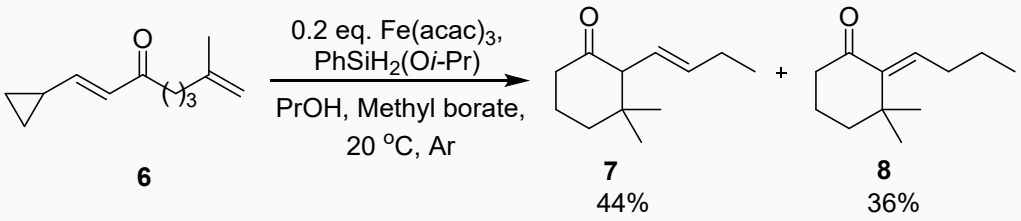
^{1}H NMR (400 MHz, Acetone-d_6) δ 3.85 (s, 1H), 1.96 – 1.76 (m, 2H), 1.54 – 1.39 (m, 1H), 1.22 – 1.12 (m, 1H), 1.09 (s, 2.44H), 1.07 – 1.05 (m, 0.44H), 1.04 (dd, *J* = 8.2, 3.2 Hz, 1H), 1.01 (s, 9H), 0.99 – 0.91 (m, 1H), 0.85 (s, 2.55H), 0.84 – 0.82 (m, 0.37H), 0.81 (d, *J* = 7.4 Hz, 1H), 0.27 (d, *J* = 7.3 Hz, 1H).

5.4 Radical inhibiting experiment

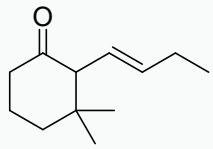


$Fe(acac)_3$ was added to the solution of compound **2a** (0.1 mmol, 20 mg) in 1.5 mL *n*-PrOH at 20 ℃ under Ar atmosphere. Then $PhSiH_2(Oi\text{-}Pr)$ (2.5 eq) and $B(OMe)_3$ (2 eq) was added to the above solution. After that, TEMPO (1.5 eq) or DMPO (1.5 eq) was added to above solution and the reaction was stirred at 20 ℃ for 5 h. The reaction didn't proceed under this condition.

5.5 Radical clock experiment



$Fe(acac)_3$ (0.2 eq) was added to the solution of a, β-unsaturated compound (35.6 mg, 0.2 mmol) in 3 mL *n*-PrOH at 20 ℃ under Ar atmosphere. Then $PhSiH_2(Oi\text{-}Pr)$ (2.5 eq) and $B(OMe)_3$ (2.0 eq) was added to the above solution and the reaction was stirred at 20 ℃ until the starting material was consumed. The resulting mixture was the direct purified by column chromatography to give the **7** (15.8 mg, 44%) and **8** (12.9 mg, 36%)



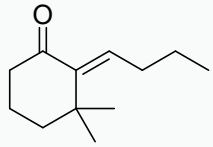
7

Physical state: colorless oil

^{1}H NMR (400 MHz, CD_3OD) δ 5.67 – 5.40 (m, 2H), 2.80 (d, *J* = 8.6 Hz, 1H), 2.40 – 2.28 (m, 2H), 2.17 – 1.99 (m, 2H), 1.98 – 1.82 (m, 2H), 1.80 – 1.47 (m, 2H), 1.00 (t, *J* = 7.5 Hz, 3H), 0.96 (s, 3H), 0.82 (s, 3H).; **^{13}C NMR** (100 MHz, CD_3OD) δ 216.22, 138.72, 125.33, 66.89, 42.15, 41.29, 39.82, 30.32, 27.60, 24.68, 24.15, 14.95.

HRMS(APCI-TOF) m/z Calculated for $C_{12}H_{21}O$ $[M+H]^+$:181.1587, found: 181.1584.

IR (thin film) ν_{max} (cm^{-1}): 2959, 2930, 1710, 1460, 1075.



8

Physical state: colorless oil

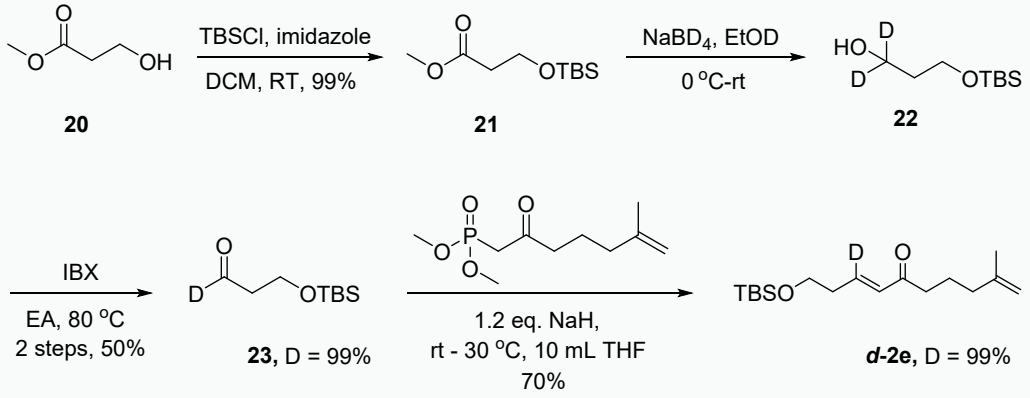
^{1}H NMR (400 MHz, CD_3OD) δ 5.57 (t, *J* = 7.5 Hz, 1H), 2.39 (t, *J* = 6.8 Hz, 2H), 2.11 (q, *J* = 7.4 Hz, 2H), 2.00 – 1.80 (m, 2H), 1.77 – 1.55 (m, 2H), 1.40 (q, *J* = 7.4 Hz, 2H), 1.08 (s, 6H), 0.89 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 211.78, 151.70, 133.91, 133.88, 64.76, 44.36, 43.34, 43.16, 43.10, 42.08, 34.81, 34.51, 32.18, 30.71, 27.57, 26.84, 26.52, 26.42, 25.41, 24.65, 24.56, 16.88, 16.63.

HRMS(APCI-TOF) m/z Calculated for $C_{12}H_{21}O[M+H]^+$: 181.1587, found: 181.1580.

IR (thin film) ν $_{max}$ (cm^{-1}): 2917, 2850, 1463, 1084, 1023.

5.6 The experiment for exploring the relative stereochemistry of cyclopropanols



Imidazole (3.4 g, 48.8 mmol) and tert-butyldimethylsilyl chloride (7.4 g, 48.8 mmol). was slowly added to a solution of 3-hydroxy-propionic acid methyl ester (1.8 g, 18 mmol) in 20 mL of CH_2Cl_2 at RT. The reaction was stirred for 2 h, Then, the reaction was poured into 50 mL of water, and extracted with CH_2Cl_2 (3 x 50 mL). The combined organic layers were dried with Na_2SO_4, filtered and concentrated. The oil was purified by flash chromatography to give the desired product **21** (3.8 g, 99%).

Physical state: colorless oil

Rf = 0.7 (PE; anisaldehyde)

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.88 (t, *J* = 6.4 Hz, 2H), 3.67 (s, 3H), 2.52 (t, *J* = 6.4 Hz, 2H), 0.86 (s, 9H), 0.04 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.26, 59.08, 51.51, 37.91, 25.81, 18.23, -5.43.

A dry flask was charged with compound **21** (1.09 g, 5 mmol) and EtOD (5 mL) under Ar atmosphere. The reaction was stirred at 0 ℃ for 30 min. Then $NaBD_4$ (246 mg, 6 mmol) was

added to the above suspension and the reaction was stirred at 0 ℃ for another 2 h. The reaction was the direct concentrated under reduced pressure to give the desired product which was used for the next step without the further purified. To a suspension of IBX (3.36 g, 12 mmol) in EA was added above residue and the mixture was stirred at 80℃ for 12 h, the reaction was filtrated and concentrated under reduced pressure. The crude product was purified on SiO_2 to give the compound **23** (472.5 mg, 50 %, D = 99%).

Physical state: colorless oil

Rf = 0.7 (PE : EA = 10:1; anisaldehyde)

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.74 (t, *J* = 2.1 Hz, 0.01 H), 3.92 (t, *J* = 6.1 Hz, 2H), 2.53 (t, *J* = 6.0 Hz, 2H), 0.82 (s, 9H), 0.00 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 202.04, 201.78, 201.51, 57.40, 46.44, 46.40, 46.37, 25.81, 18.22, -5.45.

To the solution of the phosphonate (524 mg, 2.0 mmol) in the 10 mL dry THF was added NaH (96 mg, 2.4 mmol) under Ar at rt. The reaction was stirred at rt for 30 min. Then aldehyde **23** (453.6 mg, 2.4 mmol) was added. The mixture was stirred at 30 ℃ for another 24 h and quenched with saturated NH_4Cl (10 mL). The organic layer was separated and water layer was extracted with EA and dried over Na_2SO_4. The combined organic layers were evaporated and the residue was purified via column chromatography to give desired product (415.8 mg, 70%, D = 99%).

Physical state: colorless oil

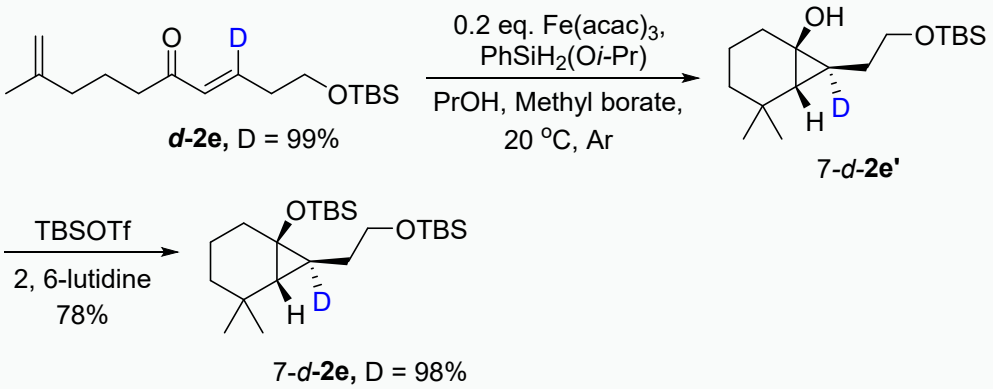
Rf = 0.8 (PE : EA = 10:1; UV)

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.78 (dt, *J* = 15.9, 7.0 Hz, 0.01H). 6.07 (s, 1H), 4.67 (s, 1H), 4.62 (s, 1H), 3.68 (t, *J* = 6.4 Hz, 2H), 2.50 – 2.45 (m, 2H), 2.41 – 2.30 (m, 2H), 2.04 – 1.93 (m, 2H), 1.76 – 1.68 (m, 2H), 1.66 (s, 3H), 0.84 (s, 9H), 0.00 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 200.52, 145.11, 131.85, 110.52, 61.59, 39.14, 37.16, 35.81, 25.88, 22.21, 21.90, 18.29, -5.32

HRMS(ESI$^+$) m/z Calculated for $C_{17}H_{32}DO_2Si$ $[M+H]^+$: 298.2307, found: 298.2301

IR (thin film) ν_{max} (cm^{-1}): 2954.14, 2925.26, 1461.96, 1377.12, 1100.72.



$Fe(acac)_3$ (0.2 eq) was added to the solution of compound ***d*-2e** (0.1 mmol, 30 mg) in 1.5 mL *n*-PrOH at 20 ℃ under Ar atmosphere. Then $PhSiH_2(Oi\text{-}Pr)$ (2.5 eq.) and $B(OMe)_3$ (2 eq.) was added to the above solution and the reaction was stirred at 20 ℃ for 4 h. The resulting mixture was directed purified by neutral alumina column chromatography. After that 2,6-lutidine (6 eq.) was added to the received compound **7-d-2e'** in dry DCM (5 mL) and the solution was stirred at 0 ℃ for 30min, then slow addition of TBSOTf (3 eq.). The reaction was stirred at 0 ℃ for another 1h. The reaction was quenched with saturated $NaHCO_3$ (5 mL) and extracted with EA, the organic layer was dried over Na_2SO_4, filtrated and concentrated under reduced pressure. the crude product was purified on SiO_2 to give the compound 7-*d*-**2e** (32 mg, 78%)

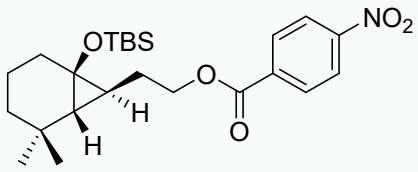
^{1}H NMR (400 MHz, Acetone-d_6) δ 3.64 (ddd, J = 7.0, 6.5, 2.4 Hz, 2H), 1.92 – 1.70 (m, 2H), 1.59 (dt, J = 13.5, 6.8 Hz, 1H), 1.54 – 1.37 (m, 2H), 1.09 (s, 3H), 1.06 – 0.88 (m, 3H), 0.85 (s, 9H), 0.82 (s, 9H), 0.81 (s, 3H), 0.49 (s, 1.02H), 0.13 (s, 3H), 0.07 (s, 3H), 0.00 (d, J = 2.1 Hz, 6H).

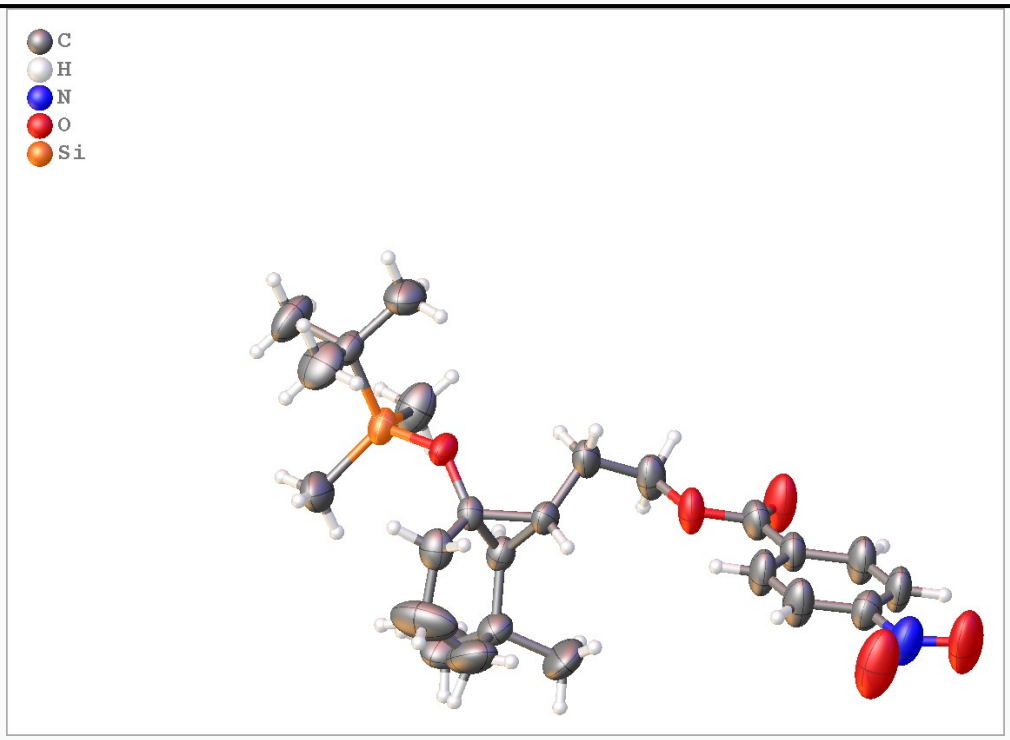
^{13}C NMR (100 MHz, Acetone-d_6) δ 62.92, 59.91, 37.76, 36.17, 32.84, 31.99, 31.06, 28.01, 25.43, 25.29, 18.46, 17.92, 17.61, -3.88, -3.94, -5.93, -5.97.

HRMS(APCI-TOF) m/z Calculated for $C_{23}DH_{47}O_2Si_2[M+H]^+$: 414.3328, found: 414.3329.

IR (thin film) ν $_{max}$ (cm^{-1}): 2928, 2856, 1462, 1195, 1092, 833.

6. X-ray Crystallographic Data:





1. X-ray crystallographic data for compound **5** (CCDC 2083784):

Table 5 Crystal data and structure refinement for compound **5**

Empirical formula	$C_{24}H_{37}NO_5Si$
Formula weight	447.63
Temperature/K	293.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	25.9894(16)
b/Å	7.4776(8)
c/Å	13.2343(12)
α/°	90
β/°	95.539(7)
γ/°	90
Volume/Å^3	2559.9(4)
Z	4

ρ_{calc}g/cm^3	1.161
μ/mm^{-1}	0.124
F(000)	968.0
Crystal size/mm^3	0.35 × 0.3 × 0.25
Radiation	MoKα(λ = 0.71073)
2Θ range for data collection/	6.186 to 52.744
Index ranges	-32 ≤ h ≤ 29, -9 ≤ k ≤ 9, -14 ≤ l ≤ 16
Reflections collected	11655
Independent reflections	5225 [R_{int} = 0.0550, R_{sigma} = 0.0834]
Data/restraints/parameters	5225/0/287
Goodness-of-fit on F^2	1.020
Final R indexes [I>=2σ (I)]	R_1 = 0.0959, wR_2 = 0.2056
Final R indexes [all data]	R_1 = 0.1638, wR_2 = 0.2474
Largest diff. peak/hole / e Å^{-3}	0.28/-0.34

2. X-ray crystallographic data for compound **2v** (CCDC 2083785):

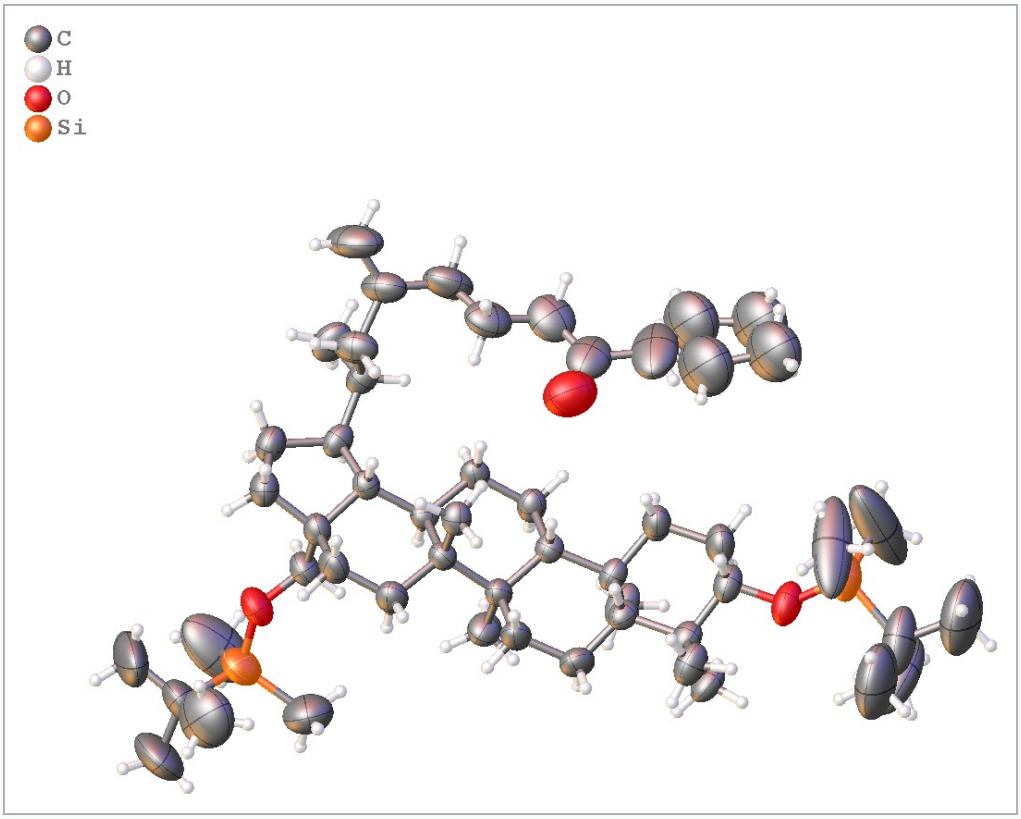


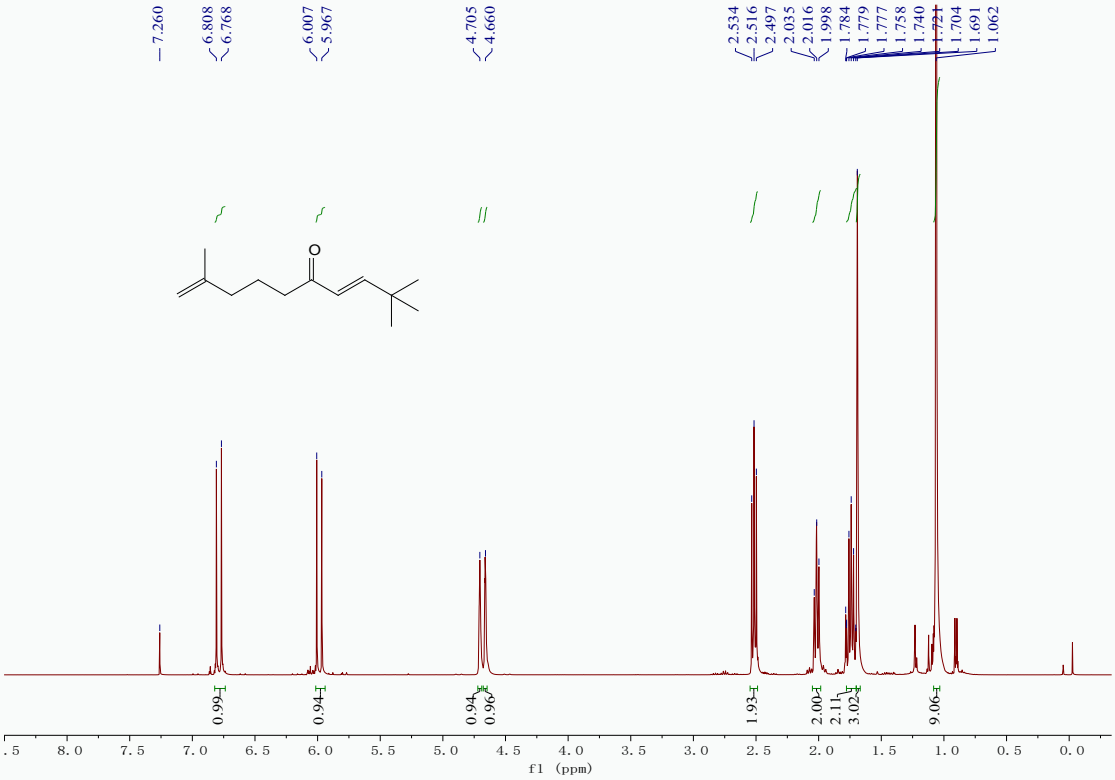
Table 6 Crystal data and structure refinement for compound 2v

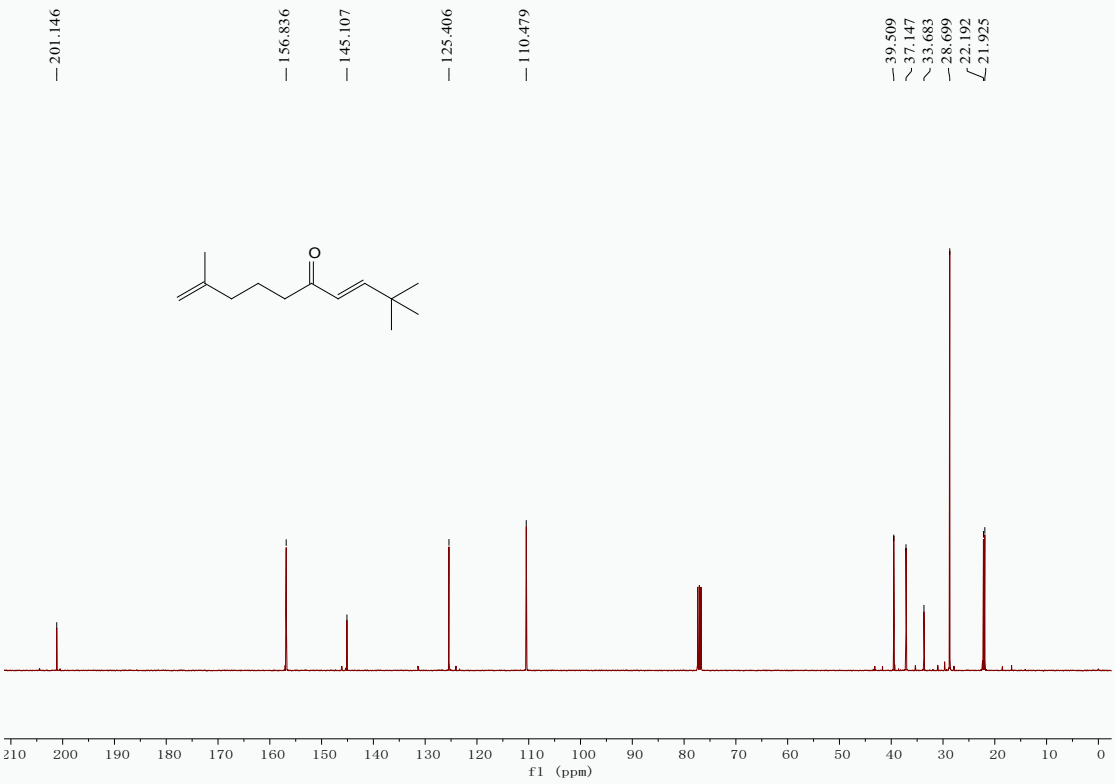
Empirical formula	$C_{51}H_{92}O_3Si_2$
Formula weight	809.42
Temperature/K	293.15
Crystal system	monoclinic
Space group	$P2_1$
a/Å	11.479(3)
b/Å	12.0136(15)
c/Å	20.224(3)
α/°	90
β/°	105.64(2)
γ/°	90
Volume/Å^3	2685.7(9)
Z	2
ρ_{calc}g/cm^3	1.001
μ/mm^{-1}	0.101
F(000)	900.0

Crystal size/mm^3	0.35 × 0.3 × 0.25
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.276 to 52.74
Index ranges	-10 ≤ h ≤ 14, -13 ≤ k ≤ 15, -22 ≤ l ≤ 25
Reflections collected	11934
Independent reflections	9462 [R_{int} = 0.0149, R_{sigma} = 0.0539]
Data/restraints/parameters	9462/6/512
Goodness-of-fit on F^2	1.010
Final R indexes [I>=2σ (I)]	R_1 = 0.0776, wR_2 = 0.1931
Final R indexes [all data]	R_1 = 0.1253, wR_2 = 0.2296
Largest diff. peak/hole / e Å^{-3}	0.33/-0.33
Flack parameter	-0.04(6)

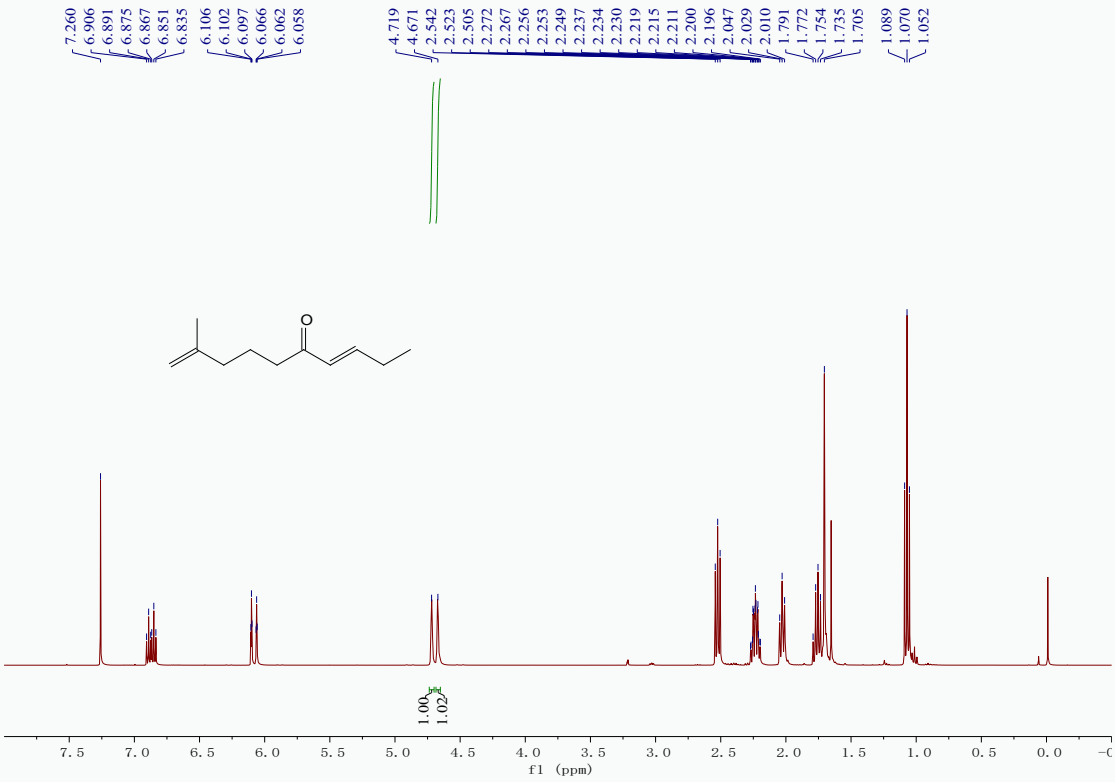
7 Spectra of Products.

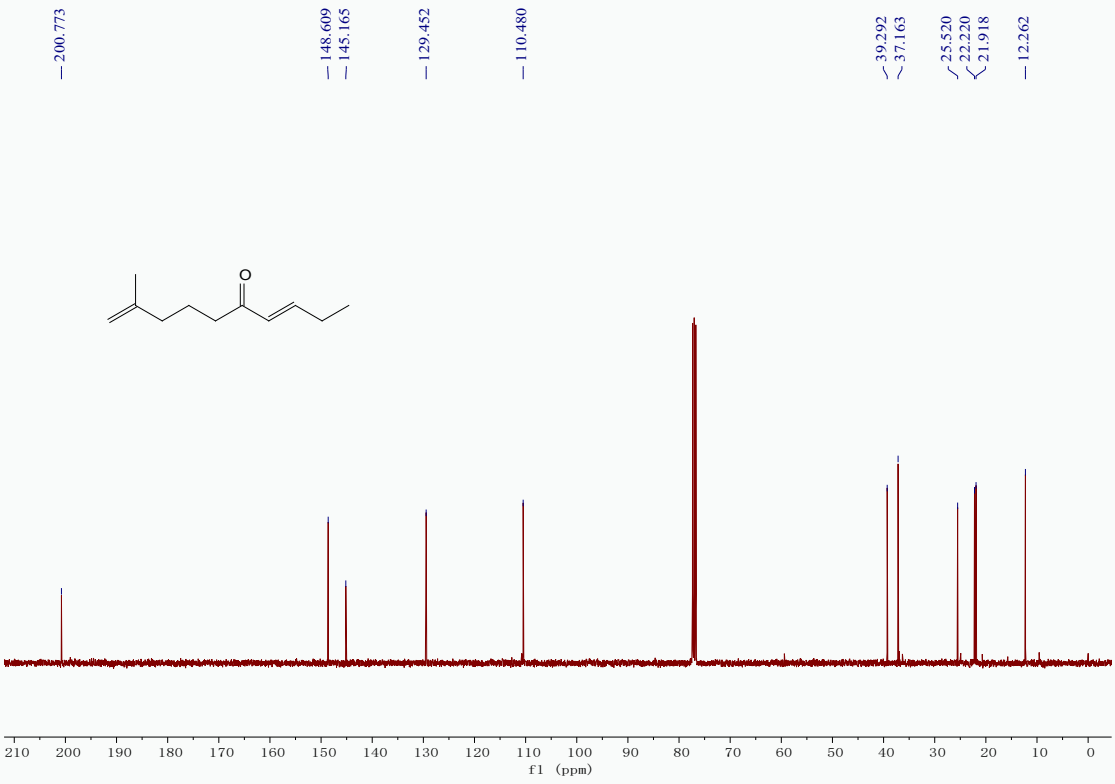
(*E*)-2,2,9-trimethyldeca-3,9-dien-5-one (**2a**) (Using $CDCl_3$ as solvent)



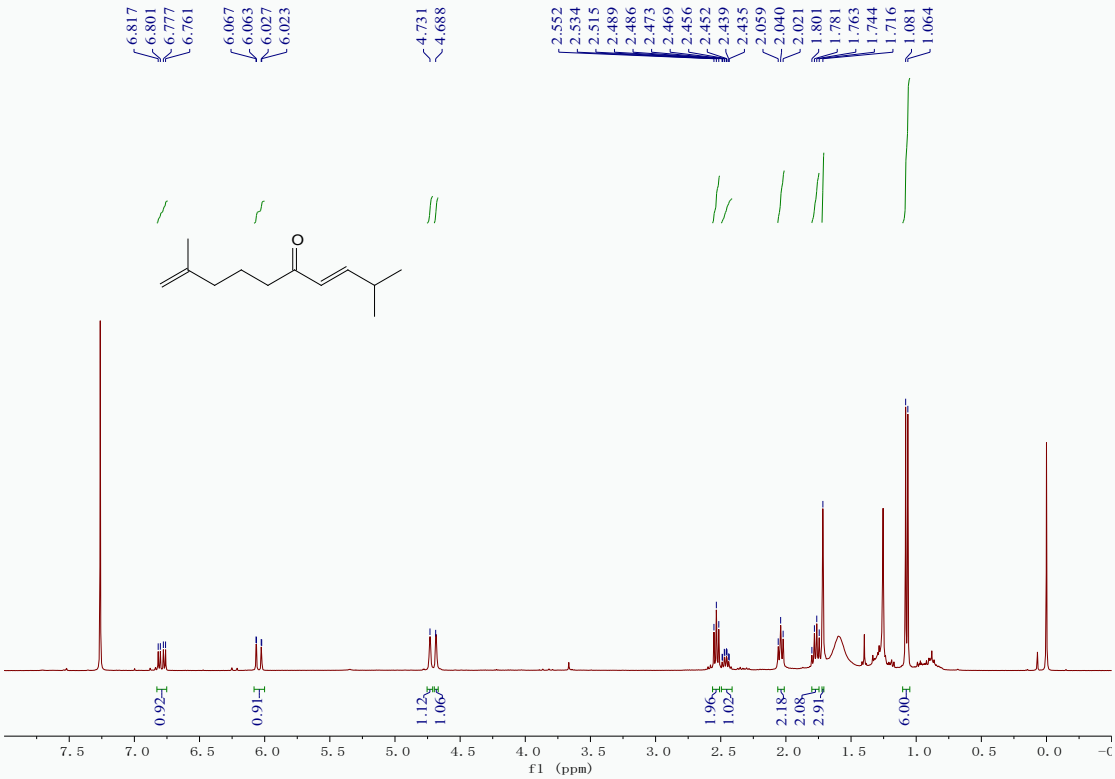


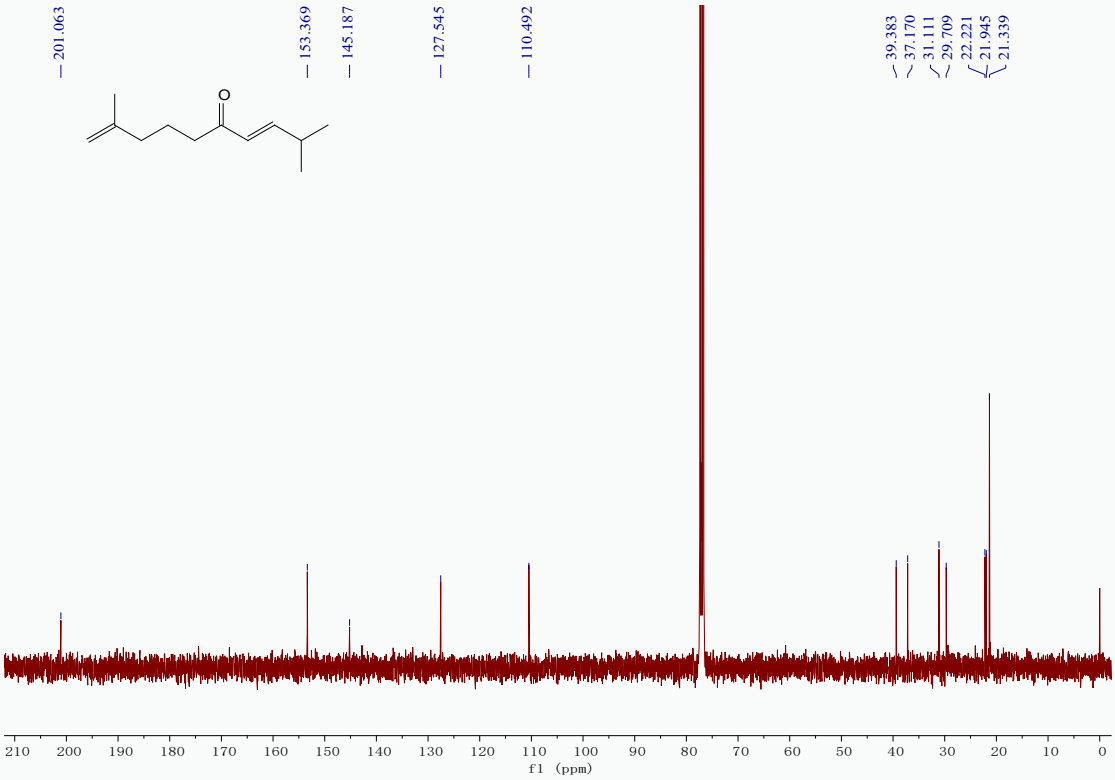
(*E*)-9-methyldeca-3,9-dien-5-one (**2b**) (Using $CDCl_3$ as solvent)



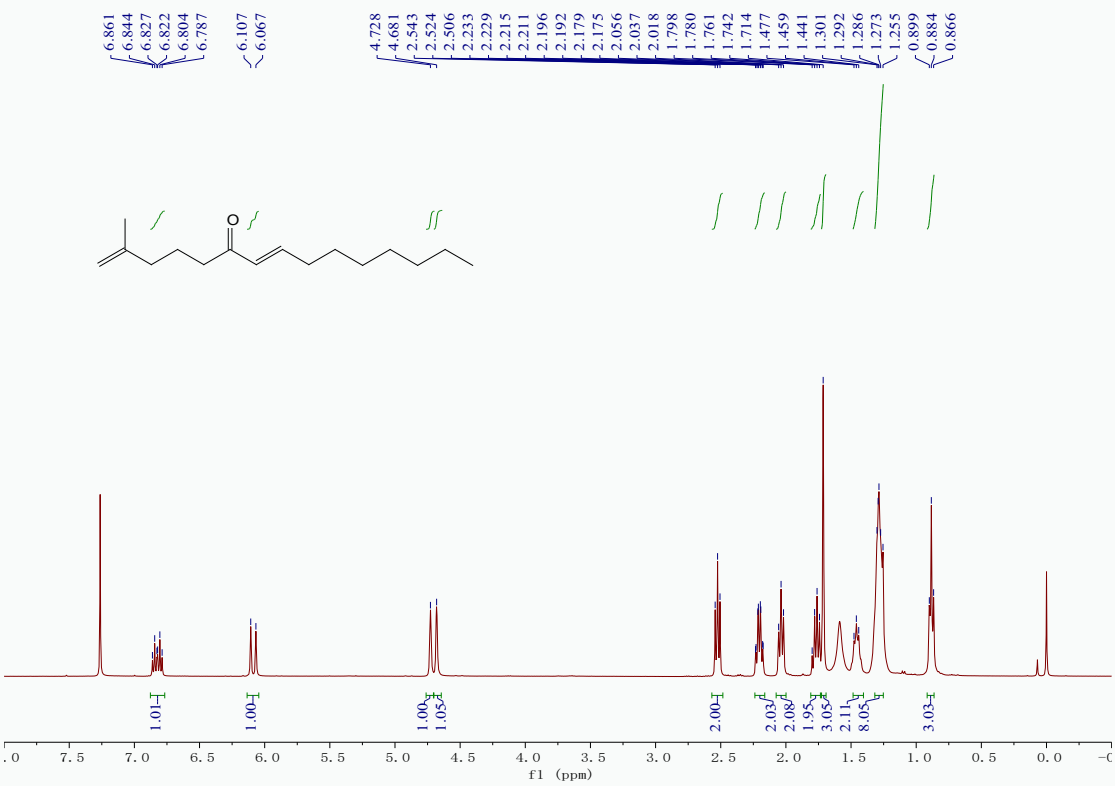


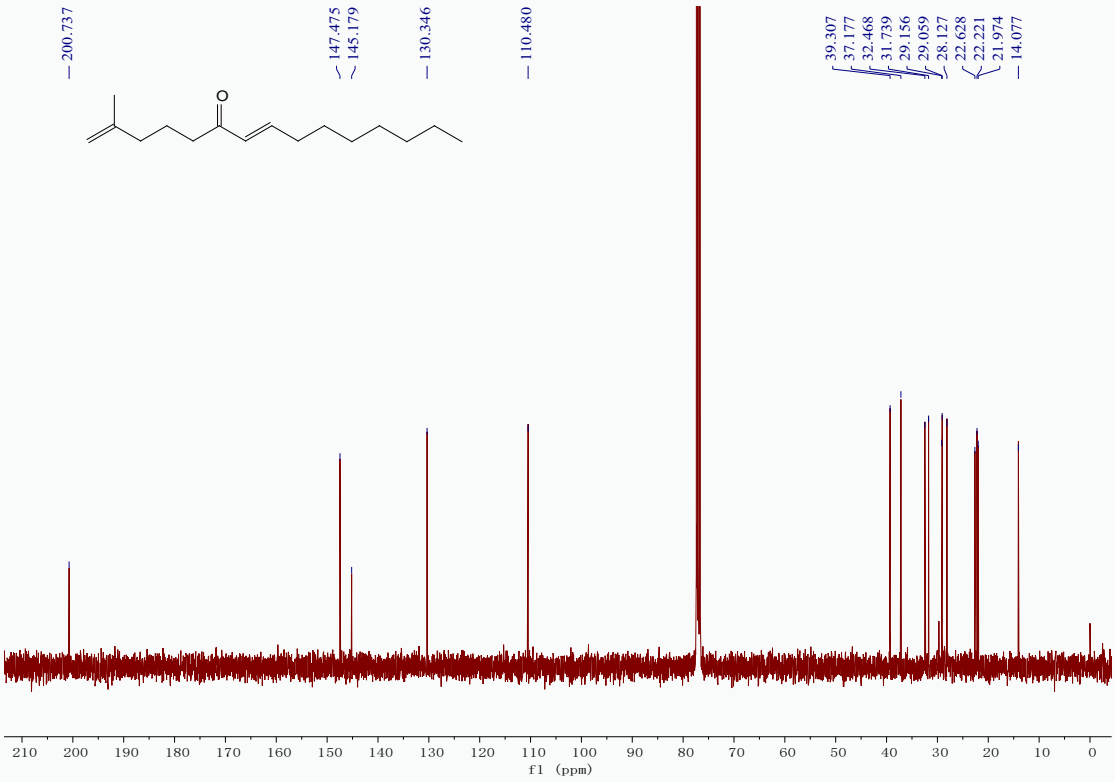
(*E*)-2,9-dimethyldeca-3, 9-dien-5-one (**2c**) (Using $CDCl_3$ as solvent)



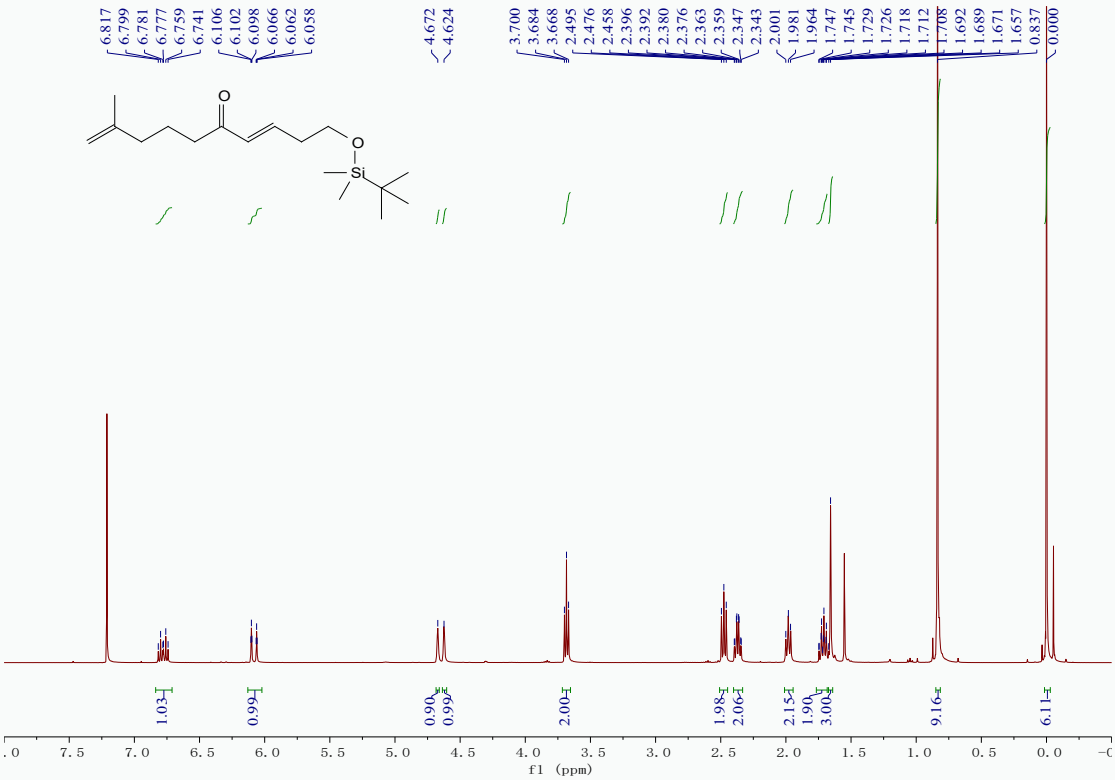


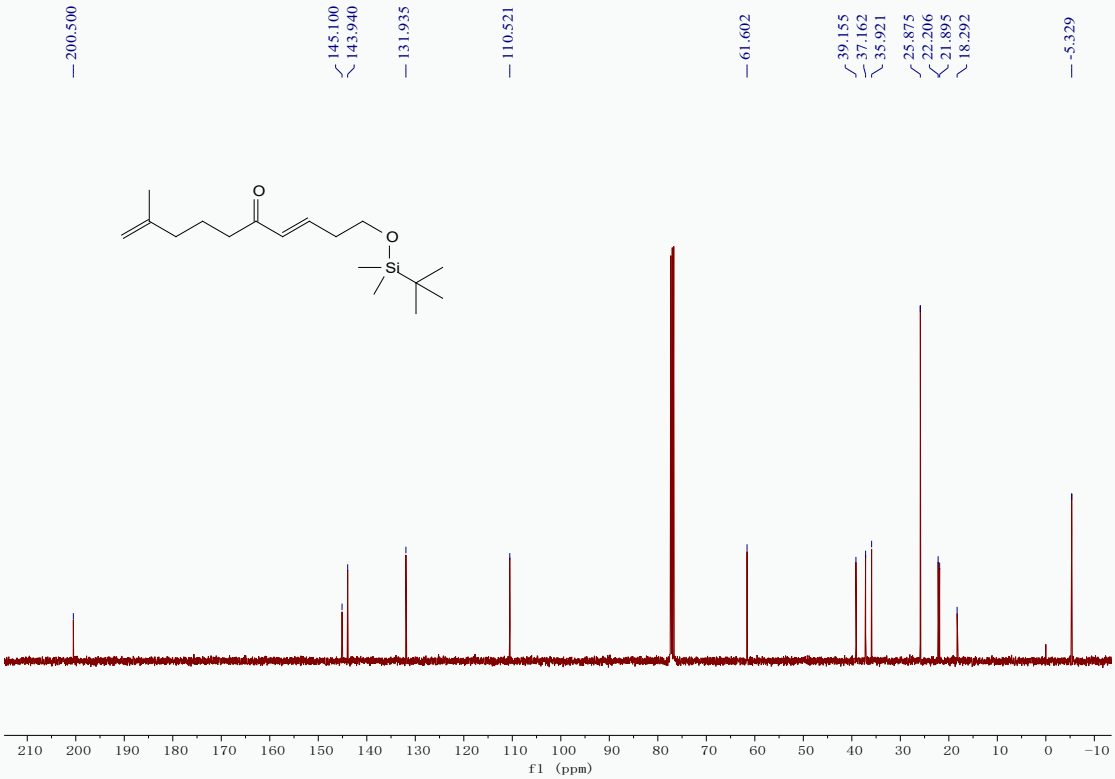
(*E*)-2-methylpentadeca-1,7-dien-6-one (**2d**) (Using $CDCl_3$ as solvent)



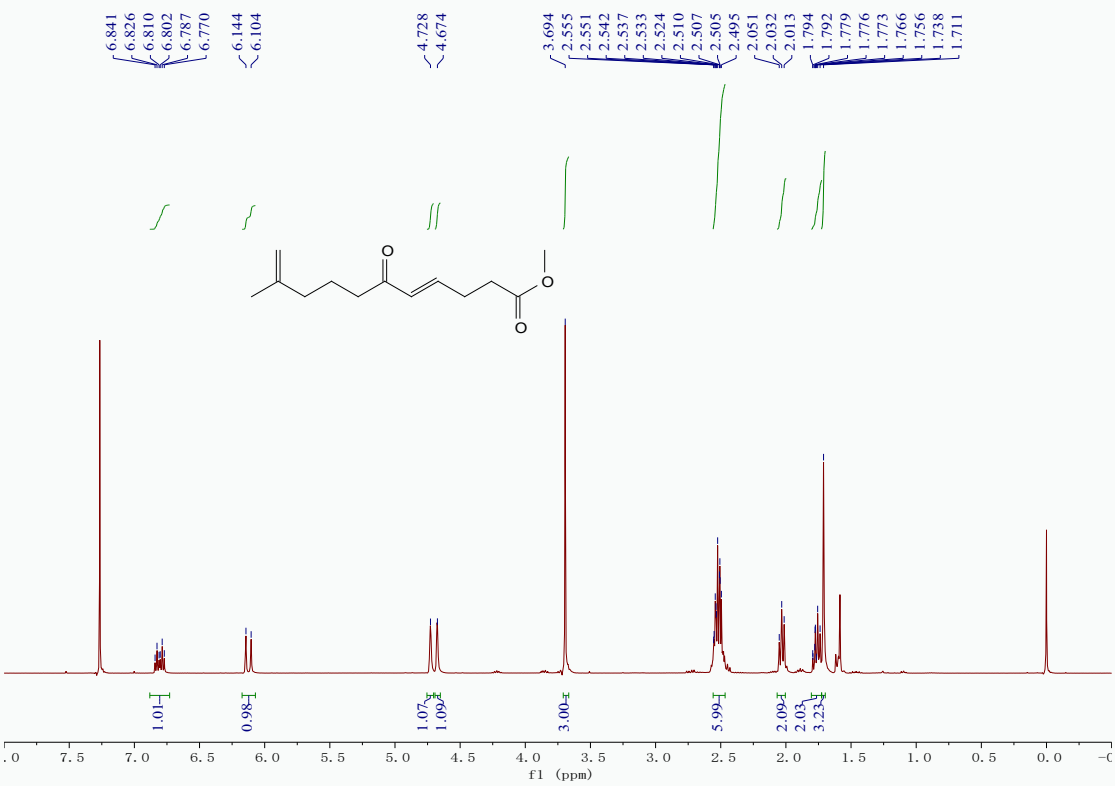


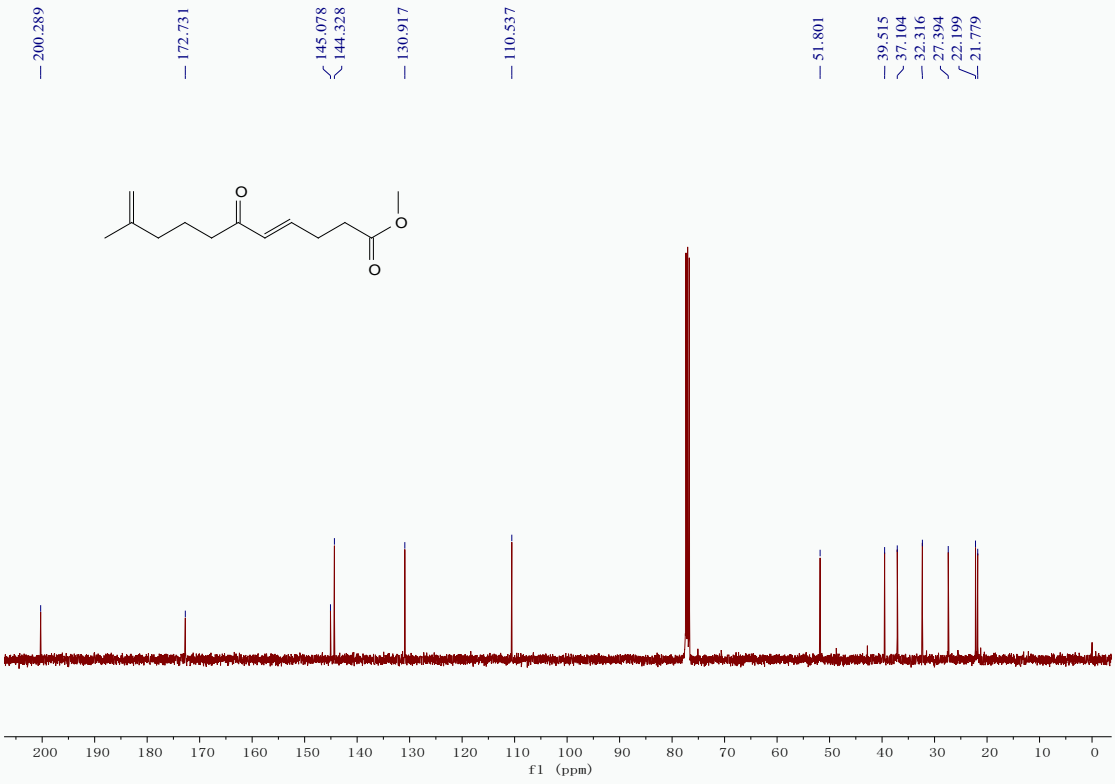
(*E*)-1-((tert-butyldimethylsilyl)oxy)-9-methyldeca-3,9-dien-5-one (**2e**) (Using $CDCl_3$ as solvent)



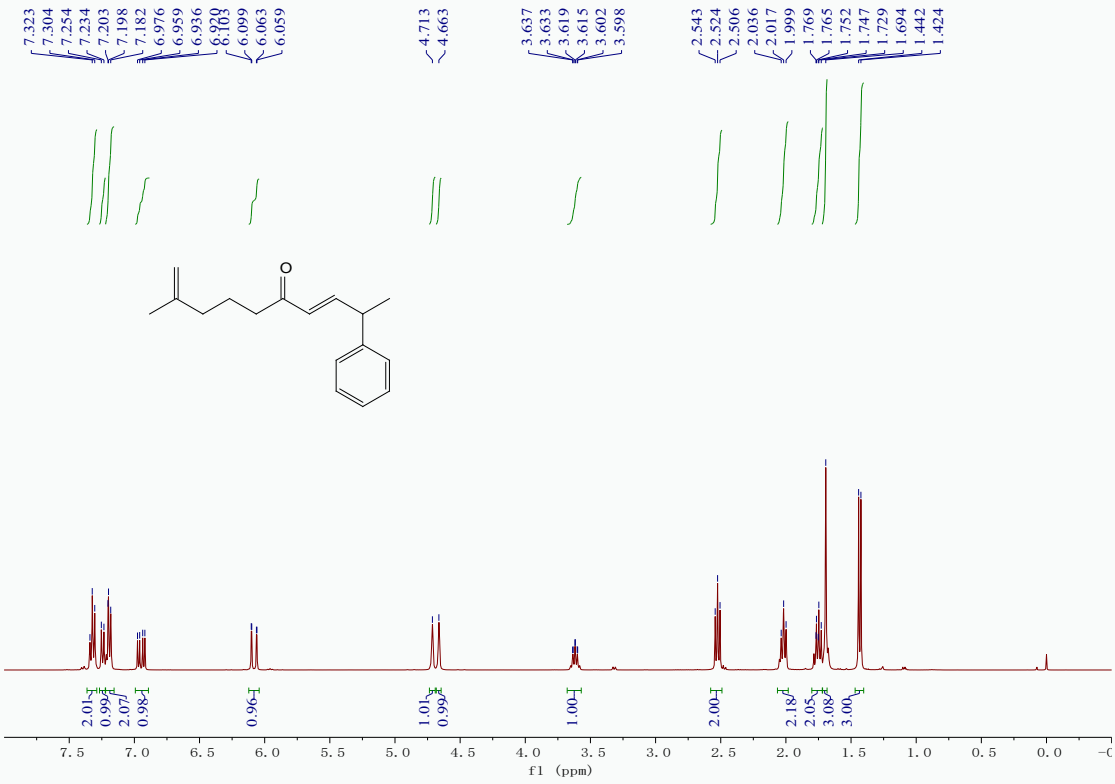


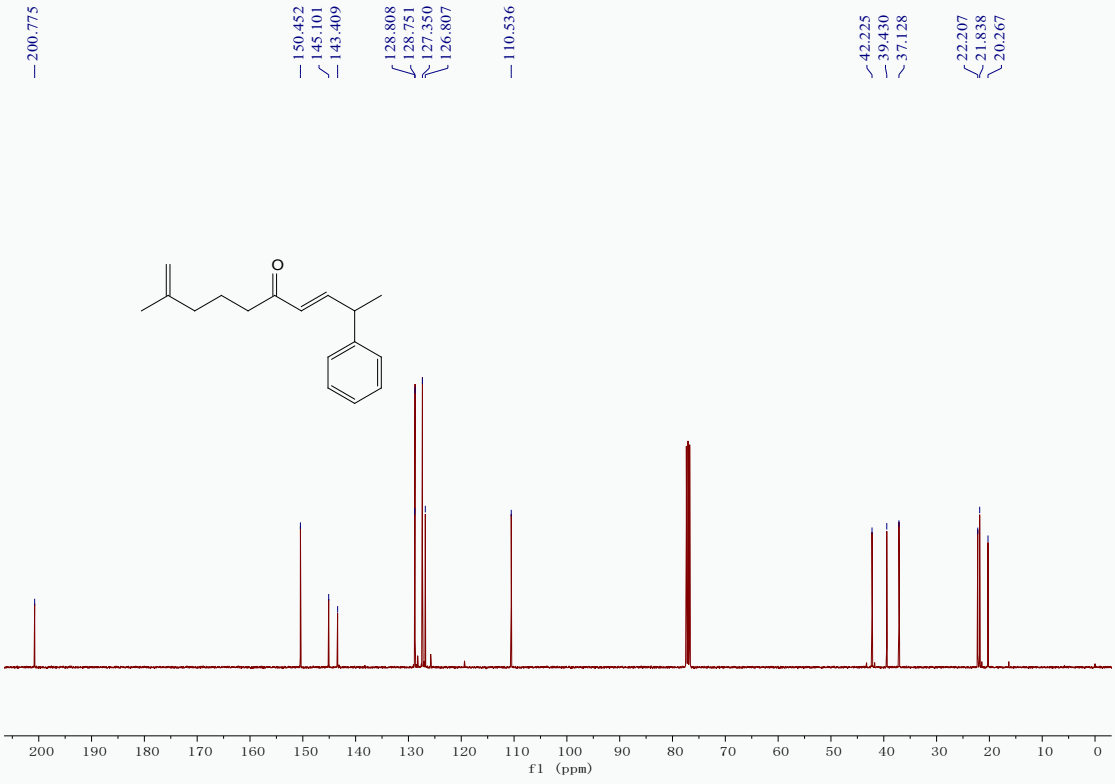
methyl (*E*)-10-methyl-6-oxoundeca-4,10-dienoate (**2f**) (Using $CDCl_3$ as solvent)



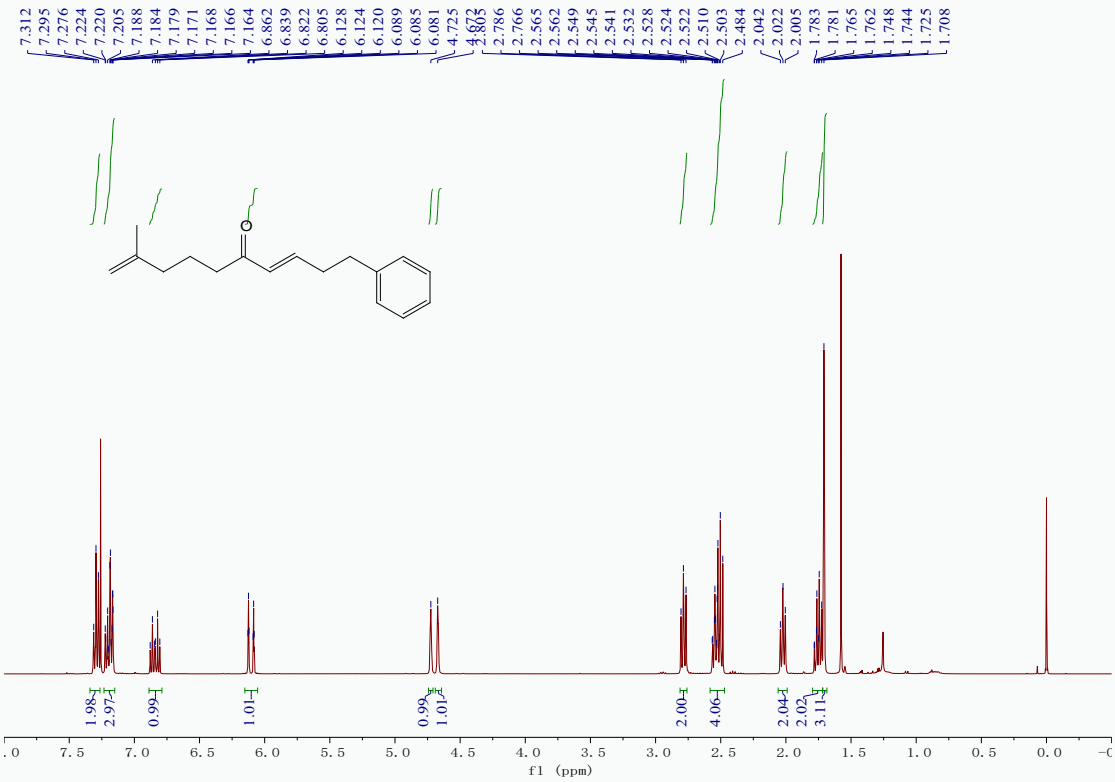


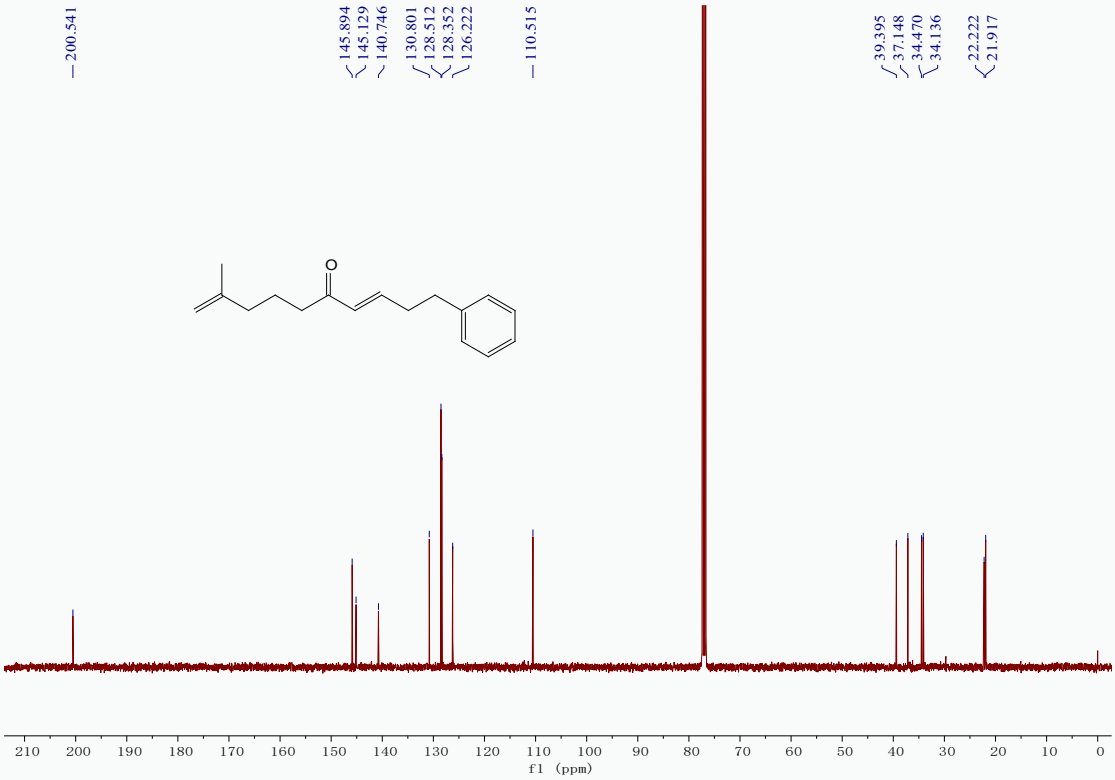
(*E*)-9-methyl-2-phenyldeca-3,9-dien-5-one (**2g**) (Using $CDCl_3$ as solvent)



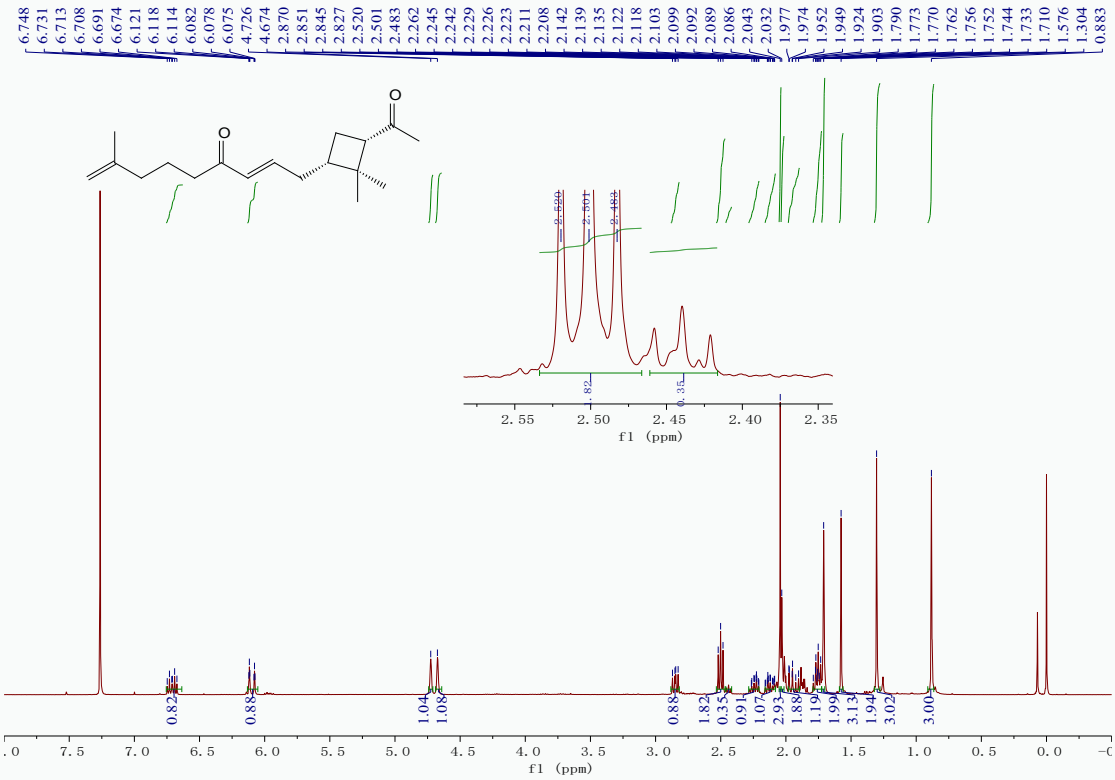


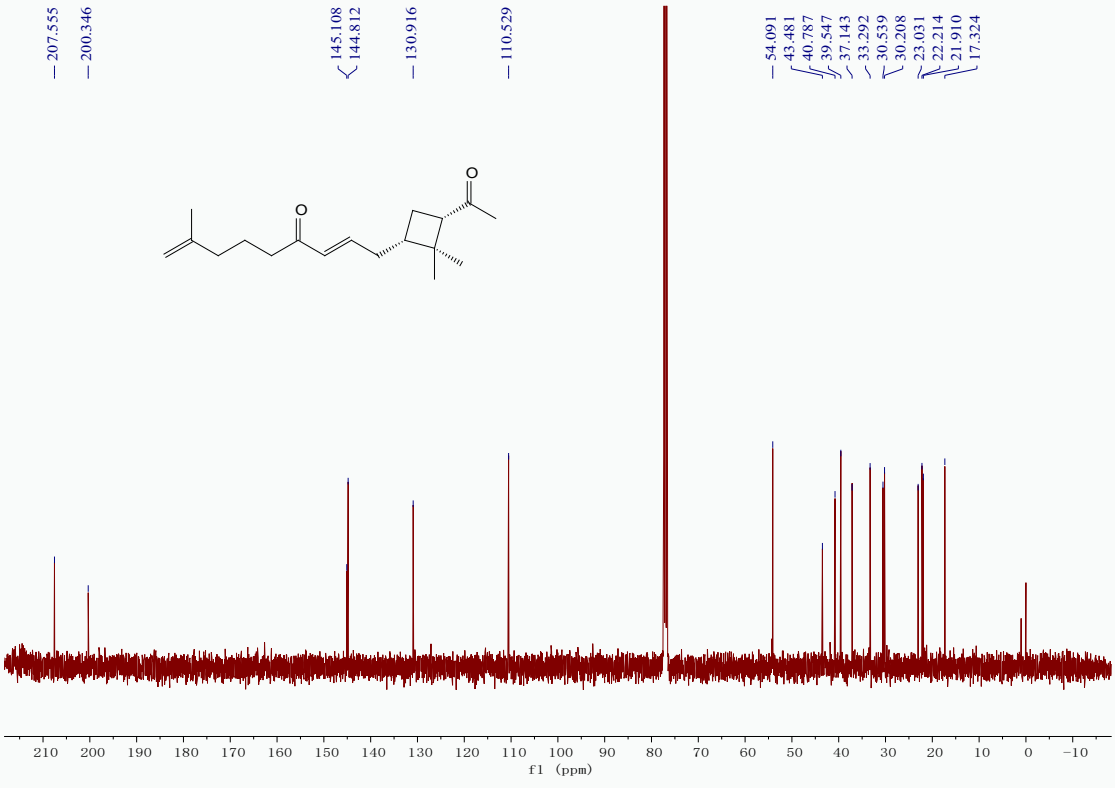
(*E*)-7-methyl-1-phenylocta-1,7-dien-3-one (**2h**) (Using $CDCl_3$ as solvent)



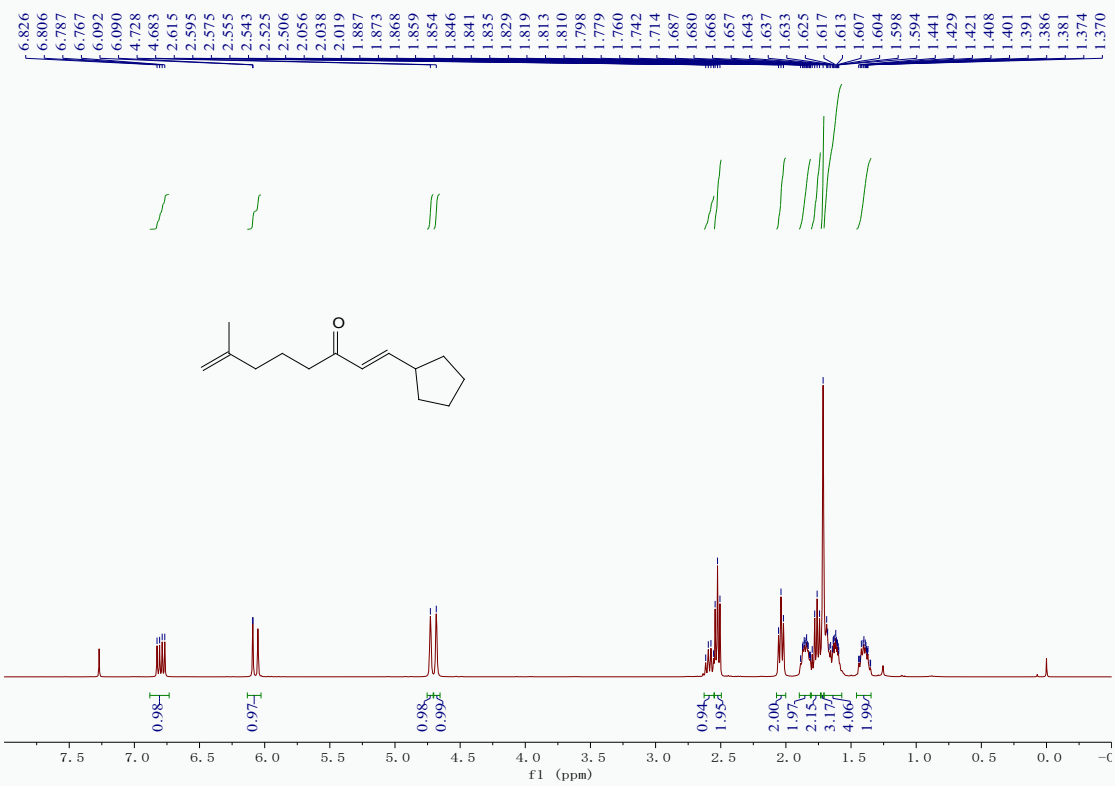


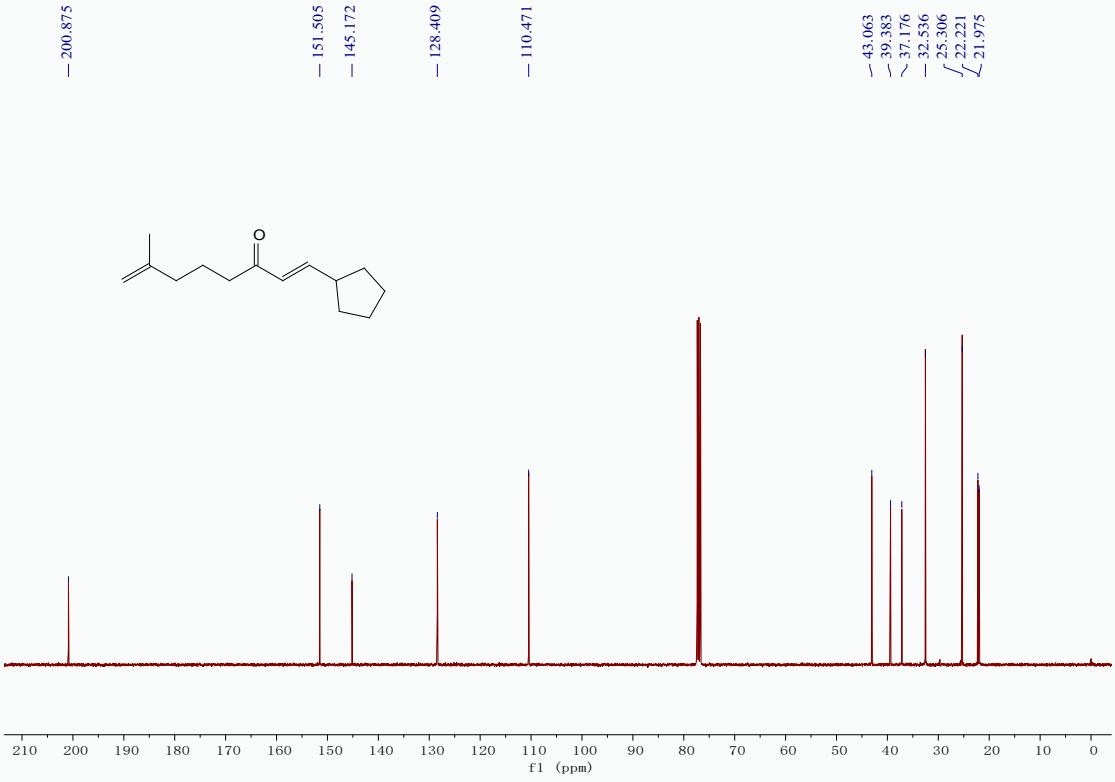
(*E*)-1-((1*R*, 3*S*)-3-acetyl-2, 2-dimethylcyclobutyl)-8-methylnona-2,8-dien-4-one (**2i**) (Using $CDCl_3$ as solvent)



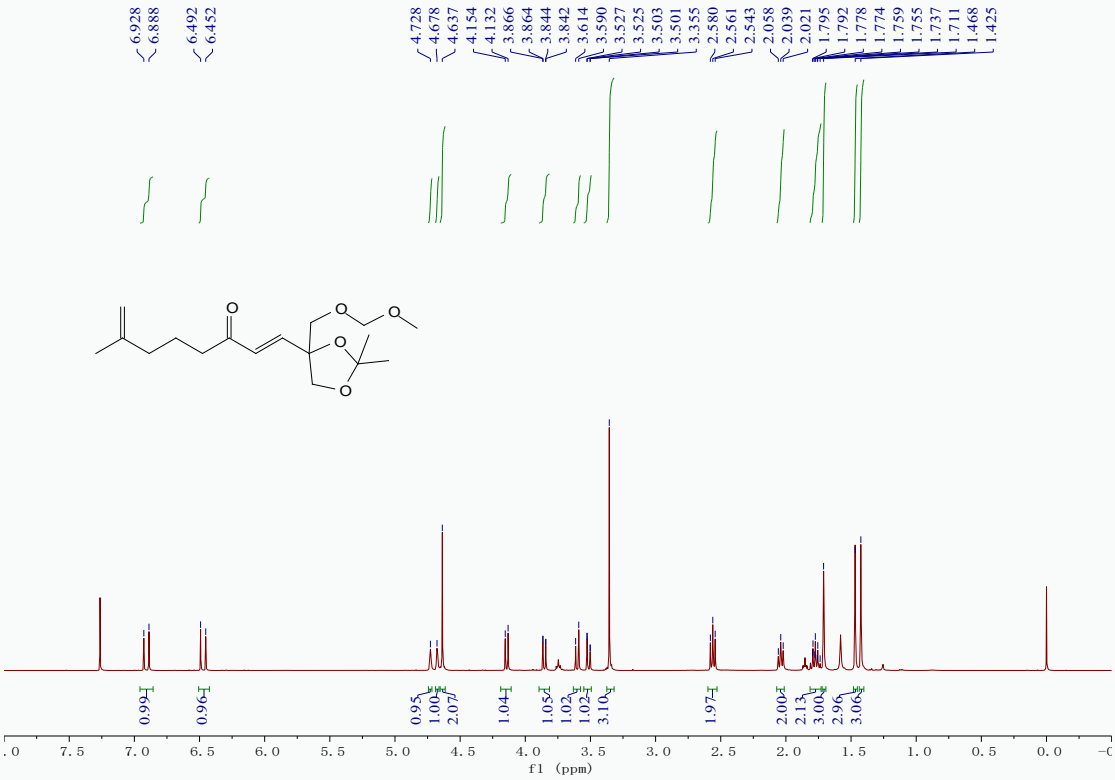


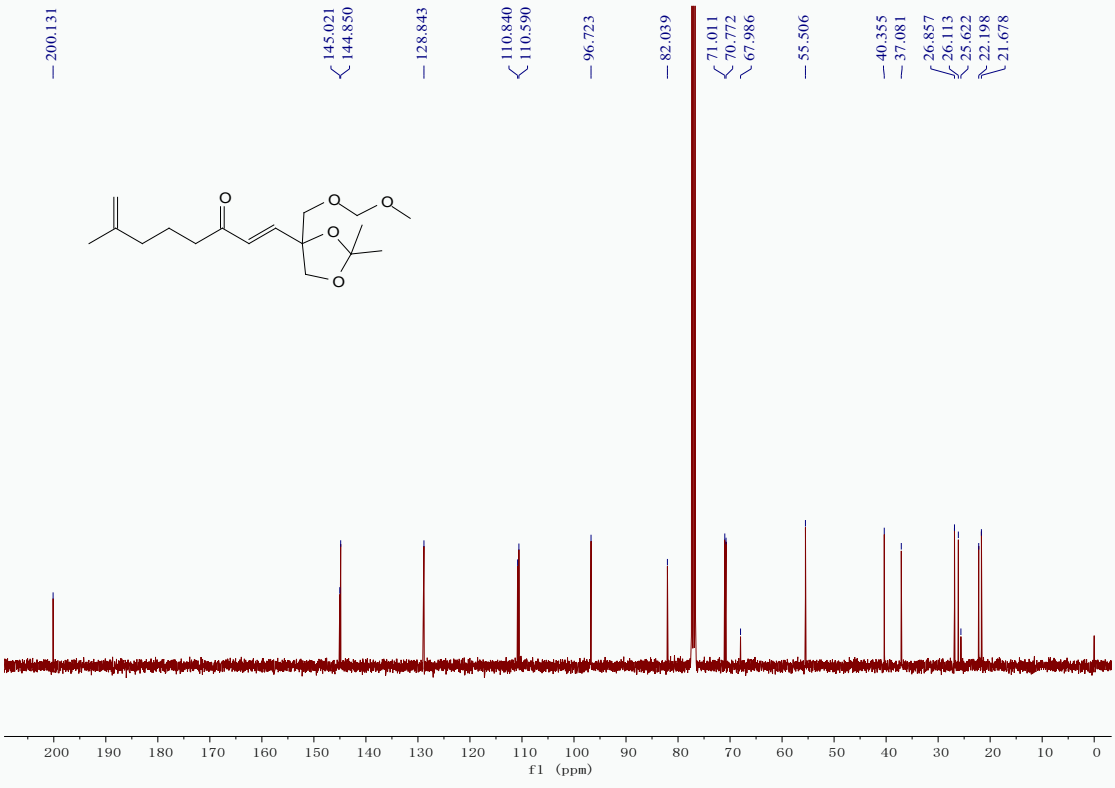
(*E*)-1-cyclopentyl-7-methylocta-1,7-dien-3-one (**2j**) (Using $CDCl_3$ as solvent)



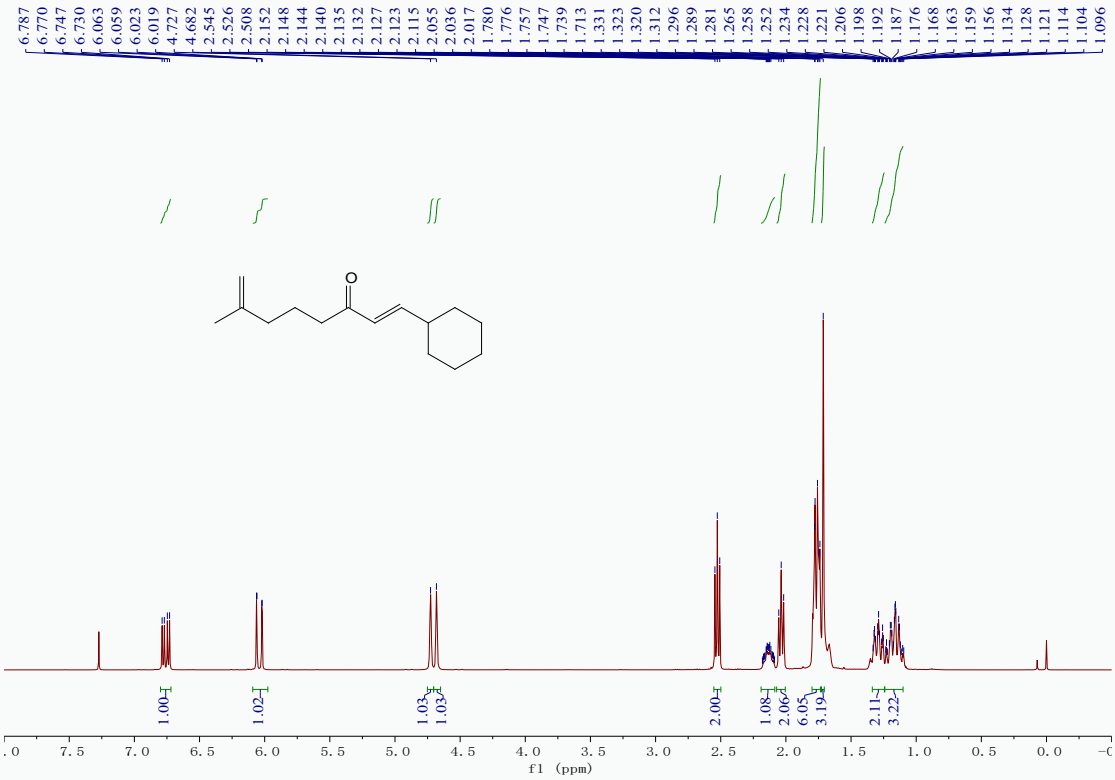


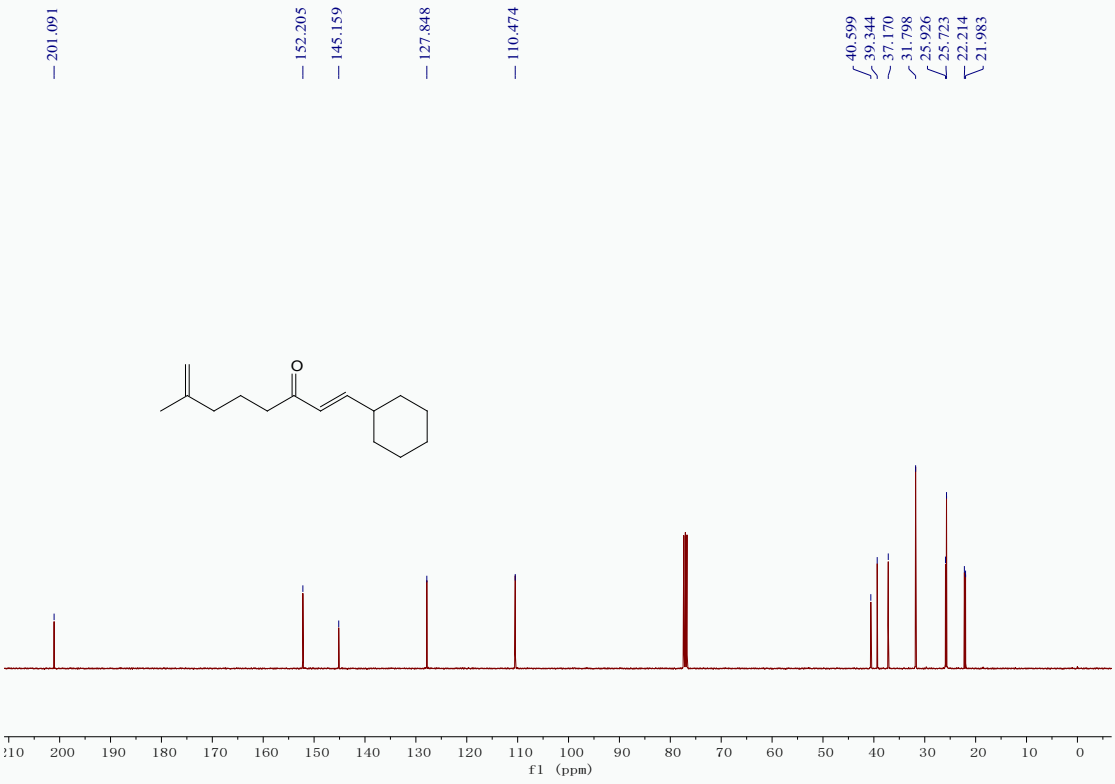
(*E*)-1-(4-((methoxymethoxy)methyl)-2,2-dimethyl-1,3-dioxolan-4-yl)-7-methylocta-1,7-dien-3-one (**2k**) (Using $CDCl_3$ as solvent)



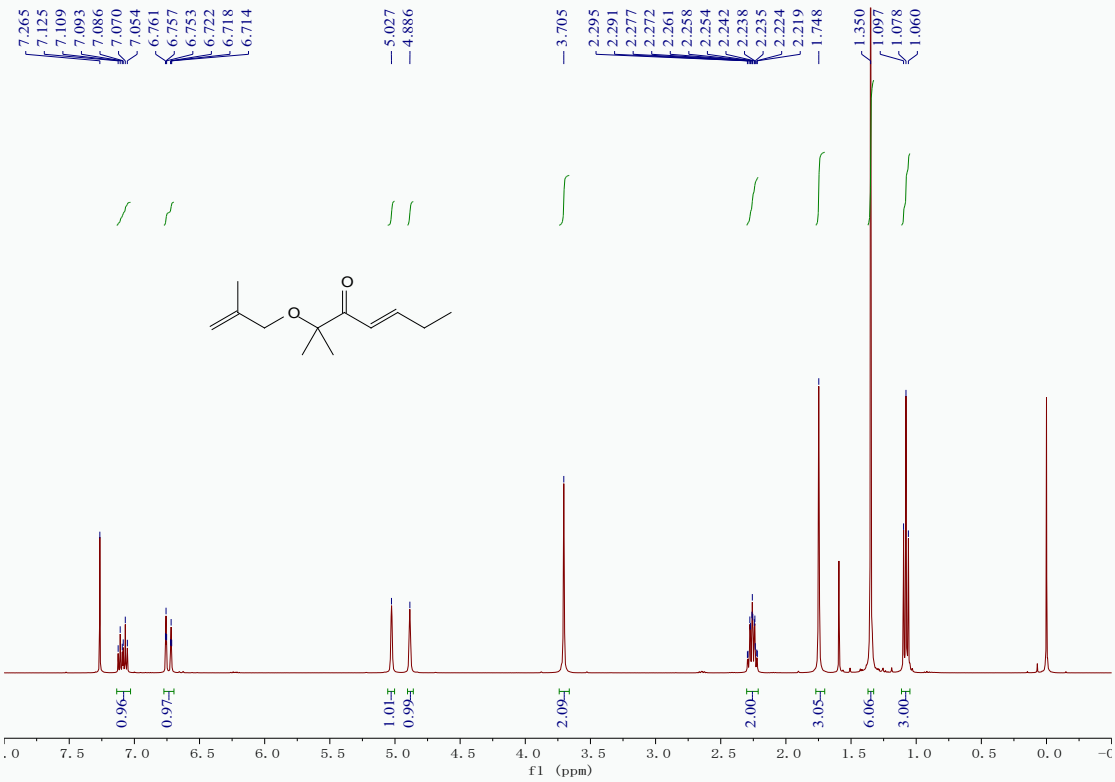


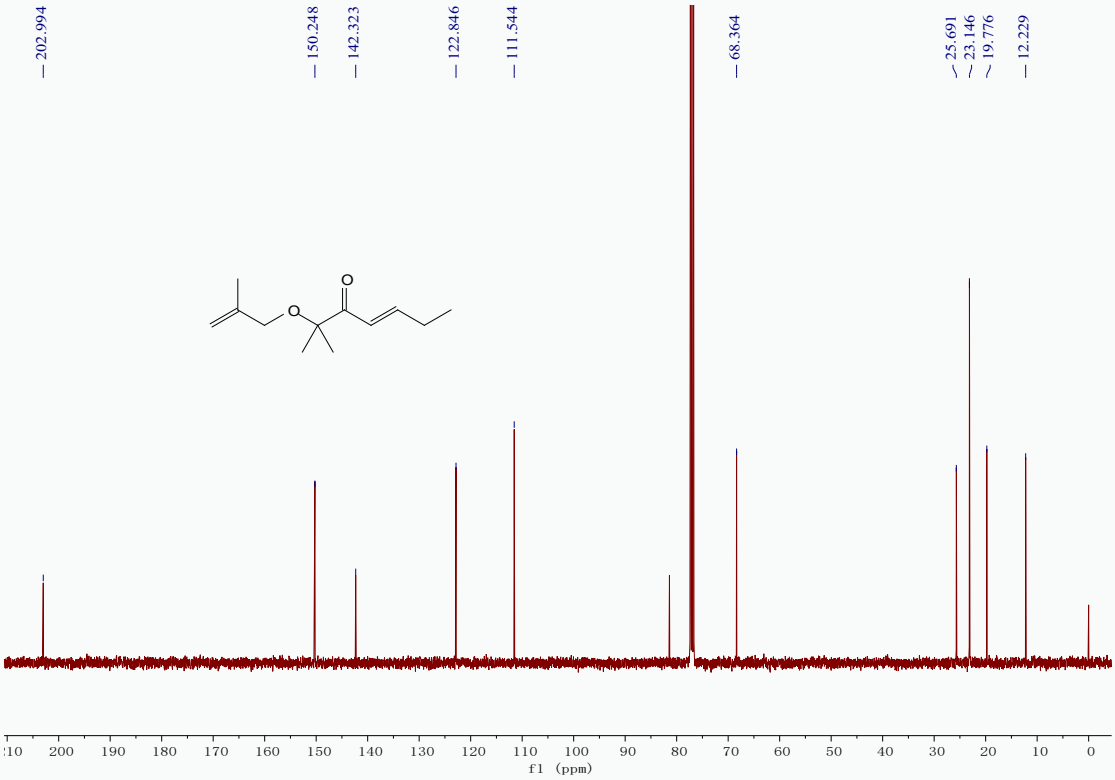
(*E*)-1-cyclohexyl-7-methylocta-1,7-dien-3-one (**2l**) (Using $CDCl_3$ as solvent)



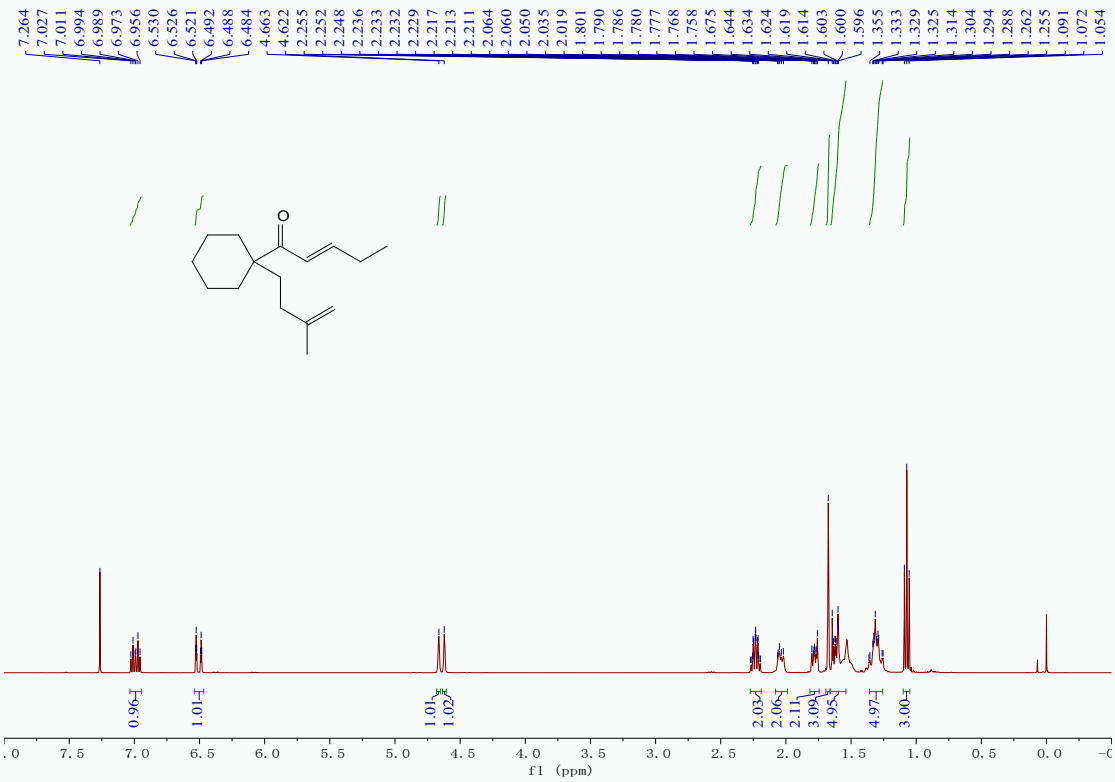


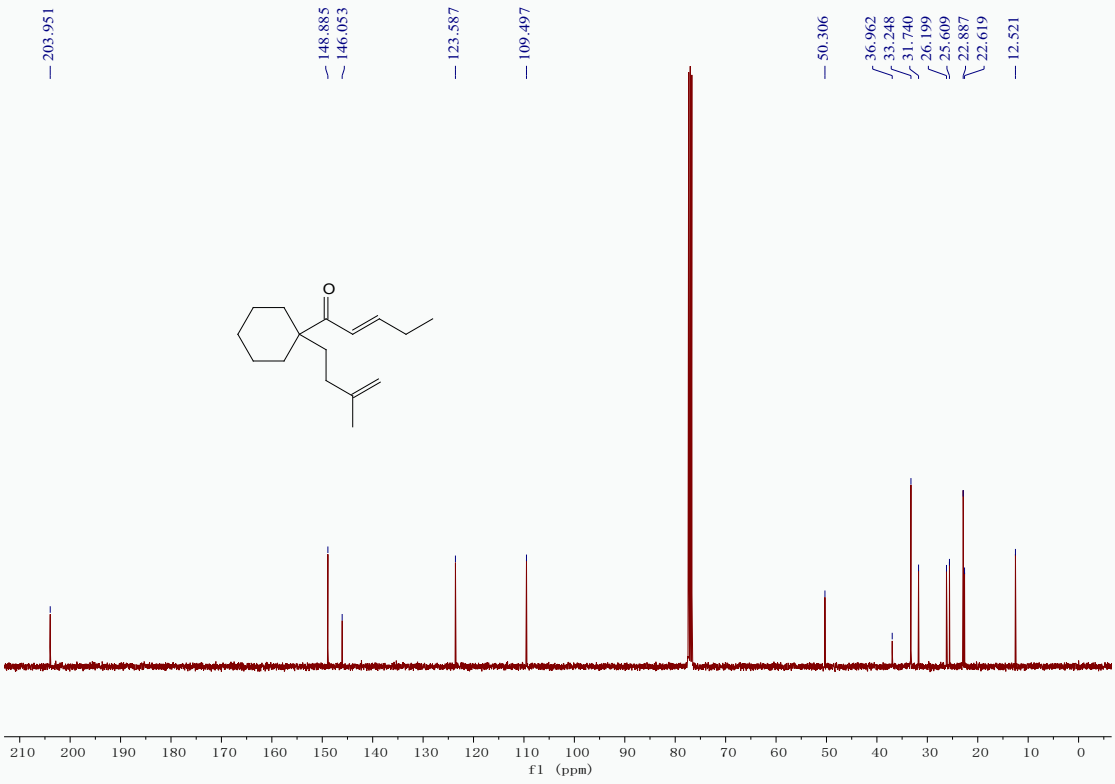
(*E*)-2-methyl-2-((2-methylallyl)oxy)hept-4-en-3-one (**2m**) (Using $CDCl_3$ as solvent)



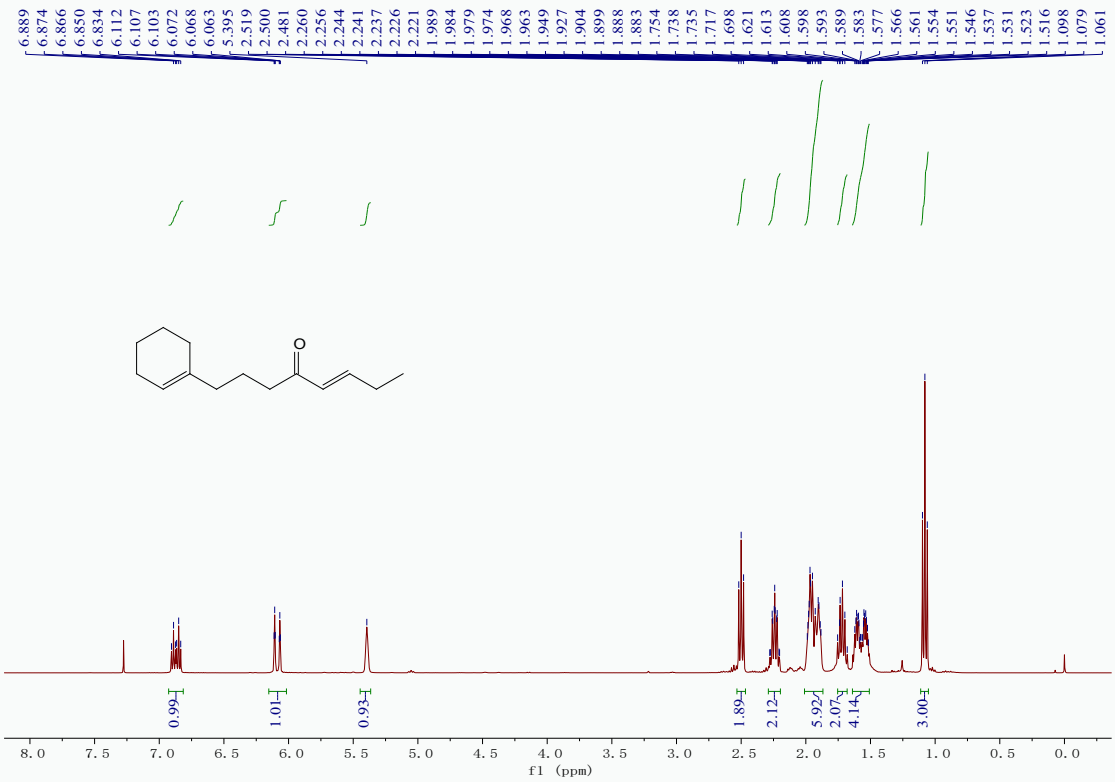


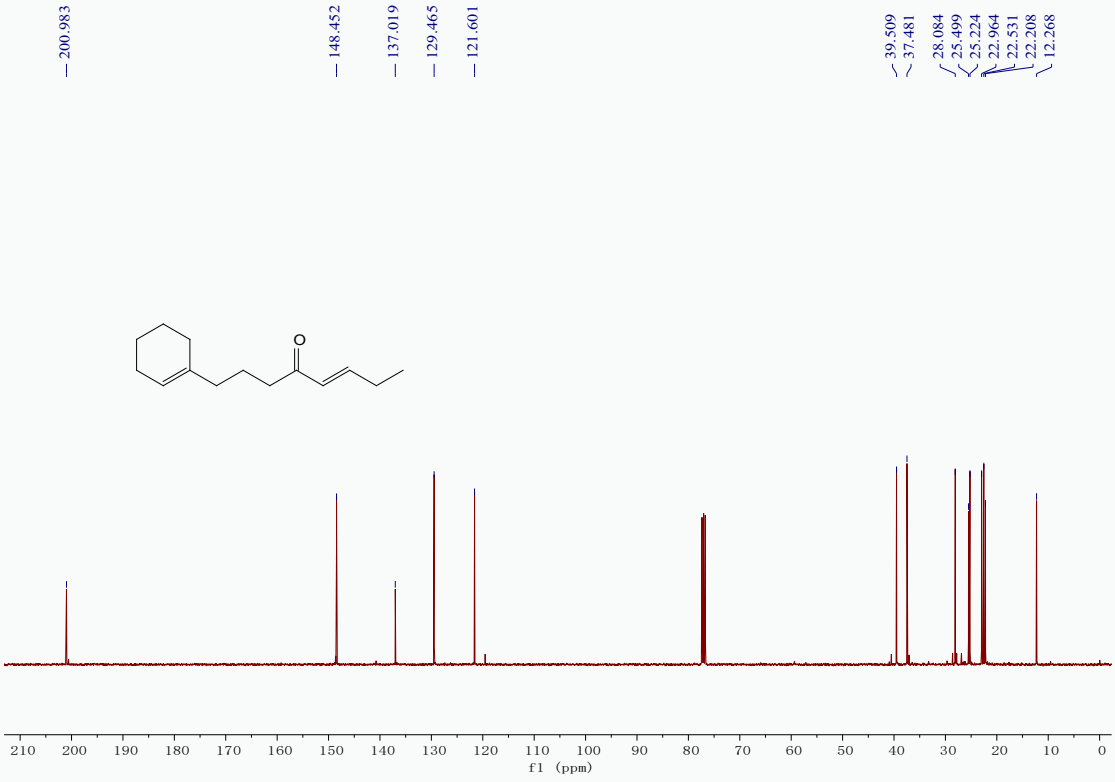
(*E*)-1-(1-(3-methylbut-3-en-1-yl)cyclohexyl)pent-2-en-1-one (**2n**) (Using $CDCl_3$ as solvent)



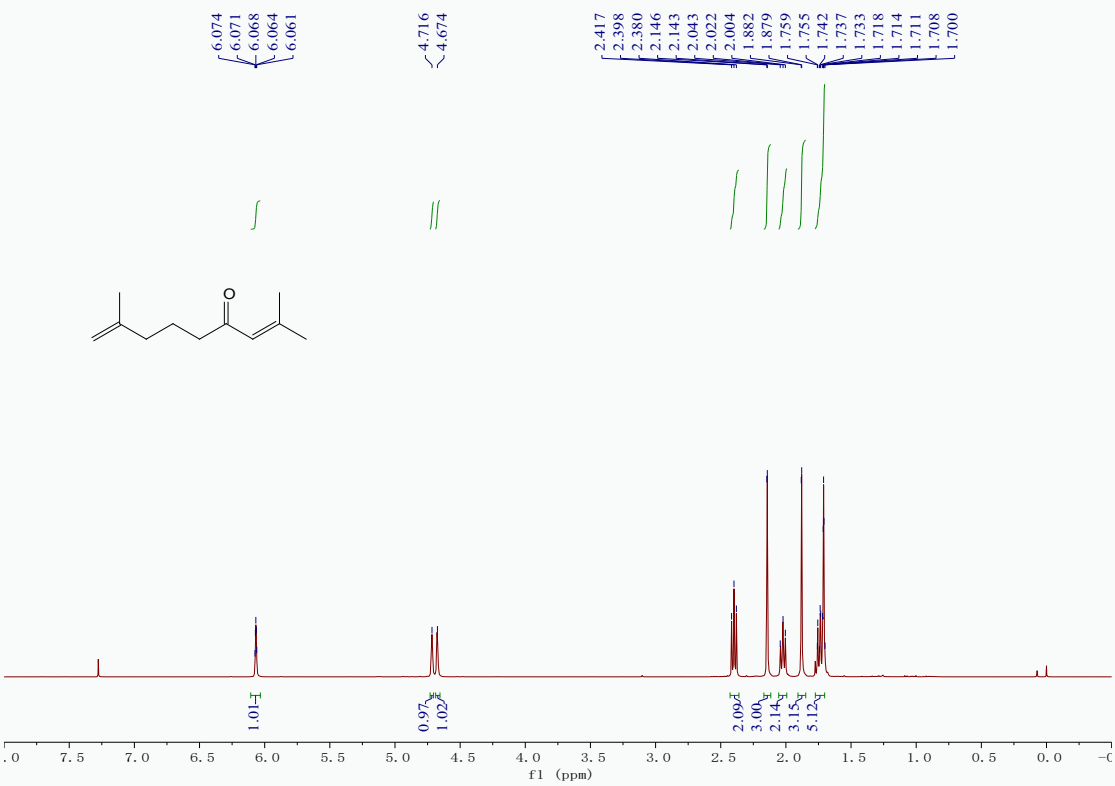


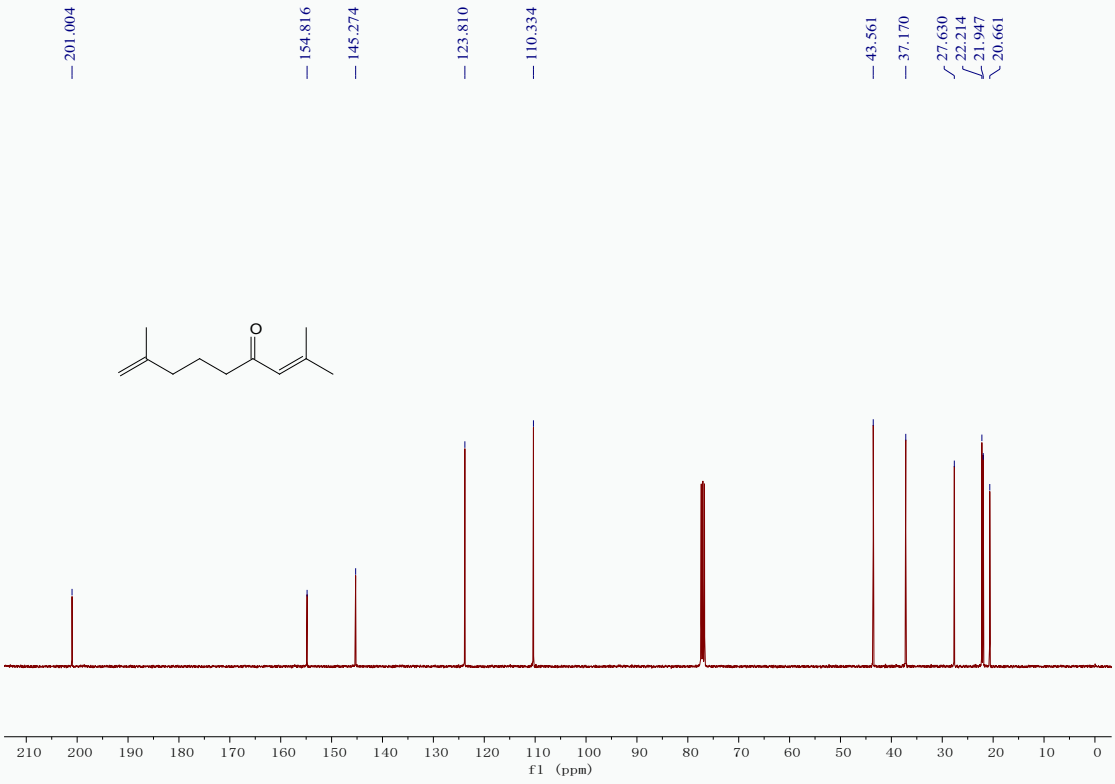
(*E*)-1-(cyclohex-1-en-1-yl)oct-5-en-4-one (**2o**) (Using $CDCl_3$ as solvent)



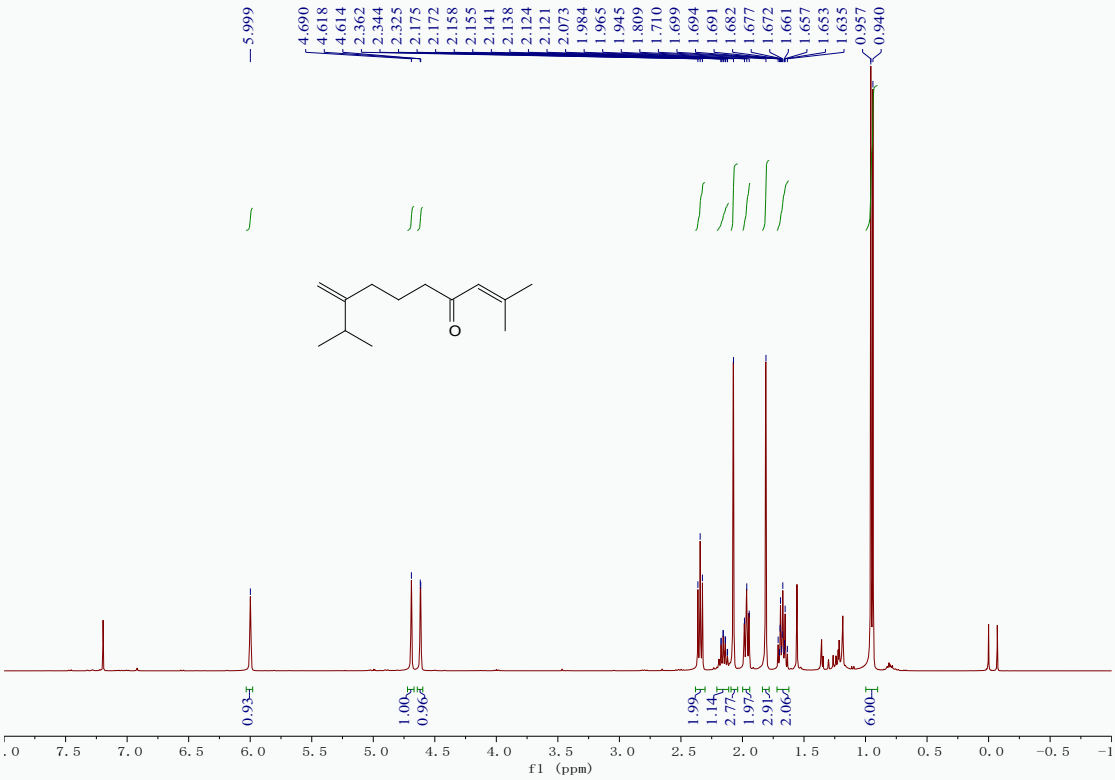


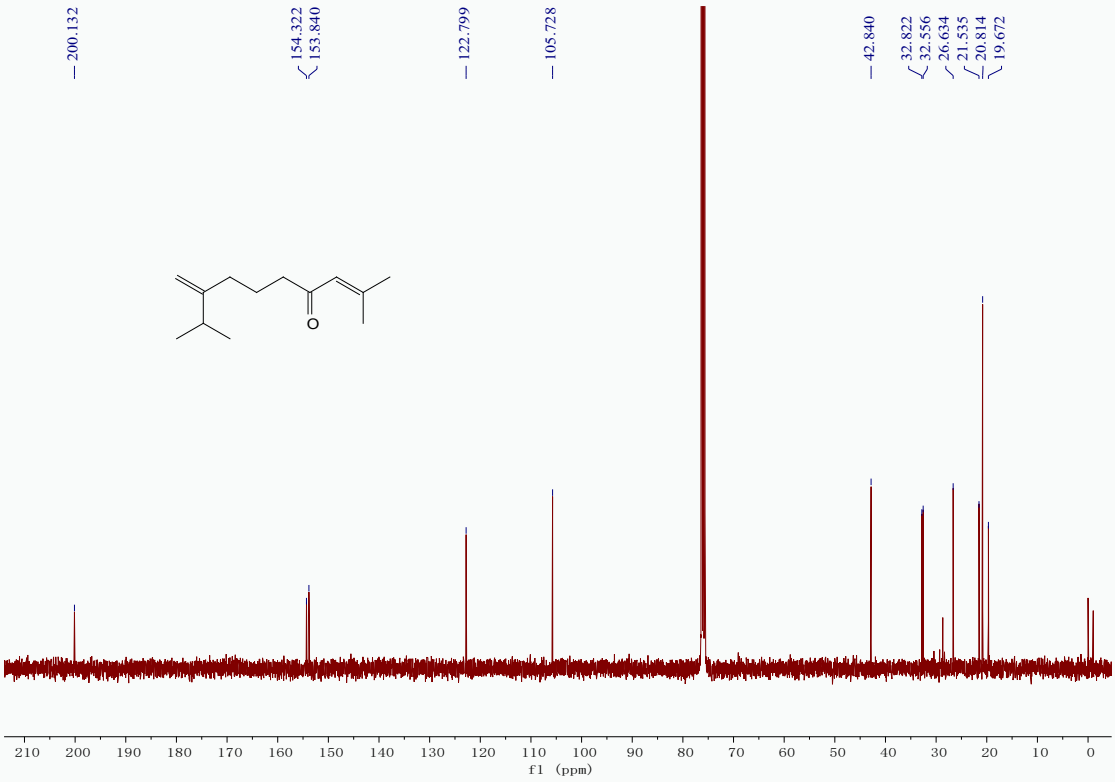
2,8-dimethylnona-2,8-dien-4-one (**2p**) (Using $CDCl_3$ as solvent)



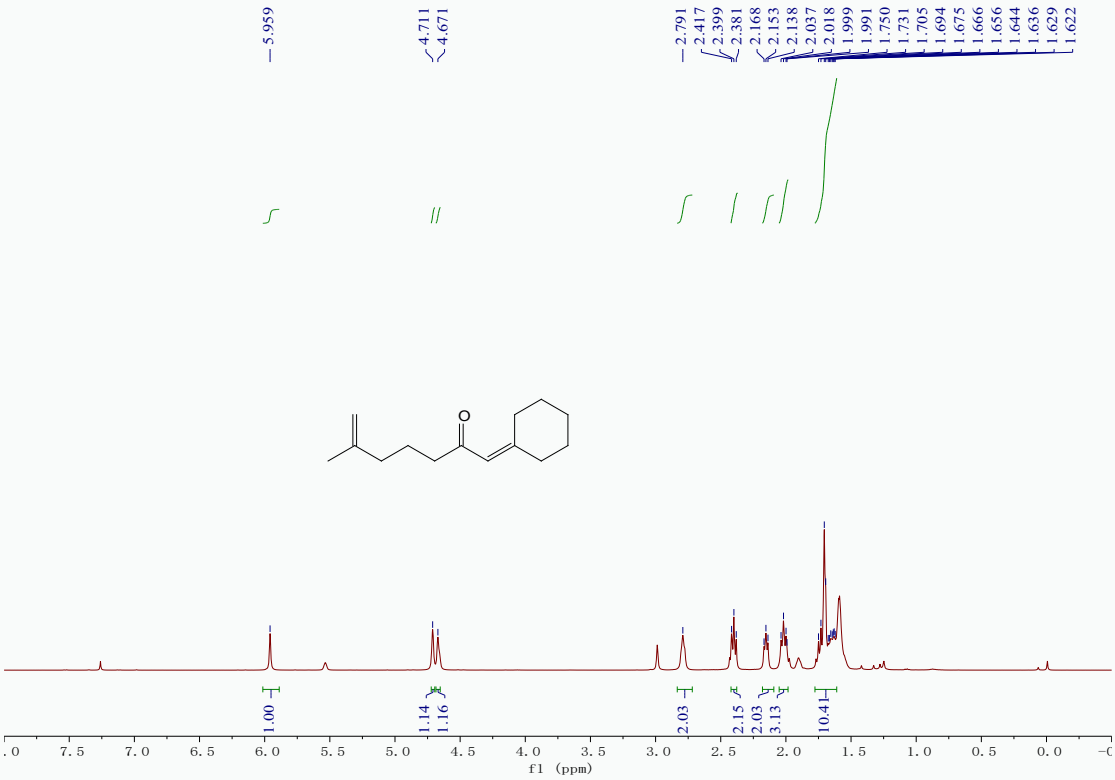


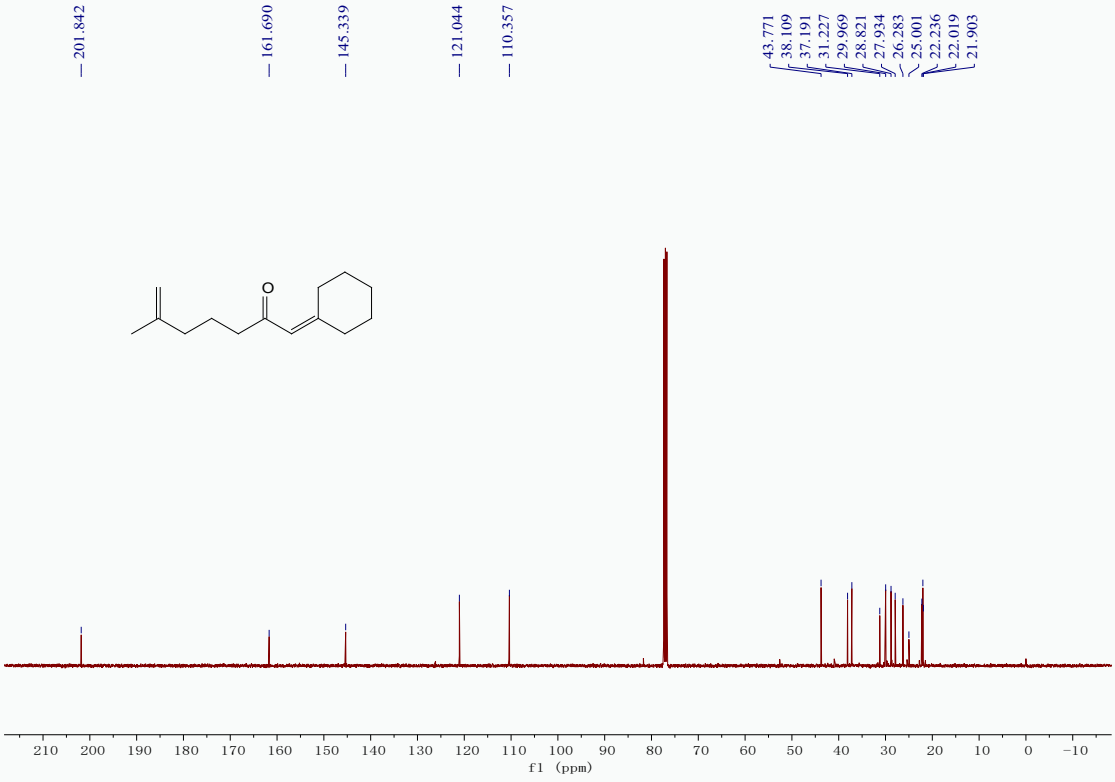
2,9-dimethyl-8-methylenedec-2-en-4-one (**2q**) (Using $CDCl_3$ as solvent)



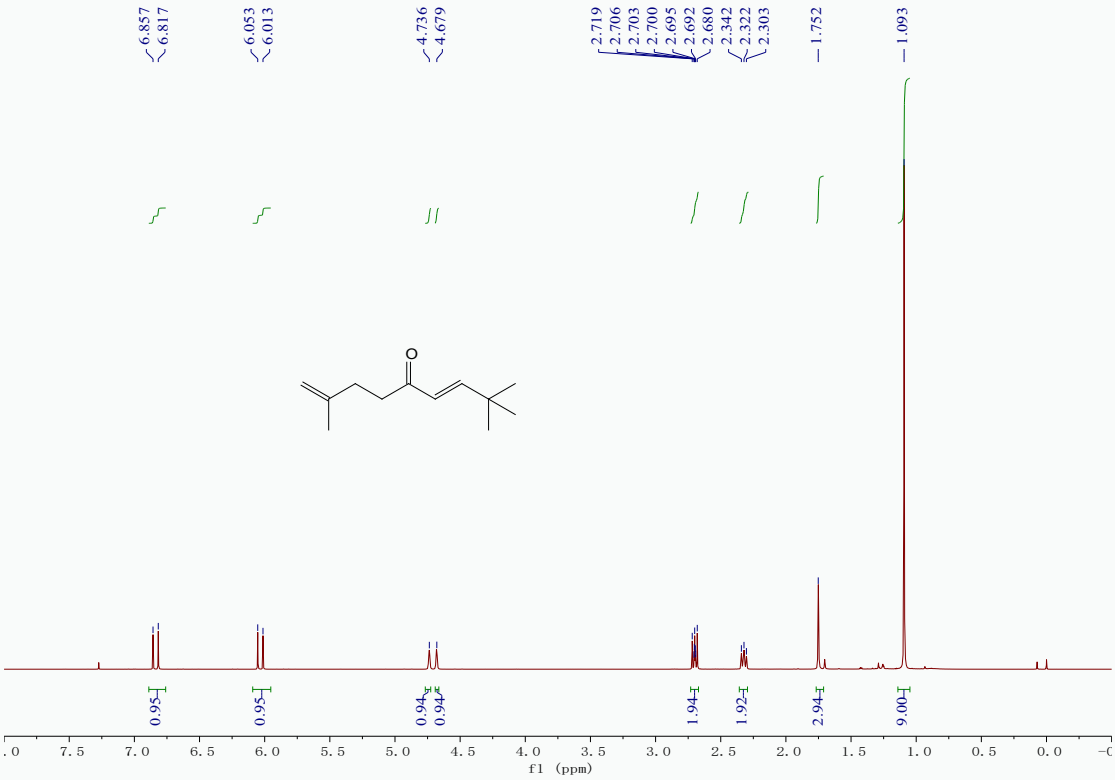


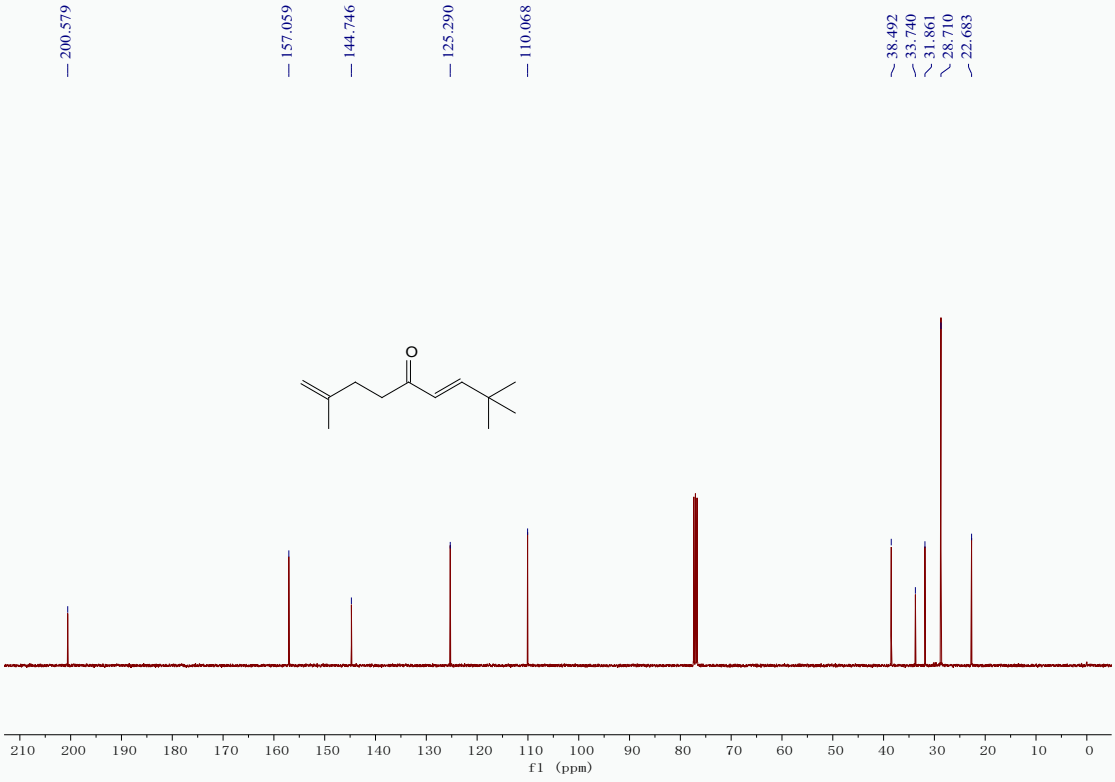
1-cyclohexylidene-6-methylhept-6-en-2-one (**2r**) (Using $CDCl_3$ as solvent)



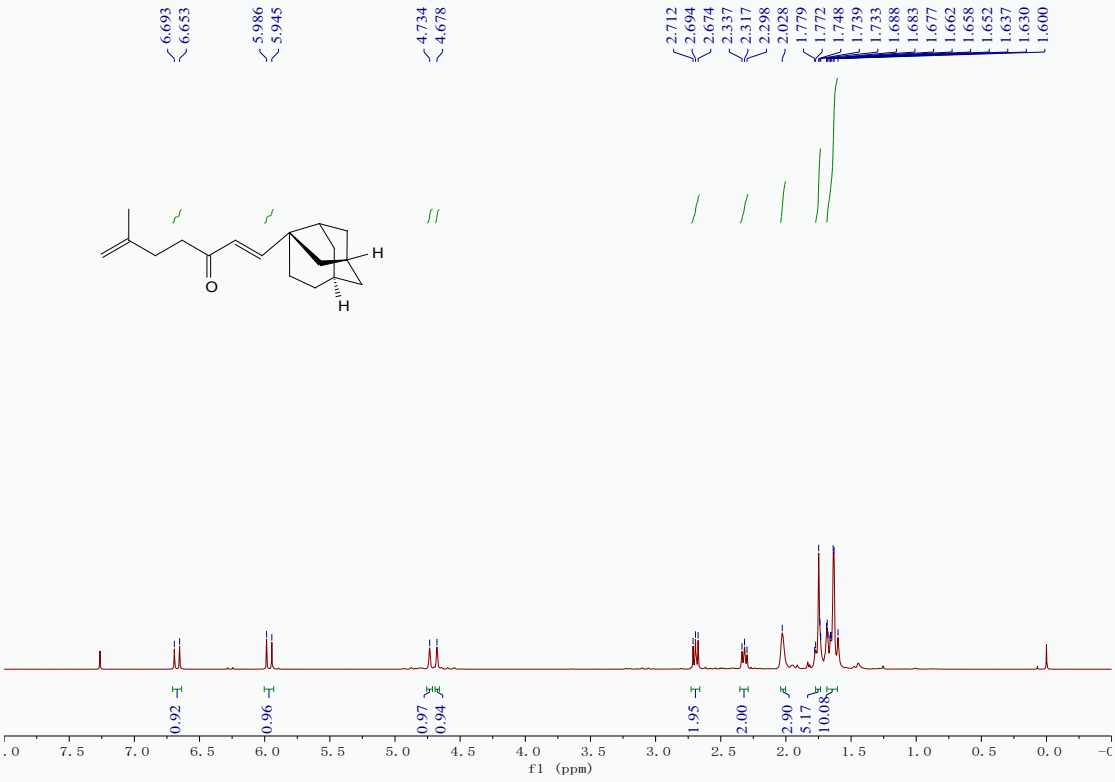


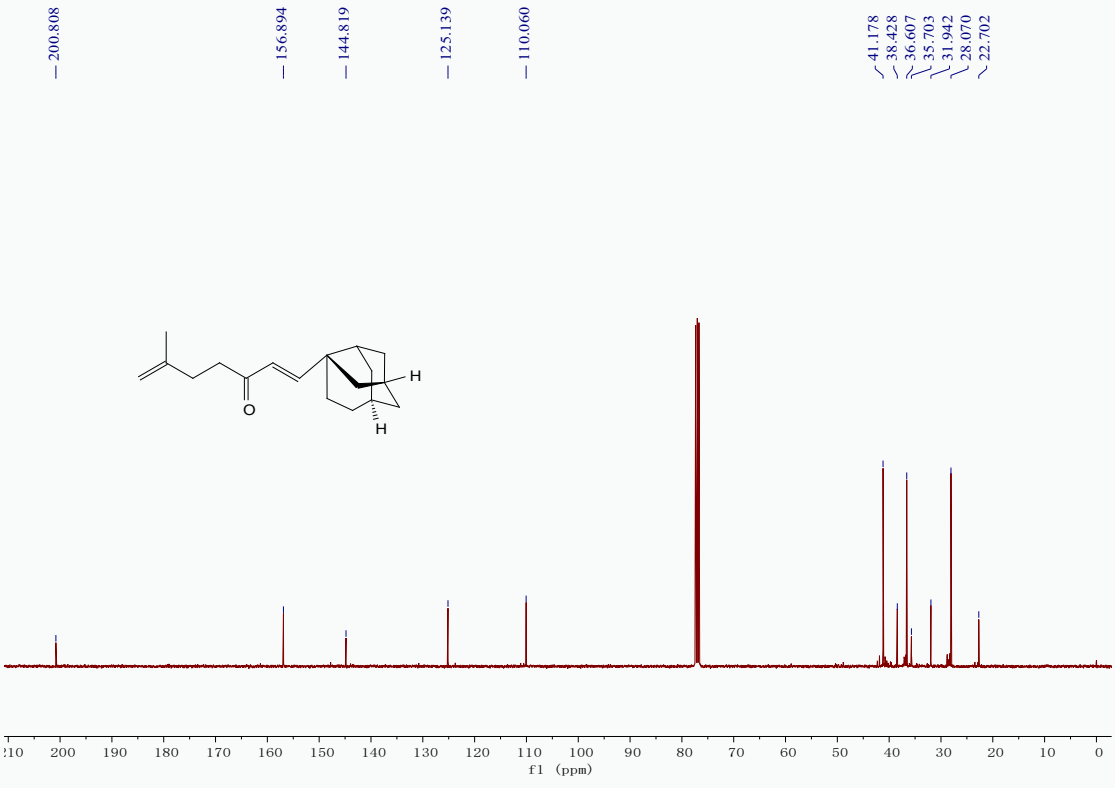
(*E*)-2,8,8-trimethylnona-1,6-dien-5-one (**2s**) (Using $CDCl_3$ as solvent)



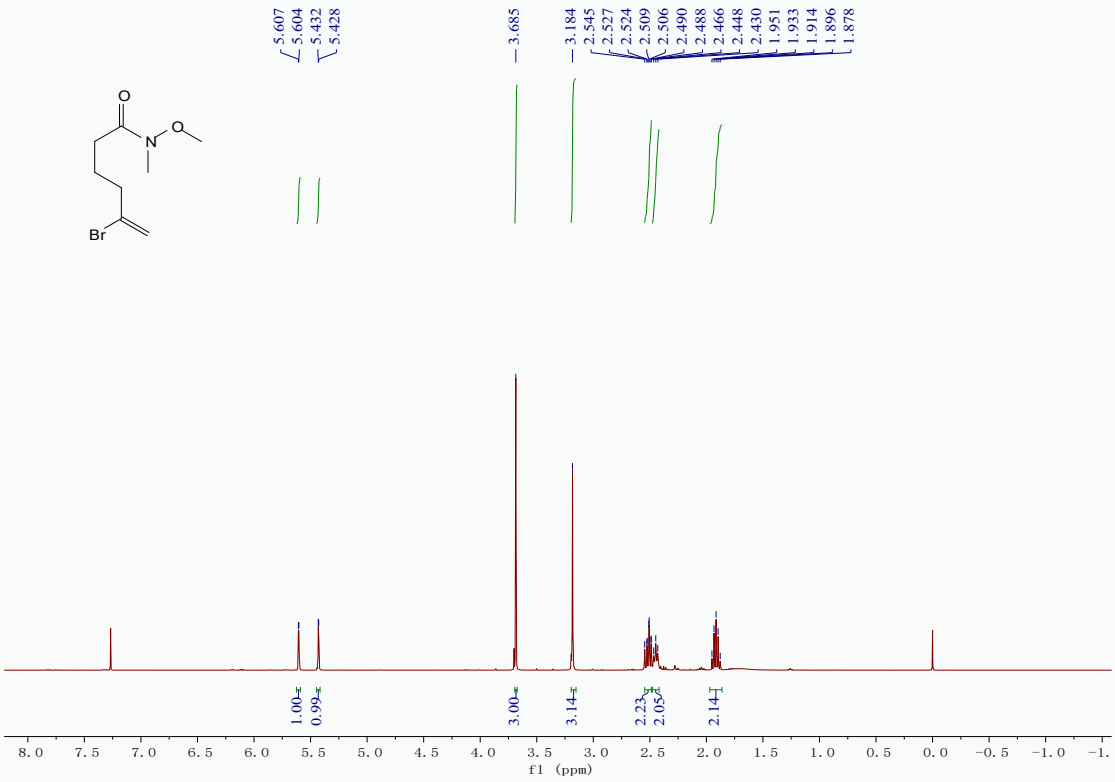


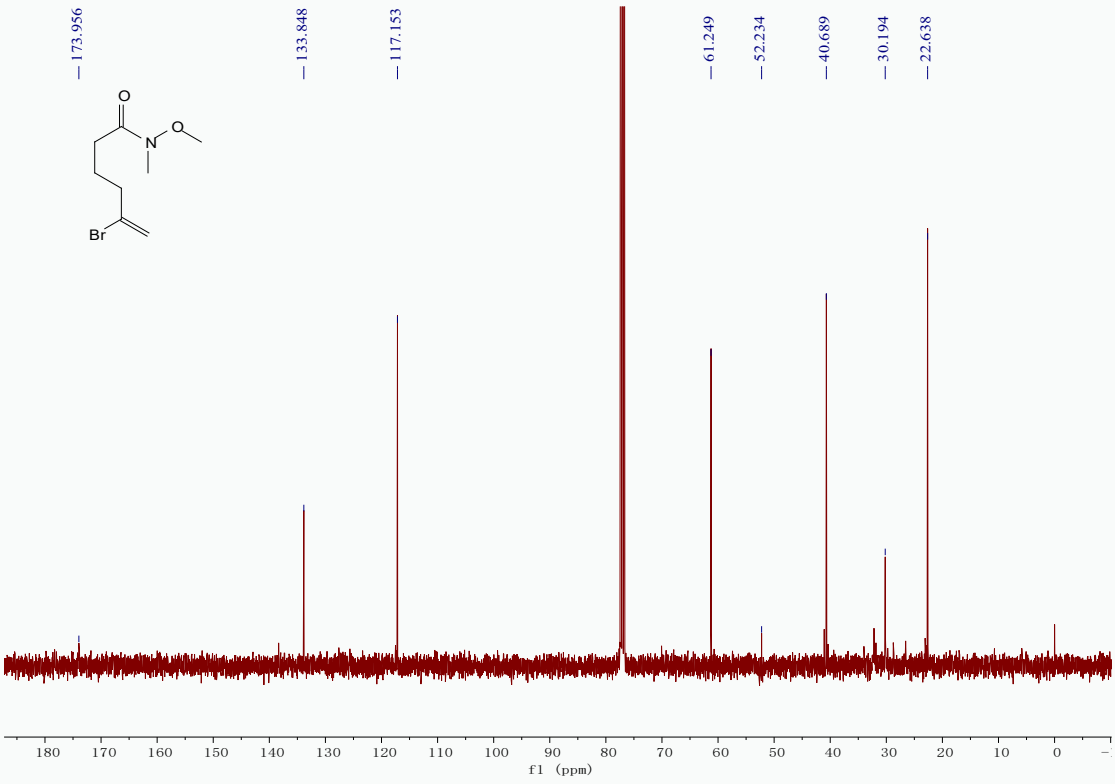
(*E*)-7-methyl-1-((*2S*, *3aS*, *5R*)-octahydro-7aH-2,5-methanoinden-7a-yl)octa-1,7-dien-3-one (**2t**) (Using $CDCl_3$ as solvent)



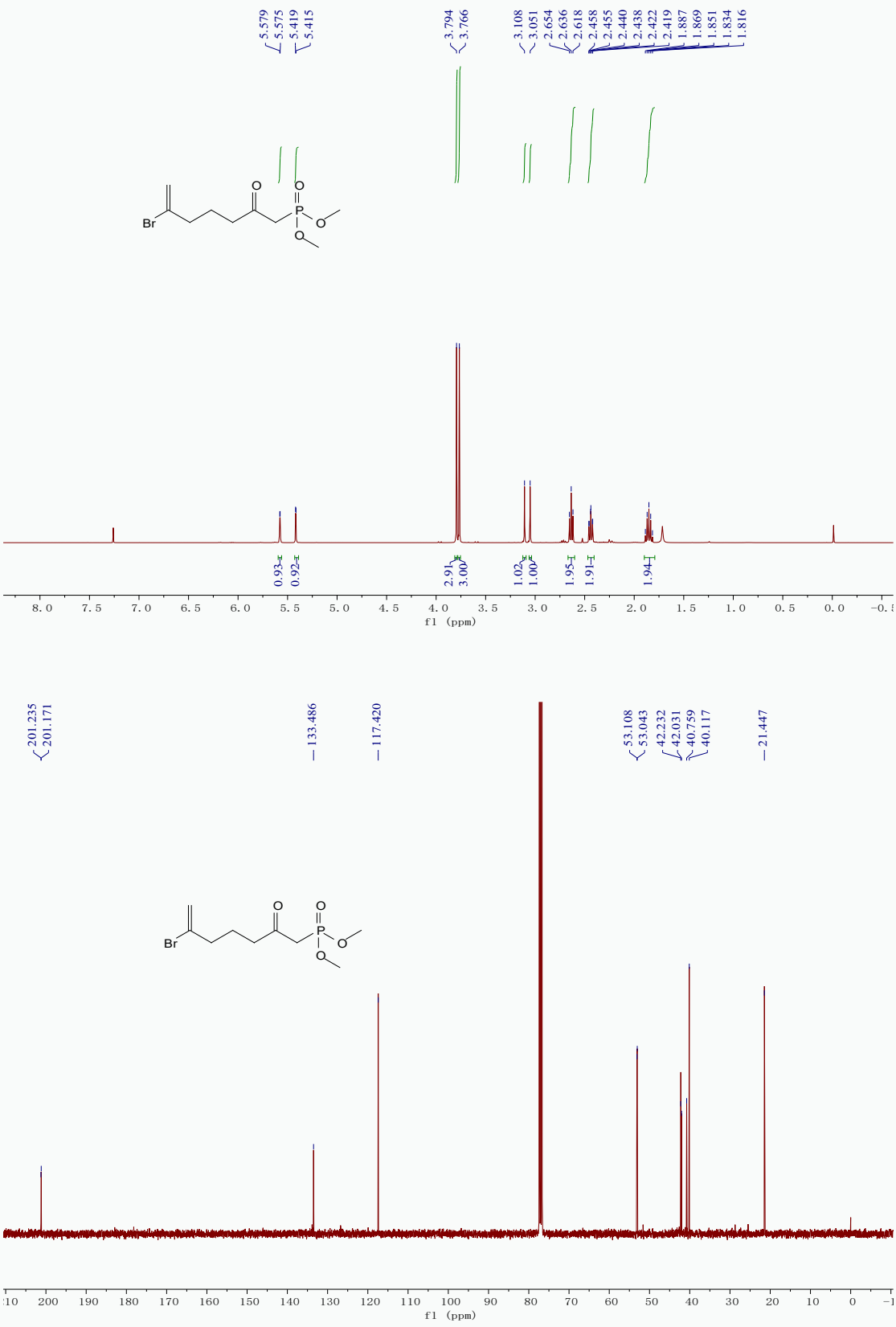


5-bromo-*N*-methoxy-*N*-methylhex-5-enamide (**15**) (Using $CDCl_3$ as solvent)

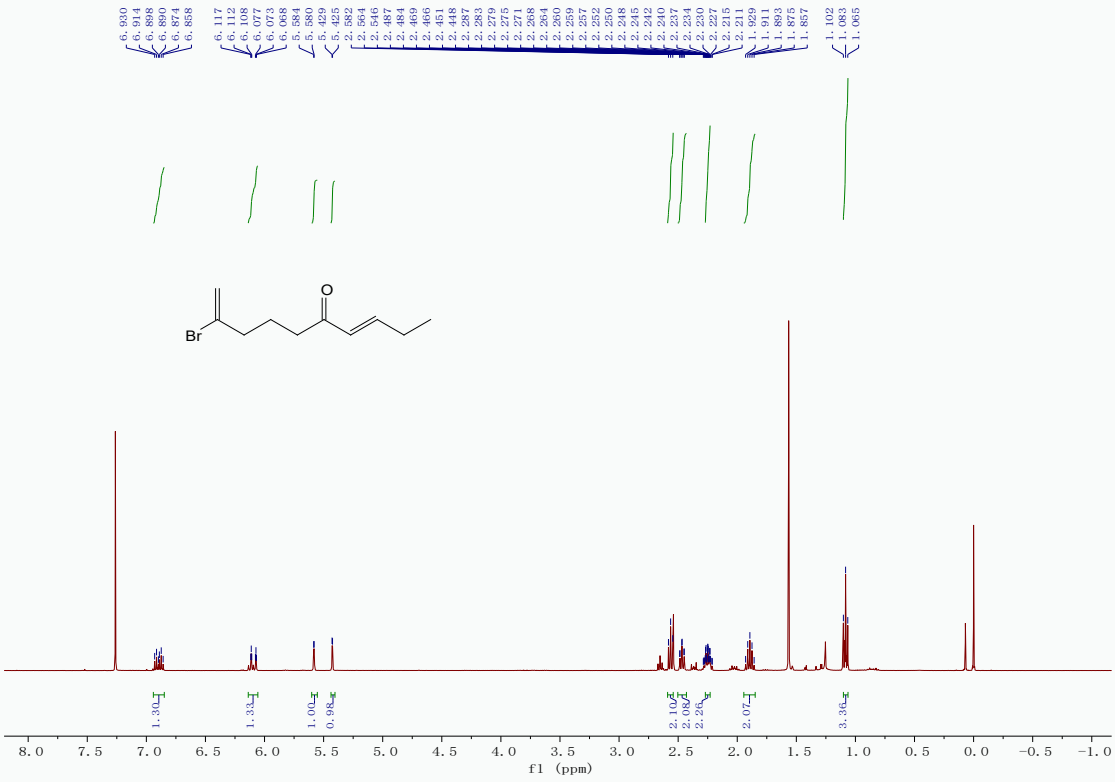


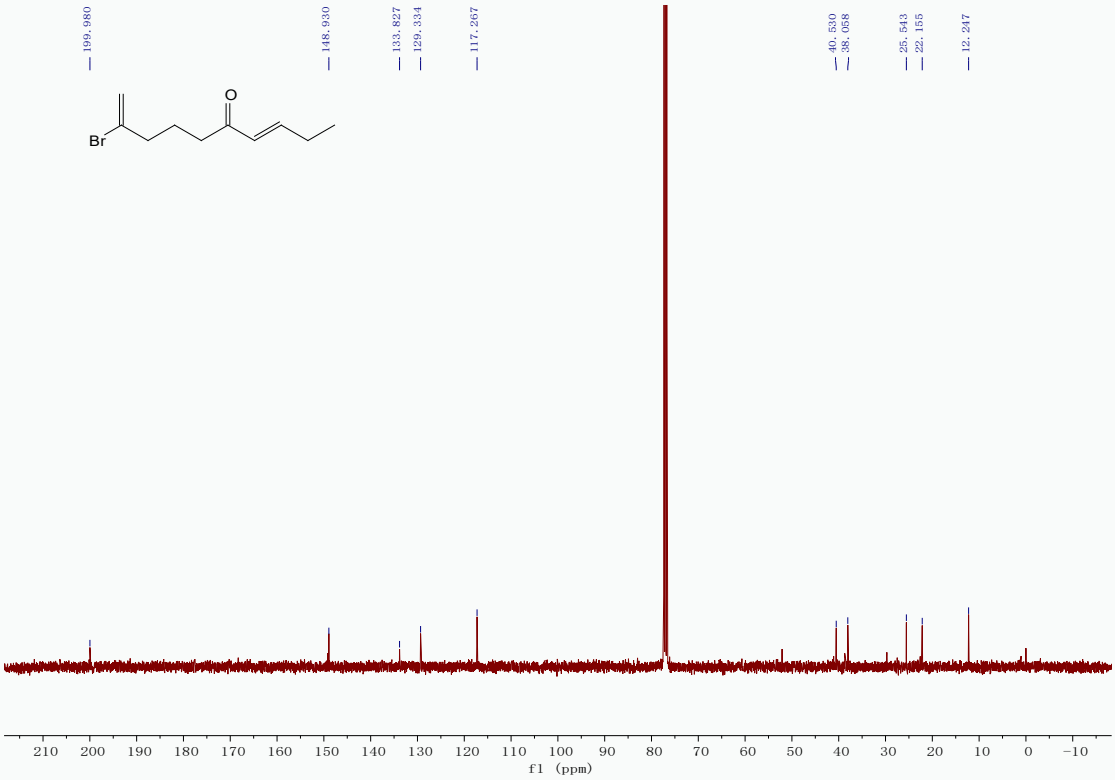


dimethyl (6-bromo-2-oxohept-6-en-1-yl)phosphonate (**16**) (Using $CDCl_3$ as solvent)

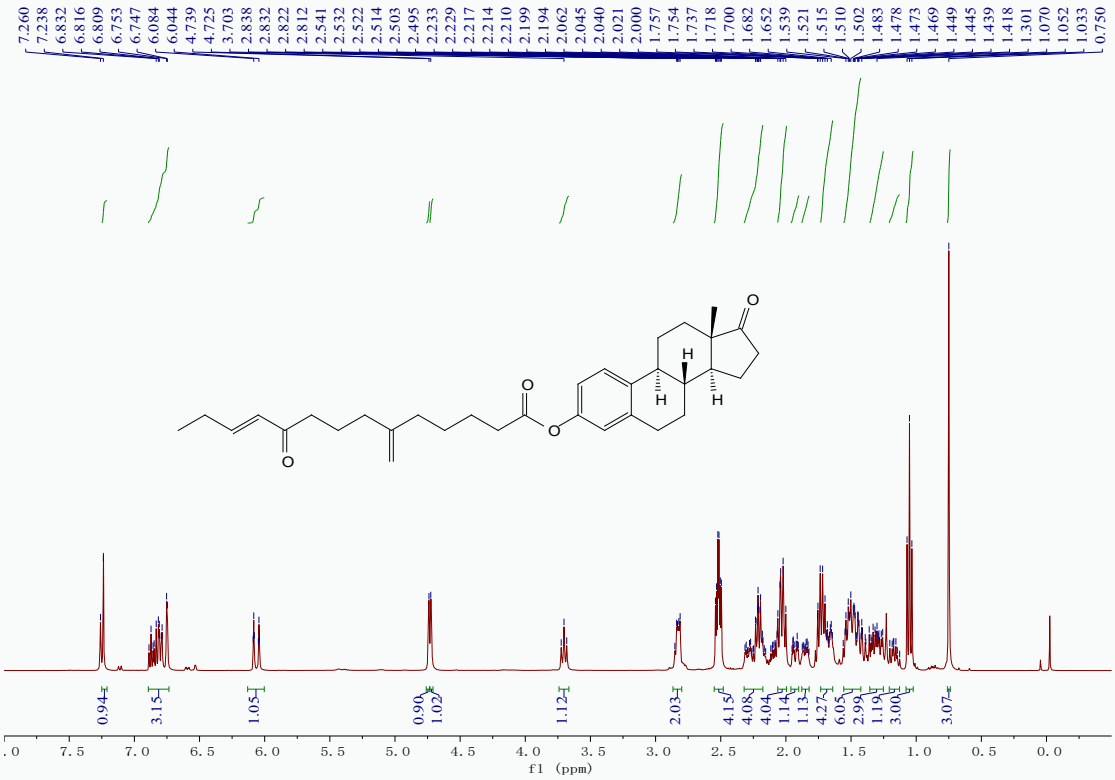


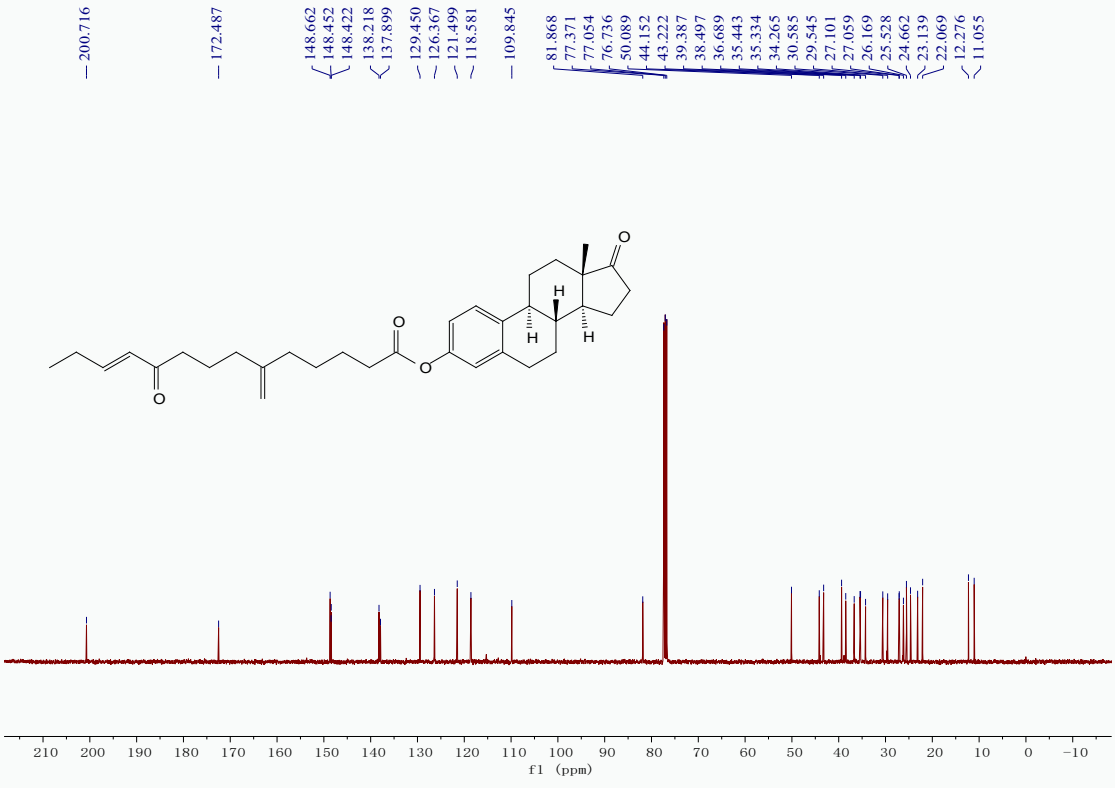
(E)-9-bromodeca-3,9-dien-5-one (**17**) (Using $CDCl_3$ as solvent)



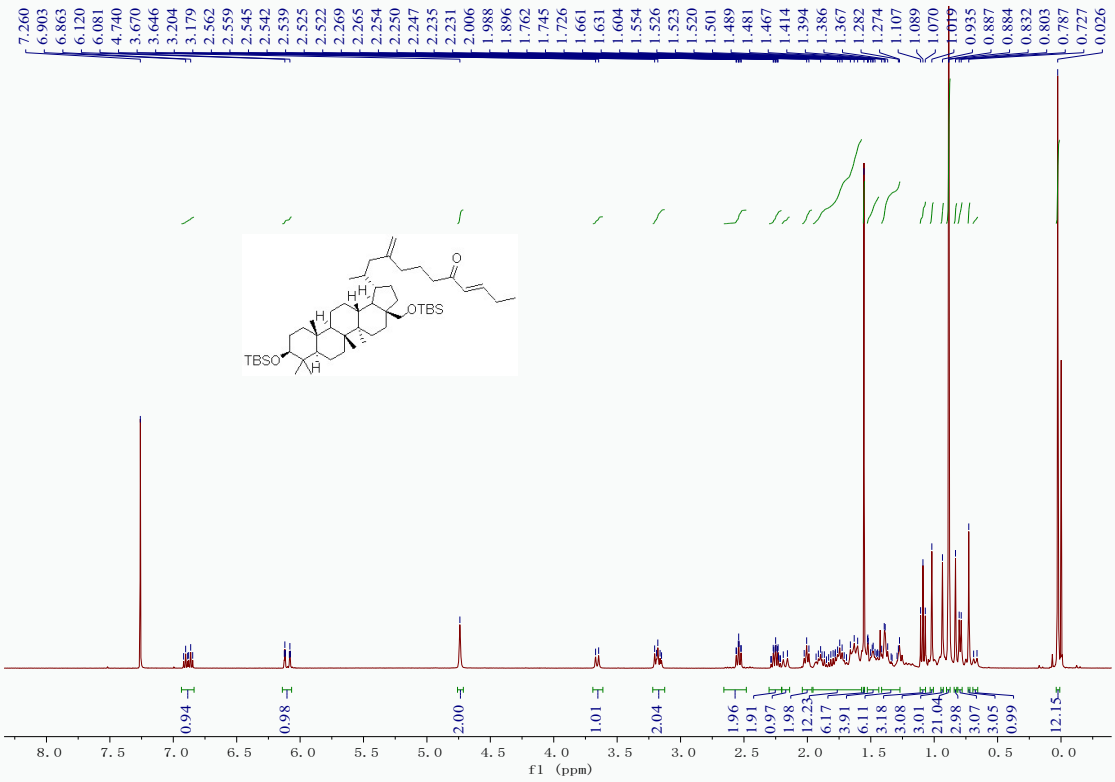


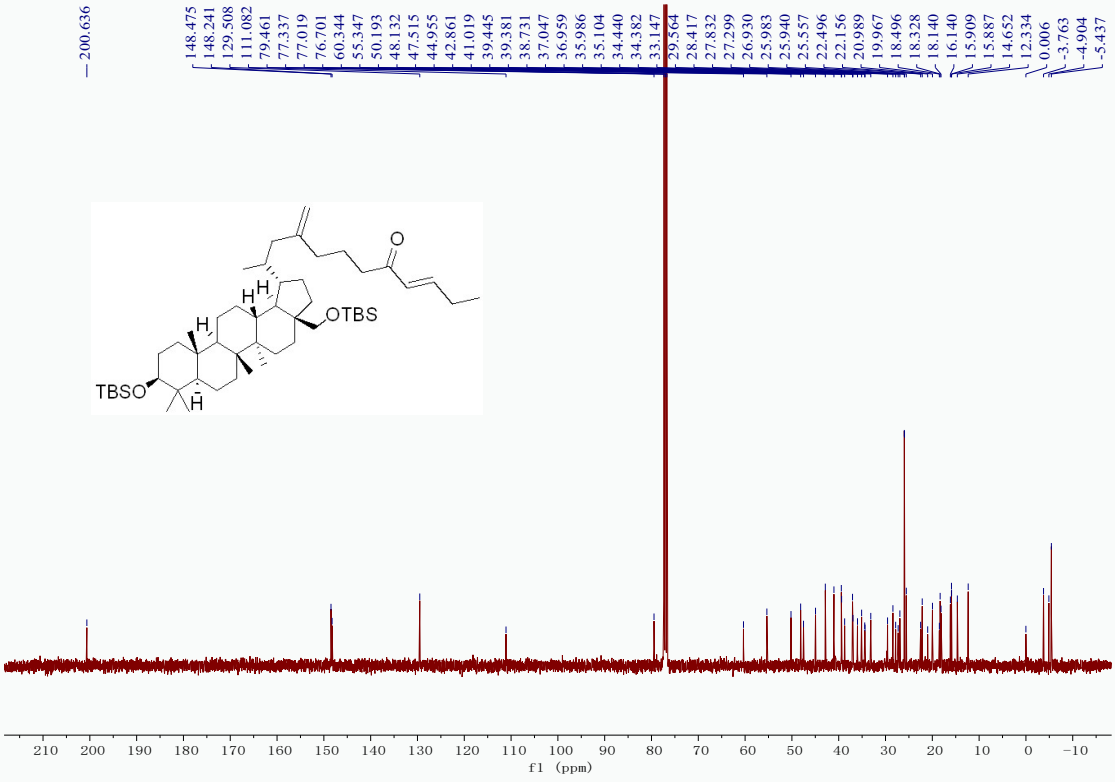
(8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta [a]phenanthren-3-yl (*E*)-6-methylene-10-oxotetradec-11-enoate (**2u**) (Using $CDCl_3$ as solvent)



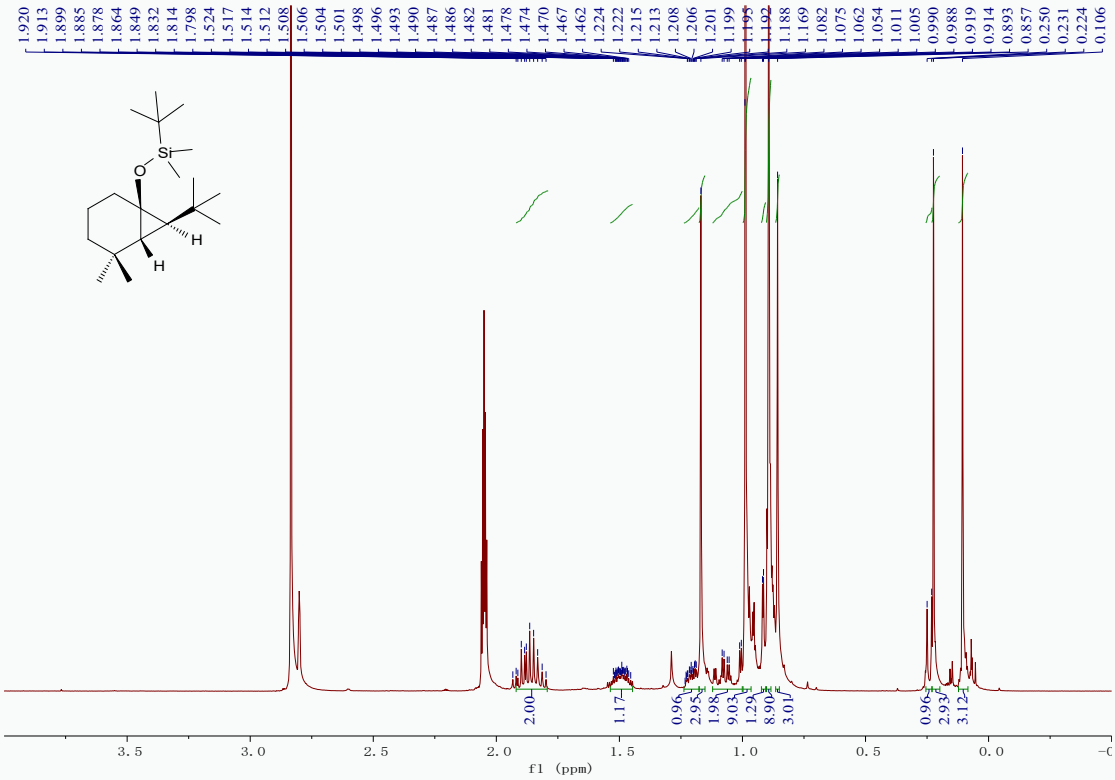


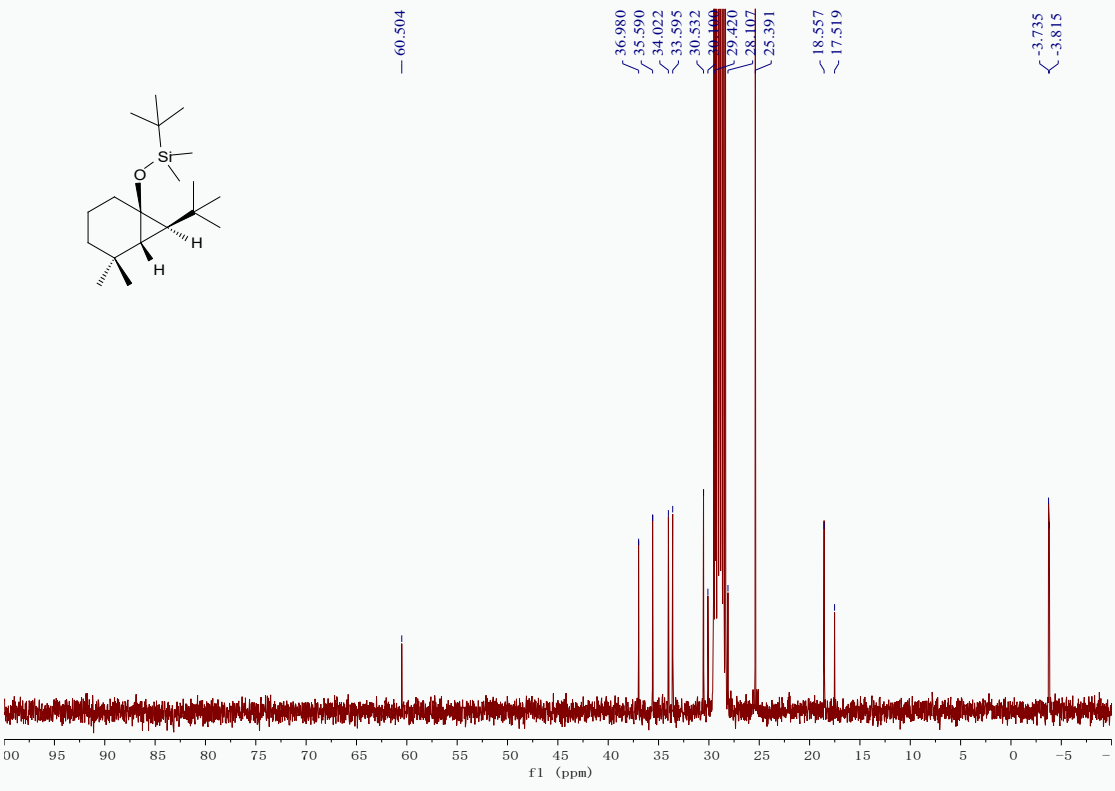
(*E*)-11-((3a*S*,5a*R*,5b*R*,7a*R*,9*S*,11a*R*,11b*R*,13a*R*,13b*R*)-9-((tert-butyldimethylsilyl)oxy)-3a-(((tert-butyldimethylsilyl)oxy)methyl)-5a,5b,8,8,11a-pentamethylicosahydro-1H-cyclopenta[a]chrysen-1-yl)-9-methylenedodec-3-en-5-one (2**v**) (Using $CDCl_3$ as solvent)



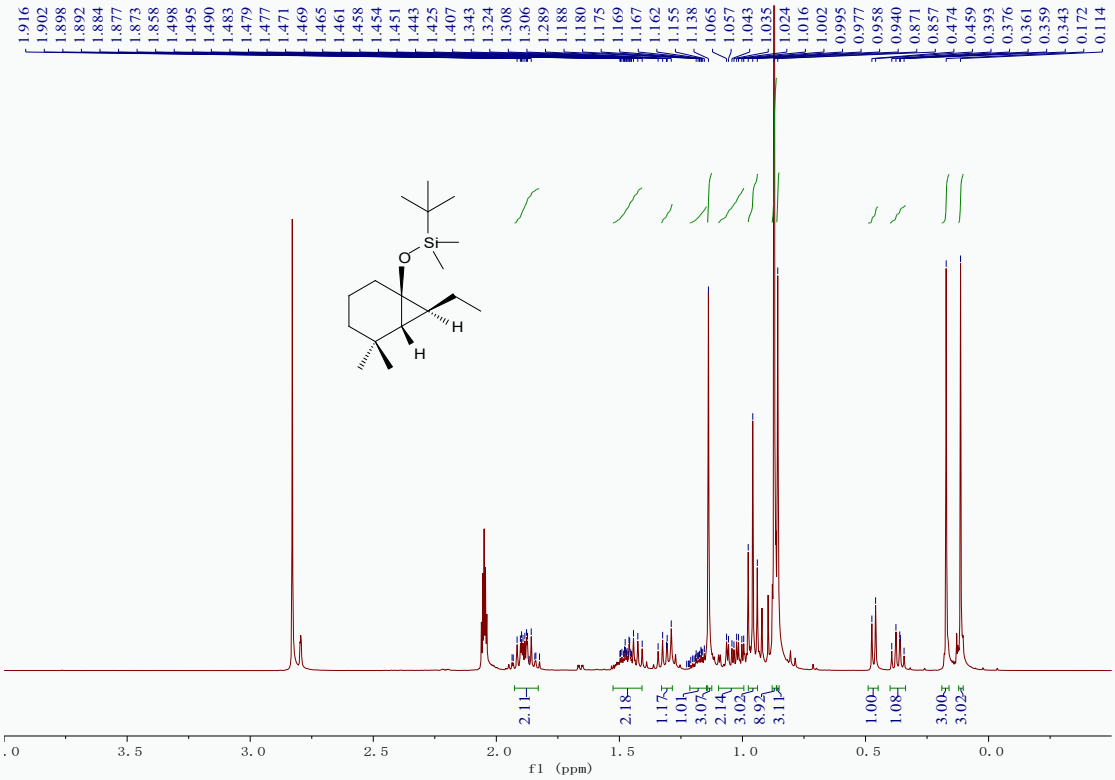


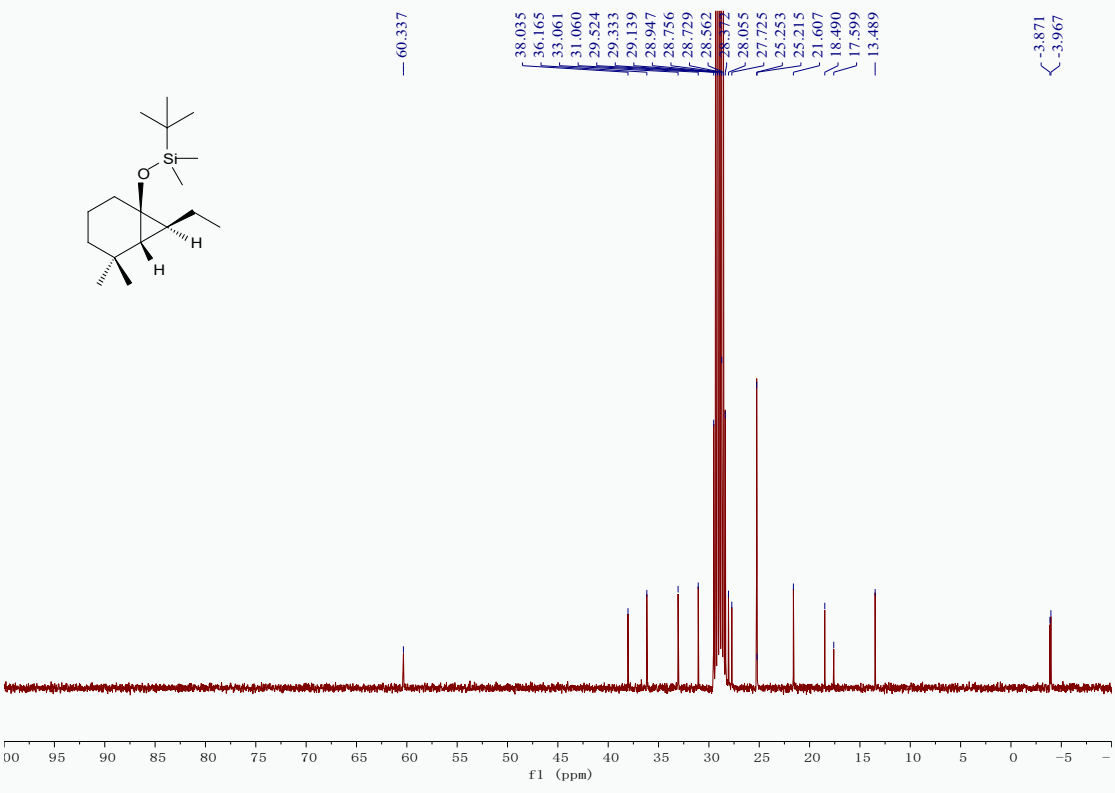
tert-butyl(((1*S*,6*R*,7*R*)-7-(tert-butyl)-5,5-dimethylbicyclo[4.1.0]heptan-1-yl)oxy) dimethylsilane **(3a)** (Using Acetone-d_6 as solvent)



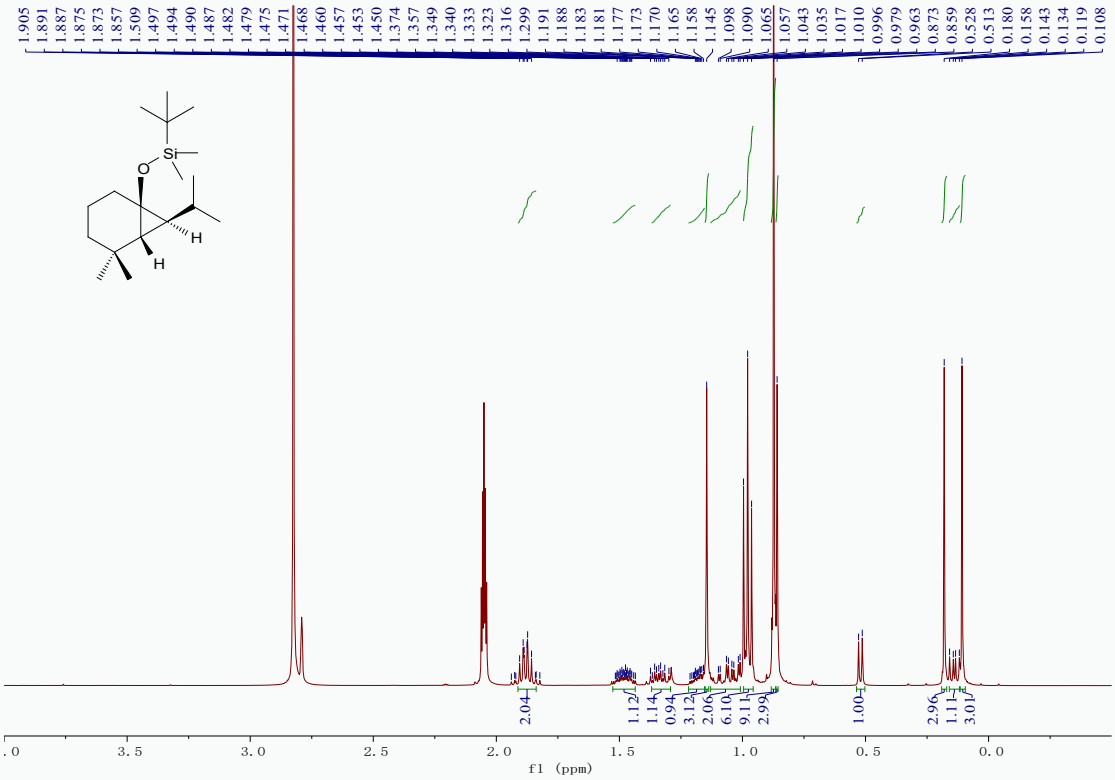


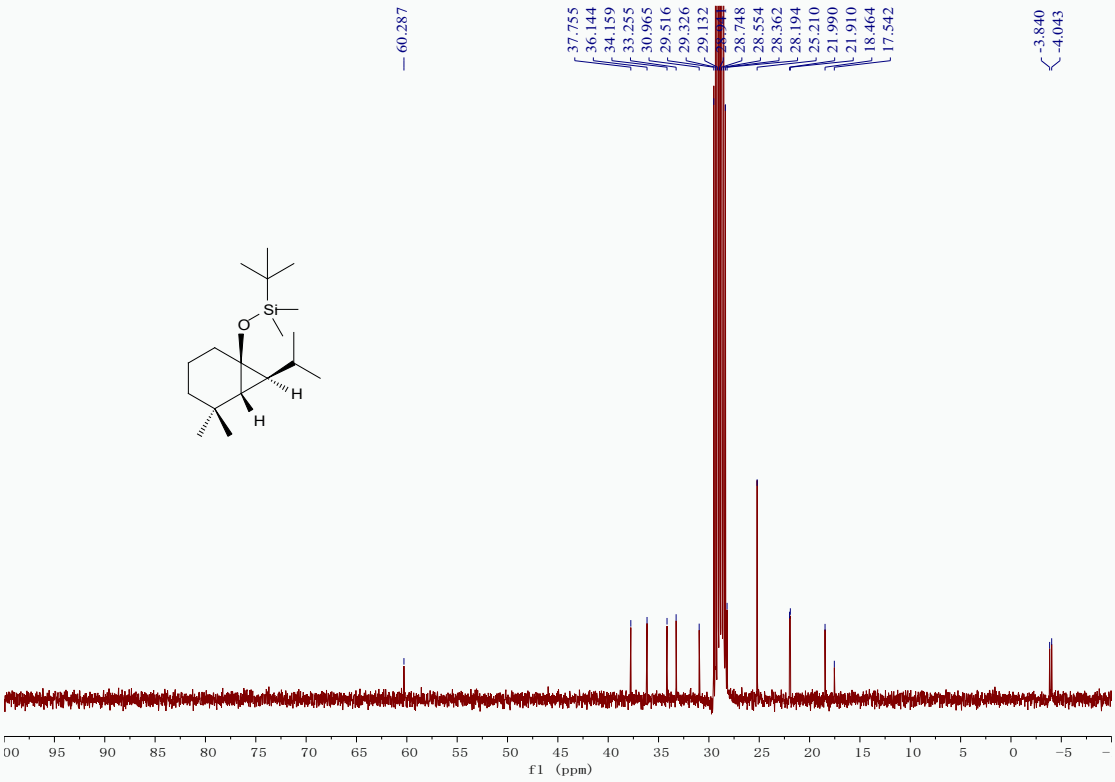
tert-butyl(((1*S*,6*R*,7*S*)-7-ethyl-5,5-dimethylbicyclo[4.1.0]heptan-1-yl)oxy)dimethylsilane **(3b)**
(Using Acetone-d_6 as solvent)



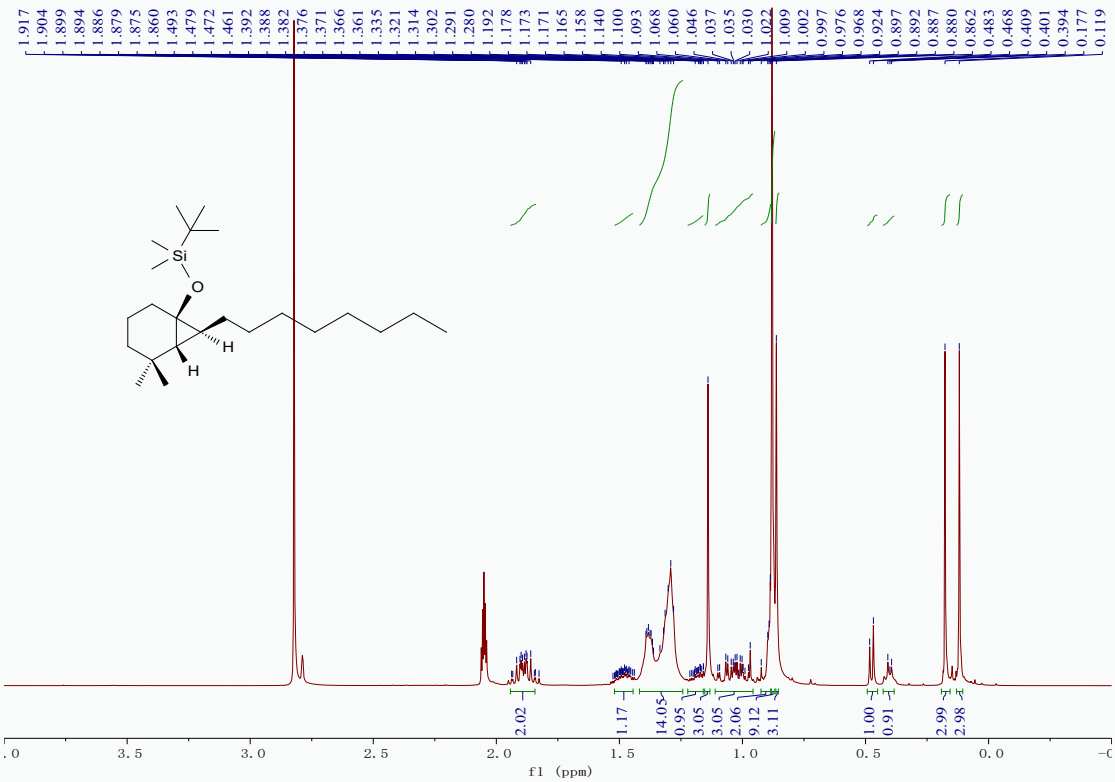


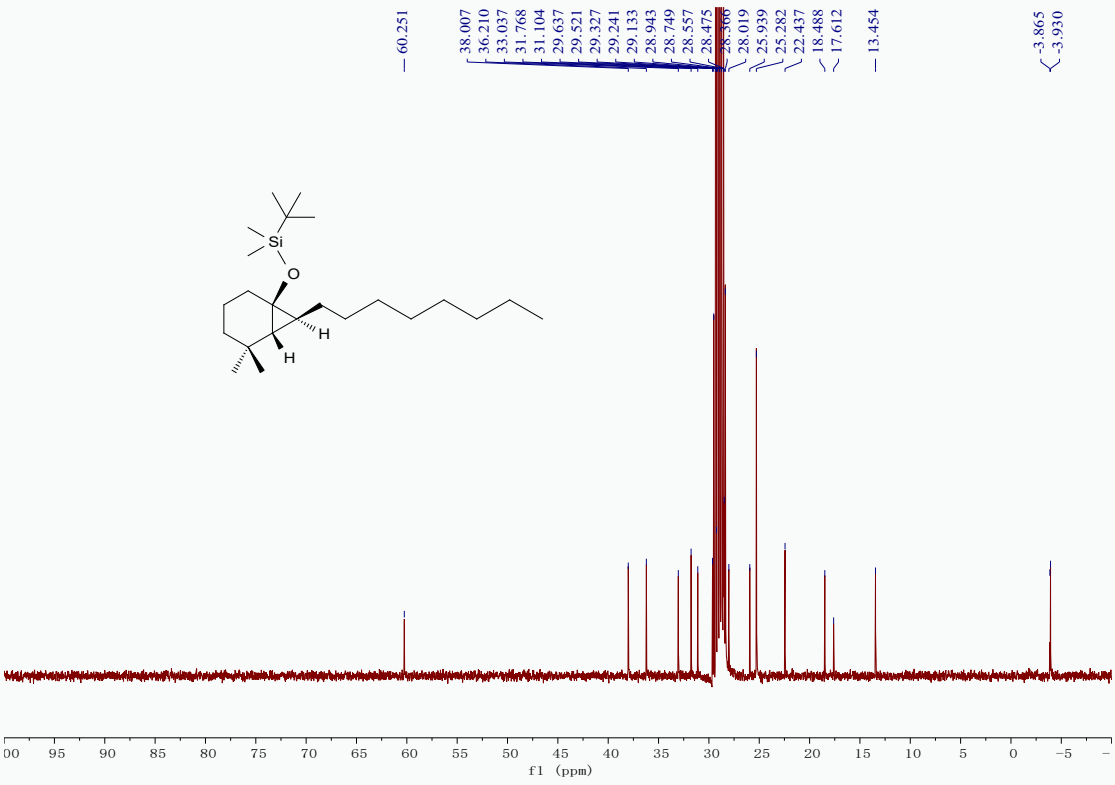
tert-butyl(((1*S*,6*R*,7*S*)-7-isopropyl-5,5-dimethylbicyclo[4.1.0]heptan-1-yl)oxy)dimethylsilane **(3c)** (Using Acetone-d_6 as solvent)



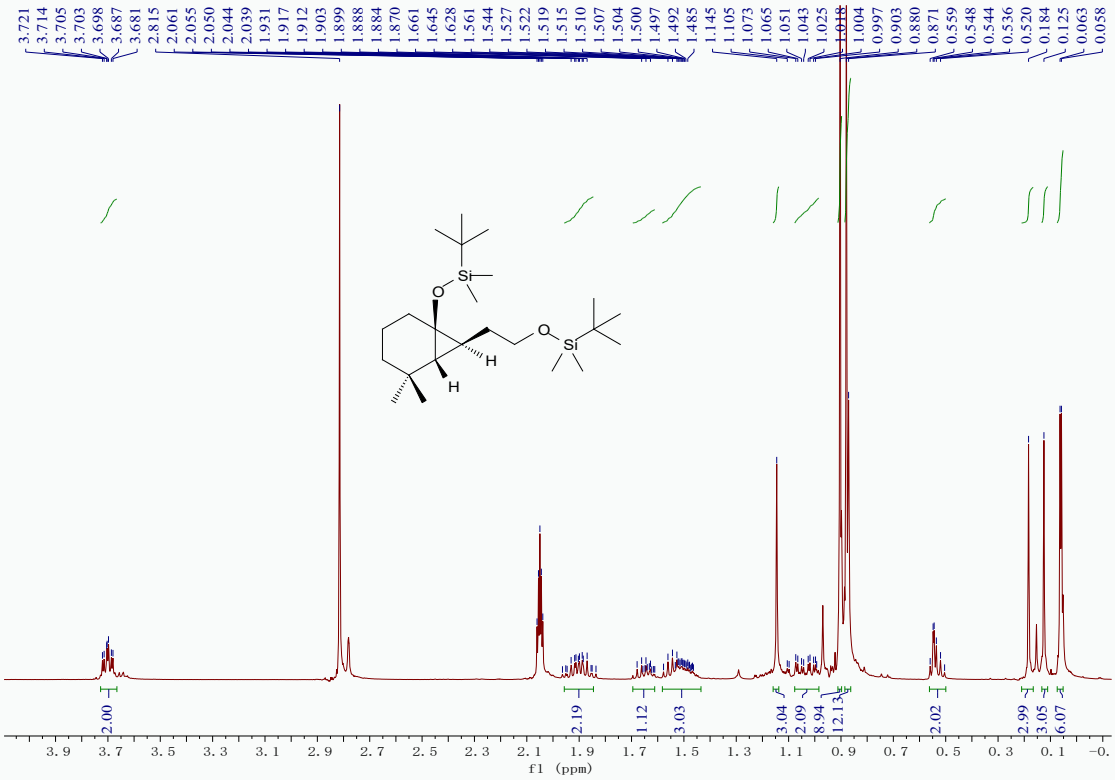


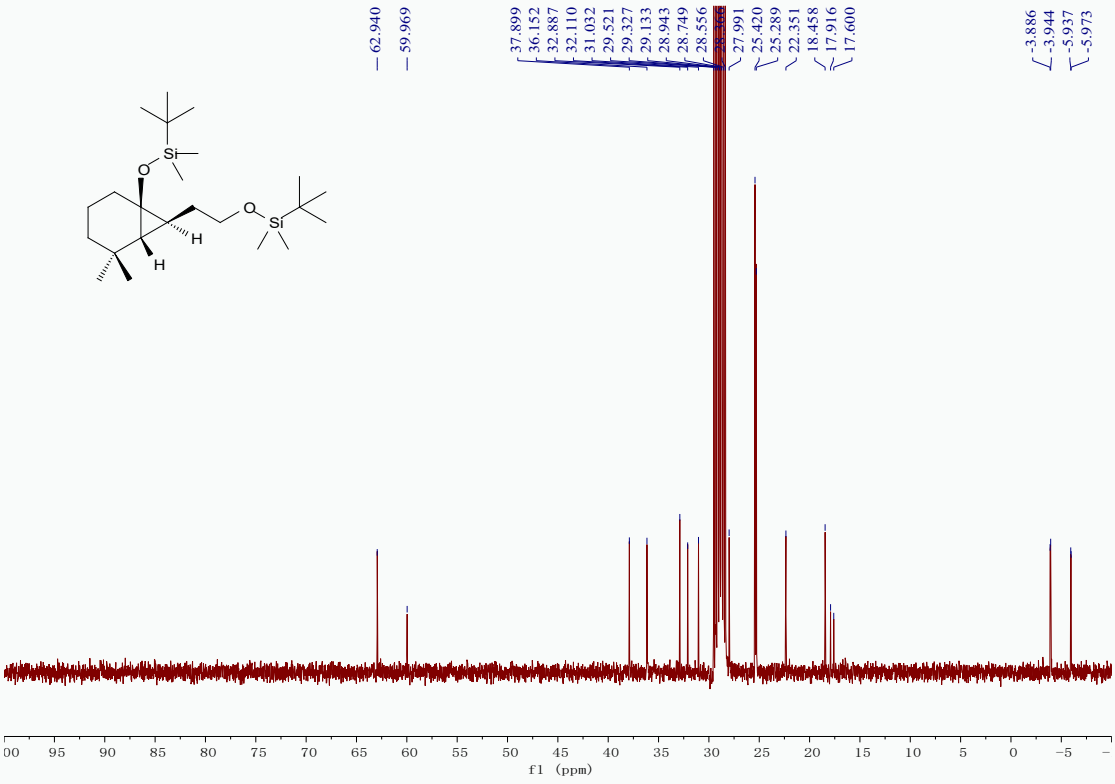
tert-butyl(((1*S*,6R,7*S*)-5,5-dimethyl-7-octylbicyclo[4.1.0]heptan-1-yl)oxy)dimethylsilane **(3d)**
(Using Acetone-d_6 as solvent)



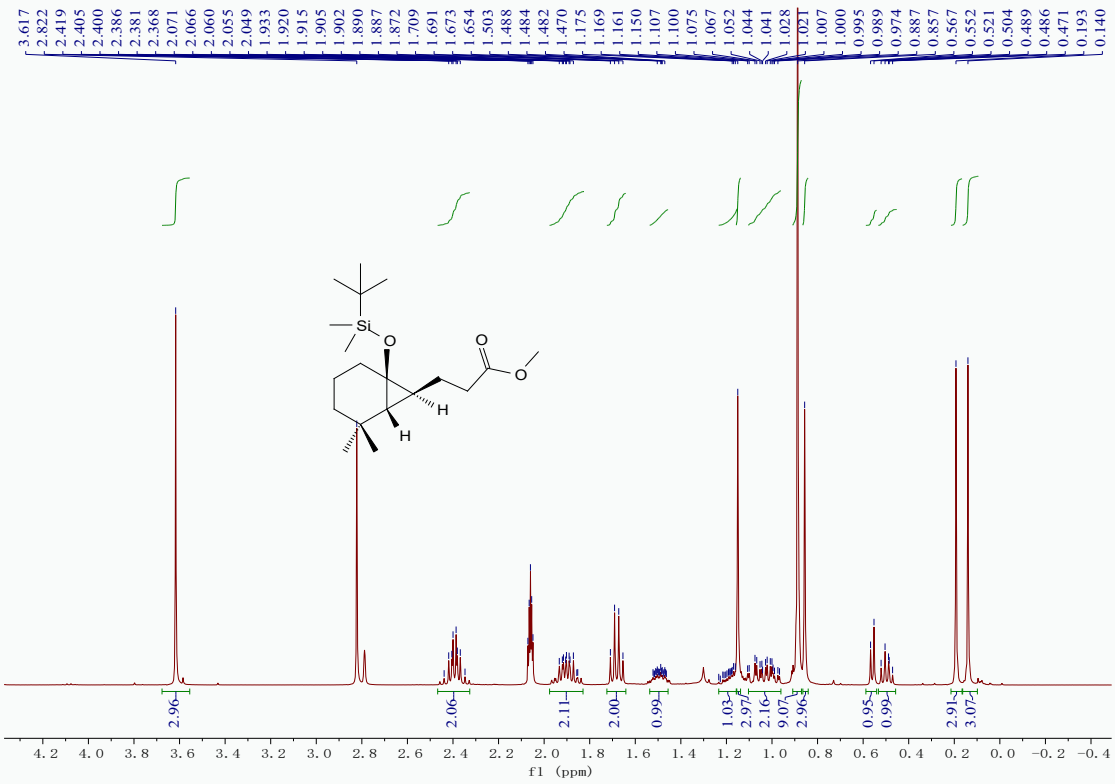


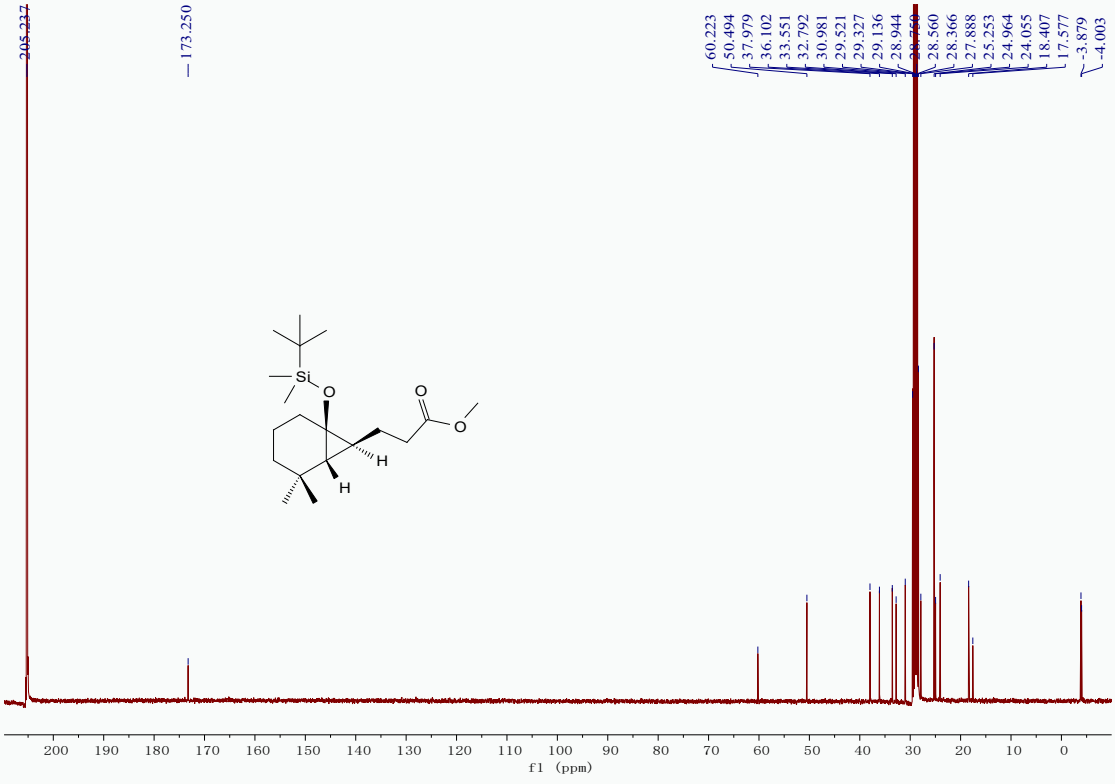
tert-butyl(2-((1*S*,6*R*,7*S*)-1-((tert-butyldimethylsilyl)oxy)-5,5-dimethylbicyclo[4.1.0]heptan-7-yl)ethoxy)dimethylsilane **(3e)** (Using Acetone-d_6 as solvent)



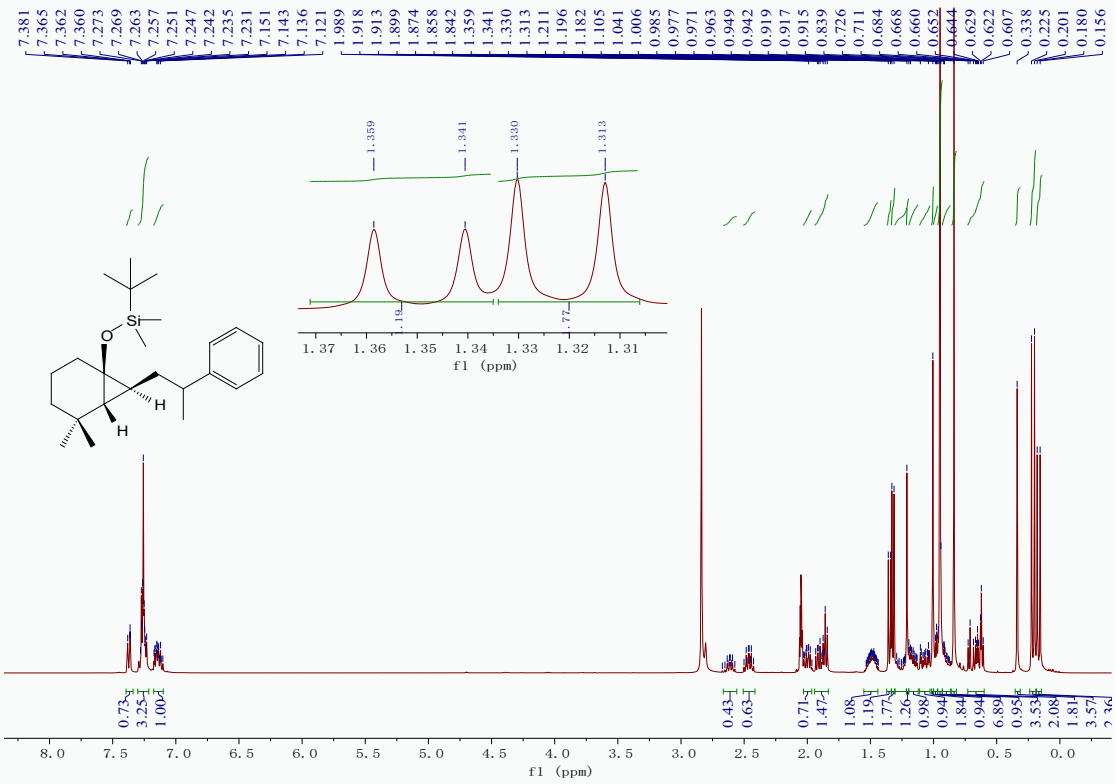


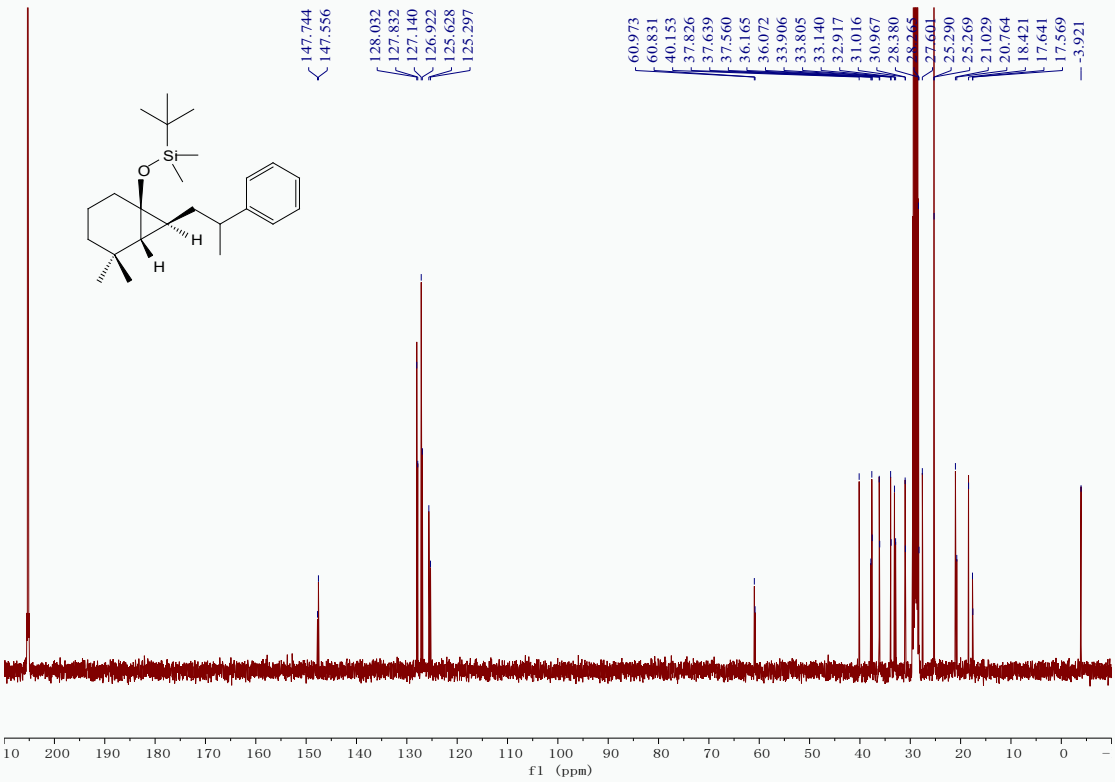
methyl 3-((1*S*,6*R*,7*S*)-1-((tert-butyldimethylsilyl)oxy)-5,5-dimethylbicyclo[4.1.0]heptan-7-yl) propanoate **(3f)** (Using Acetone-d_6 as solvent)



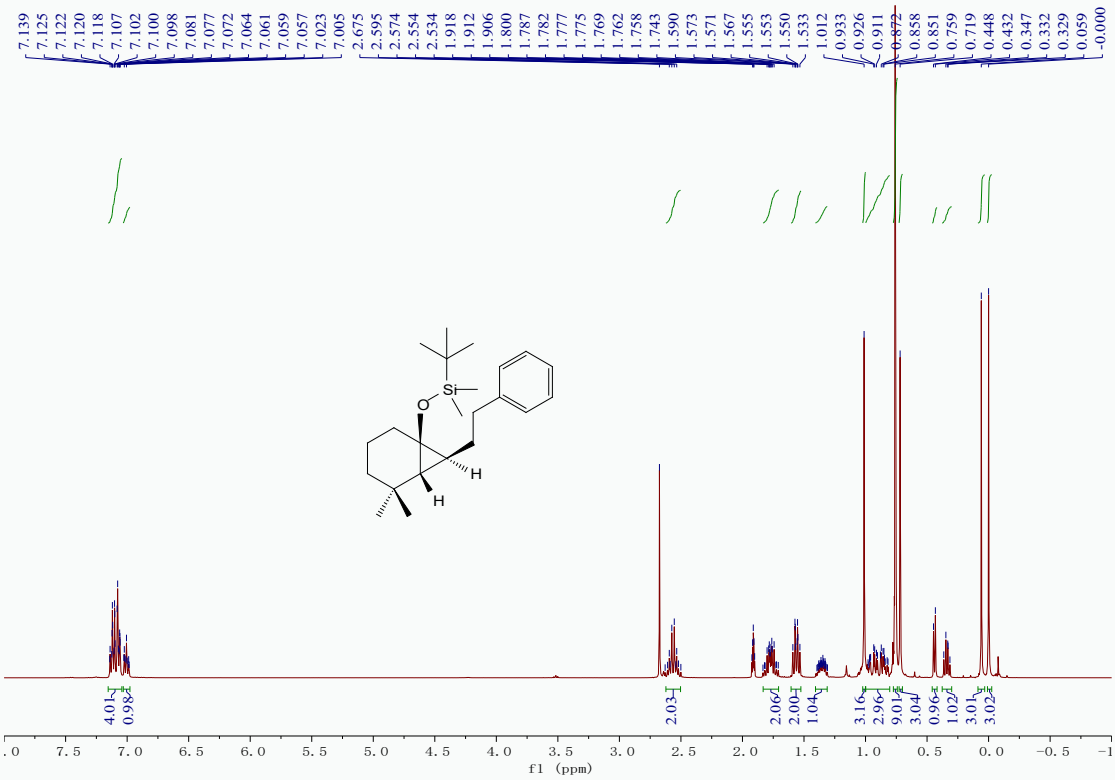


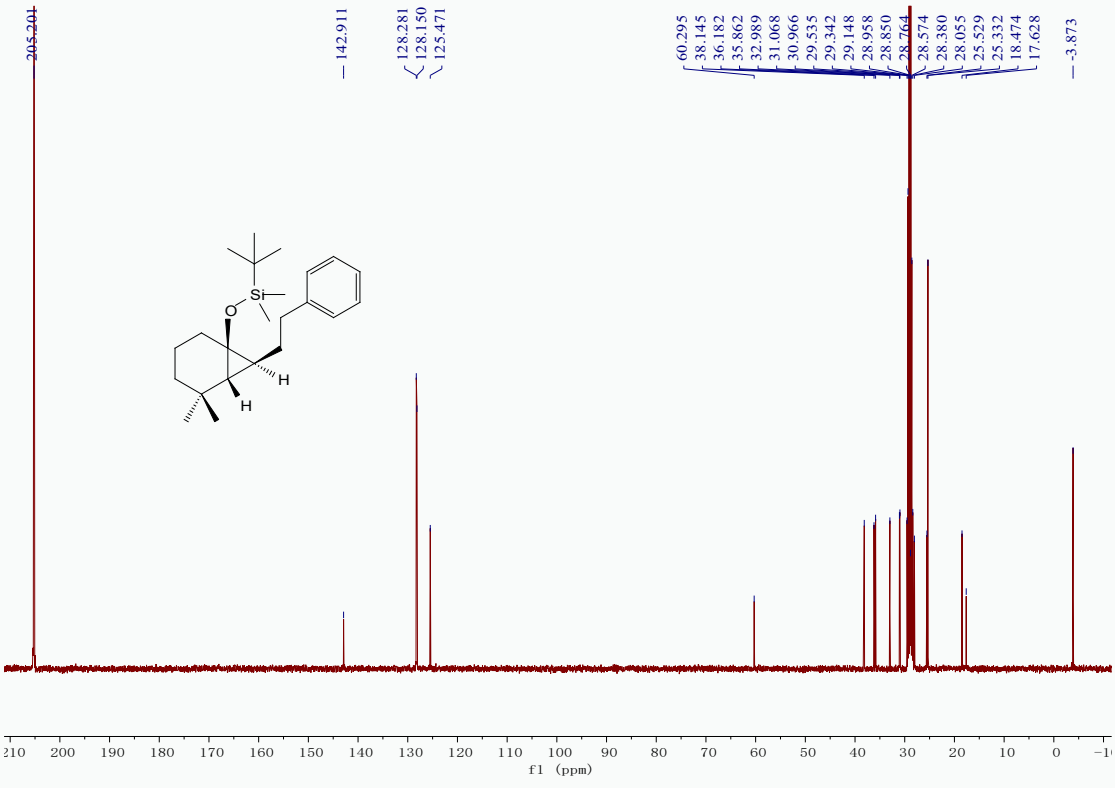
tert-butyl(((1*S*,6*R*,7*S*)-5,5-dimethyl-7-(2-phenylpropyl)bicyclo[4.1.0]heptan-1-yl)oxy)-dimethyl silane (**3g**) (Using Acetone-d_6 as solvent)



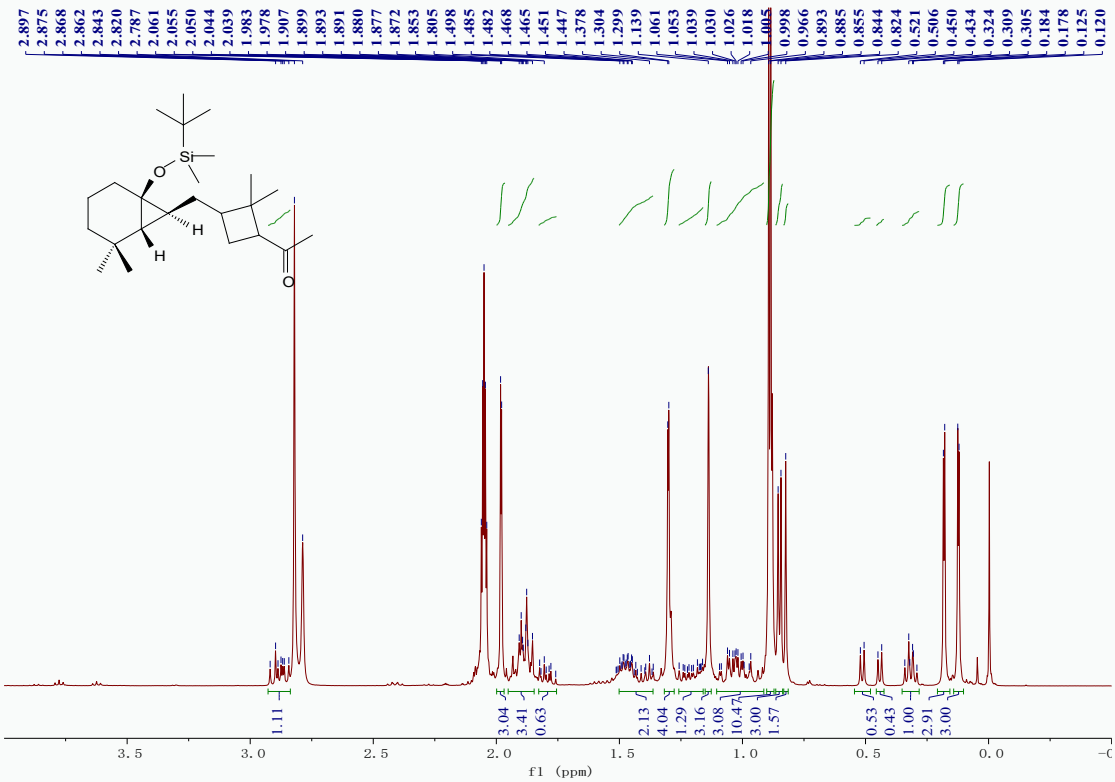


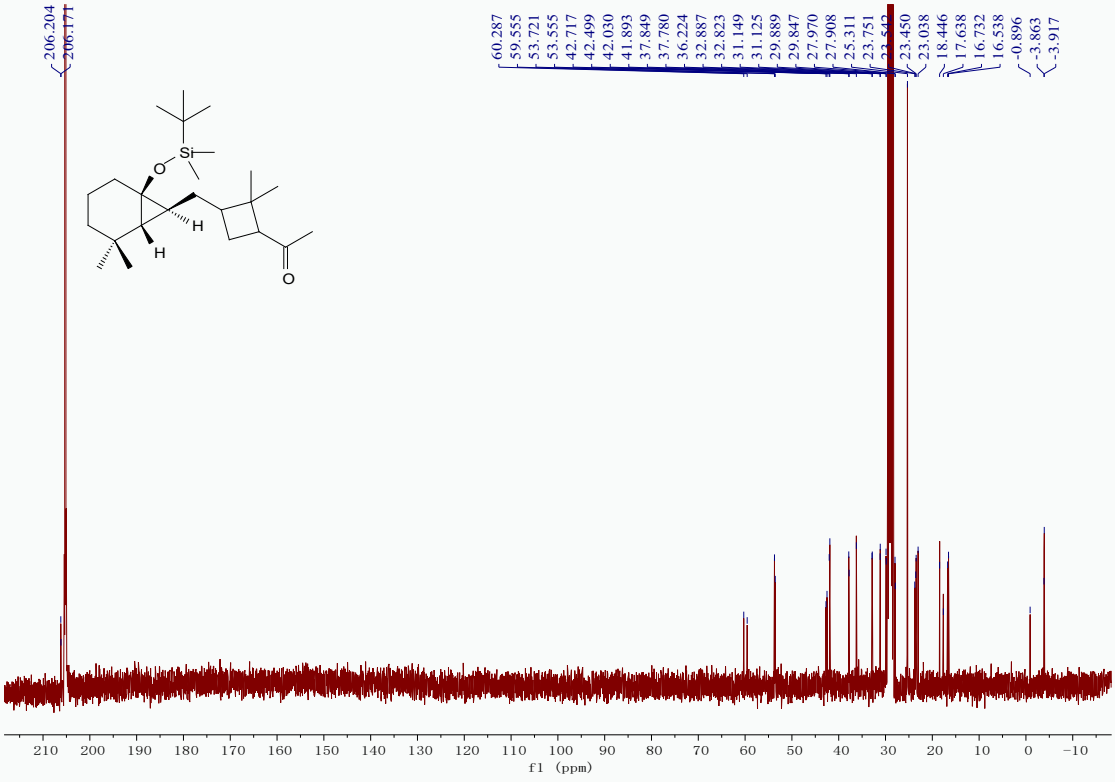
tert-butyl(((1*S*,6*R*,7*S*)-5,5-dimethyl-7-phenethylbicyclo[4.1.0]heptan-1-yl)oxy)dimethylsilane (**3h**) (Using Acetone-d_6 as solvent)



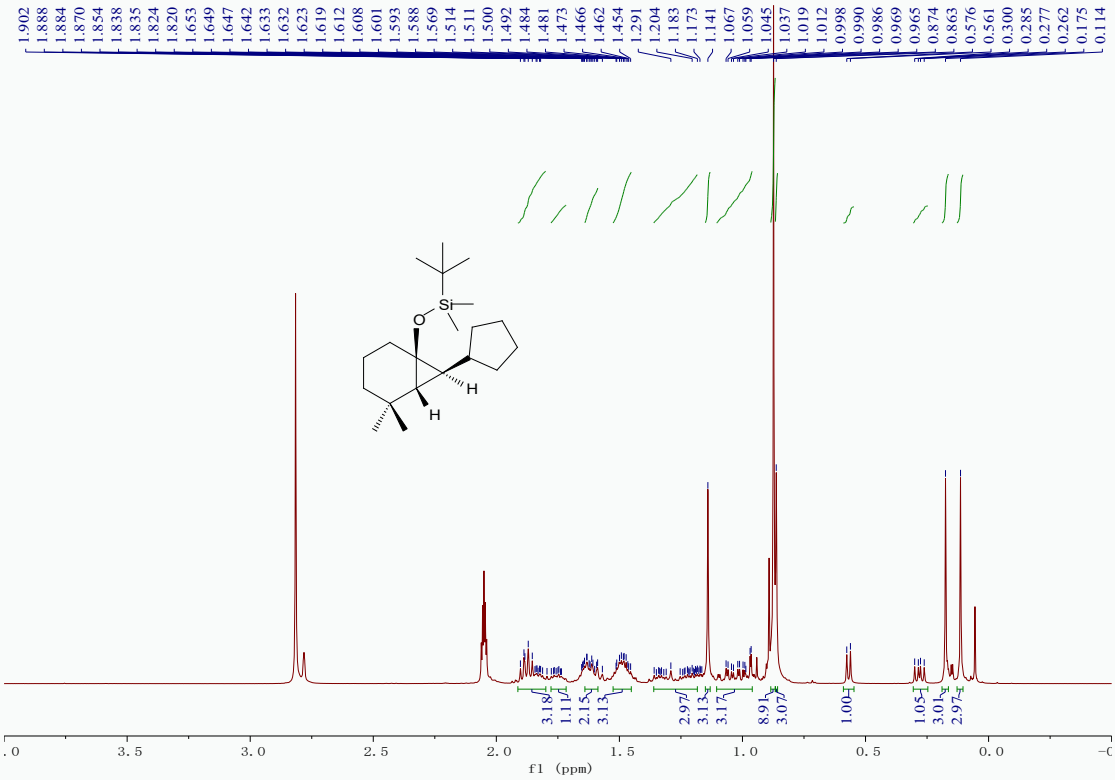


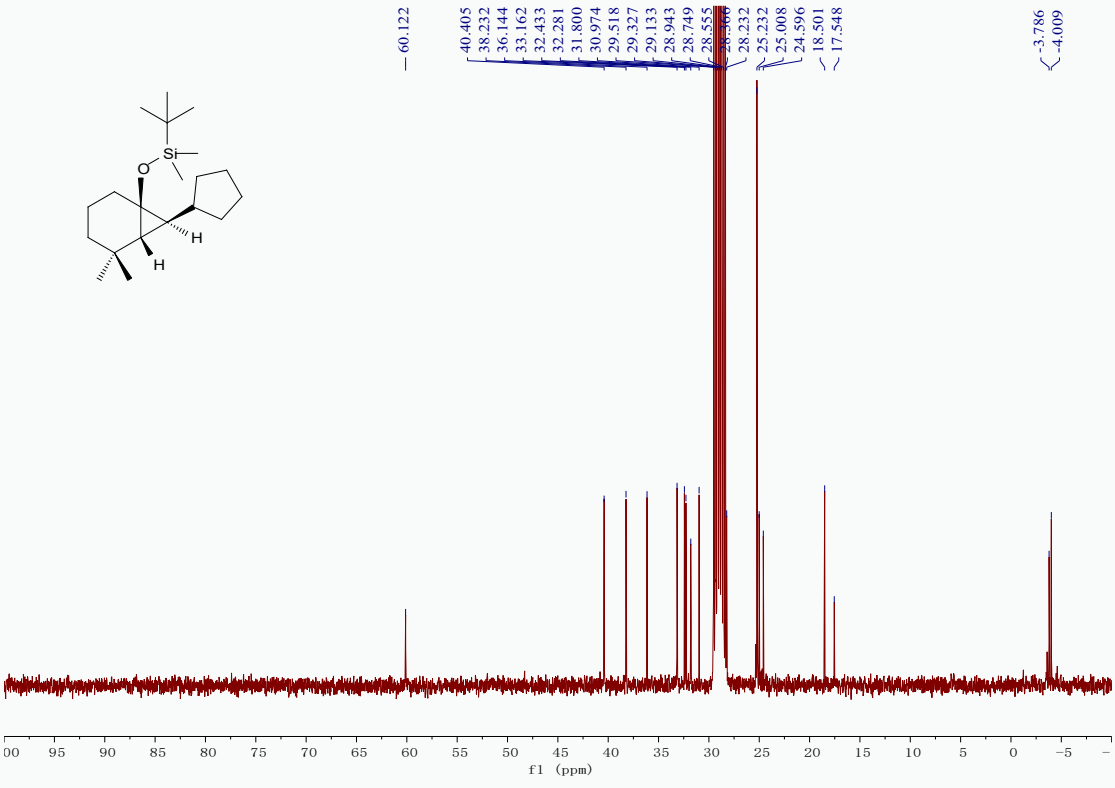
1-(3-((1*S*,6*R*,7*S*)-1-((tert-butyldimethylsilyl)oxy)-5,5-dimethylbicyclo[4.1.0] heptan-7-yl)-2,2-dimethylcyclobutyl)ethan-1-one **(3i)** (Using Acetone-d_6 as solvent)



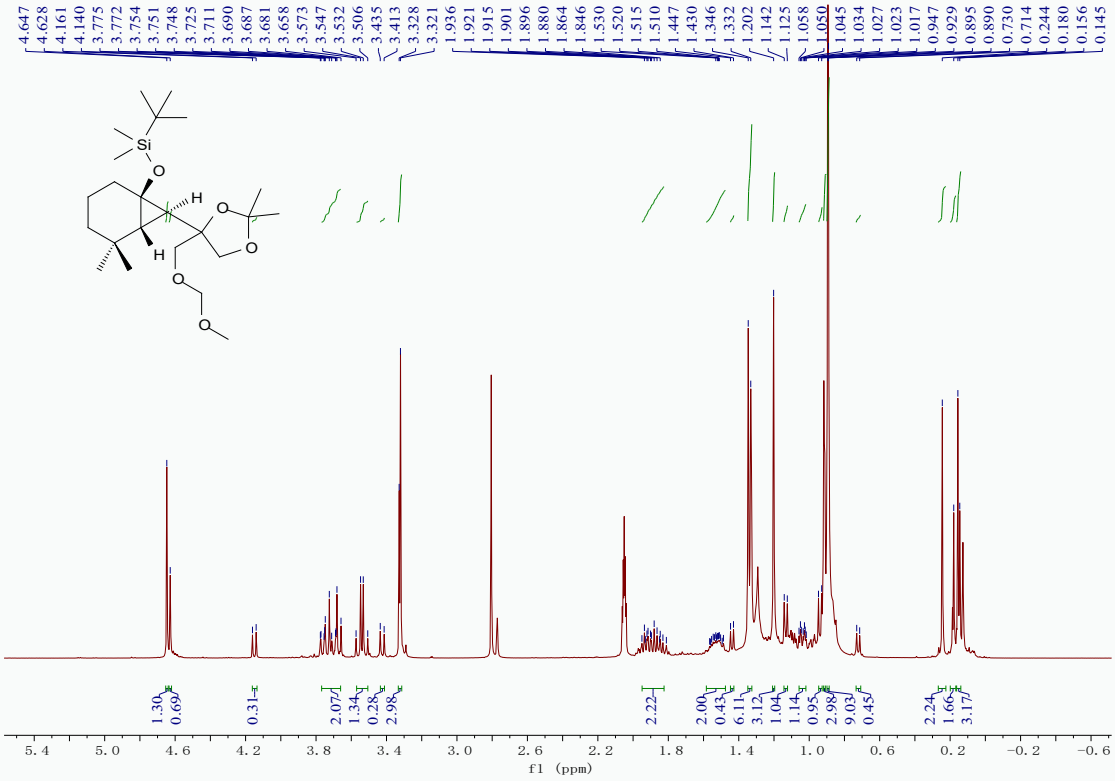


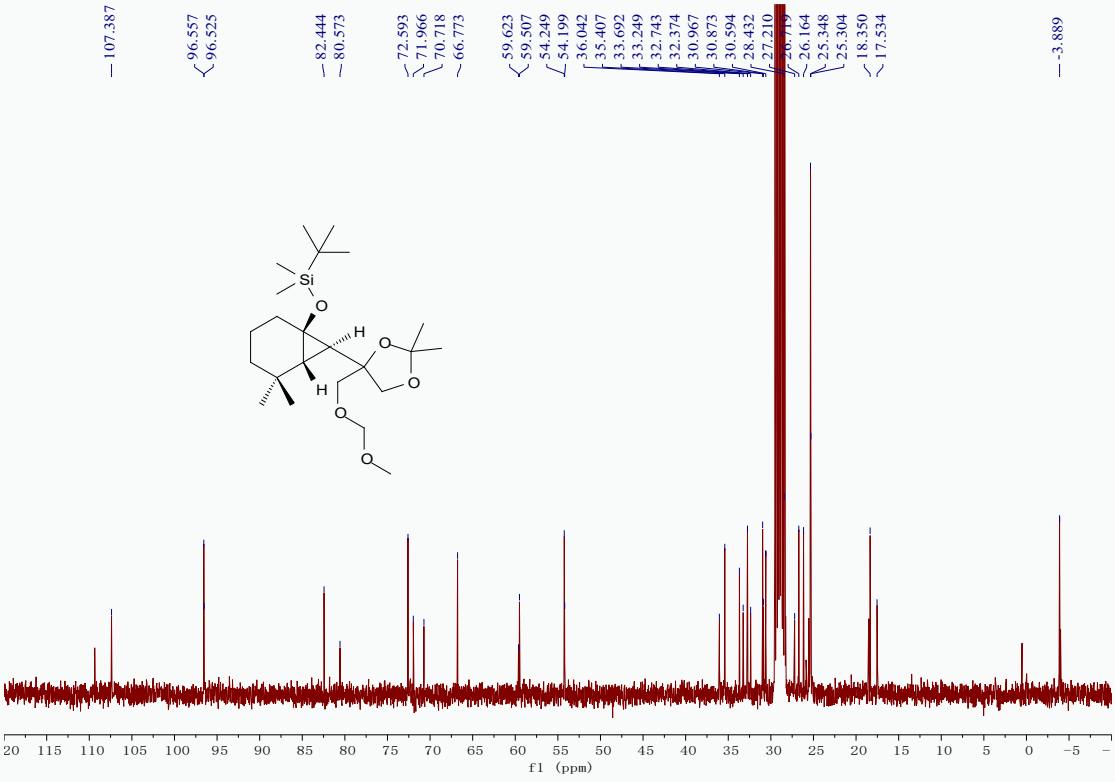
tert-butyl(((1*S*,6*R*,7*S*)-7-cyclopentyl-5,5-dimethylbicyclo[4.1.0]heptan-1-yl)oxy) dimethylsilane **(3j)** (Using Acetone-d_6 as solvent)



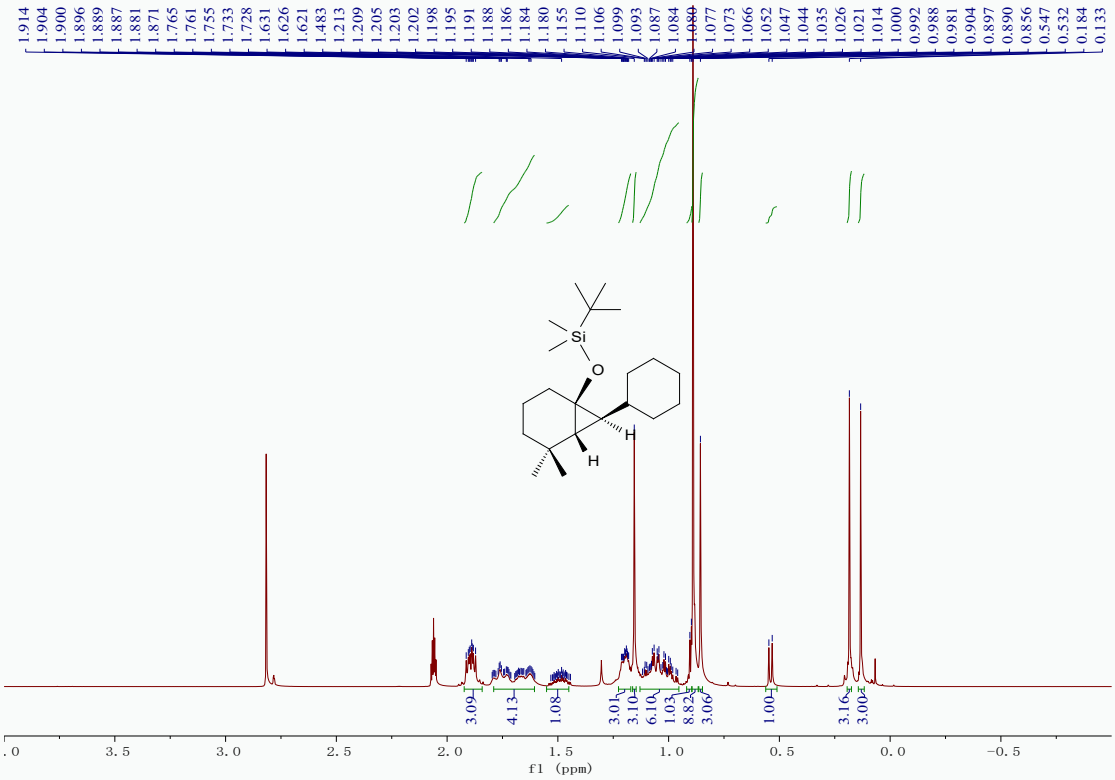


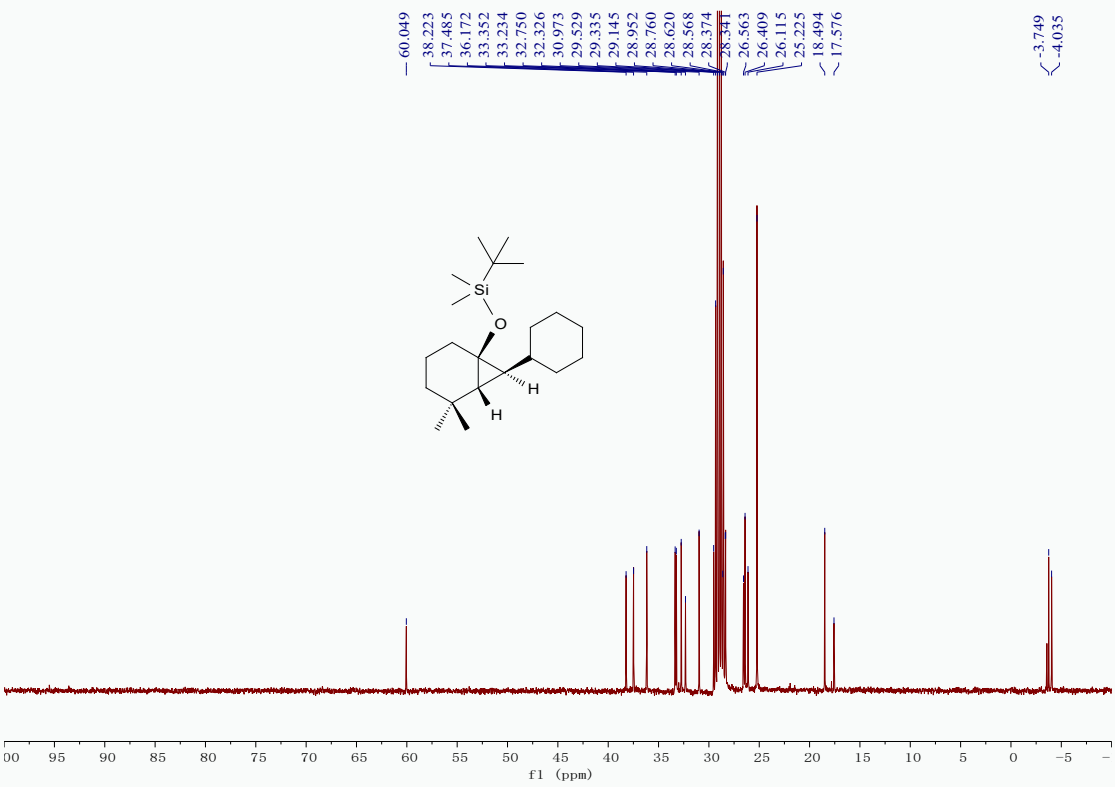
tert-butyl(((1*R*,6*R*,7*R*)-7-(4-((methoxymethoxy)methyl)-2,2-dimethyl-1,3-dioxolan-4-yl)-5,5-dimethylbicyclo[4.1.0]heptan-1-yl)oxy)dimethylsilane **(3k)** (Using Acetone-d_6 as solvent)



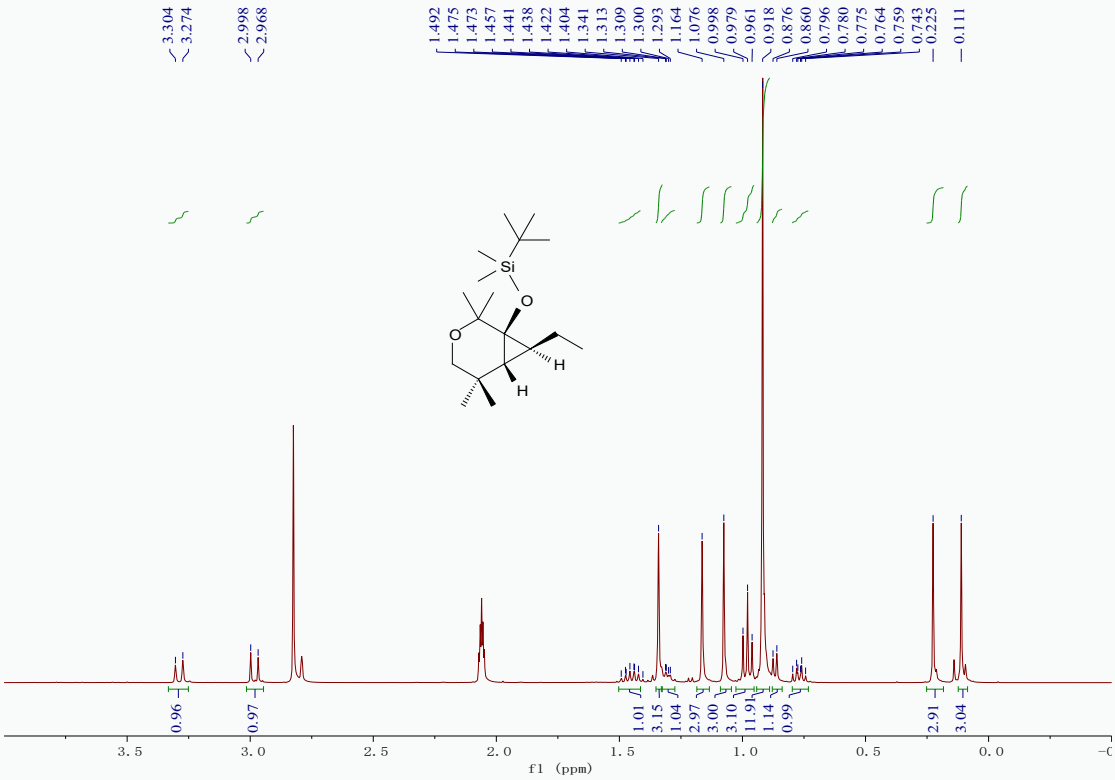


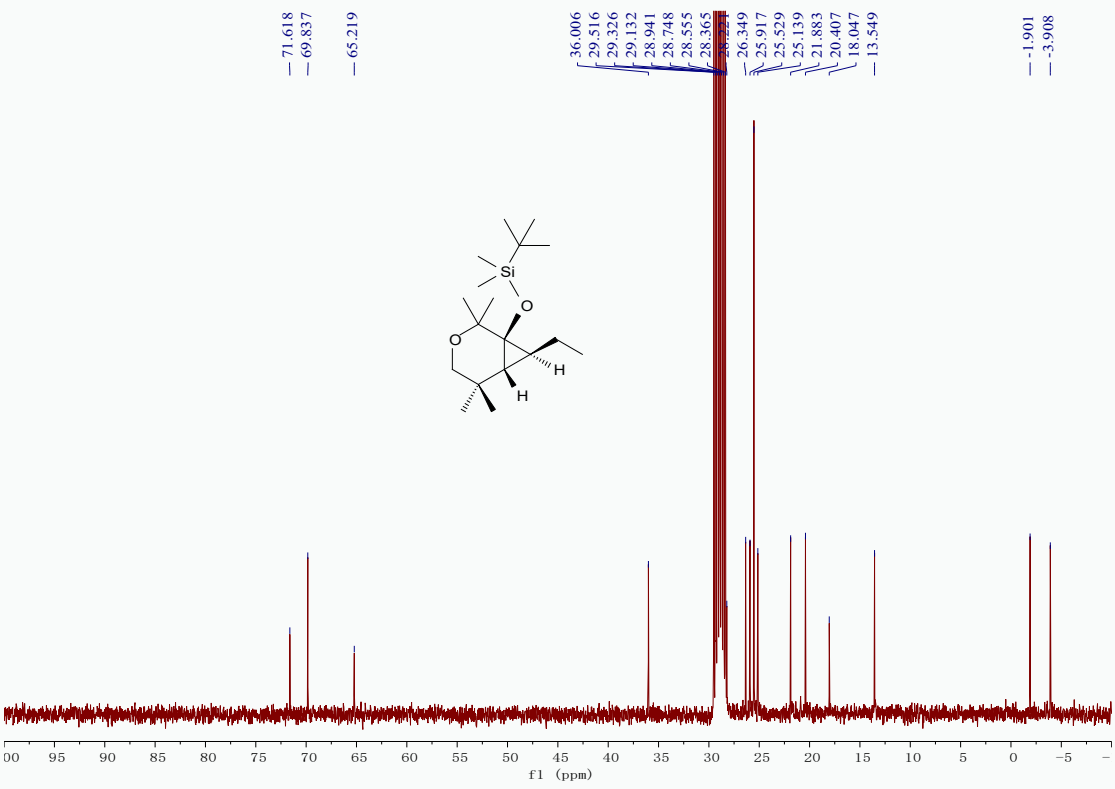
tert-butyl(((1*S*,6*R*,7*S*)-7-cyclohexyl-5,5-dimethylbicyclo[4.1.0]heptan-1-yl)oxy) dimethylsilane **(3l)** (Using Acetone-d_6 as solvent)



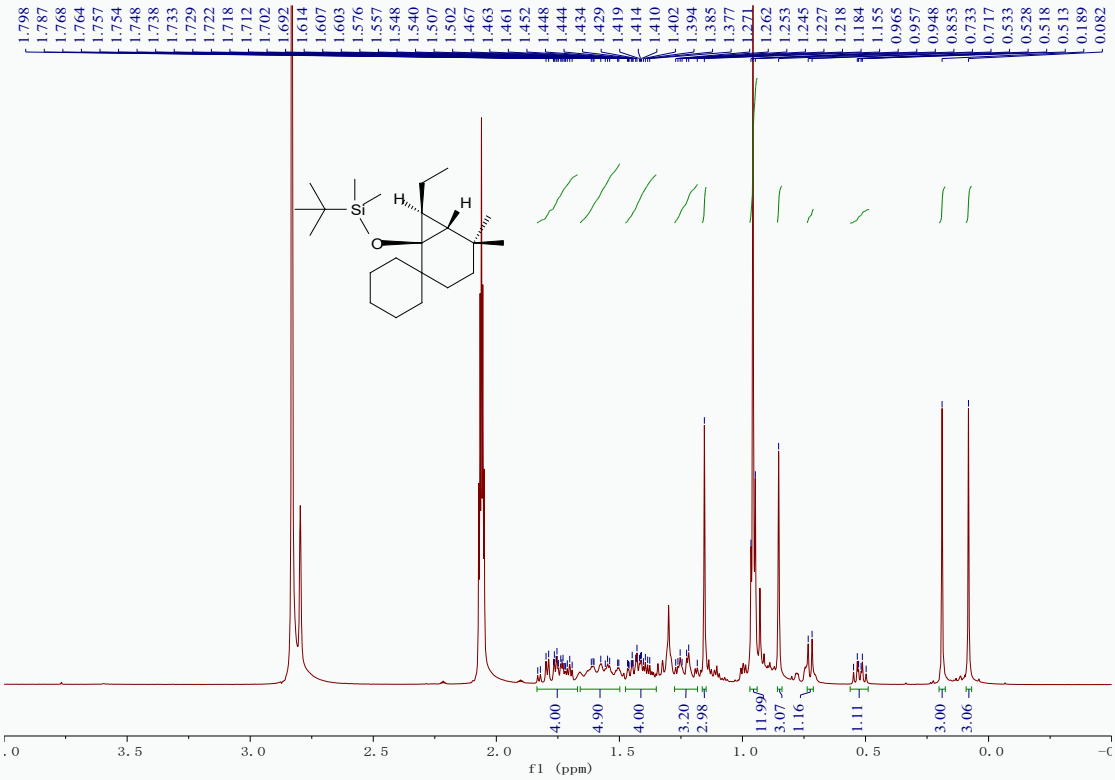


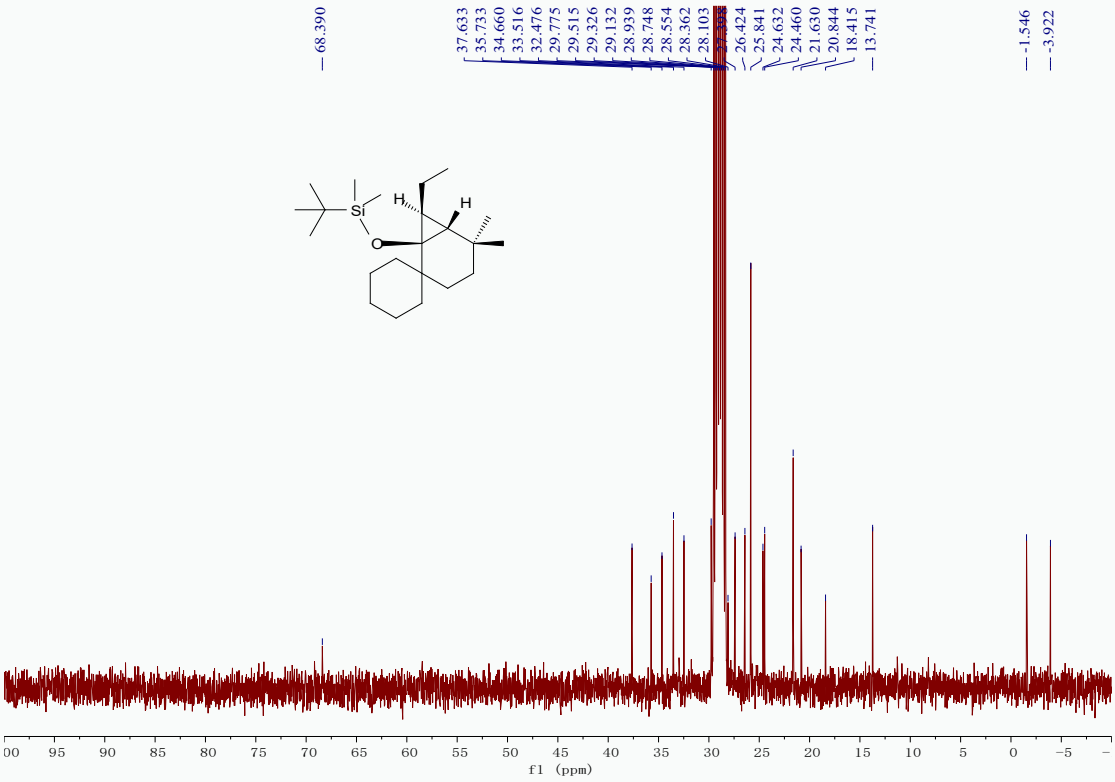
tert-butyl(((1*S*,6*R*,7*S*)-7-ethyl-2,2,5,5-tetramethyl-3-oxabicyclo[4.1.0]heptan-1-yl)oxy)-dimethylsilane **(3m)** (Using Acetone-d_6 as solvent)



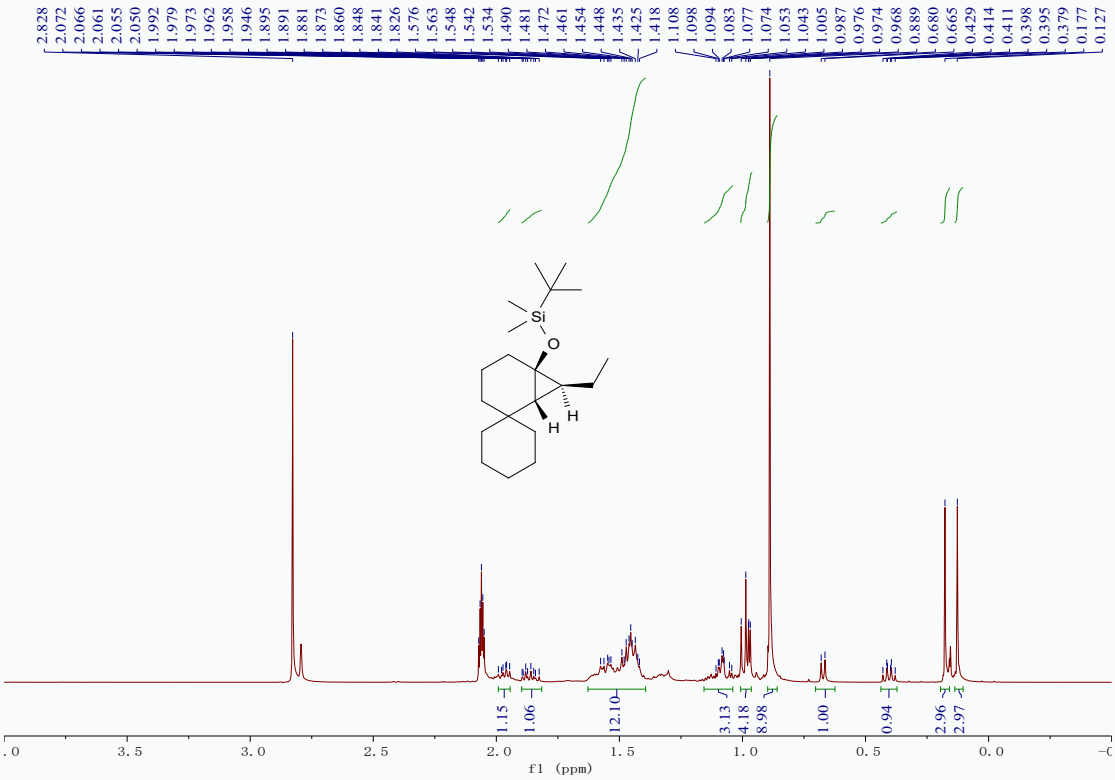


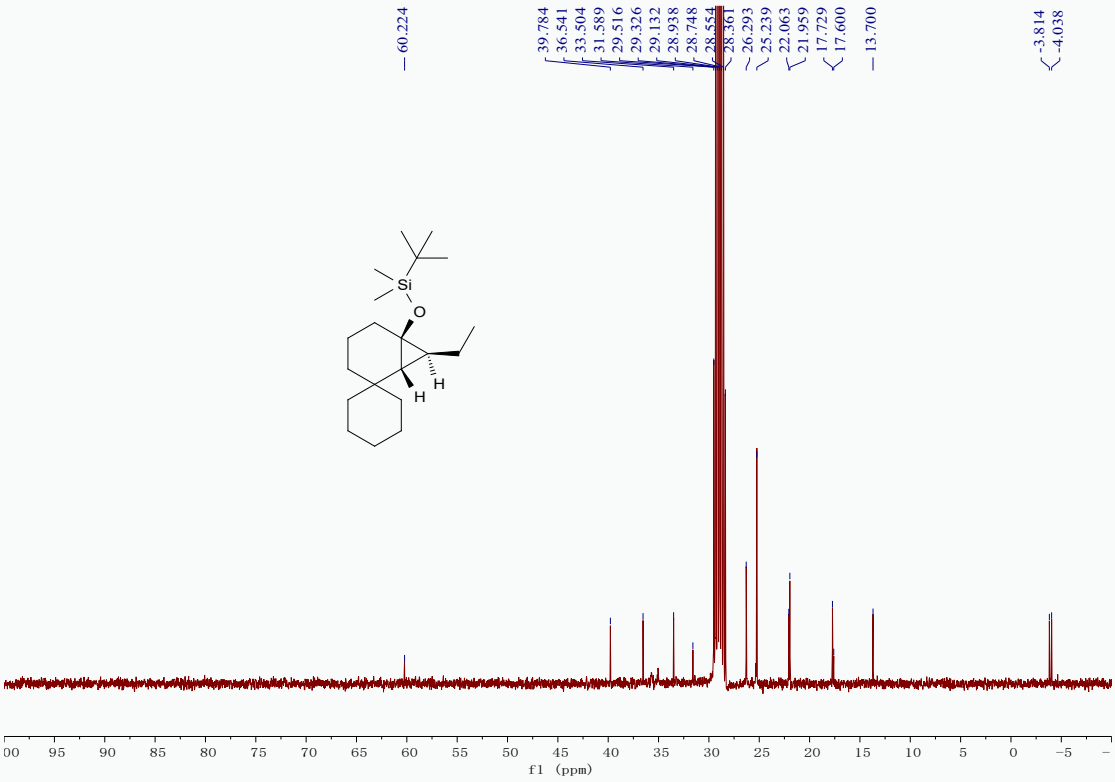
tert-butyl(((1*S*,6*R*,7*S*)-7-ethyl-5,5-dimethylspiro[bicyclo[4.1.0]heptane-2,1'-cyclohexan]-1-yl)oxy)dimethylsilane **(3n)** (Using Acetone-d_6 as solvent)



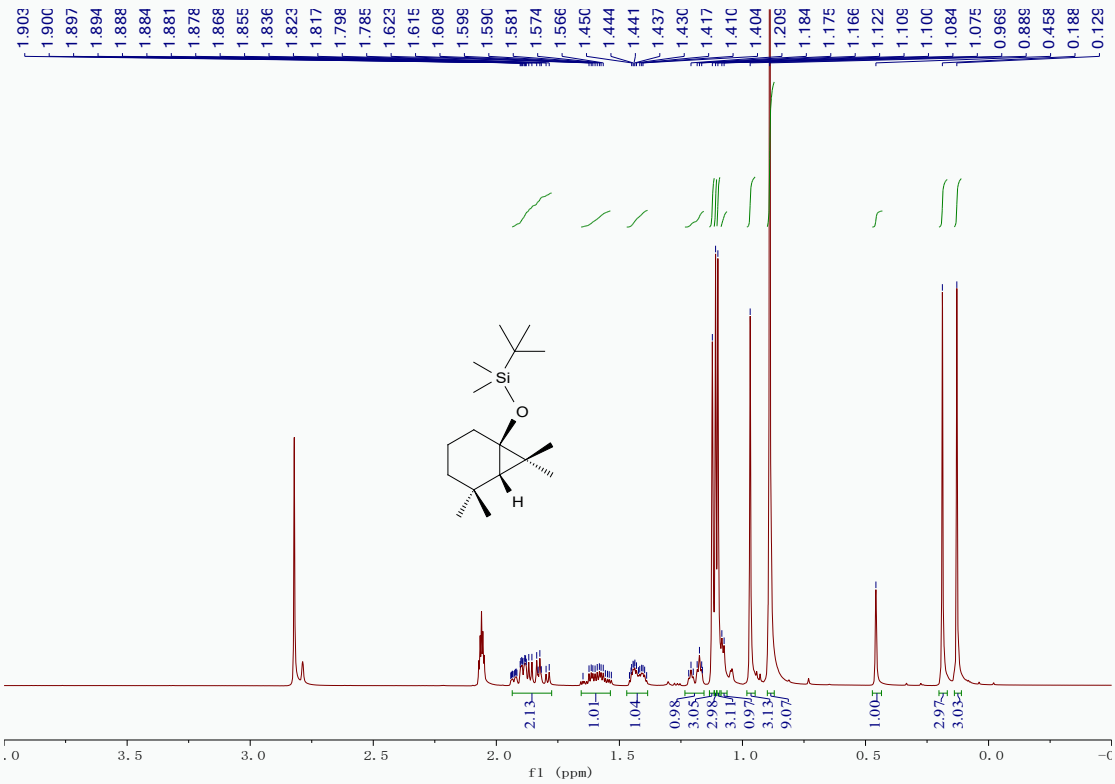


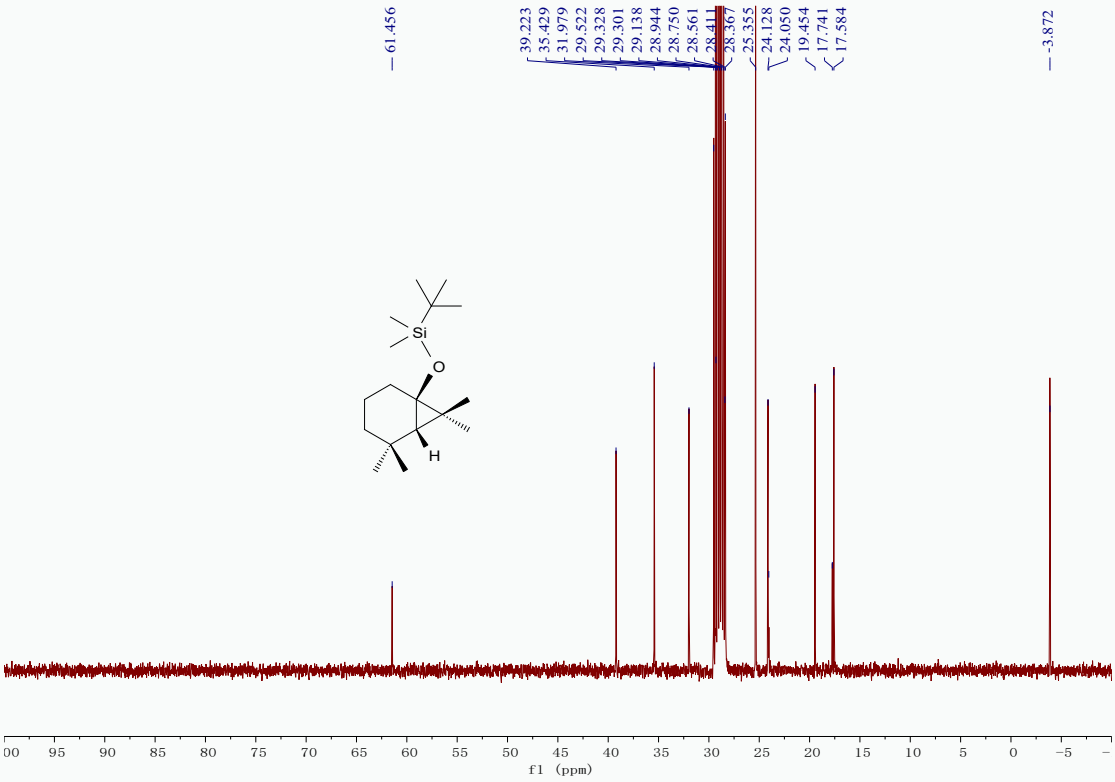
tert-butyl(((1*R*,6*S*,7*S*)-7-ethylspiro[bicyclo[4.1.0]heptane-2,1'-cyclohexan]-6-yl)oxy)-dimethylsilane **(3o)** (Using Acetone-d_6 as solvent)



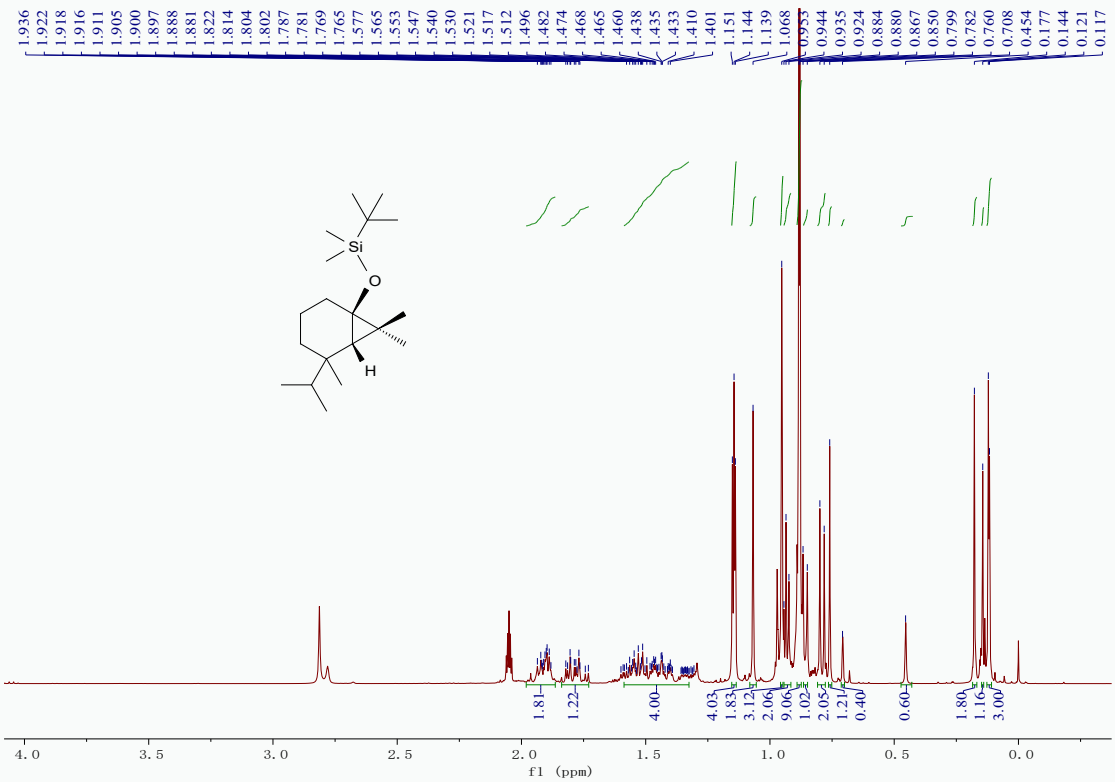


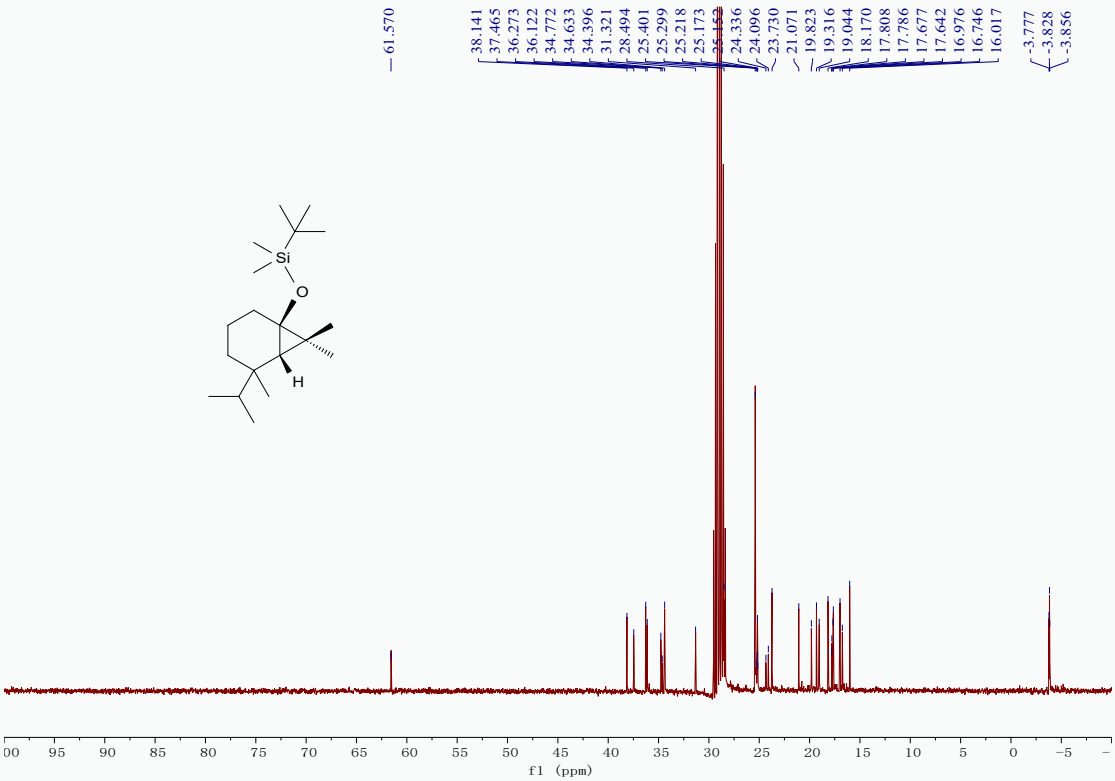
tert-butyldimethyl(((1*R*,6*S*)-5,5,7,7-tetramethylbicyclo[4.1.0]heptan-1-yl)oxy)silane **(3p)**
(Using Acetone-d_6 as solvent)



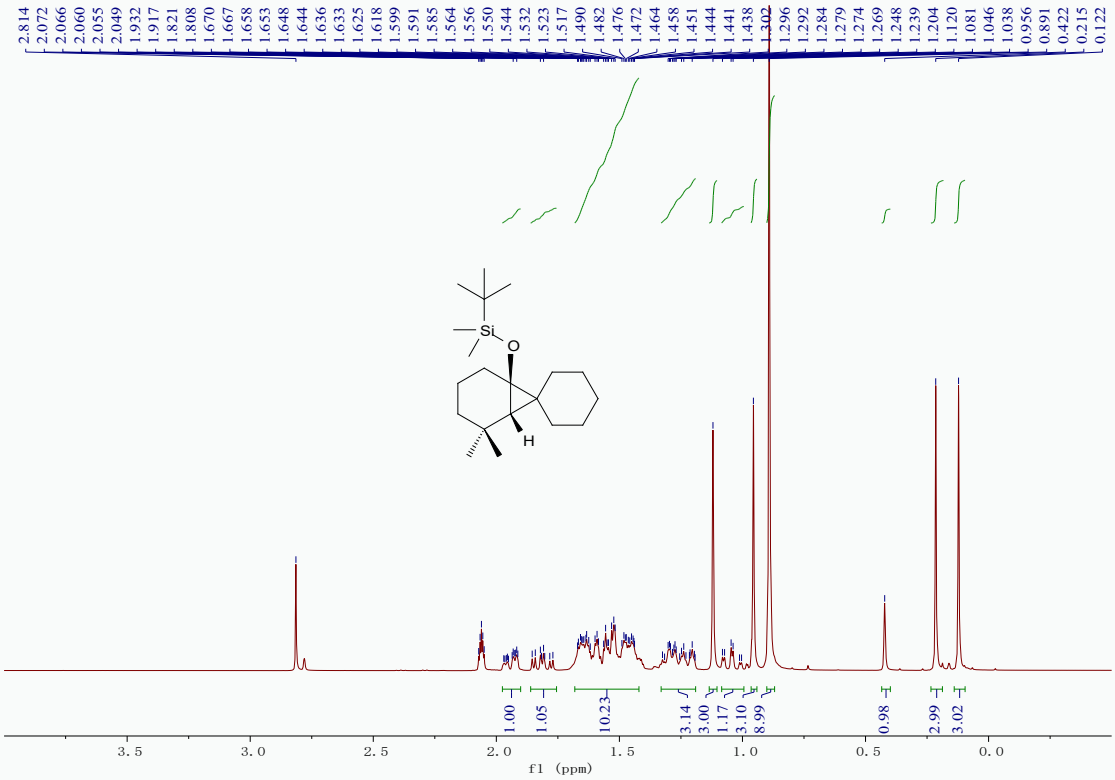


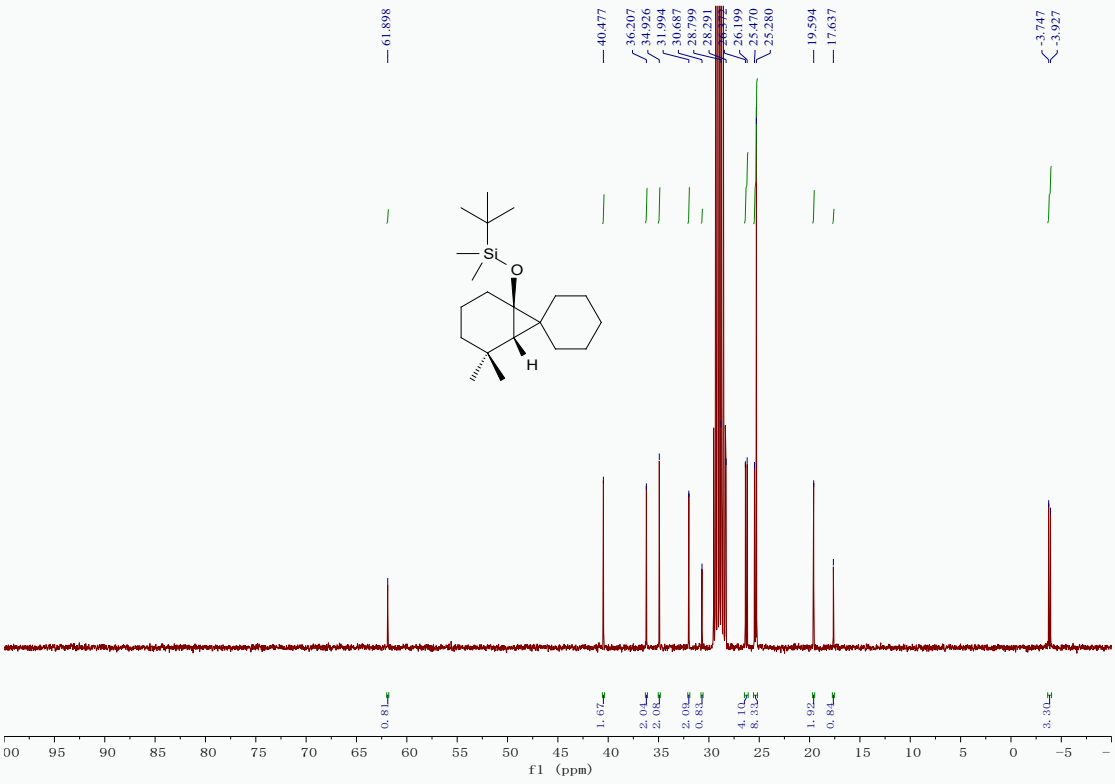
tert-butyl(((1*R*,6*S*)-5-isopropyl-5,7,7-trimethylbicyclo[4.1.0]heptan-1-yl)oxy) dimethylsilane **(3q)** (Using Acetone-d_6 as solvent)



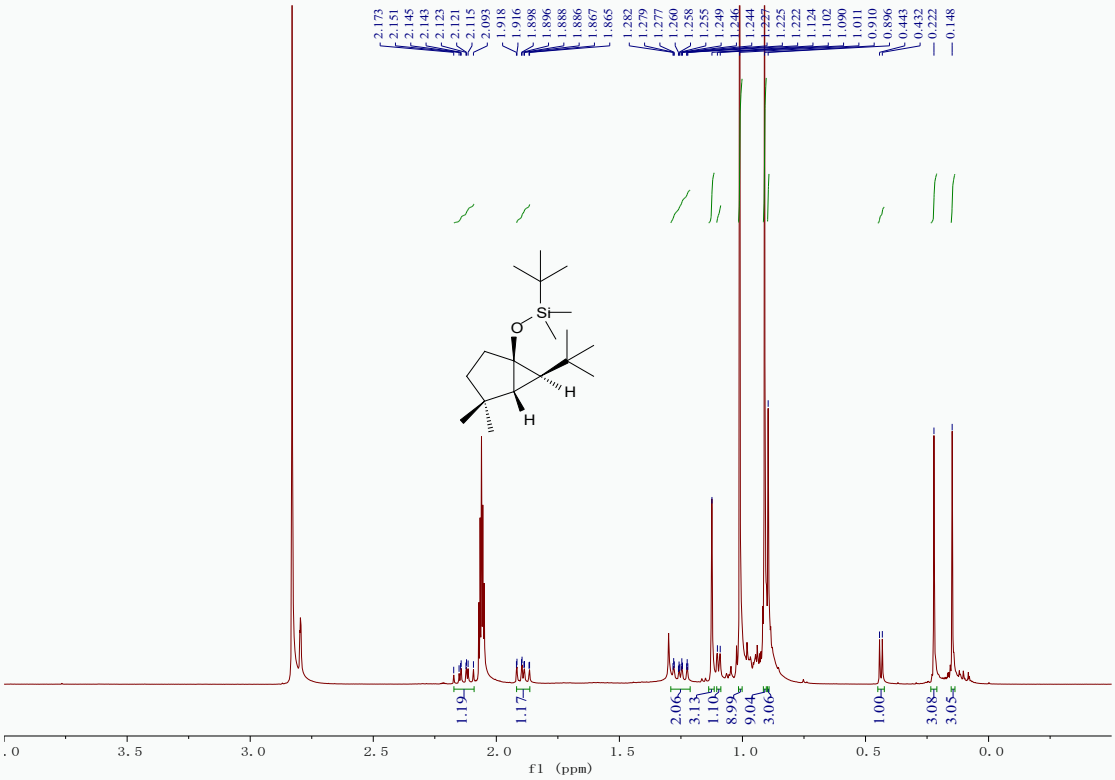


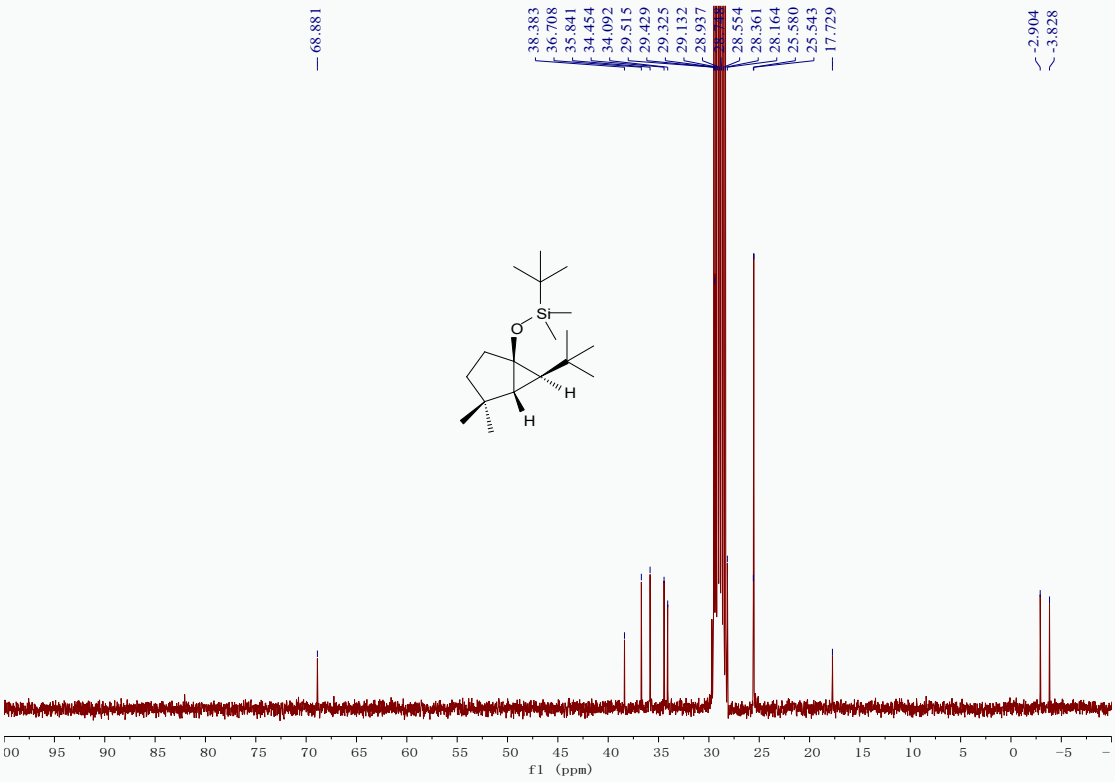
tert-butyl(((1*S*,6*R*)-2,2-dimethylspiro[bicyclo[4.1.0]heptane-7,1'-cyclohexan]-6-yl)oxy)-dimethylsilane **(3r)** (Using Acetone-d_6 as solvent)



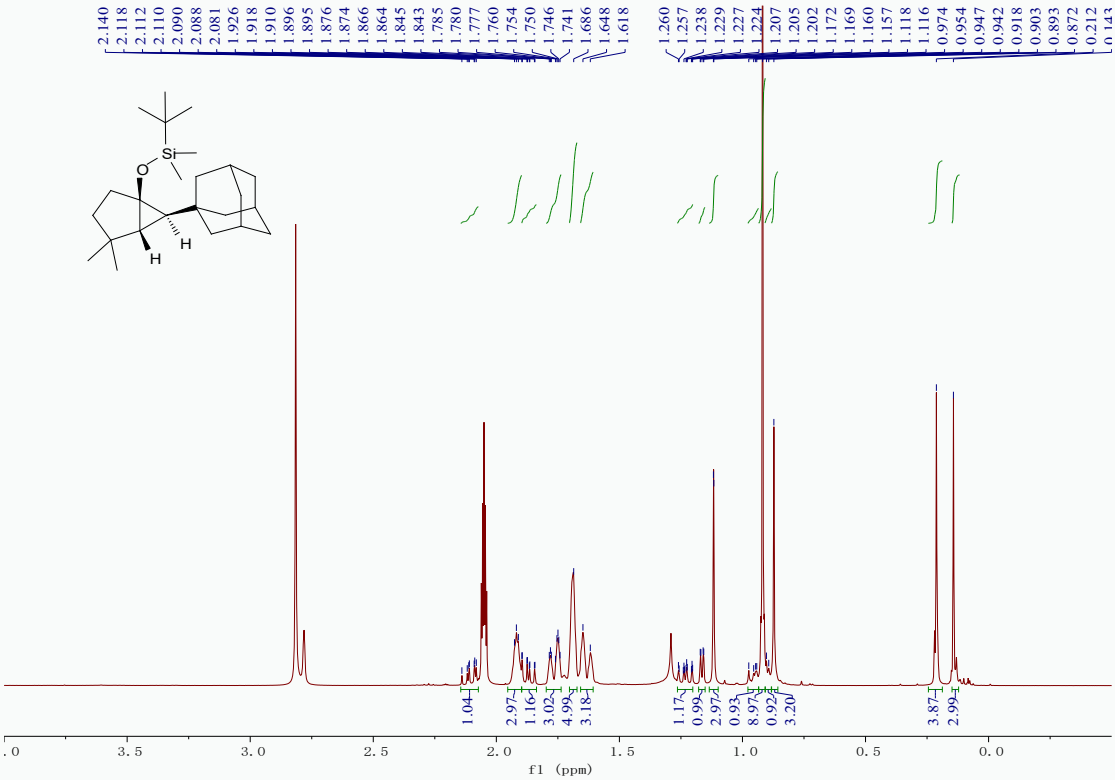


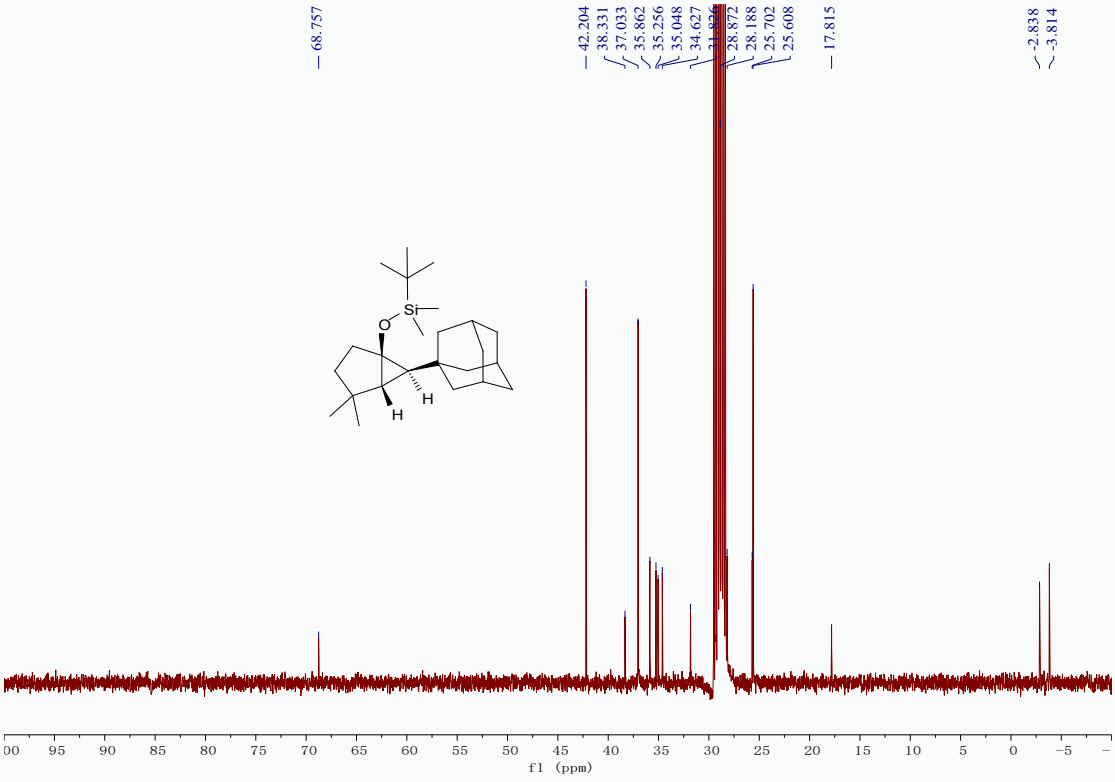
tert-butyl(((1*S*,5*R*,6*R*)-6-(tert-butyl)-4,4-dimethylbicyclo[3.1.0]hexan-1-yl)oxy) dimethylsilane **(3s)** (Using Acetone-d_6 as solvent)



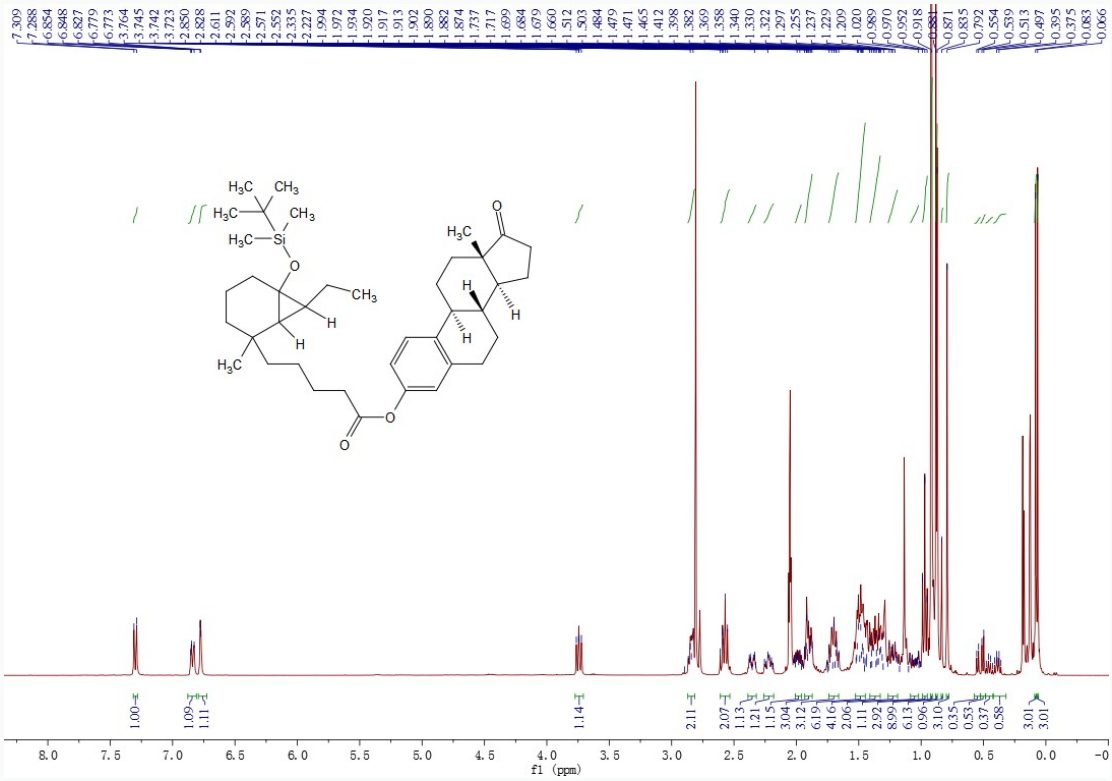


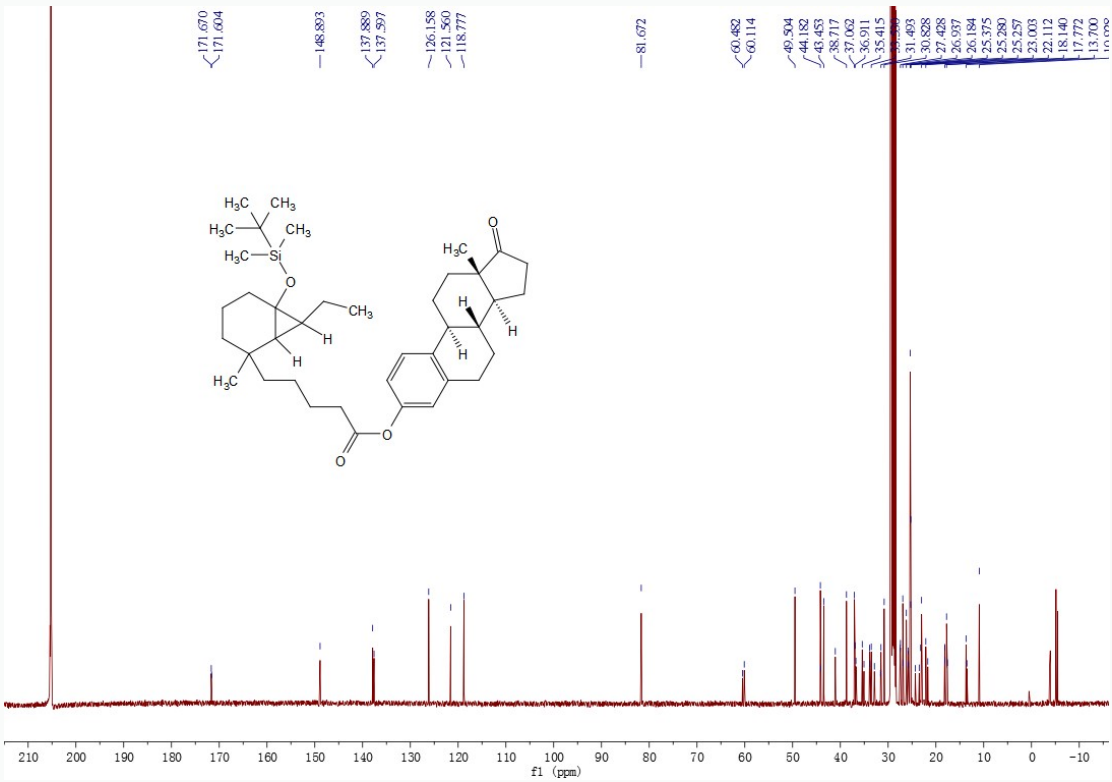
(((1*R*,5*R*,6*R*)-6-((1r,3R)-adamantan-1-yl)-4,4-dimethylbicyclo[3.1.0]hexan-1-yl) oxy)(tert-butyl)dimethylsilane **(3t)** (Using Acetone-d_6 as solvent)



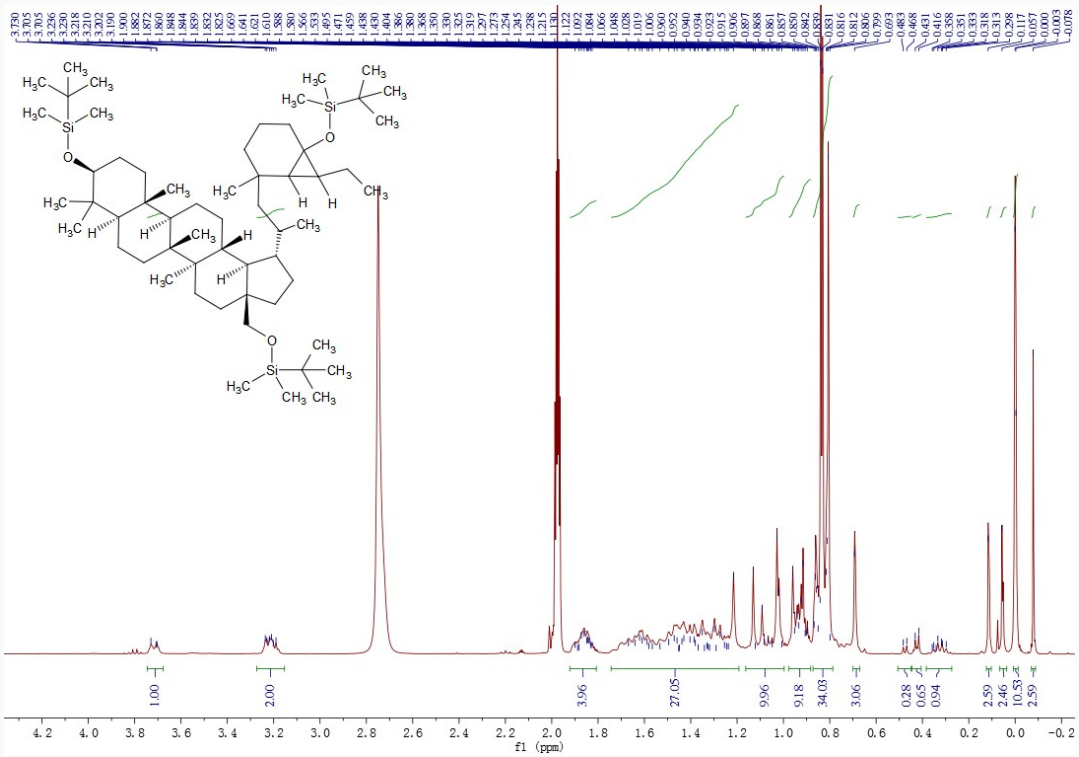


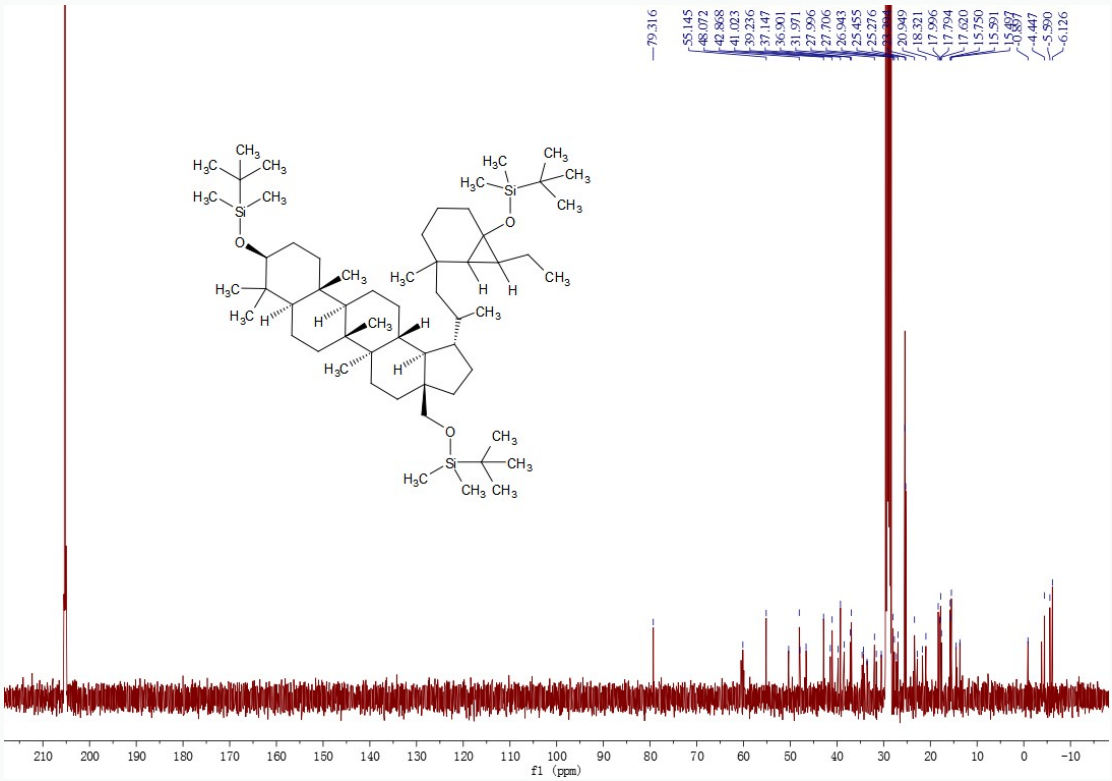
(8*R*, 9*S*, 13*S*, 14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a] phenanthren-3-yl 5-(6-((tert-butyldimethylsilyl)oxy)-7-ethyl-2-methylbicyclo[4.1.0]heptan-2-yl)pentanoate **(3u)** (Using Acetone-d_6 as solvent)



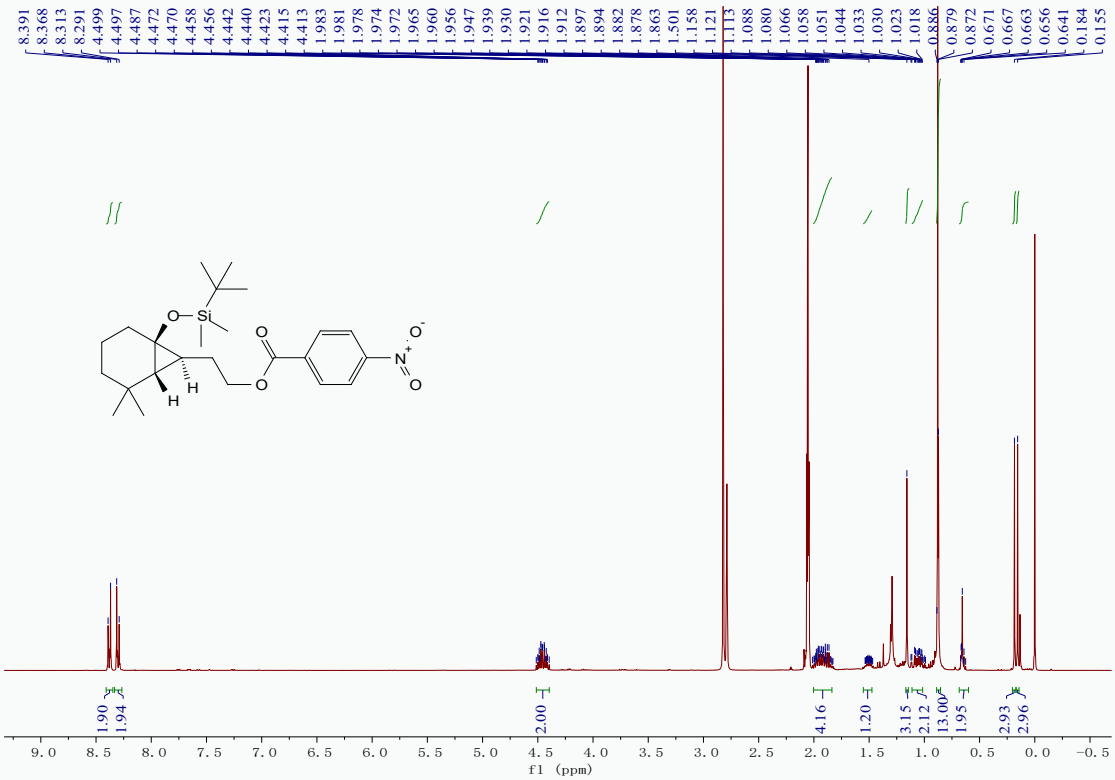


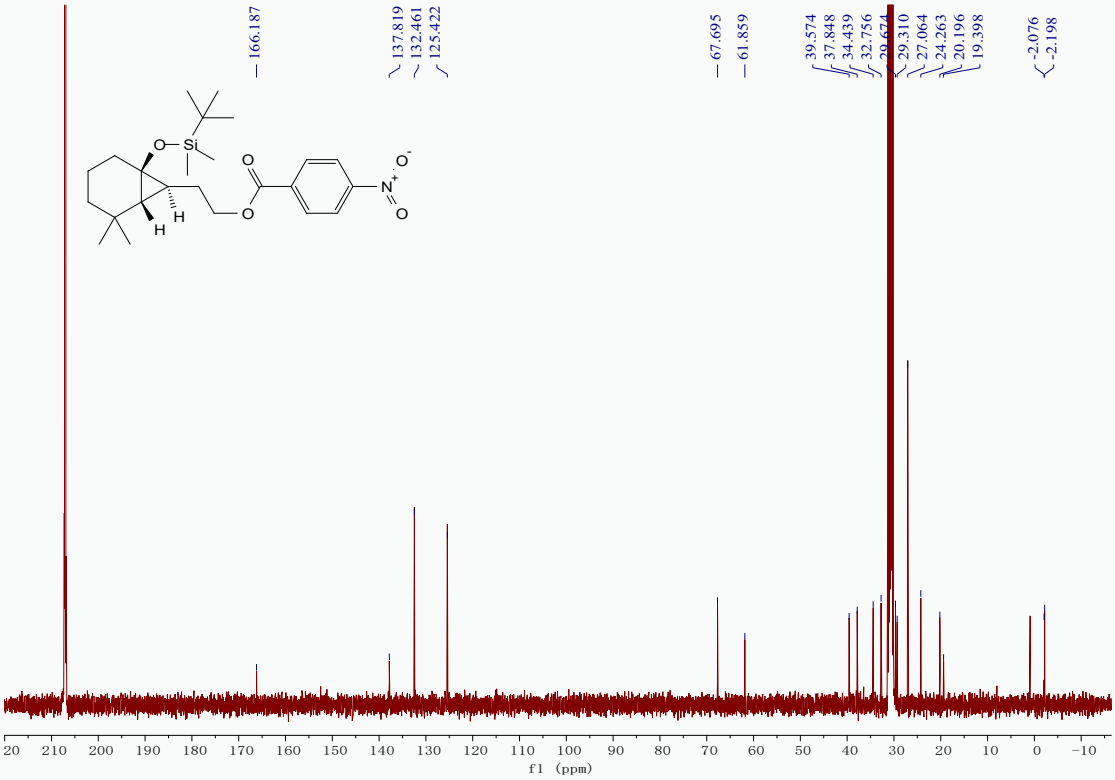
tert-butyl(((1*S*, 3*aS*, 5*aR*, 5*bR*, 7*aR*, 9*S*, 11*aR*, 11*bR*, 13*aR*, 13*bR*)-9-((tert-butyldimethylsilyl) oxy)-1-((2R)-1-(6-((tert-butyldimethylsilyl)oxy)-7-ethyl-2-methylbicyclo[4.1.0]heptan-2-yl) propan-2-yl)-5a,5b,8,8,11a-pentamethylicosahydro-3aH-cyclopenta[a]chrysen-3a-yl)methoxy) dimethylsilane **(3v)** (Using Acetone-d_6 as solvent)



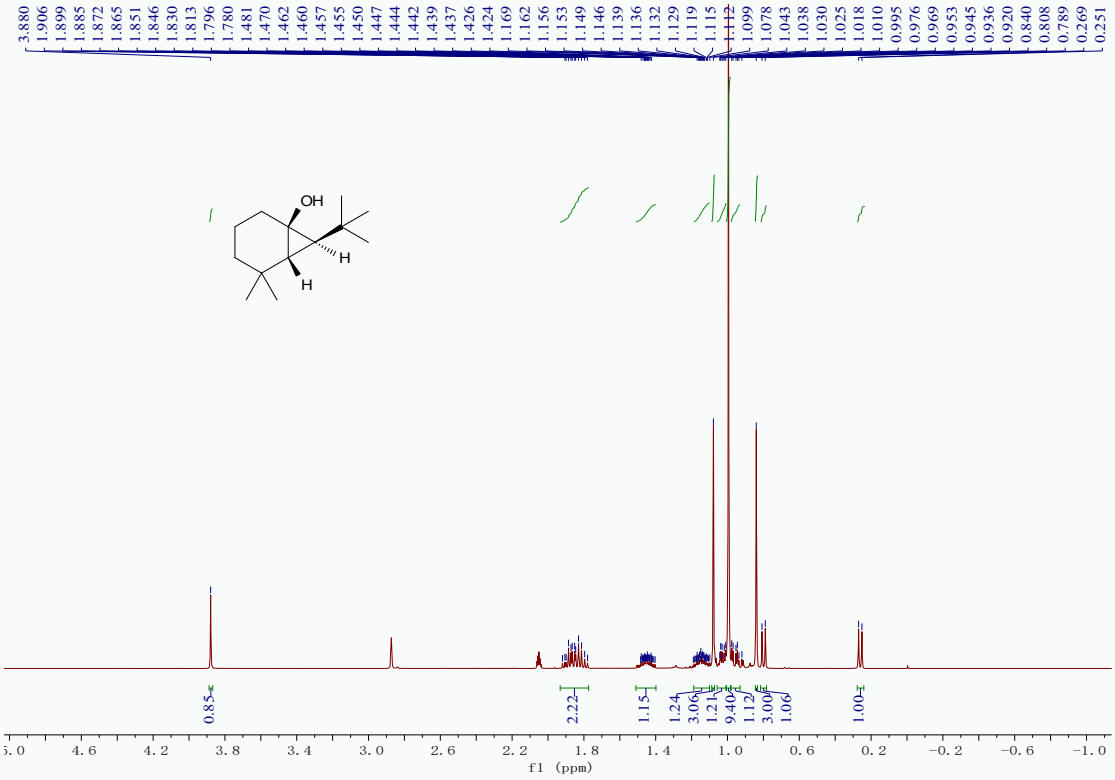


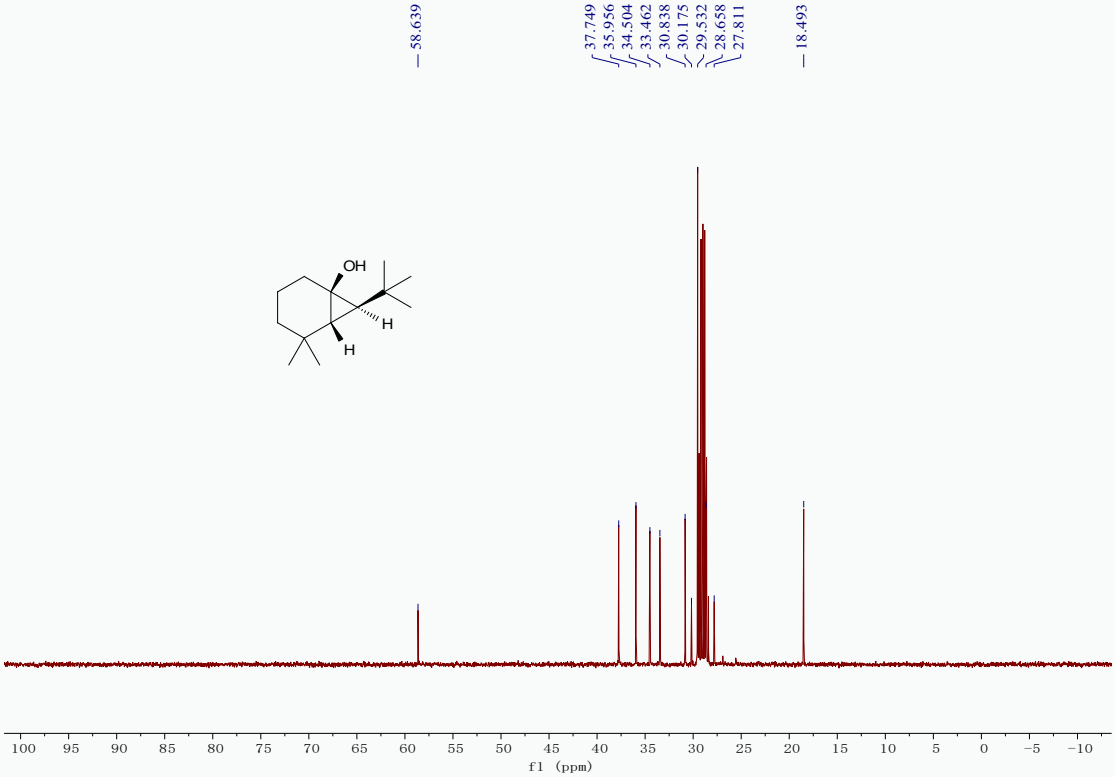
2-((1*S*, 6*R*, 7*S*)-1-((tert-butyldimethylsilyl)oxy)-5,5-dimethylbicyclo[4.1.0]heptan-7-yl)ethyl 4-nitrobenzoate (**5**) (Using Acetone-d_6 as solvent)



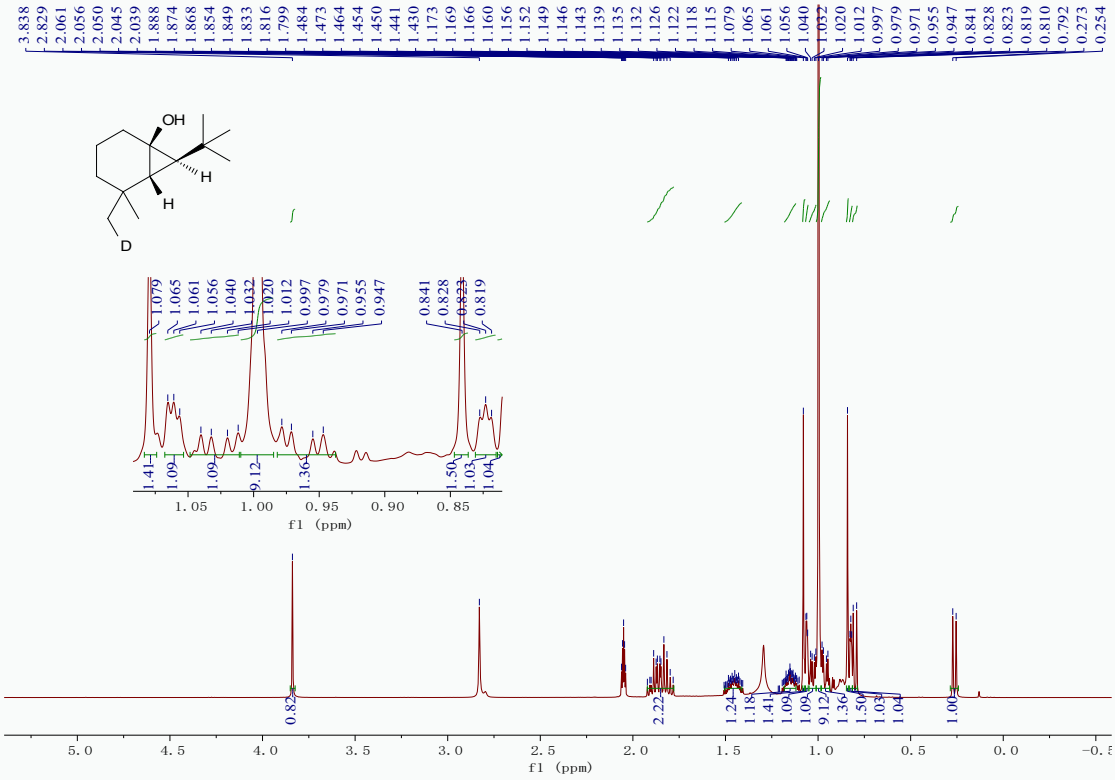


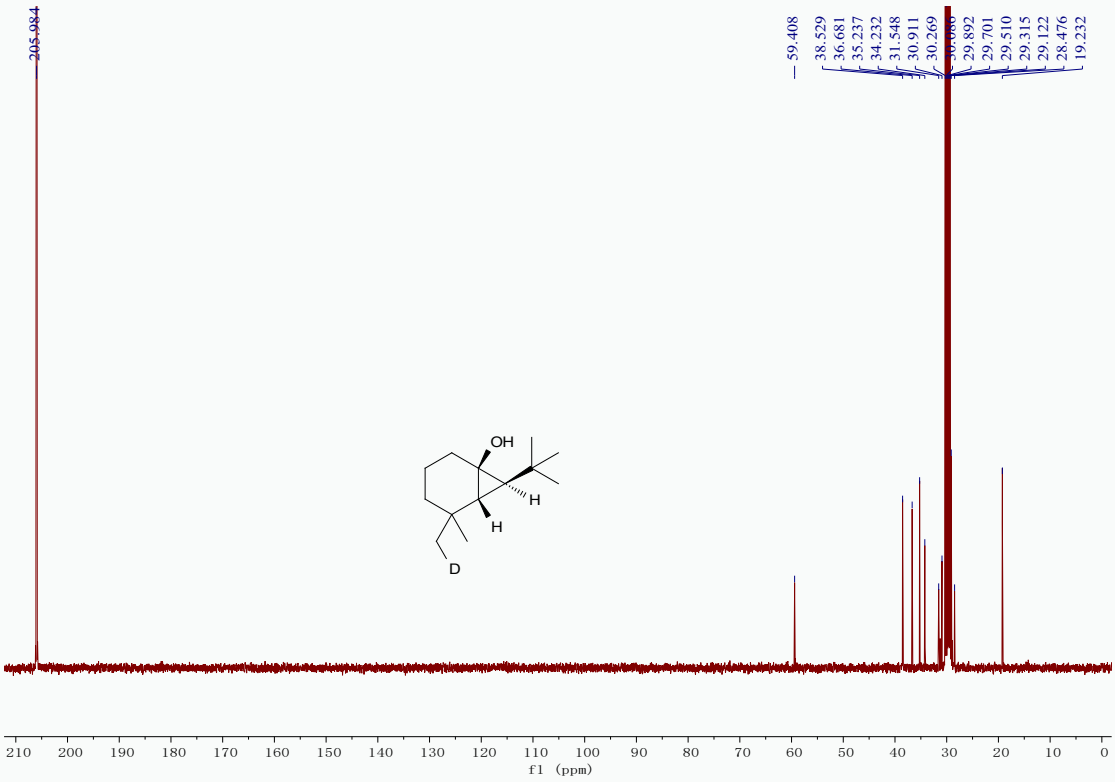
(1*S*, 6*R*,7*R*)-7-(tert-butyl)-5,5-dimethylbicyclo[4.1.0]heptan-1-ol (**3a'**) (Using Acetone-d_6 as solvent)



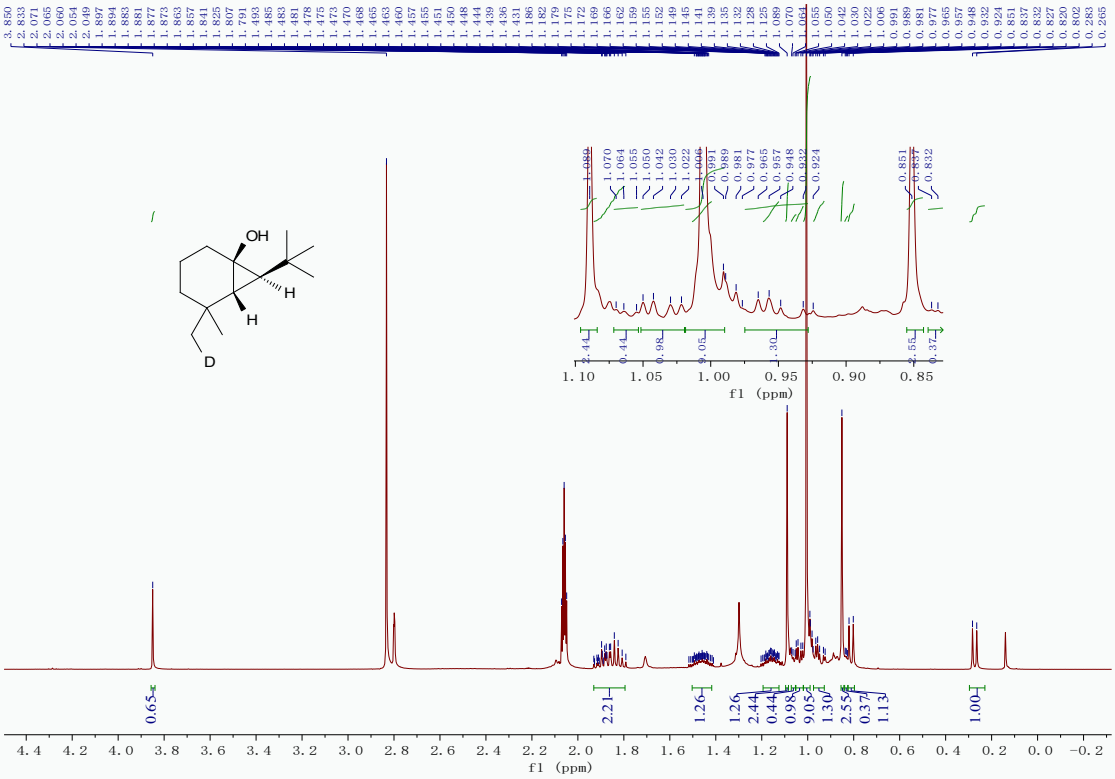


(1*S*,6*R*,7*R*)-7-(tert-butyl)-5-methyl-5-(methyl-d)bicyclo[4.1.0]heptan-1-ol (*d*-**3a'** and *epi-d*-**3a'**) (Using Acetone-d_6 as solvent)

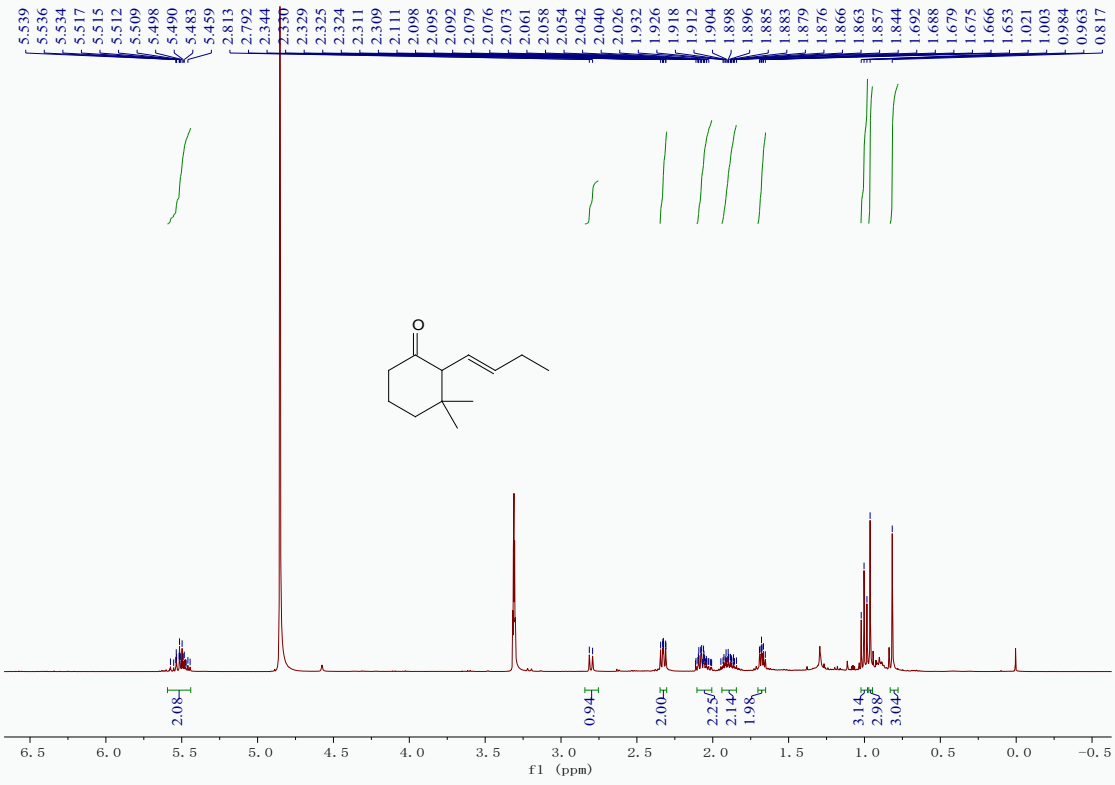


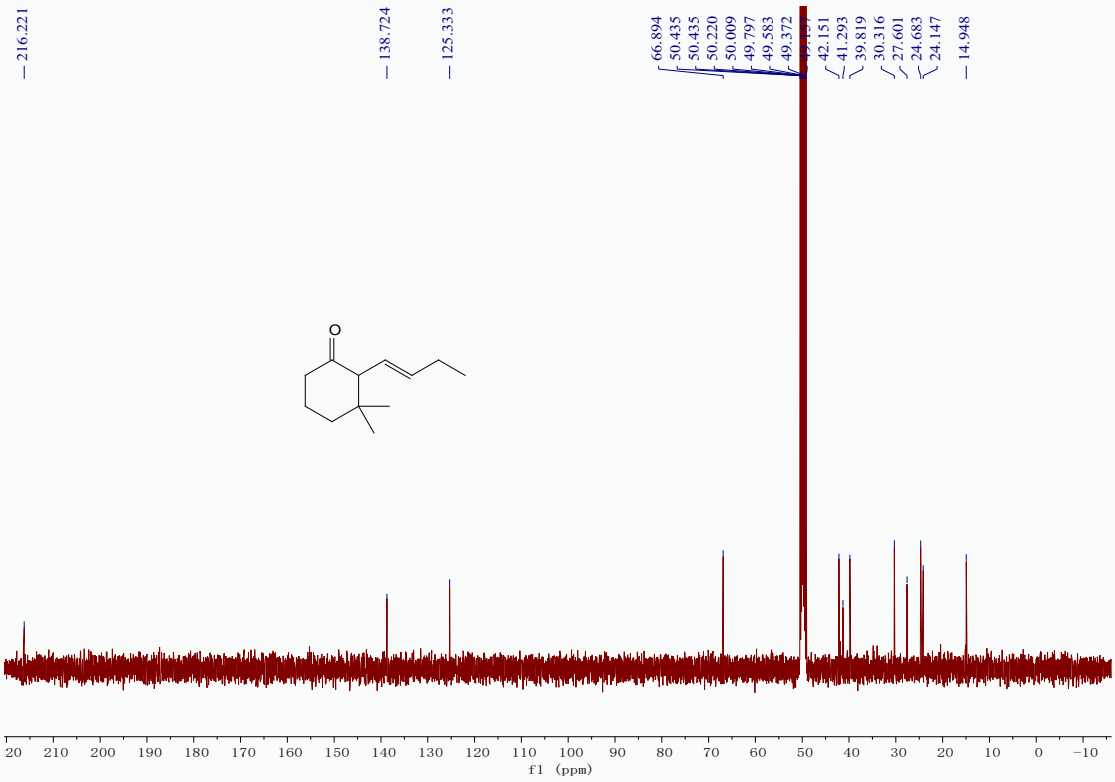


competitive experimental study, **3a'**

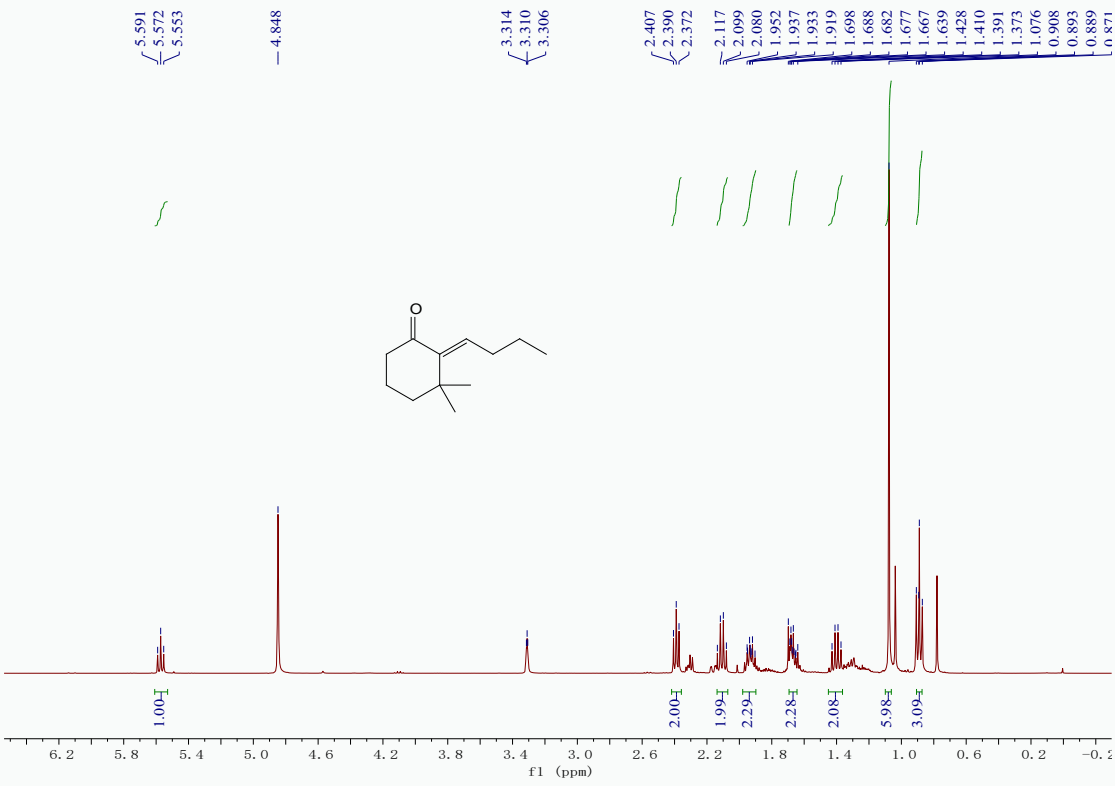


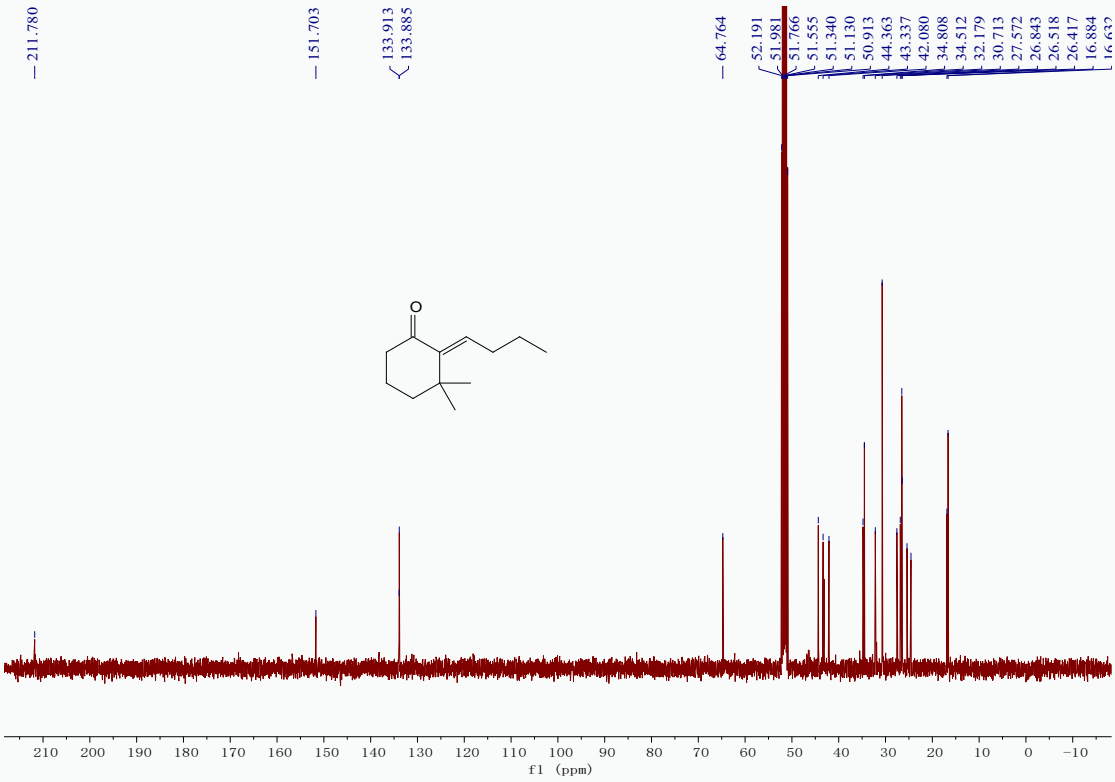
(*E*)-2-(but-1-en-1-yl)-3,3-dimethylcyclohexan-1-one (**7**) (Using CD_3OD as solvent)



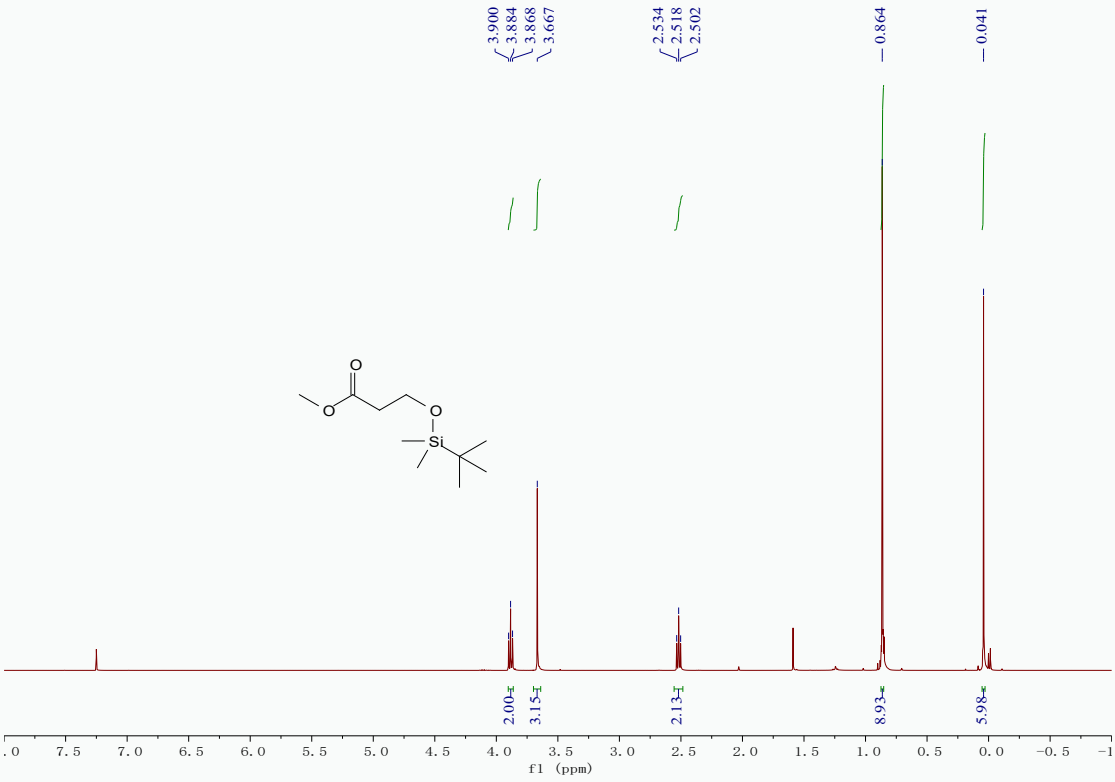


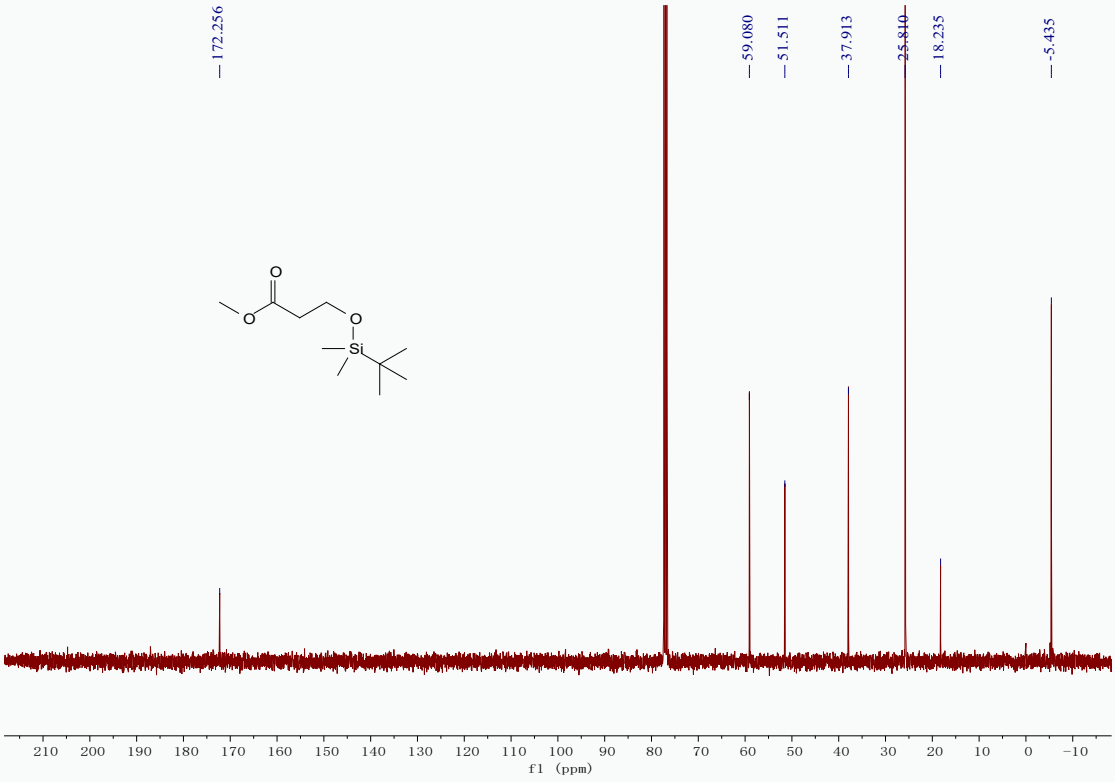
(*E*)-2-butylidene-3,3-dimethylcyclohexan-1-one (**8**) (Using CD_3OD as solvent)



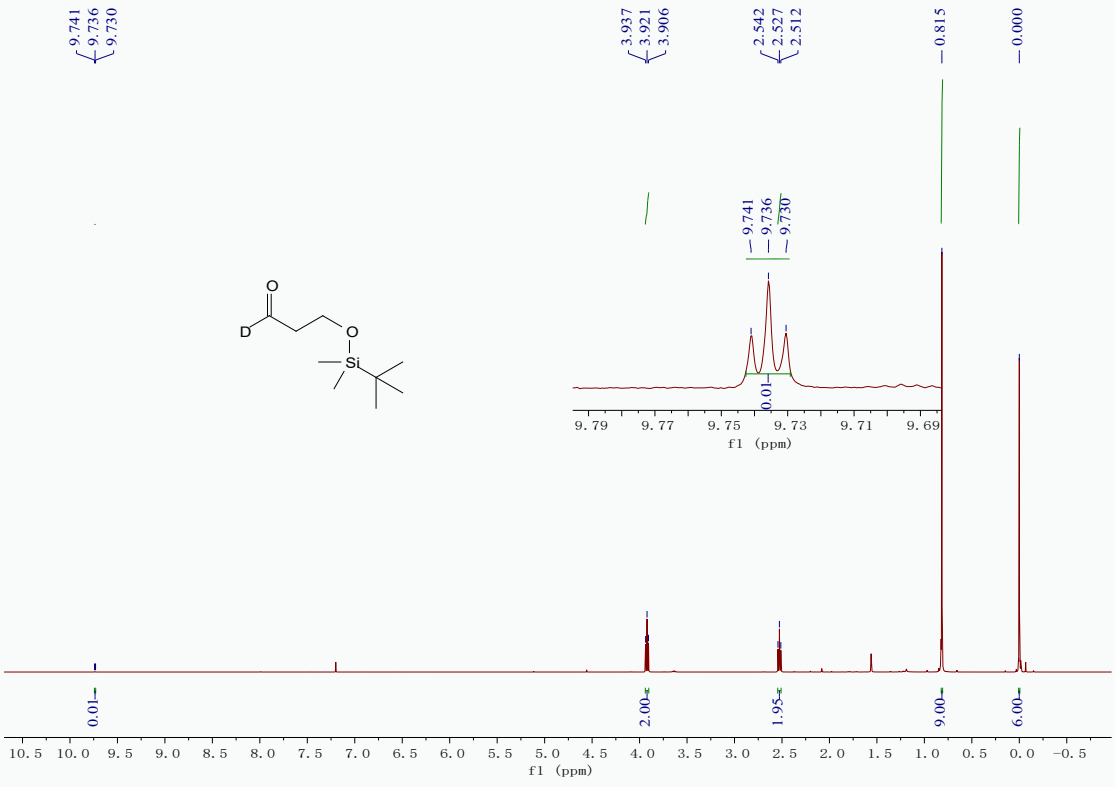


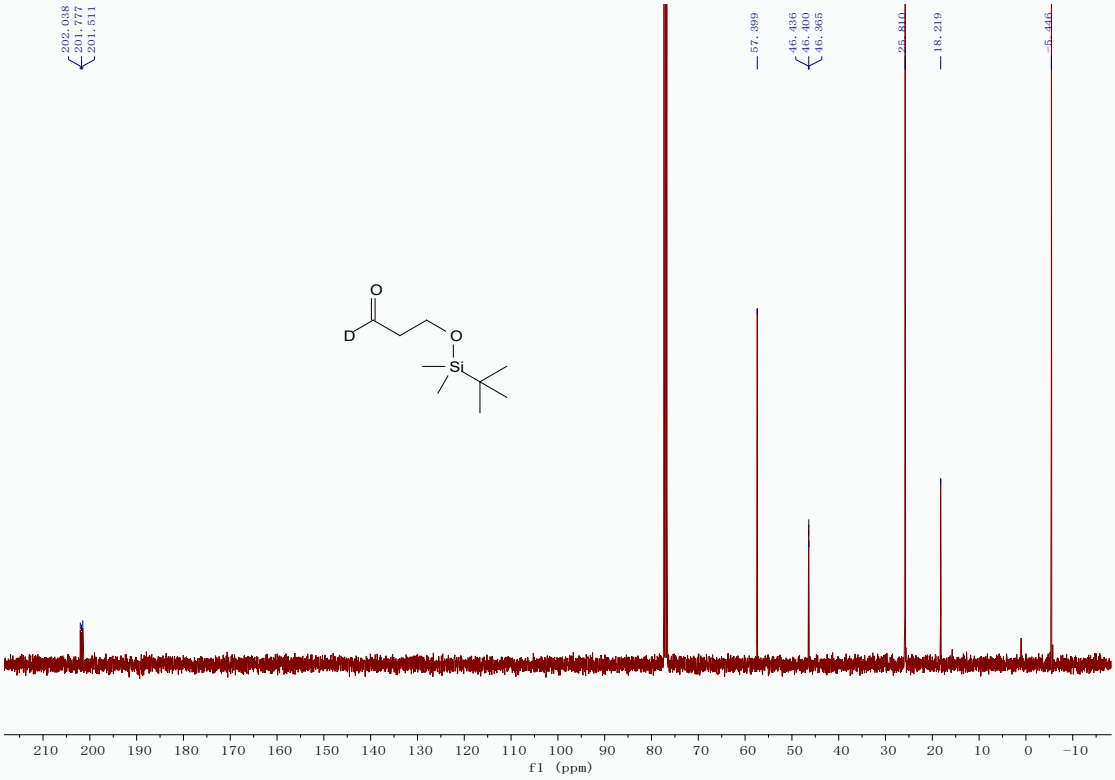
methyl 3-((tert-butyldimethylsilyl)oxy)propanoate (**21**) (Using $CDCl_3$ as solvent)



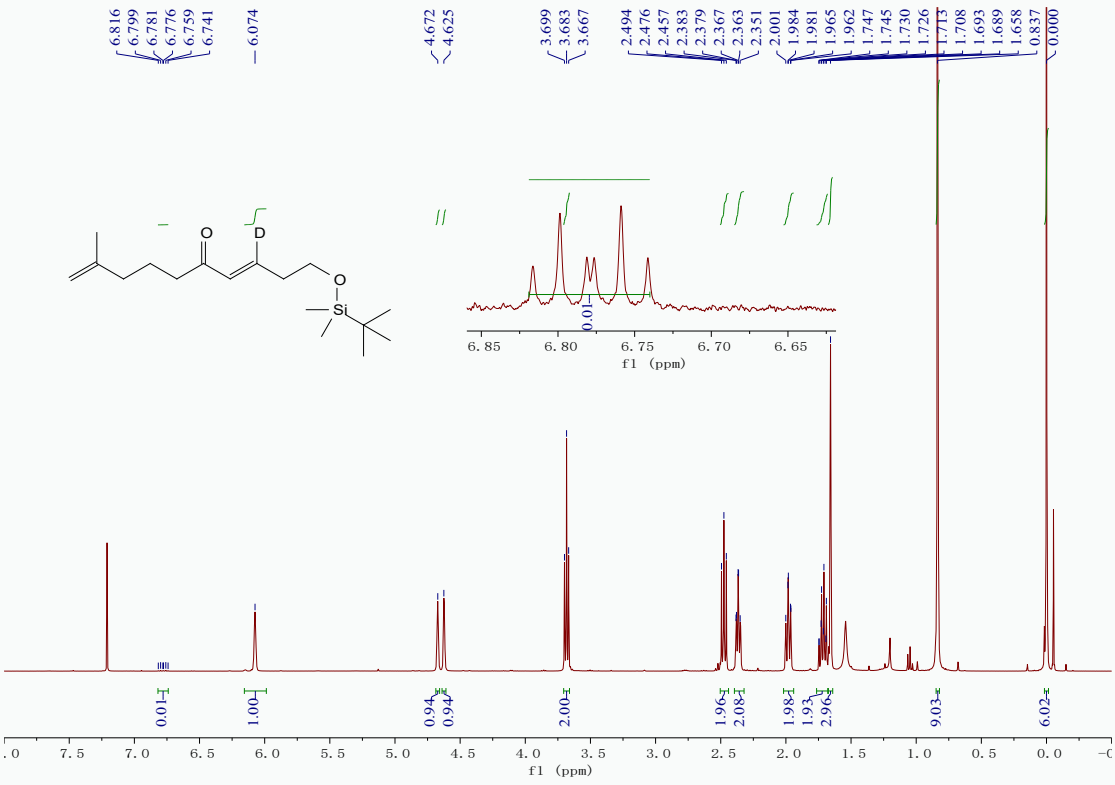


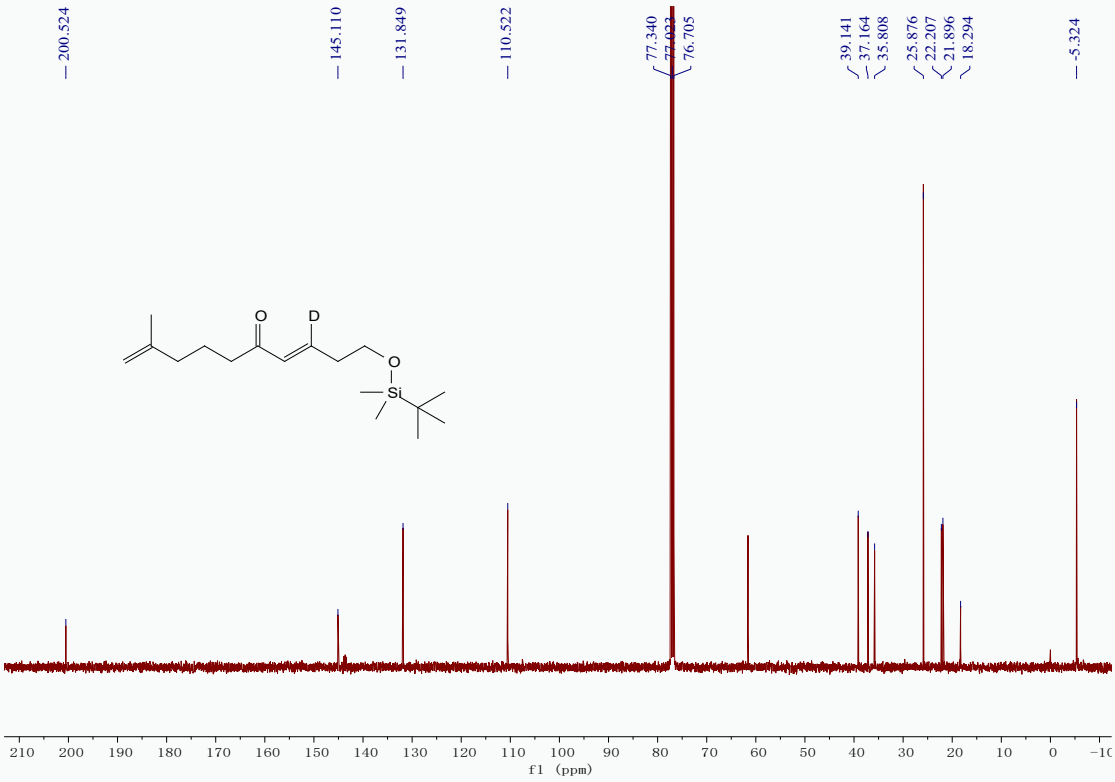
3-((tert-butyldimethylsilyl)oxy)propanal-1-d (**23**) (Using $CDCl_3$ as solvent)



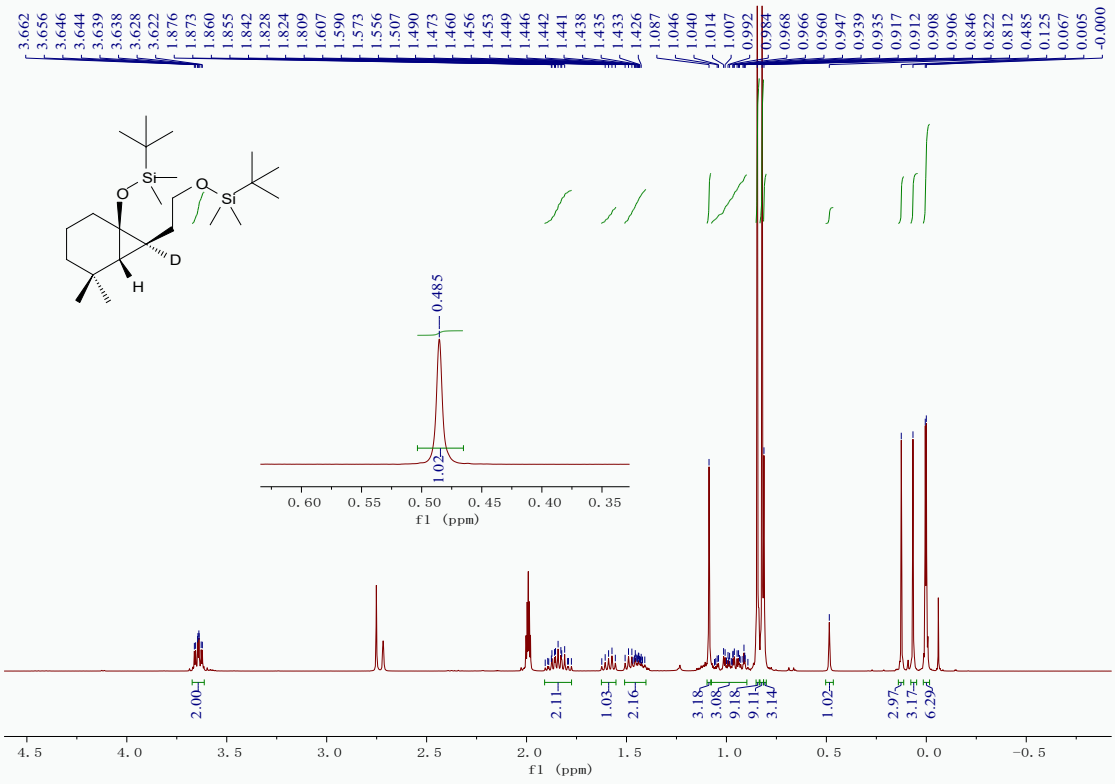


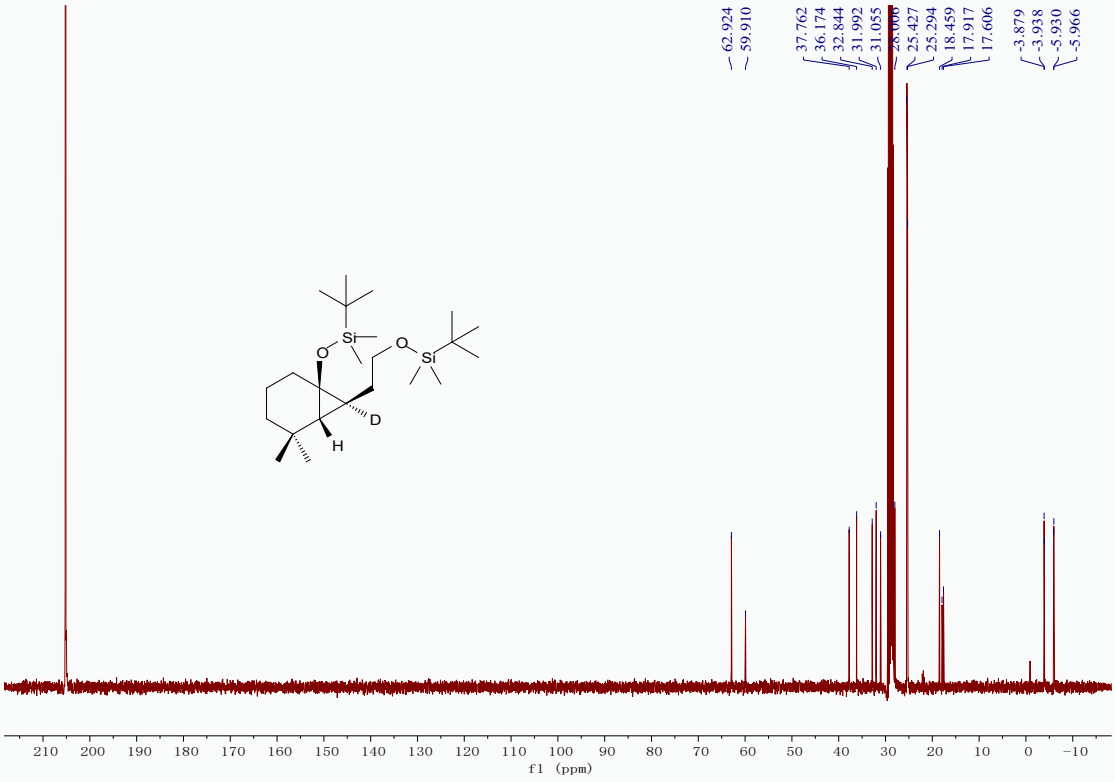
(*E*)-1-((tert-butyldimethylsilyl)oxy)-9-methyldeca-3,9-dien-5-one-3-d (*d*-**2e**) (Using $CDCl_3$ as solvent)





tert-butyl(2-((1*S*,6*R*,7*S*)-1-((tert-butyldimethylsilyl)oxy)-5,5-dimethylbicyclo[4.1.0]heptan-7-yl-7-d)ethoxy)dimethylsilane (*7-d*-**2e**) (Using Acetone-d_6 as solvent)





8. Computational procedures

All calculations were carried out using Gaussian 09 software package[10]. Since the DFT functional combined method has been demonstrated to generate accurate results for organometallics especially in the description of non-covalent interactions, the geometric structures of the intermediates and transition states were full-optimized at the B3LYP/6-31G(d,p) level in the gas-phase[11]. Frequency analyses were also performed on the optimized structures to confirm that the intermediates are local minima and the transition states have only one imaginary frequency. The solvation effect was considered into single-point calculation at the M06(PCM, *n*-PrOH)/6-311G(d,p) level[12]. This model was used for single-point energy calculations based on B3LYP-optimzed geometries. The main discussion was based on Gibbs free energies in the solution phase, which was obtained from the addition of solvation single-point energy and gas-phase thermal correction to Gibbs free energies.

Summary of energies

Table SX: Total energies (in a.u.) of various species in the reaction.

Species	B3LYP/6-31G(d,p)		M06/6-311G(d,p)
	ZPG	G	PCM-SCF
H-Fe(acac)$_2$	0.180122	-1954.5042	-1954.424057

Substrate	0.275099	-583.57672	-583.5370484
n-PrOH	0.081121	-194.278245	-194.2734448
IM0	0.478446	-2538.08589	-2537.981025
TS1	0.478719	-2538.071736	-2537.960085
IM1	0.486772	-2538.084969	-2538.019101
TS2	0.486044	-2538.071215	-2537.996743
IM2	0.486996	-2538.094099	-2538.020305
anti-TS3	0.488638	-2538.091264	-2538.017479
anti-IM3	0.494827	-2538.117945	-2538.056556
syn-TS3	0.490132	-2538.068462	-2537.998589
syn-IM3	0.493981	-2538.097548	-2538.048489
Iso-TS3	0.487235	-2538.072403	-2537.994889
Iso-IM3	0.493443	-2538.114603	-2538.048489
TS4	0.591353	-2732.378178	-2732.337232
IM4	0.593547	-2732.387779	-2732.350642
TS5	0.459373	-2863.593506	-2863.500936
Pro	0.307937	-584.757134	-584.7622298
Ph(iPrO)-SiH_2	0.168714	-715.990189	-715.9309611
Ph(iPrO)(nPrOH)SiH	0.247981	-909.125157	-909.0611194

Optimized Structures

H-Fe(acac)$_2$

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	1.340080	1.356347	0.154399
2	8	0	1.339173	-1.356577	0.153074
3	6	0	2.563958	1.230728	-0.194429
4	6	0	2.563176	-1.231396	-0.195589
5	6	0	3.209678	-0.000465	-0.386100
6	6	0	3.315559	2.524372	-0.400444
7	1	0	3.306881	3.097045	0.532814
8	1	0	2.795200	3.128653	-1.150521
9	6	0	3.313981	-2.525336	-0.402601
10	1	0	2.792911	-3.129029	-1.152650
11	1	0	4.346569	-2.365307	-0.718594
12	1	0	4.249895	-0.000659	-0.686339
13	1	0	4.348224	2.363956	-0.715989
14	1	0	3.305528	-3.098416	0.530418
15	26	0	0.000015	-0.000037	0.707169

16	8	0	-1.339165	1.356557	0.153130
17	8	0	-1.340162	-1.356349	0.154546
18	6	0	-2.563972	-1.230716	-0.194510
19	6	0	-2.563143	1.231417	-0.195611
20	6	0	-3.209629	0.000495	-0.386321
21	6	0	-3.315632	-2.524344	-0.400414
22	1	0	-4.347901	-2.363920	-0.717250
23	1	0	-2.794533	-3.129354	-1.149376
24	1	0	-3.308218	-3.096271	0.533323
25	1	0	-4.249809	0.000715	-0.686687
26	6	0	-3.313950	2.525379	-0.402486
27	1	0	-2.792747	3.129275	-1.152278
28	1	0	-3.305709	3.098232	0.530675
29	1	0	-4.346471	2.365391	-0.718720
30	1	0	0.000200	0.000030	2.364634

Substrate

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.704279	0.163710	-0.919630
2	6	0	-0.759007	1.367339	-1.145518
3	6	0	0.030976	1.736394	0.105804
4	6	0	1.300525	1.037671	0.431072
5	6	0	-3.747271	-0.733904	0.330899
6	6	0	1.897590	0.095043	-0.314272
7	1	0	-2.136853	-0.110487	-1.888903
8	1	0	-1.124788	-0.703858	-0.580961
9	1	0	-1.346938	2.249800	-1.416297
10	1	0	-0.084148	1.146695	-1.979371
11	8	0	-0.393040	2.591169	0.875297
12	1	0	1.732580	1.367191	1.372196
13	6	0	-4.628428	-1.157764	-0.819844
14	6	0	3.187394	-0.640392	-0.012596
15	6	0	4.167037	-0.382191	-1.182694
16	6	0	2.866911	-2.153352	0.052088
17	6	0	3.833840	-0.193461	1.308457
18	1	0	1.431215	-0.206175	-1.253061
19	1	0	-5.259994	-0.325023	-1.156087
20	1	0	-4.038543	-1.471708	-1.690050
21	1	0	-5.281484	-1.989332	-0.541705
22	1	0	5.094213	-0.946849	-1.035199
23	1	0	3.734880	-0.692859	-2.140382
24	1	0	3.784453	-2.731009	0.209203
25	1	0	4.760819	-0.750033	1.480909
26	1	0	4.082923	0.872490	1.292988
27	1	0	3.172348	-0.375442	2.161496
28	1	0	4.422722	0.679684	-1.256093
29	1	0	2.178966	-2.375740	0.873997
30	1	0	2.406052	-2.503496	-0.878203
31	6	0	-3.779112	-1.365555	1.509232

32	1	0	-3.152740	-1.052715	2.340351
33	1	0	-4.435332	-2.213819	1.685775
34	6	0	-2.830171	0.448733	0.094720
35	1	0	-3.420124	1.300845	-0.274006
36	1	0	-2.391936	0.768863	1.044722

n-PrOH

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	1.382174	-0.637158	-0.219660
2	6	0	0.772252	0.543796	0.291379
3	6	0	-0.634229	0.643957	-0.288533
4	6	0	-1.543268	-0.515764	0.128977
5	1	0	2.246726	-0.734844	0.197100
6	1	0	-1.677857	-0.539018	1.216952
7	1	0	-2.534283	-0.427405	-0.327652
8	1	0	-1.067174	1.601322	0.028834
9	1	0	-0.552038	0.680588	-1.381807
10	1	0	0.716032	0.516546	1.392929
11	1	0	1.351755	1.439825	0.014973
12	1	0	-1.109085	-1.471682	-0.174992

IM0

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.609172	-3.148476	1.493992
2	6	0	2.422594	-2.774764	0.240077
3	6	0	1.709948	-1.836017	-0.768191
4	6	0	1.666613	-0.362395	-0.417673
5	6	0	2.886683	0.464257	-0.410378
6	6	0	1.216379	-2.020443	2.416556
7	6	0	4.101571	0.070972	-0.830712
8	1	0	2.218029	-3.882586	2.047218
9	1	0	0.703050	-3.681381	1.180268
10	1	0	2.657971	-3.704982	-0.291406
11	1	0	3.386852	-2.344709	0.530866
12	1	0	0.681380	-2.158856	-0.945110
13	1	0	2.242629	-1.908916	-1.725111
14	8	0	0.600346	0.237977	-0.208544
15	1	0	2.712824	1.478571	-0.064094
16	6	0	2.317899	-1.194288	3.040454
17	6	0	-0.085262	-1.792253	2.732470
18	6	0	5.366742	0.899163	-0.884543
19	6	0	5.853228	0.925775	-2.353853
20	6	0	6.432828	0.190296	-0.013704
21	6	0	5.162583	2.336637	-0.381260
22	1	0	4.226488	-0.947291	-1.198569
23	1	0	3.072040	-0.858517	2.318701

24	1	0	1.911991	-0.303160	3.528078
25	1	0	2.862210	-1.768712	3.806133
26	1	0	-0.331812	-1.106639	3.536860
27	1	0	-0.952704	-0.686140	1.637975
28	1	0	-0.844991	-2.524900	2.475818
29	1	0	6.802919	1.466198	-2.427799
30	1	0	6.012862	-0.086860	-2.740114
31	1	0	7.387094	0.724368	-0.075835
32	1	0	6.104232	2.891195	-0.442254
33	1	0	4.421345	2.871966	-0.983051
34	1	0	4.831921	2.353773	0.661915
35	1	0	5.126006	1.424564	-3.002054
36	1	0	6.127428	0.159316	1.036827
37	1	0	6.603031	-0.838824	-0.348088
38	26	0	-1.464768	0.121197	0.185937
39	8	0	-3.251773	-0.725315	0.731328
40	8	0	-2.645158	1.426690	-0.950979
41	8	0	-1.433730	-1.179380	-1.357364
42	8	0	-1.123669	1.821852	1.300862
43	6	0	-1.591042	3.004592	1.224991
44	6	0	-2.934551	2.657700	-0.813749
45	6	0	-2.469715	3.470229	0.233150
46	6	0	-1.122273	3.956582	2.307373
47	6	0	-2.373500	-1.940978	-1.781589
48	6	0	-3.969761	-1.543022	0.077918
49	6	0	-3.597651	-2.154002	-1.139712
50	6	0	-2.082900	-2.652530	-3.086390
51	1	0	-1.178963	-3.261869	-2.978834
52	1	0	-2.906196	-3.291406	-3.412289
53	1	0	-1.876688	-1.908105	-3.862538
54	1	0	-4.302603	-2.833412	-1.602860
55	6	0	-5.316262	-1.869332	0.689817
56	1	0	-5.897339	-0.947207	0.793520
57	1	0	-5.167320	-2.268370	1.698265
58	1	0	-5.886349	-2.588620	0.098139
59	1	0	-1.528448	4.963810	2.191128
60	1	0	-0.028488	4.004937	2.297568
61	6	0	-3.844747	3.243231	-1.873598
62	1	0	-4.776820	2.669909	-1.905627
63	1	0	-4.075094	4.296497	-1.698334
64	1	0	-2.787293	4.505186	0.268888
65	1	0	-1.415819	3.561790	3.285629
66	1	0	-3.370982	3.138064	-2.855299

IM0’

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-6.421925	-0.680864	-0.025042
2	6	0	-5.128068	-0.669445	-0.850160
3	6	0	-4.171873	0.464536	-0.468441
4	6	0	-2.876568	0.460733	-1.274622

5	6	0	-1.850293	1.500190	-1.024919
6	6	0	-6.326572	-1.082326	1.436391
7	6	0	-1.942510	2.464837	-0.096090
8	1	0	-7.144289	-1.357899	-0.506036
9	1	0	-6.894735	0.311828	-0.079135
10	1	0	-5.384175	-0.571051	-1.910255
11	1	0	-4.610710	-1.630506	-0.767049
12	1	0	-3.921444	0.416937	0.598161
13	1	0	-4.662970	1.437543	-0.610425
14	8	0	-2.681917	-0.395085	-2.133776
15	1	0	-0.975826	1.412315	-1.663732
16	6	0	-5.255240	-1.662096	1.988255
17	6	0	-0.936886	3.552364	0.215083
18	6	0	-0.431381	3.327972	1.661496
19	6	0	-1.672901	4.911779	0.139779
20	6	0	0.256317	3.559667	-0.753969
21	1	0	-2.831526	2.498131	0.535349
22	1	0	-4.351160	-1.876129	1.427557
23	1	0	-5.251587	-1.953692	3.034854
24	1	0	0.255689	4.132138	1.949104
25	1	0	-1.260587	3.325619	2.378085
26	1	0	-0.994659	5.725759	0.418547
27	1	0	0.924413	4.392466	-0.507294
28	1	0	0.839788	2.636453	-0.694036
29	1	0	-0.072304	3.695296	-1.790015
30	1	0	0.097652	2.373956	1.747901
31	1	0	-2.040554	5.108471	-0.872902
32	1	0	-2.529539	4.942127	0.822627
33	6	0	-7.573897	-0.809642	2.242815
34	1	0	-7.799163	0.264648	2.269382
35	1	0	-8.448445	-1.298321	1.793250
36	1	0	-7.479058	-1.163753	3.272730
37	1	0	1.181474	0.005417	1.526340
38	26	0	2.227647	-0.638783	0.412478
39	8	0	4.008783	-0.971313	1.200740
40	8	0	3.020605	1.046580	-0.335691
41	6	0	4.168371	1.576295	-0.157716
42	6	0	5.065797	-0.248388	1.235008
43	6	0	5.202629	0.988980	0.591446
44	6	0	4.380103	2.919870	-0.815409
45	1	0	3.641730	3.629874	-0.428835
46	1	0	5.383645	3.315529	-0.647891
47	1	0	4.200612	2.826624	-1.891295
48	1	0	6.143189	1.517907	0.680051
49	6	0	6.210036	-0.819484	2.038297
50	1	0	6.471217	-1.806457	1.642980
51	1	0	5.884279	-0.966512	3.073322
52	1	0	7.093315	-0.178111	2.025193
53	8	0	1.396823	-0.837780	-1.362592
54	8	0	1.917588	-2.582123	0.655891
55	6	0	1.338160	-3.435366	-0.101576
56	6	0	0.869526	-1.857264	-1.937364
57	6	0	0.831220	-3.143539	-1.375671
58	6	0	1.218748	-4.830441	0.464669

59	1	0	0.747197	-5.526455	-0.231726
60	1	0	0.633588	-4.793397	1.389619
61	6	0	0.238611	-1.596100	-3.279132
62	1	0	0.878875	-0.927974	-3.861746
63	1	0	0.059030	-2.518574	-3.835724
64	1	0	0.362122	-3.938044	-1.942115
65	1	0	2.214493	-5.199146	0.731087
66	1	0	-0.721875	-1.090508	-3.115706

TS1

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.120290	-3.405471	0.551387
2	6	0	1.994010	-2.856976	-0.595898
3	6	0	1.414788	-1.585310	-1.251453
4	6	0	1.548309	-0.309698	-0.444195
5	6	0	2.865584	0.257890	-0.091981
6	6	0	0.990347	-2.508637	1.757218
7	6	0	4.046011	-0.110271	-0.616964
8	1	0	1.561176	-4.367355	0.861674
9	1	0	0.123647	-3.633668	0.155248
10	1	0	2.089730	-3.628746	-1.370286
11	1	0	3.008827	-2.673368	-0.227752
12	1	0	0.350351	-1.716231	-1.458288
13	1	0	1.916690	-1.421061	-2.215385
14	8	0	0.550000	0.345574	-0.109023
15	1	0	2.797823	1.088081	0.605495
16	6	0	2.245142	-2.185069	2.526158
17	6	0	-0.250384	-2.022386	2.157715
18	6	0	5.405421	0.501066	-0.347655
19	6	0	5.957313	1.041988	-1.688691
20	6	0	6.339765	-0.621595	0.164161
21	6	0	5.354702	1.637912	0.685281
22	1	0	4.065847	-0.925920	-1.340197
23	1	0	2.960415	-1.572168	1.961514
24	1	0	2.016508	-1.651216	3.453209
25	1	0	2.783196	-3.106384	2.797010
26	1	0	-0.350108	-1.553141	3.133496
27	1	0	-0.725560	-0.713358	1.405499
28	1	0	-1.145875	-2.516711	1.787666
29	1	0	6.967443	1.442982	-1.551164
30	1	0	6.011051	0.251430	-2.445152
31	1	0	7.353274	-0.234235	0.315351
32	1	0	6.359261	2.040533	0.850243
33	1	0	4.717661	2.461215	0.346793
34	1	0	4.973228	1.286752	1.649374
35	1	0	5.322746	1.842524	-2.081657
36	1	0	5.984287	-1.026542	1.116930
37	1	0	6.400533	-1.447662	-0.552784
38	26	0	-1.712829	0.286342	0.291331
39	8	0	-3.601098	-0.057530	0.833316

40	8	0	-1.728848	1.573586	-1.300681
41	8	0	-1.918447	-1.303913	-0.968679
42	8	0	-1.607254	1.883189	1.478063
43	6	0	-1.243414	3.069852	1.169398
44	6	0	-1.403791	2.803007	-1.295311
45	6	0	-1.113448	3.557492	-0.139903
46	6	0	-0.977567	3.989157	2.341383
47	6	0	-2.986972	-1.901505	-1.330316
48	6	0	-4.491515	-0.798567	0.295424
49	6	0	-4.255535	-1.689169	-0.764662
50	6	0	-2.826276	-2.919242	-2.439061
51	1	0	-2.111811	-3.687689	-2.125164
52	1	0	-3.768413	-3.398193	-2.712613
53	1	0	-2.402661	-2.426933	-3.320468
54	1	0	-5.090070	-2.263165	-1.147692
55	6	0	-5.878728	-0.680197	0.885320
56	1	0	-6.214983	0.358865	0.808974
57	1	0	-5.838336	-0.924567	1.951830
58	1	0	-6.603632	-1.331667	0.393265
59	1	0	-0.692331	4.996857	2.032197
60	1	0	-0.180864	3.562711	2.959962
61	6	0	-1.344947	3.472668	-2.653176
62	1	0	-2.315780	3.368639	-3.148412
63	1	0	-1.084248	4.531431	-2.593065
64	1	0	-0.831278	4.595320	-0.268550
65	1	0	-1.873623	4.043430	2.968187
66	1	0	-0.610036	2.955439	-3.278941

TS1’

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.143457	-3.366982	-2.036069
2	6	0	-1.819626	-2.030755	-1.669150
3	6	0	-1.598408	-1.651561	-0.182714
4	6	0	-1.752969	-0.158967	0.007802
5	6	0	-3.074029	0.463844	0.226988
6	6	0	0.362619	-3.347160	-1.841877
7	6	0	-4.231181	-0.203489	0.364985
8	1	0	-1.396281	-3.598332	-3.082226
9	1	0	-1.584161	-4.174132	-1.435974
10	1	0	-2.892393	-2.073152	-1.893589
11	1	0	-1.400044	-1.239641	-2.298919
12	1	0	-0.576662	-1.896735	0.109198
13	1	0	-2.284675	-2.213784	0.459063
14	8	0	-0.773793	0.591201	-0.077398
15	1	0	-3.036897	1.548305	0.278567
16	6	0	1.116063	-2.308816	-2.328153
17	6	0	-5.608699	0.379523	0.597004
18	6	0	-6.154126	-0.205545	1.922439
19	6	0	-6.518805	-0.077667	-0.568934
20	6	0	-5.602027	1.914522	0.674788

21	1	0	-4.216127	-1.292461	0.309539
22	1	0	0.727498	-1.656752	-3.105541
23	1	0	2.199943	-2.354285	-2.273786
24	1	0	-7.176485	0.145776	2.099508
25	1	0	-6.175706	-1.300547	1.896530
26	1	0	-7.544504	0.271877	-0.408691
27	1	0	-6.617736	2.285984	0.844633
28	1	0	-4.974532	2.272234	1.497413
29	1	0	-5.234333	2.362484	-0.253965
30	1	0	-5.536321	0.100500	2.772644
31	1	0	-6.167070	0.323793	-1.524607
32	1	0	-6.545910	-1.169831	-0.650059
33	6	0	0.962684	-4.410425	-0.962646
34	1	0	0.562780	-4.370988	0.062774
35	1	0	0.736011	-5.418938	-1.338039
36	1	0	2.050596	-4.314579	-0.897269
37	1	0	1.044337	-0.934970	-1.282783
38	26	0	1.559980	0.320083	-0.158683
39	8	0	3.515195	-0.019149	0.028874
40	8	0	1.285884	-0.882426	1.452767
41	6	0	2.164787	-1.403297	2.216521
42	6	0	4.152371	-0.641129	0.945451
43	6	0	3.555078	-1.316239	2.022493
44	6	0	1.625315	-2.173594	3.402916
45	1	0	0.988498	-2.989507	3.044437
46	1	0	2.414984	-2.586980	4.033637
47	1	0	0.992226	-1.511952	4.003097
48	1	0	4.202366	-1.804773	2.740404
49	6	0	5.659256	-0.622338	0.813932
50	1	0	6.008058	0.415587	0.826008
51	1	0	5.941976	-1.042392	-0.156874
52	1	0	6.159411	-1.179707	1.608600
53	8	0	1.284637	2.021176	0.945409
54	8	0	1.771436	1.523995	-1.753727
55	6	0	1.592921	2.786413	-1.852956
56	6	0	1.174172	3.223867	0.551427
57	6	0	1.283989	3.646241	-0.788653
58	6	0	1.755972	3.352356	-3.247969
59	1	0	1.602568	4.433001	-3.286954
60	1	0	1.045113	2.862953	-3.922165
61	6	0	0.922699	4.252277	1.635981
62	1	0	1.742630	4.219722	2.361183
63	1	0	0.831163	5.267697	1.244141
64	1	0	1.168573	4.701880	-1.002790
65	1	0	2.759713	3.116518	-3.616839
66	1	0	0.007436	3.989126	2.176432

IM1

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.088396	-2.484536	1.740372

2	6	0	1.526878	-2.524884	1.191568
3	6	0	1.738356	-1.944361	-0.233447
4	6	0	1.875707	-0.441101	-0.227491
5	6	0	3.186248	0.229827	-0.317006
6	6	0	-0.560873	-1.131126	2.070962
7	6	0	4.379434	-0.384643	-0.377736
8	1	0	0.106763	-3.080732	2.673183
9	1	0	-0.557144	-3.040905	1.048977
10	1	0	1.833115	-3.577308	1.150980
11	1	0	2.218656	-2.041369	1.892358
12	1	0	0.870778	-2.184737	-0.853944
13	1	0	2.621839	-2.401790	-0.686006
14	8	0	0.880720	0.286748	-0.109002
15	1	0	3.112216	1.313600	-0.304428
16	6	0	0.321671	-0.269020	2.971938
17	6	0	-1.900098	-1.393531	2.776391
18	6	0	5.744971	0.264473	-0.437997
19	6	0	6.451747	-0.239625	-1.719925
20	6	0	6.547195	-0.207597	0.799464
21	6	0	5.678483	1.799967	-0.455139
22	1	0	4.410707	-1.474114	-0.378397
23	1	0	1.266282	0.023990	2.502984
24	1	0	-0.194199	0.651859	3.256054
25	1	0	0.576461	-0.810259	3.901289
26	1	0	-1.726624	-1.891025	3.748188
27	1	0	-2.446817	-0.467497	2.982379
28	1	0	-2.558646	-2.048958	2.195760
29	1	0	7.470055	0.160571	-1.772397
30	1	0	6.520286	-1.332886	-1.735161
31	1	0	7.566111	0.193202	0.764597
32	1	0	6.688946	2.218035	-0.505297
33	1	0	5.122029	2.168207	-1.323050
34	1	0	5.200164	2.192243	0.447965
35	1	0	5.914178	0.078412	-2.618877
36	1	0	6.077926	0.133521	1.727584
37	1	0	6.618061	-1.300085	0.837484
38	26	0	-1.291406	-0.025646	0.310765
39	8	0	-3.307915	-0.171629	0.297247
40	8	0	-1.271067	1.204079	-1.410825
41	8	0	-1.329028	-1.600743	-0.987975
42	8	0	-1.448997	1.687067	1.333885
43	6	0	-1.600136	2.898132	0.945700
44	6	0	-1.437944	2.456507	-1.489676
45	6	0	-1.597645	3.325429	-0.386134
46	6	0	-1.794427	3.907557	2.057105
47	6	0	-2.304767	-2.051282	-1.679397
48	6	0	-4.078053	-0.783763	-0.512713
49	6	0	-3.647692	-1.688678	-1.499669
50	6	0	-1.938597	-3.059821	-2.747163
51	1	0	-1.426032	-3.910285	-2.284905
52	1	0	-2.807313	-3.423789	-3.299603
53	1	0	-1.233927	-2.600166	-3.448248
54	1	0	-4.393547	-2.146438	-2.137663
55	6	0	-5.554719	-0.491539	-0.356542

56	1	0	-5.726987	0.579611	-0.504948
57	1	0	-5.862377	-0.725761	0.667788
58	1	0	-6.173202	-1.056108	-1.057424
59	1	0	-1.909585	4.927903	1.685112
60	1	0	-0.937593	3.866465	2.737918
61	6	0	-1.464180	3.036578	-2.891890
62	1	0	-2.254359	2.546675	-3.470188
63	1	0	-1.627523	4.116541	-2.902627
64	1	0	-1.735817	4.381743	-0.582934
65	1	0	-2.679863	3.634640	2.641084
66	1	0	-0.515905	2.811833	-3.391553

TS2

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-2.461387	-1.125129	0.878851
2	6	0	-3.657322	-1.550145	0.792930
3	6	0	-4.631224	-1.030384	-0.083939
4	6	0	-4.393262	0.025597	-0.977567
5	8	0	-3.273841	0.628079	-1.123518
6	6	0	-5.516767	0.523039	-1.863067
7	6	0	-4.023720	-2.692926	1.719721
8	1	0	-5.623708	-1.464578	-0.060516
9	1	0	-6.447076	-0.030481	-1.717588
10	1	0	-5.211161	0.446235	-2.911928
11	1	0	-5.695212	1.584601	-1.660745
12	1	0	-3.361544	-3.543869	1.526947
13	1	0	-5.061028	-3.015307	1.605416
14	1	0	-3.855211	-2.385506	2.757315
15	6	0	1.548731	-3.588195	-0.153353
16	6	0	2.064706	-3.354793	-1.583870
17	6	0	1.258140	-2.222665	-2.259459
18	6	0	0.861795	-1.170803	-1.243859
19	6	0	1.885721	-0.602207	-0.353626
20	6	0	1.861954	-2.450749	0.815754
21	6	0	3.146078	-0.252105	-0.856924
22	1	0	1.990889	-4.513449	0.246923
23	1	0	0.465097	-3.754323	-0.191376
24	1	0	1.976275	-4.270794	-2.177333
25	1	0	3.129862	-3.102209	-1.554710
26	1	0	0.331034	-2.603679	-2.695284
27	1	0	1.836058	-1.759508	-3.068511
28	8	0	-0.338819	-0.882313	-1.116210
29	1	0	1.465538	0.015248	0.435322
30	6	0	3.268622	-2.484539	1.362858
31	6	0	0.790096	-2.170784	1.839340
32	6	0	4.093337	0.804824	-0.323508
33	6	0	4.188895	1.920526	-1.398289
34	6	0	5.502231	0.190572	-0.136816
35	6	0	3.624970	1.432725	1.000955
36	1	0	3.485186	-0.727600	-1.776768

37	1	0	4.022903	-2.565389	0.574588
38	1	0	3.494508	-1.599070	1.962794
39	1	0	3.382844	-3.361348	2.018685
40	1	0	0.669931	-3.049681	2.493635
41	1	0	1.046145	-1.322342	2.480648
42	1	0	-0.185302	-1.971766	1.387143
43	1	0	4.900346	2.693712	-1.085324
44	1	0	4.530983	1.518662	-2.358445
45	1	0	6.223685	0.965728	0.145970
46	1	0	4.353202	2.179250	1.335740
47	1	0	2.659952	1.938060	0.893297
48	1	0	3.532217	0.685004	1.795465
49	1	0	3.215517	2.394632	-1.557532
50	1	0	5.504329	-0.573551	0.645928
51	1	0	5.858214	-0.273501	-1.063649
52	26	0	-1.574227	0.425542	-0.098661
53	8	0	-0.743844	2.050693	-1.003935
54	6	0	-0.263879	3.101214	-0.477901
55	6	0	-0.019308	3.263926	0.905418
56	6	0	-0.287746	2.274601	1.863377
57	8	0	-0.740889	1.104095	1.603629
58	6	0	0.054065	4.239272	-1.428175
59	6	0	-0.031288	2.562512	3.328320
60	1	0	0.366988	4.216351	1.248761
61	1	0	0.779861	3.898484	-2.174559
62	1	0	0.452300	5.119664	-0.918694
63	1	0	-0.854292	4.517455	-1.972628
64	1	0	0.375908	3.561667	3.498257
65	1	0	0.663569	1.817596	3.730782
66	1	0	-0.967621	2.457026	3.886688

IM2

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-1.560464	-1.720831	0.660305
2	6	0	-2.524066	-2.547487	0.593528
3	6	0	-3.691923	-2.359648	-0.176557
4	6	0	-3.936673	-1.231845	-0.973594
5	8	0	-3.145360	-0.232448	-1.106214
6	6	0	-5.223863	-1.142370	-1.765410
7	6	0	-2.371001	-3.816400	1.409438
8	1	0	-4.446655	-3.136710	-0.153490
9	1	0	-5.861623	-2.019263	-1.635459
10	1	0	-4.986627	-1.022147	-2.827796
11	1	0	-5.776219	-0.247302	-1.459832
12	1	0	-1.465489	-4.345563	1.093427
13	1	0	-3.227094	-4.487835	1.314435
14	1	0	-2.236114	-3.553147	2.463851
15	6	0	2.866195	-3.123382	-0.062273
16	6	0	3.060487	-2.778813	-1.543694
17	6	0	1.845295	-1.982318	-2.045940

18	6	0	1.326392	-0.992949	-1.019549
19	6	0	2.230492	-0.614813	0.142518
20	6	0	2.840834	-1.880565	0.876206
21	6	0	3.195634	0.333434	-0.513667
22	1	0	3.647202	-3.812006	0.280498
23	1	0	1.916040	-3.666103	0.035368
24	1	0	3.170585	-3.691484	-2.139109
25	1	0	3.987047	-2.210647	-1.685266
26	1	0	1.007841	-2.655639	-2.265612
27	1	0	2.053426	-1.448294	-2.981637
28	8	0	0.203285	-0.490329	-1.169214
29	1	0	1.614169	-0.066773	0.859065
30	6	0	4.262412	-1.575185	1.383074
31	6	0	1.933110	-2.196755	2.082079
32	6	0	3.098724	1.843789	-0.539503
33	6	0	2.412380	2.303431	-1.855935
34	6	0	4.541557	2.403324	-0.513984
35	6	0	2.315404	2.411165	0.659352
36	1	0	3.943747	-0.095140	-1.177608
37	1	0	4.978220	-1.452093	0.564355
38	1	0	4.283087	-0.657903	1.980918
39	1	0	4.616787	-2.396585	2.015871
40	1	0	2.245424	-3.130878	2.563771
41	1	0	1.983164	-1.400124	2.832735
42	1	0	0.886462	-2.300507	1.775435
43	1	0	2.424984	3.398184	-1.925434
44	1	0	2.937168	1.908272	-2.732951
45	1	0	4.529102	3.497187	-0.575372
46	1	0	2.331111	3.505790	0.630226
47	1	0	1.268038	2.100521	0.649126
48	1	0	2.758903	2.096701	1.610902
49	1	0	1.370772	1.973392	-1.895596
50	1	0	5.060755	2.120288	0.407761
51	1	0	5.128109	2.027932	-1.360294
52	26	0	-1.438902	0.149947	-0.166845
53	8	0	-1.319696	2.043603	-0.944160
54	6	0	-1.511153	3.136247	-0.326452
55	6	0	-1.554064	3.265860	1.080714
56	6	0	-1.361462	2.200073	1.969893
57	8	0	-1.128083	0.984994	1.627953
58	6	0	-1.683965	4.369480	-1.190430
59	6	0	-1.402923	2.453697	3.461835
60	1	0	-1.736463	4.249247	1.497279
61	1	0	-0.789309	4.506245	-1.807248
62	1	0	-1.858063	5.276351	-0.607047
63	1	0	-2.523174	4.213673	-1.876096
64	1	0	-1.579436	3.502949	3.707937
65	1	0	-0.456996	2.131935	3.910373
66	1	0	-2.191820	1.841105	3.911220

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syn-TS3

Standard orientation:

Center	Atomic	Atomic	Coordinates (Angstroms)		

Number	Number	Type	X	Y	Z
1	8	0	-1.269275	-1.841548	0.654344
2	6	0	-2.083913	-2.810723	0.543750
3	6	0	-3.231770	-2.804295	-0.278018
4	6	0	-3.617249	-1.718856	-1.075744
5	8	0	-2.995480	-0.599494	-1.152671
6	6	0	-4.858566	-1.821908	-1.934670
7	6	0	-1.762586	-4.047944	1.358455
8	1	0	-3.849889	-3.693749	-0.297107
9	1	0	-5.350349	-2.793377	-1.851715
10	1	0	-4.589606	-1.640814	-2.980667
11	1	0	-5.564387	-1.035377	-1.647104
12	1	0	-0.787113	-4.441765	1.052668
13	1	0	-2.512775	-4.834024	1.248892
14	1	0	-1.679961	-3.772407	2.414828
15	6	0	3.250336	-2.768360	-0.032019
16	6	0	3.292927	-2.404929	-1.521114
17	6	0	1.975954	-1.725776	-1.925512
18	6	0	1.481280	-0.720968	-0.902055
19	6	0	2.356829	-0.365447	0.273675
20	6	0	3.167031	-1.542223	0.923466
21	6	0	3.052595	0.644155	-0.577574
22	1	0	4.122061	-3.374324	0.242544
23	1	0	2.370561	-3.405519	0.130966
24	1	0	3.437713	-3.306268	-2.126923
25	1	0	4.151812	-1.757612	-1.735109
26	1	0	1.182331	-2.482367	-1.996542
27	1	0	2.032789	-1.259082	-2.916148
28	8	0	0.322730	-0.236153	-1.034817
29	1	0	1.740624	0.123653	1.030315
30	6	0	4.580841	-1.067896	1.306790
31	6	0	2.411415	-1.970511	2.197782
32	6	0	2.771925	2.131369	-0.658480
33	6	0	2.171008	2.480346	-2.045238
34	6	0	4.134234	2.858568	-0.516314
35	6	0	1.821444	2.628327	0.444998
36	1	0	3.838083	0.287791	-1.238402
37	1	0	5.195262	-0.848737	0.427828
38	1	0	4.541940	-0.159309	1.917440
39	1	0	5.094120	-1.841588	1.888585
40	1	0	2.866307	-2.865978	2.637434
41	1	0	2.432525	-1.178625	2.955018
42	1	0	1.362318	-2.192855	1.972991
43	1	0	2.064906	3.566621	-2.152327
44	1	0	2.819489	2.127584	-2.855247
45	1	0	3.997685	3.942304	-0.607783
46	1	0	1.685141	3.711418	0.356777
47	1	0	0.836189	2.164424	0.369822
48	1	0	2.224591	2.426456	1.443749
49	1	0	1.184840	2.025447	-2.167322
50	1	0	4.595055	2.654820	0.455938
51	1	0	4.836740	2.543570	-1.296104
52	26	0	-1.401944	0.035225	-0.164474

53	8	0	-1.655212	1.937174	-0.878805
54	6	0	-2.054916	2.955758	-0.234961
55	6	0	-2.145823	3.029656	1.173799
56	6	0	-1.789689	1.984480	2.035147
57	8	0	-1.358208	0.833586	1.664180
58	6	0	-2.434820	4.162846	-1.067816
59	6	0	-1.888275	2.180448	3.532377
60	1	0	-2.498117	3.954396	1.614492
61	1	0	-3.236566	3.883435	-1.759265
62	1	0	-1.577560	4.464268	-1.678710
63	1	0	-2.760873	5.011139	-0.462156
64	1	0	-2.246165	3.175160	3.806042
65	1	0	-0.904584	2.013892	3.984134
66	1	0	-2.562321	1.426328	3.952296

syn-IM3

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-0.959011	-1.741831	1.074641
2	6	0	-1.171055	-2.987419	0.887996
3	6	0	-1.834226	-3.519032	-0.230738
4	6	0	-2.347693	-2.717671	-1.261480
5	8	0	-2.271331	-1.441081	-1.292502
6	6	0	-3.051456	-3.351657	-2.438272
7	6	0	-0.654415	-3.907858	1.969523
8	1	0	-1.962038	-4.592169	-0.296159
9	1	0	-3.102720	-4.439373	-2.360442
10	1	0	-2.528112	-3.078473	-3.360455
11	1	0	-4.064886	-2.944540	-2.514391
12	1	0	0.430613	-3.789221	2.058415
13	1	0	-0.886383	-4.956653	1.774208
14	1	0	-1.087457	-3.612198	2.930464
15	6	0	3.252466	-2.218322	0.007900
16	6	0	2.969095	-1.940557	-1.473582
17	6	0	1.620469	-1.225302	-1.636525
18	6	0	1.481295	0.009420	-0.750844
19	6	0	2.408805	0.151891	0.450526
20	6	0	3.411378	-0.942809	0.880131
21	6	0	2.591978	1.040526	-0.771752
22	1	0	4.149454	-2.841301	0.117215
23	1	0	2.415075	-2.811043	0.401569
24	1	0	2.948133	-2.884340	-2.031392
25	1	0	3.780474	-1.349441	-1.917004
26	1	0	0.822003	-1.923688	-1.353645
27	1	0	1.440840	-0.947493	-2.683052
28	8	0	0.179712	0.457384	-0.628501
29	1	0	1.928963	0.656163	1.285931
30	6	0	4.859692	-0.419151	0.793742
31	6	0	3.111490	-1.317866	2.345905
32	6	0	2.393896	2.568515	-0.796717
33	6	0	1.735663	2.943211	-2.141895

34	6	0	3.786705	3.229597	-0.710141
35	6	0	1.530808	3.107057	0.360077
36	1	0	3.417706	0.752070	-1.422829
37	1	0	5.157837	-0.204032	-0.237098
38	1	0	4.975836	0.505649	1.369291
39	1	0	5.563238	-1.157331	1.196685
40	1	0	3.743796	-2.150312	2.677118
41	1	0	3.296887	-0.470702	3.016377
42	1	0	2.063374	-1.614657	2.464014
43	1	0	1.638851	4.031020	-2.242842
44	1	0	2.335563	2.583498	-2.986349
45	1	0	3.701741	4.322217	-0.738041
46	1	0	1.408815	4.191437	0.255003
47	1	0	0.540492	2.648400	0.368122
48	1	0	2.003912	2.924953	1.331242
49	1	0	0.740598	2.496254	-2.218463
50	1	0	4.296986	2.955264	0.219886
51	1	0	4.426526	2.924049	-1.546230
52	26	0	-1.424625	-0.142618	-0.045854
53	8	0	-2.660391	1.199658	-0.871389
54	6	0	-3.160302	2.266053	-0.381604
55	6	0	-3.071917	2.635133	0.972647
56	6	0	-2.430871	1.844652	1.935771
57	8	0	-1.842623	0.733254	1.690230
58	6	0	-3.894414	3.152036	-1.361219
59	6	0	-2.406509	2.279872	3.382328
60	1	0	-3.539319	3.559093	1.289064
61	1	0	-3.200406	3.470577	-2.146039
62	1	0	-4.329759	4.033237	-0.886024
63	1	0	-4.685110	2.573188	-1.849140
64	1	0	-2.941775	3.216888	3.547311
65	1	0	-1.366786	2.395678	3.705812
66	1	0	-2.848846	1.494411	4.003593

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anti-TS3

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-2.054713	-1.532402	0.635445
2	6	0	-3.149375	-2.169450	0.551316
3	6	0	-4.259913	-1.760333	-0.220226
4	6	0	-4.285396	-0.593924	-0.994259
5	8	0	-3.323755	0.249490	-1.094818
6	6	0	-5.520498	-0.254496	-1.799647
7	6	0	-3.230679	-3.461421	1.340311
8	1	0	-5.142171	-2.388945	-0.218273
9	1	0	-6.309387	-1.002825	-1.698397
10	1	0	-5.246795	-0.158196	-2.855623
11	1	0	-5.904974	0.720141	-1.480592
12	1	0	-2.461818	-4.154213	0.981254
13	1	0	-4.207126	-3.944646	1.263819
14	1	0	-3.010644	-3.255591	2.392846

15	6	0	2.562106	-3.178344	-0.283092
16	6	0	2.864376	-2.617469	-1.675138
17	6	0	1.721598	-1.699424	-2.144932
18	6	0	1.065468	-0.917640	-1.020276
19	6	0	1.742041	-0.814048	0.329051
20	6	0	2.488208	-2.100887	0.834769
21	6	0	2.276326	0.524819	-0.126507
22	1	0	3.309671	-3.929960	-0.002058
23	1	0	1.599032	-3.705301	-0.327490
24	1	0	2.984280	-3.436189	-2.393535
25	1	0	3.816636	-2.083899	-1.663910
26	1	0	0.910371	-2.305480	-2.566977
27	1	0	2.037234	-1.028003	-2.952146
28	8	0	-0.110961	-0.485041	-1.206240
29	1	0	0.960617	-0.579245	1.056880
30	6	0	3.884544	-1.808484	1.408777
31	6	0	1.620378	-2.675607	1.978692
32	1	0	4.607494	-1.526288	0.640894
33	1	0	3.845707	-1.002353	2.148247
34	1	0	4.273830	-2.700554	1.912508
35	1	0	2.005555	-3.649571	2.302641
36	1	0	1.619941	-2.007647	2.847285
37	1	0	0.581198	-2.805316	1.658526
38	26	0	-1.573459	0.294684	-0.174583
39	8	0	-1.282612	2.218904	-0.787539
40	6	0	-1.005501	3.250891	-0.105440
41	6	0	-0.707299	3.238386	1.278159
42	6	0	-0.712033	2.079499	2.062327
43	8	0	-0.963429	0.894913	1.631129
44	6	0	-0.998040	4.566723	-0.856923
45	6	0	-0.401523	2.170838	3.540456
46	1	0	-0.486244	4.181757	1.762841
47	1	0	-0.271536	4.512519	-1.674497
48	1	0	-0.756839	5.418781	-0.217640
49	1	0	-1.980420	4.724819	-1.313741
50	1	0	-0.167239	3.188240	3.860679
51	1	0	0.442777	1.514263	3.776144
52	1	0	-1.259209	1.802271	4.113305
53	6	0	3.550892	1.207689	-0.616127
54	6	0	4.299075	1.762322	0.629962
55	1	0	3.632314	2.374052	1.246383
56	1	0	4.694136	0.956753	1.253714
57	1	0	5.139778	2.392930	0.315429
58	6	0	3.096966	2.419330	-1.471139
59	1	0	2.436266	3.080008	-0.900198
60	1	0	3.962789	3.006982	-1.795956
61	1	0	2.552783	2.089360	-2.361800
62	1	0	1.506500	1.271141	0.056814
63	6	0	4.541294	0.394980	-1.468665
64	1	0	4.970217	-0.451595	-0.930973
65	1	0	4.076339	0.026814	-2.386973
66	1	0	5.374543	1.042599	-1.762778

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anti-IM3

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	1.461846	1.552075	0.905565
2	6	0	1.923767	2.721888	0.668914
3	6	0	2.660000	3.069342	-0.473107
4	6	0	2.976120	2.147089	-1.484756
5	8	0	2.644627	0.914706	-1.467465
6	6	0	3.763377	2.591071	-2.695900
7	6	0	1.627493	3.763559	1.722989
8	1	0	3.000951	4.091495	-0.578703
9	1	0	4.036737	3.647258	-2.655394
10	1	0	3.170511	2.404704	-3.597417
11	1	0	4.670171	1.983462	-2.779183
12	1	0	0.543339	3.877546	1.827032
13	1	0	2.069583	4.733940	1.488799
14	1	0	2.005858	3.415381	2.689446
15	6	0	-2.550704	2.435735	0.565418
16	6	0	-2.741568	2.233291	-0.938458
17	6	0	-1.671189	1.284929	-1.504175
18	6	0	-1.390717	0.032819	-0.667646
19	6	0	-2.010725	-0.053315	0.726048
20	6	0	-2.724571	1.142893	1.404890
21	6	0	-2.407489	-1.049384	-0.390031
22	1	0	-3.239326	3.204466	0.939495
23	1	0	-1.534384	2.818746	0.730649
24	1	0	-2.663241	3.197498	-1.455725
25	1	0	-3.749583	1.866302	-1.141623
26	1	0	-0.721120	1.832019	-1.529331
27	1	0	-1.889793	1.010505	-2.543081
28	8	0	-0.087176	-0.418379	-0.847587
29	1	0	-1.360242	-0.563235	1.433597
30	6	0	-4.213794	0.872820	1.694101
31	6	0	-2.020669	1.371397	2.762608
32	1	0	-4.810564	0.796628	0.782922
33	1	0	-4.339063	-0.059858	2.254172
34	1	0	-4.637499	1.684027	2.298574
35	1	0	-2.416742	2.265671	3.258709
36	1	0	-2.175751	0.520287	3.435865
37	1	0	-0.942266	1.501327	2.625328
38	26	0	1.557714	-0.140753	-0.162649
39	8	0	2.637499	-1.690790	-0.811844
40	6	0	2.914998	-2.801206	-0.247427
41	6	0	2.620328	-3.107861	1.092089
42	6	0	1.987759	-2.204140	1.957639
43	8	0	1.602926	-1.029061	1.627662
44	6	0	3.616353	-3.815916	-1.120420
45	6	0	1.723341	-2.590608	3.394652
46	1	0	2.905837	-4.079164	1.475961
47	1	0	2.985141	-4.040628	-1.986383
48	1	0	3.844002	-4.741913	-0.588814
49	1	0	4.544073	-3.380597	-1.505752

50	1	0	2.091625	-3.589794	3.635083
51	1	0	0.646356	-2.546225	3.587718
52	1	0	2.196757	-1.859603	4.058037
53	6	0	-3.674891	-1.522036	-1.144390
54	6	0	-4.524039	-2.373237	-0.174530
55	1	0	-3.920572	-3.161730	0.288796
56	1	0	-4.948616	-1.762331	0.627115
57	1	0	-5.352611	-2.856228	-0.706106
58	6	0	-3.158568	-2.441087	-2.280126
59	1	0	-2.567514	-3.273014	-1.882247
60	1	0	-3.995914	-2.865103	-2.846619
61	1	0	-2.521769	-1.885826	-2.976523
62	1	0	-1.848748	-1.959527	-0.171151
63	6	0	-4.584157	-0.467398	-1.798545
64	1	0	-5.048047	0.201923	-1.071525
65	1	0	-4.050057	0.136281	-2.536589
66	1	0	-5.398585	-0.977380	-2.325922

iso-TS3

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-3.180091	-0.848717	1.093553
2	6	0	-4.336150	-1.297550	0.768867
3	6	0	-4.922358	-1.164897	-0.496598
4	6	0	-4.306372	-0.491712	-1.572224
5	8	0	-3.160797	0.057476	-1.516739
6	6	0	-5.025401	-0.387243	-2.900945
7	6	0	-5.081701	-2.014860	1.872992
8	1	0	-5.906228	-1.590345	-0.652876
9	1	0	-6.007543	-0.864773	-2.889209
10	1	0	-4.410544	-0.848629	-3.680903
11	1	0	-5.139943	0.668553	-3.167624
12	1	0	-4.474981	-2.851856	2.234344
13	1	0	-6.055513	-2.388724	1.549696
14	1	0	-5.220185	-1.333406	2.719142
15	6	0	2.395805	-2.422888	1.093534
16	6	0	1.657460	-3.302243	0.066785
17	6	0	1.204388	-2.580821	-1.227470
18	6	0	0.690618	-1.193864	-0.913739
19	6	0	1.591200	-0.106071	-0.771998
20	6	0	3.710007	-1.781307	0.708422
21	6	0	2.956185	-0.170700	-1.028034
22	1	0	2.590248	-3.050033	1.982643
23	1	0	1.709938	-1.642348	1.448247
24	1	0	0.764936	-3.694548	0.566803
25	1	0	2.265838	-4.173135	-0.204303
26	1	0	0.401279	-3.149801	-1.703836
27	1	0	2.033091	-2.525448	-1.940288
28	8	0	-0.560298	-1.063916	-0.702169

29	1	0	1.154615	0.816227	-0.399650
30	6	0	4.682883	-2.619743	-0.079410
31	6	0	4.311423	-0.975540	1.831682
32	6	0	3.805660	1.099757	-1.148944
33	6	0	3.356866	1.803364	-2.459921
34	6	0	5.300886	0.755506	-1.291512
35	6	0	3.609128	2.077859	0.026275
36	1	0	3.319666	-0.991904	-1.638103
37	1	0	4.243239	-3.038109	-0.990809
38	1	0	5.575207	-2.054335	-0.362293
39	1	0	5.025913	-3.477866	0.524306
40	1	0	4.619305	-1.647383	2.652597
41	1	0	5.203890	-0.420972	1.529961
42	1	0	3.590276	-0.270137	2.256619
43	1	0	3.965340	2.698299	-2.636687
44	1	0	3.472209	1.141937	-3.325446
45	1	0	5.881885	1.661554	-1.494607
46	1	0	4.188846	2.990954	-0.149112
47	1	0	2.562823	2.372968	0.148458
48	1	0	3.947396	1.644501	0.970329
49	1	0	2.306873	2.104842	-2.406708
50	1	0	5.705247	0.300225	-0.384801
51	1	0	5.469593	0.061472	-2.122835
52	26	0	-1.855222	0.163640	0.018480
53	8	0	-1.506831	2.078642	-0.421214
54	6	0	-0.956323	3.010155	0.263009
55	6	0	-0.339630	2.829788	1.510229
56	6	0	-0.288778	1.586837	2.178731
57	8	0	-0.763150	0.501981	1.718034
58	6	0	-1.001950	4.387132	-0.362837
59	6	0	0.363100	1.501966	3.543816
60	1	0	0.088789	3.695447	2.000771
61	1	0	-0.551609	4.347759	-1.360094
62	1	0	-0.487963	5.140850	0.237409
63	1	0	-2.046690	4.686675	-0.498382
64	1	0	0.790114	2.452976	3.869397
65	1	0	1.149105	0.739985	3.524581
66	1	0	-0.381016	1.172598	4.276804

iso-IM3

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-3.177095	-0.796173	1.165443
2	6	0	-4.280919	-1.367973	0.860045
3	6	0	-4.879413	-1.315695	-0.406875
4	6	0	-4.322536	-0.604090	-1.483113
5	8	0	-3.228020	0.050321	-1.424449
6	6	0	-5.028339	-0.572324	-2.818896
7	6	0	-4.943475	-2.131925	1.982611
8	1	0	-5.817121	-1.835309	-0.558461
9	1	0	-5.970690	-1.123609	-2.809945

10	1	0	-4.368724	-0.996322	-3.583219
11	1	0	-5.218188	0.467935	-3.102259
12	1	0	-4.261598	-2.911144	2.338787
13	1	0	-5.887144	-2.589160	1.678879
14	1	0	-5.122113	-1.455044	2.824427
15	6	0	2.634935	-2.509772	1.014014
16	6	0	1.927267	-3.379570	-0.042580
17	6	0	1.122391	-2.604727	-1.124458
18	6	0	0.693773	-1.229630	-0.656763
19	6	0	1.620119	-0.279963	-0.374262
20	6	0	3.712337	-1.476223	0.556539
21	6	0	3.107479	-0.509534	-0.565911
22	1	0	3.127055	-3.189062	1.722696
23	1	0	1.869018	-1.979738	1.589291
24	1	0	1.240125	-4.037328	0.503021
25	1	0	2.646964	-4.042451	-0.536937
26	1	0	0.234496	-3.170493	-1.418063
27	1	0	1.737708	-2.491761	-2.025714
28	8	0	-0.618434	-1.055675	-0.497629
29	1	0	1.272474	0.671569	0.013821
30	6	0	4.917821	-2.275944	0.010724
31	6	0	4.145719	-0.737327	1.839140
32	6	0	3.821049	0.855325	-0.943123
33	6	0	3.181028	1.335362	-2.270146
34	6	0	5.330209	0.688932	-1.215612
35	6	0	3.644544	1.988118	0.094821
36	1	0	3.213220	-1.104495	-1.484699
37	1	0	4.666396	-2.802213	-0.916745
38	1	0	5.785709	-1.647438	-0.192700
39	1	0	5.229422	-3.031045	0.742119
40	1	0	4.422465	-1.463373	2.612858
41	1	0	5.013949	-0.092597	1.679020
42	1	0	3.332530	-0.124191	2.241793
43	1	0	3.634312	2.279532	-2.593104
44	1	0	3.334427	0.601510	-3.069834
45	1	0	5.733358	1.618477	-1.634258
46	1	0	4.091287	2.909518	-0.297088
47	1	0	2.593465	2.207625	0.303464
48	1	0	4.136234	1.769023	1.044035
49	1	0	2.103304	1.491383	-2.169535
50	1	0	5.900301	0.472235	-0.308770
51	1	0	5.524581	-0.108497	-1.940484
52	26	0	-1.867167	0.171014	0.030894
53	8	0	-1.450642	1.959476	-0.729665
54	6	0	-0.853543	2.972868	-0.225947
55	6	0	-0.399949	3.047038	1.100067
56	6	0	-0.578256	2.002271	2.024684
57	8	0	-1.145865	0.892274	1.752619
58	6	0	-0.654399	4.139785	-1.164238
59	6	0	-0.087155	2.154665	3.445454
60	1	0	0.087127	3.955457	1.431339
61	1	0	-0.069969	3.810771	-2.029692
62	1	0	-0.149127	4.981093	-0.686078
63	1	0	-1.627936	4.467823	-1.542825

64	1	0	0.374652	3.126804	3.628399
65	1	0	0.637735	1.363098	3.661920
66	1	0	-0.927032	2.015273	4.133676

TS4

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-1.163427	-1.788714	-0.254639
2	6	0	-2.016119	-2.701064	0.017218
3	6	0	-3.326812	-2.458057	0.458144
4	6	0	-3.853318	-1.167086	0.620347
5	8	0	-3.194685	-0.087229	0.433788
6	6	0	-5.296264	-0.984633	1.030601
7	6	0	-1.539066	-4.121486	-0.180307
8	1	0	-3.972252	-3.306018	0.649759
9	1	0	-5.815485	-1.934304	1.173124
10	1	0	-5.816767	-0.398658	0.266024
11	1	0	-5.337456	-0.405944	1.959159
12	1	0	-1.195754	-4.249424	-1.212013
13	1	0	-2.314640	-4.858875	0.035413
14	1	0	-0.677014	-4.303921	0.469844
15	6	0	2.894874	-2.895259	-0.504216
16	6	0	2.774933	-2.373809	-1.941679
17	6	0	1.662076	-1.319161	-2.034070
18	6	0	1.787482	-0.222866	-0.981412
19	6	0	2.659730	-0.464970	0.232002
20	6	0	3.339414	-1.821802	0.525809
21	6	0	3.114798	0.499154	-0.856778
22	1	0	3.588884	-3.744601	-0.459139
23	1	0	1.910090	-3.279061	-0.205577
24	1	0	2.544732	-3.203281	-2.620970
25	1	0	3.733901	-1.964261	-2.284365
26	1	0	0.698842	-1.815337	-1.872848
27	1	0	1.634512	-0.867688	-3.035785
28	8	0	0.610530	0.515992	-0.798306
29	1	0	2.283905	0.034974	1.121170
30	6	0	4.874905	-1.679039	0.516012
31	6	0	2.901909	-2.287360	1.929748
32	6	0	3.312774	2.016205	-0.677874
33	6	0	2.875343	2.714527	-1.983547
34	6	0	4.817114	2.275684	-0.444809
35	6	0	2.527221	2.616026	0.503198
36	1	0	3.870579	0.096239	-1.532122
37	1	0	5.258279	-1.420864	-0.476069
38	1	0	5.199059	-0.893449	1.207334
39	1	0	5.352800	-2.616848	0.823445
40	1	0	3.291232	-3.288032	2.152004
41	1	0	3.277106	-1.605960	2.703178
42	1	0	1.809727	-2.318462	2.006448
43	1	0	3.082616	3.790632	-1.942002
44	1	0	3.411673	2.306260	-2.848415

45	1	0	5.013884	3.347972	-0.328755
46	1	0	2.698215	3.698248	0.546931
47	1	0	1.456224	2.437002	0.397978
48	1	0	2.857523	2.196218	1.459668
49	1	0	1.803396	2.579226	-2.153255
50	1	0	5.169811	1.769112	0.460423
51	1	0	5.420505	1.915439	-1.286253
52	26	0	-1.238252	0.196169	0.104671
53	8	0	-1.398556	0.744207	-1.847840
54	6	0	-2.056141	0.051674	-2.897079
55	6	0	-3.393679	0.711569	-3.232880
56	6	0	-3.247602	2.153367	-3.725420
57	1	0	-0.197015	0.646745	-1.677350
58	1	0	-2.660451	2.197032	-4.650736
59	1	0	-4.223850	2.605915	-3.928766
60	1	0	-3.896703	0.098517	-3.993777
61	1	0	-4.024372	0.686629	-2.335708
62	1	0	-1.407590	0.060639	-3.787027
63	1	0	-2.218229	-1.002131	-2.625586
64	1	0	-2.736237	2.761857	-2.974906
65	8	0	-1.420776	2.077334	0.735691
66	6	0	-1.217749	2.596531	1.883253
67	6	0	-0.761352	1.886414	3.007445
68	6	0	-0.466359	0.516004	2.982942
69	8	0	-0.578895	-0.236329	1.952446
70	6	0	-1.495167	4.077945	1.984766
71	6	0	0.023444	-0.172744	4.235885
72	1	0	-0.626099	2.425938	3.936373
73	1	0	-0.846388	4.611853	1.282695
74	1	0	-1.333886	4.467143	2.991863
75	1	0	-2.527793	4.272526	1.678289
76	1	0	0.102843	0.507968	5.085695
77	1	0	1.001195	-0.624896	4.040611
78	1	0	-0.660869	-0.989136	4.489632

IM4

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	1.207509	1.737247	-0.758771
2	6	0	2.019343	2.708567	-0.621407
3	6	0	3.303561	2.605990	-0.051937
4	6	0	3.856687	1.403271	0.406371
5	8	0	3.257868	0.270267	0.397574
6	6	0	5.266532	1.379090	0.950487
7	6	0	1.536105	4.047621	-1.133725
8	1	0	3.909117	3.501701	0.006474
9	1	0	5.739066	2.363195	0.937435
10	1	0	5.869033	0.680982	0.360031
11	1	0	5.250915	0.998276	1.976936
12	1	0	1.282274	3.958952	-2.195098
13	1	0	2.276831	4.839514	-1.006599

14	1	0	0.618166	4.324724	-0.604860
15	6	0	-3.009204	2.760446	-0.826951
16	6	0	-2.937941	2.049709	-2.184468
17	6	0	-1.843297	0.971682	-2.162173
18	6	0	-1.977128	0.032157	-0.974765
19	6	0	-2.784167	0.444234	0.224467
20	6	0	-3.429190	1.843602	0.354882
21	6	0	-3.298496	-0.651603	-0.703396
22	1	0	-3.696161	3.614805	-0.877522
23	1	0	-2.013303	3.171680	-0.613731
24	1	0	-2.711494	2.775718	-2.973767
25	1	0	-3.911587	1.615434	-2.446108
26	1	0	-0.867258	1.462098	-2.079989
27	1	0	-1.844000	0.395498	-3.098286
28	8	0	-0.779916	-0.683203	-0.687692
29	1	0	-2.375089	0.061175	1.155691
30	6	0	-4.965453	1.728984	0.421242
31	6	0	-2.926770	2.483729	1.664717
32	6	0	-3.505583	-2.125162	-0.300497
33	6	0	-3.125083	-3.015466	-1.503129
34	6	0	-5.005232	-2.319227	0.013220
35	6	0	-2.692486	-2.561486	0.933644
36	1	0	-4.075641	-0.331471	-1.398039
37	1	0	-5.392563	1.353924	-0.514212
38	1	0	-5.272223	1.044887	1.219928
39	1	0	-5.416579	2.707297	0.623901
40	1	0	-3.292695	3.512276	1.765789
41	1	0	-3.277819	1.919340	2.537183
42	1	0	-1.832229	2.503564	1.689964
43	1	0	-3.358900	-4.067348	-1.301935
44	1	0	-3.673289	-2.718573	-2.404823
45	1	0	-5.212072	-3.357637	0.296496
46	1	0	-2.874159	-3.623568	1.134657
47	1	0	-1.620942	-2.417305	0.785485
48	1	0	-2.994757	-2.006205	1.828064
49	1	0	-2.054454	-2.947016	-1.719118
50	1	0	-5.321077	-1.675448	0.841417
51	1	0	-5.630720	-2.079635	-0.854578
52	26	0	1.370554	-0.164005	-0.051049
53	8	0	1.528018	-0.949014	-1.727884
54	6	0	2.471934	-0.724854	-2.743538
55	6	0	3.627636	-1.732634	-2.687749
56	6	0	3.166768	-3.184289	-2.837070
57	1	0	-0.397416	-1.048424	-1.509876
58	1	0	2.668043	-3.343098	-3.801077
59	1	0	4.011283	-3.879464	-2.780717
60	1	0	4.343414	-1.476843	-3.482000
61	1	0	4.150258	-1.602897	-1.732195
62	1	0	1.970647	-0.806993	-3.722941
63	1	0	2.880502	0.297185	-2.680535
64	1	0	2.457594	-3.441094	-2.045642
65	8	0	1.459270	-1.900915	0.948216
66	6	0	1.365411	-2.138877	2.199312
67	6	0	0.977022	-1.198160	3.165914

68	6	0	0.610146	0.122458	2.854628
69	8	0	0.605221	0.621825	1.680013
70	6	0	1.694961	-3.554790	2.615645
71	6	0	0.169270	1.052511	3.964745
72	1	0	0.935949	-1.512579	4.201415
73	1	0	1.022596	-4.247533	2.098897
74	1	0	1.610210	-3.707412	3.693509
75	1	0	2.712709	-3.796844	2.292962
76	1	0	0.245367	0.594495	4.953058
77	1	0	-0.867460	1.359250	3.791240
78	1	0	0.779674	1.960882	3.937947

TS5

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	2.854546	-0.203760	-0.742753
2	8	0	1.397683	-1.355329	1.259287
3	6	0	2.380810	-2.165905	1.332991
4	6	0	3.707020	-1.118106	-0.464425
5	6	0	3.531228	-2.092389	0.527768
6	6	0	2.247567	-3.258294	2.367941
7	1	0	1.335120	-3.830110	2.170695
8	1	0	3.104619	-3.934534	2.378899
9	1	0	2.132270	-2.803075	3.357052
10	1	0	4.314477	-2.824750	0.677305
11	6	0	4.967658	-1.104179	-1.297682
12	1	0	5.661790	-1.900118	-1.021161
13	1	0	5.464008	-0.134812	-1.184687
14	1	0	4.704150	-1.206133	-2.355673
15	14	0	-1.639561	-0.145197	-0.828693
16	8	0	-0.012314	-0.445678	-1.421054
17	26	0	1.138651	0.300636	0.159248
18	8	0	1.185031	2.037886	-0.827510
19	8	0	1.516310	1.362990	1.785791
20	6	0	1.022148	3.219334	-0.377736
21	6	0	1.363335	2.622129	1.989877
22	6	0	1.090309	3.559062	0.987576
23	6	0	0.753596	4.281900	-1.414264
24	1	0	1.515497	4.228455	-2.197753
25	1	0	0.730932	5.288071	-0.991040
26	6	0	1.511931	3.062461	3.426454
27	1	0	2.498882	2.764540	3.795397
28	1	0	1.391302	4.140572	3.548473
29	1	0	0.967693	4.597427	1.268589
30	1	0	-0.212139	4.064268	-1.882784
31	1	0	0.769832	2.542924	4.041566
32	1	0	-0.584913	0.169004	0.545153
33	6	0	0.321301	-0.625309	-2.816108
34	6	0	0.174307	-2.081615	-3.248825
35	6	0	1.105326	-3.049529	-2.514331
36	1	0	0.944382	-4.079242	-2.849477

37	1	0	0.932696	-3.015559	-1.435206
38	1	0	2.157866	-2.801409	-2.692259
39	1	0	0.365638	-2.124093	-4.330077
40	1	0	-0.869951	-2.381072	-3.104171
41	1	0	1.353319	-0.281011	-2.928508
42	1	0	-0.327858	0.019220	-3.417275
43	1	0	-2.288242	-0.552540	-2.130223
44	8	0	-2.043952	1.492857	-0.760958
45	6	0	-3.301688	2.017347	-0.327658
46	1	0	-3.653797	1.441218	0.541971
47	6	0	-4.349885	1.916740	-1.439542
48	1	0	-4.520861	0.875786	-1.727328
49	1	0	-5.305085	2.342507	-1.112114
50	1	0	-4.011369	2.463460	-2.326137
51	6	0	-3.070782	3.461867	0.112045
52	1	0	-3.991185	3.900980	0.512069
53	1	0	-2.295661	3.505632	0.882254
54	1	0	-2.742813	4.068959	-0.739242
55	6	0	-2.547148	-1.367719	0.311290
56	6	0	-2.275959	-1.524712	1.681897
57	6	0	-3.573727	-2.153224	-0.245169
58	6	0	-3.003408	-2.421680	2.465762
59	1	0	-1.477318	-0.942178	2.132872
60	6	0	-4.305527	-3.053371	0.532129
61	1	0	-3.799374	-2.058675	-1.305032
62	6	0	-4.021205	-3.187576	1.892147
63	1	0	-2.775914	-2.525993	3.523677
64	1	0	-5.093519	-3.649223	0.078575
65	1	0	-4.587197	-3.887413	2.501588

Product

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.706949	0.329838	-0.402308
2	6	0	-1.954384	1.345505	-1.270881
3	6	0	-0.913138	2.096048	-0.428267
4	6	0	0.003925	1.164966	0.351970
5	6	0	-0.430082	-0.255113	0.602675
6	6	0	-1.814687	-0.800946	0.180842
7	6	0	0.704947	0.036095	-0.374140
8	1	0	-3.530945	-0.121684	-0.968919
9	1	0	-3.168767	0.879214	0.429424
10	1	0	-2.661129	2.065067	-1.700097
11	1	0	-1.477265	0.847021	-2.124643
12	1	0	-1.436034	2.721545	0.307190
13	1	0	-0.318089	2.774107	-1.057239
14	8	0	0.642708	1.797161	1.444394
15	1	0	-0.086107	-0.634220	1.562116
16	6	0	-1.659638	-1.939399	-0.847980
17	6	0	-2.510137	-1.369931	1.434506
18	6	0	2.170204	-0.400873	-0.179500

19	6	0	3.086535	0.715710	-0.726600
20	6	0	2.398544	-1.682940	-1.008783
21	6	0	2.546359	-0.695966	1.285399
22	1	0	0.422838	-0.024813	-1.425663
23	1	0	-1.242087	-1.585176	-1.795609
24	1	0	-0.994749	-2.722559	-0.467908
25	1	0	-2.631178	-2.398473	-1.064838
26	1	0	-3.524694	-1.711980	1.199499
27	1	0	-1.955436	-2.223480	1.840928
28	1	0	-2.583660	-0.611251	2.221375
29	1	0	4.138072	0.406700	-0.710547
30	1	0	2.828498	0.970537	-1.760889
31	1	0	3.433012	-2.031822	-0.910197
32	1	0	3.611991	-0.943556	1.351276
33	1	0	2.345933	0.159983	1.932496
34	1	0	1.988269	-1.554261	1.674177
35	1	0	3.001634	1.626773	-0.124399
36	1	0	1.738265	-2.490147	-0.673900
37	1	0	2.204309	-1.511308	-2.073863
38	1	0	1.226664	2.478526	1.083478

Ph(iPrO)-SiH_2

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.646252	0.604219	-0.068129
2	1	0	3.666517	0.662443	-0.469462
3	6	0	2.740285	0.331122	1.433407
4	1	0	1.747260	0.304991	1.897170
5	1	0	3.238329	-0.623130	1.628131
6	1	0	3.314828	1.122893	1.925351
7	6	0	1.929518	1.918382	-0.380570
8	1	0	2.469245	2.764130	0.059272
9	1	0	1.872949	2.070901	-1.462018
10	1	0	0.911037	1.914412	0.020160
11	6	0	-0.883383	-0.584134	-0.137449
12	6	0	-1.491583	-0.564817	1.130689
13	6	0	-1.555923	0.052525	-1.198442
14	6	0	-2.718964	0.068938	1.336630
15	1	0	-1.002498	-1.056093	1.969121
16	6	0	-2.780959	0.688675	-0.998930
17	1	0	-1.118408	0.050469	-2.194479
18	6	0	-3.364132	0.697824	0.270965
19	1	0	-3.171143	0.070476	2.324675
20	1	0	-3.283555	1.173392	-1.831501
21	1	0	-4.319631	1.191051	0.427057
22	14	0	0.756899	-1.463829	-0.400298
23	1	0	1.013509	-2.254123	0.838293
24	1	0	0.661527	-2.372376	-1.569110
25	8	0	2.034597	-0.475281	-0.785938

Ph(iPrO)(nPrOH)SiH

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	14	0	0.323425	0.161793	-0.681316
2	8	0	1.527517	-0.890172	-0.261205
3	6	0	2.917481	-0.630053	-0.478174
4	6	0	3.720564	-1.897344	-0.205556
5	6	0	3.602279	-2.391073	1.238930
6	1	0	4.176656	-3.310559	1.390588
7	1	0	2.558169	-2.594243	1.491064
8	1	0	3.978347	-1.641088	1.944607
9	1	0	4.770512	-1.689278	-0.451089
10	1	0	3.382409	-2.678213	-0.897808
11	1	0	3.244771	0.179748	0.188387
12	1	0	3.081595	-0.297675	-1.514105
13	1	0	0.379852	0.428179	-2.149662
14	8	0	0.575019	1.555798	0.183929
15	6	0	-0.209468	2.754864	0.086493
16	1	0	-1.247708	2.490849	-0.166953
17	6	0	0.356919	3.660066	-1.007705
18	1	0	0.343378	3.157252	-1.979249
19	1	0	-0.229194	4.581450	-1.092009
20	1	0	1.392756	3.928136	-0.775212
21	6	0	-0.198803	3.422995	1.458175
22	1	0	-0.791526	4.343582	1.447336
23	1	0	-0.613308	2.752097	2.215852
24	1	0	0.827366	3.672629	1.747099
25	6	0	-1.323322	-0.611203	-0.264750
26	6	0	-1.833181	-0.589684	1.046592
27	6	0	-2.092898	-1.231605	-1.264183
28	6	0	-3.061545	-1.177255	1.349806
29	1	0	-1.262760	-0.107092	1.836367
30	6	0	-3.322195	-1.822167	-0.966256
31	1	0	-1.728441	-1.253604	-2.289149
32	6	0	-3.806788	-1.795547	0.342717
33	1	0	-3.439277	-1.152948	2.368382
34	1	0	-3.901750	-2.298957	-1.752003
35	1	0	-4.764343	-2.252342	0.577653

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