Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

An Entry to Vinylcyclopropane through Palladium-catalyzed Intramolecular Cyclopropanation of Alkenes with Unstabilized Allylictosylhydrazones

Table of Contents

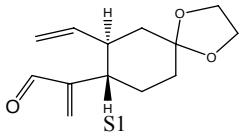
General information

CH_2Cl_2 ,DMF, toluene and diisopropylamine (DIPA) were distilled from calcium hydride under argon; CH_3OH was distilled from magnesium chips and I_2 ; Tetrahydrofuran was distilled from sodium-benzophenone, DMA was distilled from Barium Oxide. All other reagents were obtained from commercial sources and used as received, unless otherwise stated. Flash chromatography was performed using silica gel (200-300 mesh). Reactions were monitored by thin layer chromatography (TLC). Visualization was achieved under a UV lamp (254 nm and 365 nm), I_2 and by developing the plates with *p*-anisaldehyde or phosphomolybdic acid. ^1H and ^{13}C NMR were recorded on Bruker DRX-400 MHz NMR spectrometer with TMS as the internal standard and were calibrated using residual undeuterated solvent as an internal reference ($CDCl_3$: ^1H NMR = 7.26, ^{13}C NMR = 77.16; d_6-acetone: ^1H NMR = 2.05, ^{13}C NMR = 29.84). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad. Coupling constants (*J*) are reported in Hertz (Hz). Optical rotations were measured at the sodium D line with a 100 mm path length cell, and are reported as follows: $[\quad]_D^T$, concentration (g/100 mL), and solvent. High resolution Mass spectra (HRMS) were recorded by using FTMS-7 spectrometers.

Experimental Procedures

Procedure for the preparation of unsaturated aldehyde S2-S7.

General procedure: To a dichloromethane(30 mL) solution of aldehyde S1(333mg,1.50mmol) was added Grrubbs II catalyst(250mg,0.29mmol) and styrene(1.7 mL,15.98mmol) successively under argon at room temperature, and the mixture was refluxed at 45℃ for 24h. The resulting mixture was concentrated and purified on a silica gel column chromatography(petroluem ether/ EtOAc=10:1), which furnished aldehyde S2 (204mg,0.68mmol,46%) as a colourless oil.



S1

S1: colourless liquid

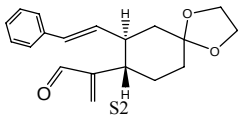
$[\alpha]_D^{14}$=53.0(c 0.79，$CHCl_3$)

IR(thin film):3361.78cm^{-1}，2944.30 cm^{-1}，2881.63 cm^{-1}，1690.79 cm^{-1}，1125.30 cm^{-1}，1064.48 cm^{-1};

^{1}H NMR (400MHz , d_6-acetone): δ 9.45 (s，1H)， 6.35(s，1H)，6.15(s，1H)，5.47(ddd，*J*=8.0, 10.4, 17.2Hz，1H)，4.86(dd, *J*=1.6，17.2Hz，1H)，4.82(dd，1.6，10.0Hz，1H)，3.89-3.97(m，4H)，2.40-2.51(m，2H)，1.71-1.76(m，2H)，1.59-1.66(m，2H)，1.45-1.55(m，2H)；

^{13}C NMR(100MHz，d_6-acetone): δ 194.9，154.1，142.3，135.2，114.7，108.7，65.0，64.8，45.0，42.0，40.1，35.5，30.7；

HRMS(ESI):m/z calcd for $C_{13}H_{18}O_3$ Na $[M+Na]^+$ 245.1148, found 245.1151



S2

S2: colourless liquid

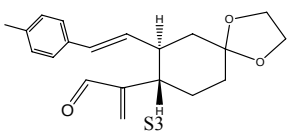
$[\alpha]_D^{14}$=42.8(c 0.80，$CHCl_3$)

IR(thin film):3360.52 cm^{-1}，3057.75 cm^{-1}，3025.52 cm^{-1}，2944.94 cm^{-1}，2881.66 cm^{-1}，1689.43 cm^{-1}，1124.98 cm^{-1}，1065.92 cm^{-1};

^{1}H NMR (400MHz , d_6-acetone): δ 9.47(s，1H)，7.24-7.30(m，4H)，7.15-7.19(m，1H)，6.42(s，1H)，6.28(d，*J*=16.0Hz，1H)，6.15(s，1H)，5.93(dd，*J*=8.4，16.0Hz，1H)，3.91-4.00(m，4H)，2.53-2.67(m，2H)，1.76-1.85(m，2H)，1.66-1.73(m，2H)，1.56-1.63(m，2H)；

^{13}C NMR(100MHz，d_6-acetone): δ 195.0，154.1，138.5，135.3，134.0，130.5，129.3，127.8，126.8，108.7，65.0，64.9，44.7，42.2，40.6，35.5，30.4；

HRMS(ESI):m/z calcd for $C_{19}H_{21}O_3[M-H]^-$ 297.1496, found 297.1489



S3

S3:colourless liquid,79%

$[\alpha]_D^{14}$=48.2(c 0.77，$CHCl_3$)

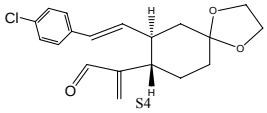
IR(thin film):3361.11 cm^{-1}，2926.63 cm^{-1}，2880.08 cm^{-1}，1689.88 cm^{-1}，1124.15 cm^{-1}，1065.42 cm^{-1};

^{1}H NMR (400MHz , d_6-acetone): δ 9.46(s，1H)，7.17(d，*J*=8.0Hz，2H)，7.07(d，*J*=8.0Hz，

2H)，6.40(s，1H)，6.23(d，*J*=16.0Hz，1H)，6.14(s，1H)，5.86(dd，*J*=8.4，16.0Hz，1H)，3.90-4.00(m，4H)，2.51-2.64(m，2H)，2.26(s，3H)，1.75-1.84(m，2H)，1.66-1.72(m，2H)，1.56-1.63(m，2H)；

^{13}C NMR(100MHz，d_6-acetone): δ 195.0，154.2，137.4，135.7，135.3，132.9，130.3，129.9，126.8，108.7，65.0，64.9，44.7，42.3，40.6，35.5，30.4，21.1；

HRMS(ESI):m/z calcd for $C_{20}H_{24}O_3$ Na $[M+Na]^+$ 335.1618, found 335.1623



S4:white solid,97%

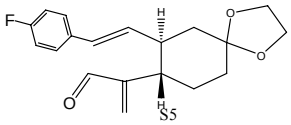
$[\alpha]_D^{14}$=47.9(c 0.58，$CHCl_3$)

IR(thin film),3361.16 cm^{-1}，2946.40 cm^{-1}，2882.75 cm^{-1}，1689.58 cm^{-1}，1124.82 cm^{-1}，1065.31 cm^{-1}；

^{1}H NMR (400MHz , d_6-acetone): δ 9.46(s，1H)，7.27-7.32(m，4H)，6.42(s，1H)，6.28(d，*J*=16.0Hz，1H)，6.16(s，1H)，5.96(dd，*J*=8.4，16.0Hz，1H)，3.91-3.98(m，4H)，2.52-2.66(m，2H)，1.76-1.84(m，2H)，1.66-1.73(m，2H)，1.57-1.63(m，2H)；

^{13}C NMR(100MHz，d_6-acetone): δ 195.0，154.0，137.3，135.4，135.1，132.9，129.3，129.2，128.4，108.6，65.0，64.9，44.7，42.1，40.5，35.5，30.4；

HRMS(ESI):m/z calcd for $C_{19}H_{21}O_3Cl$ Na $[M+Na]^+$ 355.1071, found 355.1078



S5:colourless liquid,45%

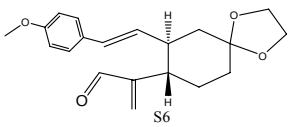
$[\alpha]_D^{14}$=52.1(c 1.52，$CHCl_3$)

IR(thin film):3360.99 cm^{-1}，2945.78 cm^{-1}，2882.03 cm^{-1}，1690.13 cm^{-1}，1126.09 cm^{-1}，1065.02 cm^{-1}；

^{1}H NMR (400MHz , d_6-acetone): δ 9.46(s，1H)，7.30-7.35(m，2H)，7.00-7.06(m，2H)，6.41(s，1H)，6.27(d，*J*=16.0Hz，1H)，6.15(s，1H)，5.87(dd，*J*=8.0，16.0Hz，1H)，3.90-3.98(m，4H)，2.52-2.64(m，2H)，1.75-1.83(m，2H)，1.66-1.72(m，2H)，1.57-1.63(m，2H);

^{13}C NMR(100MHz，d_6-acetone): δ 195.0，164.0，161.5，154.0，135.4，134.9(2C)，133.9(2C)，129.2，128.5(2C)，116.0，115.8，108.6，65.0，64.8，44.7，42.2，40.5，35.5，30.4；

HRMS(ESI):m/z calcd for $C_{19}H_{21}O_3F$ Na $[M+Na]^+$ 339.1367, found 339.1373



S6:white solid,55%

$[\alpha]_D^{14}$=70.9(c 0.89，$CHCl_3$)

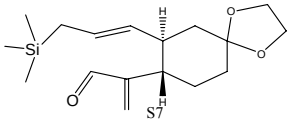
IR(thin film):3343.70 cm^{-1}，2952.62 cm^{-1}，2891.34 cm^{-1}，2861.26 cm^{-1}，2838.93 cm^{-1}，1681.15 cm^{-1}，1134.82 cm^{-1}，1030.50 cm^{-1}；

^{1}H NMR (400MHz , d_6-acetone): δ 9.46(s，1H)，7.22(d，*J*=8.8，2H)，6.83(d，*J*=8.8，2H)，6.39(s，1H)，6.21(d，*J*=16.0Hz，1H)，6.14(s，1H)，5.76(dd，*J*=8.0，16.0Hz，1H)，3.90-3.98(m，

4H)，3.76(s，3H)，2.50-2.62(m，2H)，1.73-1.83(m，2H)，1.66-1.72(m，2H)，1.55-1.62(m，2H)；

^{13}C NMR(100MHz，d_6-acetone)：δ 195.0，159.9，154.2，135.2，131.7，131.1，129.9，128.0，114.7，108.7，65.0，64.8，55.5，44.7，42.4，40.7，35.5，30.5；

HRMS(ESI):m/z calcd for $C_{20}H_{24}O_4$ Na $[M+Na]^+$ 351.1567, found 351.1569



S7

S7:colourless liquid,79%

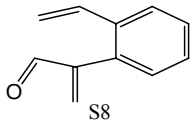
$[\alpha]_D^{14}$=11.6(c 0.45，$CHCl_3$)

IR(thin film): 3435.91 cm^{-1}，2950.71 cm^{-1}，1691.76 cm^{-1}，1123.73 cm^{-1}，1071.81 cm^{-1}；

^{1}H NMR (400MHz , d_6-acetone)：δ 9.49(s，1H)，6.33(s，1H)，6.14(s，1H)，5.28(dq，*J*=8.0，8.0Hz，1H)，4.90(dd，*J*=8.0，15.2Hz，1H)，3.89-3.95(m，4H)，2.36-2.46(m，2H)，1.69-1.73(m，2H)，1.45-1.67(m，4H)，1.30-1.37(m，3H)，-0.07(s，8H)；

^{13}C NMR(100MHz，d_6-acetone)：δ 194.9，154.4，135.2，132.4，127.2，108.8，64.9，64.8，43.9，43.2，40.8，35.5，30.9，23.0，-1.89；

HRMS(ESI):m/z calcd for $C_{17}H_{28}O_3$ Na $[M+Na]^+$ 331.1700, found 331.1708



S8

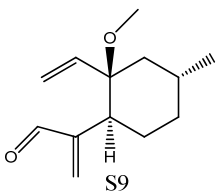
S8: colourless liquid

IR(thin film): 3374.47 cm^{-1}，3087.95 cm^{-1}，3062.01 cm^{-1}，2819.85 cm^{-1}，1736.01 cm^{-1}，1697.10 cm^{-1}；

^{1}H NMR (400MHz , d_6-acetone)：δ 9.79(s，1H)，7.66(dd，*J*=1.0，8.0Hz，1H)，7.37(ddd，*J*=1.2，7.2，8.0Hz，1H)，7.30(ddd，*J*=1.2，7.2，7.2Hz，1H)，7.11(dd，*J*=1.6，7.6Hz，1H)，6.61(dd，*J*=10.8，17.2Hz，1H)，6.57(s，1H)，6.49(s，1H)，5.71(dd，*J*=1.0，17.2Hz，1H)，5.20 (dd，*J*=0.8，11.2Hz，1H)；

^{13}C NMR(100MHz，d_6-acetone)：δ 193.4，150.5，138.2，137.1，135.9，134.9，130.8，129.3，128.4，125.9，115.6；

HRMS(ESI):m/z calcd for $C_{11}H_{10}O$ Na $[M+Na]^+$ 181.0624, found 181.0626



S9

S9: colourless liquid

$[\alpha]_D^{14}$=18.9(c 1.64，$CHCl_3$)

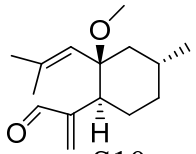
IR(thin film):3365.59 cm^{-1}，2926.30 cm^{-1}，1693.18 cm^{-1}，1075.12 cm^{-1}；

^{1}H NMR (400MHz , $CDCl_3$+D_2O)：δ 9.39(s，1H)，6.66(s，1H)，6.08(s，1H)，5.46(dd，*J*=11.2，17.6Hz，1H)，5.03(dd，*J*=1.2，11.2Hz，1H)，4.96(dd，*J*=1.2，17.6Hz，1H)，3.08(s，3H)，2.65(dd，*J*=3.4，12.8Hz，1H)，2.00(d，*J*=14.4，1H)，1.84(qd，*J*=3.6，12.9Hz，1H)，1.62-1.74(m，

2H)，1,38(ddd，*J*=3.3，6.6，12.8Hz，1H)，1.08(dd，*J*=12.4，14.0，1H)，0.96-1.05(m，1H)，0.93(d，*J*=6.4，3H);

^{13}C NMR(100MHz，$CDCl_3$+D_2O): δ 195.1，150.9，141.0，138.1，115.3，77.4，49.4，42.2，38.9，34.9，28.6，27.2，22.5；

HRMS(ESI):m/z calcd for $C_{13}H_{20}O_2$ Na $[M+Na]^+$ 231.1356, found 231.1360



S10

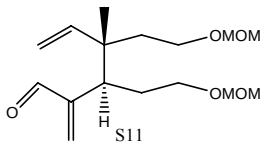
S10: colourless solid

$[\alpha]_D^{17}$=-130.0(c 1.06，$CHCl_3$)

^{1}H NMR (400MHz , $CDCl_3$): δ 9.37(s，1H)，6.50(s，1H)，6.02(s，1H)，4.72(s，1H)，3.06(s，3H)，2.75(dd，*J*=3.2，13.2Hz，1H)，2.00-2.04(m，1H)，1.90(qd，*J*=3.6，12.8Hz，1H)，1.68-1.72(m，1H)，1.56(s，6H，2CH_3)，1.56-1.61(m，1H)，1.31-1.35(m，1H)，0.95-1.02(m，2H)，0.88(d，*J*=6.8Hz，3H)；

^{13}C NMR(100MHz，$CDCl_3$): δ 194.7，151.6，137.3，133.2，127.0，78.7，49.3，43.0，41.6，35.0，28.0，27.7，27.0，22.4，19.3;

HRMS(ESI):m/z calcd for $C_{15}H_{24}O_2$ Na $[M+Na]^+$ 323.1829, found 323.1828



S11

S11: colourless liquid

$[\alpha]_D^{14}$=-38.4(c 0.19,$CHCl_3$)

IR(thin film):3369.38 cm^{-1}，2926.99 cm^{-1}，1762.60 cm^{-1}，1693.12 cm^{-1}，1110.00 cm^{-1}，1040.89 cm^{-1}；

^{1}H NMR (400MHz , $CDCl_3$+ D_2O): δ 9.48(s，1H)，6.27(s，1H)，6.17(s，1H)，5.68(dd，*J*=10.8，17.6Hz，1H)，5.02(dd，*J*=1.2，10.8Hz，1H)，4.84(dd，*J*=0.8，17.6Hz，1H)，4.56(s，2H)，4.51(q，*J*=6.8Hz，2H)，3.41-3.51(m，2H)，3.33(s，3H)，3.29(s，3H)，3.22-3.36(m，2H)，2.93(dd，*J*=2.4，12.8Hz，1H)，1.98-2.06(m，1H)，1.68-1.75(m，1H)，1.57-1.64(m，2H)，0.98(s，3H)；

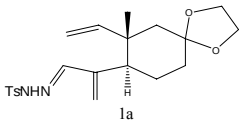
^{13}C NMR(100MHz，$CDCl_3$+D_2O): δ 194.9，150.5，143.6，135.8，113.9，96.6，96.5，66.2，64.8，55.3，41.6，37.8，29.1，19.3；

HRMS(ESI):m/z calcd for $C_{16}H_{28}O_5$ Na $[M+Na]^+$ 259.1669, found 259.1674

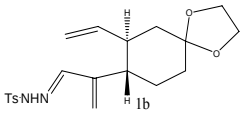
Procedure for the preparation of unsaturated hydrazone 1a-1l.

General procedure: To a methanol(3.5 mL) solution of aldehyde S2(204mg,0.68mmol) was added p-Toluenesulfonhydrazide(191mg,1.03mmol) under argon, and the mixture was heated up to 60℃. After 20 minutes the resulting mixture was quenched by the addtion of saturated aqueous $NaHCO_3$ and extracted with EtOAc for two times. The organic extract was dried over Na_2SO_4 and concentrated. The residue was purified on a silica gel column chromatography(petroluem

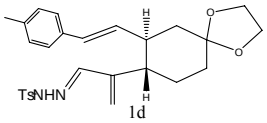
ether/EtOAc=3:1), which furnished hydrazone 1c(252mg,0.54mmol,79%) as a colourless thick liquid.



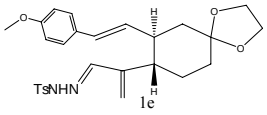
1a: white solid, 87%



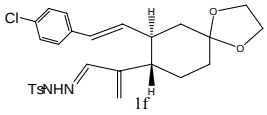
1b: white solid, 82%



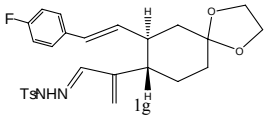
1d: white solid, 47%



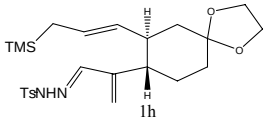
1e: white solid, 73%



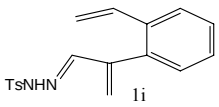
1f: white solid, 62%



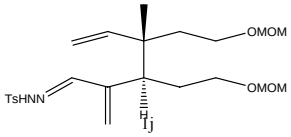
1g: white solid, 73%



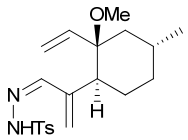
1h: white solid, 57%



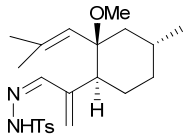
1i: white solid, 65%



1j: white solid,85%



1k: white solid,81%

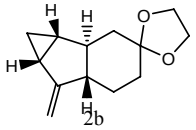


1l: white solid,89%

Procedure for the cyclopropanation reactions of unsaturated hydrazone 1b-9b.

Method A: To a methanol(1.8 mL) solution of hydrazone 1a(75mg,0.19mmol) was added dropwise CH_3ONa (0.28 mL,0.28mmol,1.0M in CH_3OH) at 0℃ under argon. The resulting mixture was stired at 0℃ for 5 minutes and 15 minutes for ambient temperature, then concentrated. To the resulting solid was added $Pd_2(dba)_3$(26mg,0.028mmol) and dry DMF(9.3 mL) successively under argon, and the mixture was stired at 35℃ for 5h and diluted with Et_2O. The resulting mixture was washed with water for two times, and the organic extract was dried over Na_2SO_4 and concentrated. The residue was purified on a silica gel column chromatography(petroluem ether/EtOAc=30:1), which furnished the cyclopropanation product 2a (33mg,0.15mmol,81%) as a colourless liquid.

The characterization data of 2a is in accord with the literature.[1]



2b

2b: colourless liquid

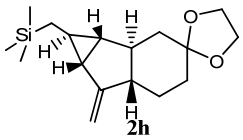
$[\alpha]_D^{14}$=-48.8(c 0.41,$CHCl_3$)

IR(thin film):3066.48 cm^{-1}；2933.02 cm^{-1}；2879.29 cm^{-1}；

^{1}H NMR (400MHz , $CDCl_3$+D_2O): δ 4.88(m，1H)，4.67(s，1H)，3.91-3.97(m，4H)，2.18-2.26(m，1H)，2.09-2.13(m，1H)，1.87-1.91(m，1H)，1.73-1.81(m，2H)，1.55-1.62(m，1H)，1.47-1.54(m，1H)，1.20-1.28(m，2H)，1.11-1.18(m，1H)，1.01(ddd，*J*=4.4，7.6，9.2Hz，1H)，0.37-0.39(m，1H)；

^{13}C NMR(100MHz，$CDCl_3$+D_2O): δ 154.3，110.2，103.6，64.5(2C)，59.2，47.4，40.8，34.8，24.3，24.2，22.5，21.1;

HRMS(ESI):m/z calcd for $C_{13}H_{18}O_2Na$ $[M+Na]^+$ 229.1199, found 229.1202.



2h

2h: colourless liquid

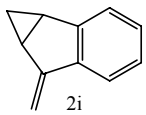
$[\alpha]_D^{14}$=-43.8(c 0.52,$CHCl_3$)

IR(thin film):2950.15 cm^{-1}，2876.56 cm^{-1}，1248.03 cm^{-1}，1069.62 cm^{-1}；

^{1}H NMR (400MHz , d_6-DMSO): δ 4.81-4.83(m，1H)，4.62(s，1H)，3.82-3.86(m，4H)，2.07(dd，*J*=8.6，11.8Hz，1H)，1.95-2.00(m，1H)，1.62-1.73(m，2H)，1.56-1.60(m，1H)，1.50(t，*J*=12.4Hz，1H)，1.42(td，*J*=4.4，13.2Hz，1H)，0.98-1.10(m，3H)，0.61(dd，*J*=6.0，14.0Hz，1H)，0.50-0.55(m，1H)，0.36(dd，*J*=8.0，14.0Hz，1H)，-0.01-0.04(m，9H)；

^{13}C NMR(100MHz，d_6-DMSO): δ 153.6，109.1，103.0，63.7(2C)，58.1，46.4，40.2，34.0，32.9，31.7，29.6，23.7，20.3，-1.3；

HRMS(ESI):m/z calcd for $C_{17}H_{29}O_2$ $[M+H]^+$ 293.1931, found 293.1934



2i

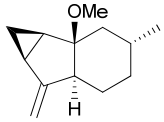
2i: colourless liquid

IR(thin film):3430.62 cm^{-1}，3072.53 cm^{-1}，3044.09 cm^{-1}，2994.30 cm^{-1}，1640.72 cm^{-1}，1463.88 cm^{-1}，1035.87 cm^{-1}；

^{1}H NMR (400MHz , $CDCl_3$): δ 7.46-7.48(m，1H)，7.34(d，*J*=7.2Hz，1H)，7.14-7.22(m，2H)，5.51(s，1H)，5.26(s，1H)，2.61-2.65(m，1H)，2.48-2.52(m，1H)，1.21-1.27(m，1H)，0.53-0.56(m，1H)；

^{13}C NMR(100MHz，$CDCl_3$): δ 150.6，148.5，138.3，128.0，125.9，124.0，121.5，104.0，23.4，23.1，22.9；

HRMS(ESI):m/z calcd for $C_{11}H_{11}$ $[M+H]^+$ 143.0855, found 143.0858



2k: colourless liquid

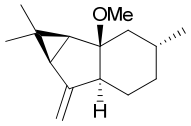
$[\alpha]_D^{14}$=-62.3(c 0.13,$CHCl_3$)

IR(thin film):3426.22 cm^{-1}；2922.79 cm^{-1}；1762.48 cm^{-1}；1073.53 cm^{-1}；

^{1}H NMR (400MHz , $CDCl_3$): δ 4.94 (t，*J*=1.2Hz，1H)，4.70(s，1H)，3.04(s，3H)，2.30-2.34(m，1H)，2.25(dd，*J*=2.8，13.2Hz，1H)，1.96-2.00(m，1H)，1.64-1.76(m，2H)，1.45-1.51(m，2H)，1.31(td，*J*=3.6,7.2Hz，1H)，1.06(dd，*J*=11.6，13.2Hz，1H)，0.98-1.02(m，1H)，0.93(d，*J*=6.4Hz，3H)，0.90-0.95(m，1H)，0.83(q，*J*=4.0Hz，1H)；

^{13}C NMR(100MHz，$CDCl_3$): δ 153.0，104.4，80.6，63.9，48.7，40.2，34.1，28.2，24.7，24.0，22.5，21.7，16.8；

HRMS(ESI):m/z calcd for $C_{13}H_{20}O$ Na $[M+Na]^+$ 215.1406, found 215.1415



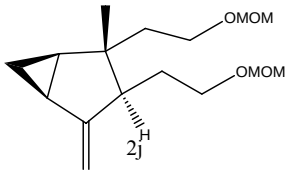
2l: colourless liquid

$[\alpha]_D^{14}$=-39.2(c 0.12,$CHCl_3$)

IR(thin film):3438.19 cm^{-1}，2948.22 cm^{-1}，2922.25 cm^{-1}，1661.74 cm^{-1}，1078.40 cm^{-1}；

^{1}H NMR (600MHz , $CDCl_3$): δ 4.78-4.79(m，1H)，4.72(s，1H)，2.99(s，3H)，2.30-2.33(m，1H)，2.23(dd，*J*=3.6，13.2Hz，1H)，1.85(dd，*J*=1.2，7.8Hz，1H)，1.70-1.75(m，2H)，1.45-1.55(m，2H)，1.24(s，3H)，1.02(s，3H)，1.02-1.03(m，1H)，0.97(dd，*J*=11.4，13.2Hz，1H)，0.88-0.93(m，1H)，0.91(d，*J*=6.6Hz，3H)；

^{13}C NMR(150MHz，$CDCl_3$): δ 150.6，104.8，81.8，65.0，49.6，42.0，37.4，36.6，34.4，29.4，29.0，27.7，22.5，21.1，17.9;



2j: colourless liquid

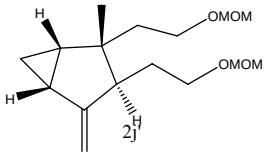
[α]$_D^{14}$=30.7(c 0.73,$CHCl_3$)

IR(thin film):3077.67 cm^{-1}，2930.38 cm^{-1}，2881.82 cm^{-1}，1647.47 cm^{-1}，1109.36 cm^{-1}，1141.00 cm^{-1}；

^{1}H NMR (400MHz , $CDCl_3$): δ 4.99(s，1H)，4.64(s，1H)，4.59(s，4H)，3.62(t，*J*=7.6Hz，2H)，3.47-3.57(m，2H)，3.34(s，6H)，2.19(dd，*J*=4.4，11.6Hz，1H)，1.79-1.83(m，1H)，1.68-1.77(m，3H)，1.44-1.48(m，1H)，1.20-1.29(m，1H)，1.03(s，3H)，0.61(td，*J*=5.2，8.0Hz，1H)，0.51-0.54(m，1H)；

^{13}C NMR(100MHz，$CDCl_3$): δ 156.0，106.8，96.6，67.1，64.9，55.4，55.3，46.9，43.9，43.4，33.5，32.5，25.0，20.8，11.8；

HRMS(ESI):m/z calcd for $C_{16}H_{28}O_4$ Na $[M+Na]^+$ 307.1880, found 307.1888



2j': colourless liquid

[α]$_D^{14}$=45.7(c 0.07,$CHCl_3$)

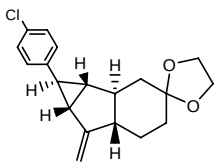
IR(thin film):3440.71 cm^{-1}，2923.75 cm^{-1}，2881.23 cm^{-1}，1652.08 cm^{-1}，1109.50 cm^{-1}，1041.42 cm^{-1}；

^{1}H NMR (400MHz , $CDCl_3$): δ 4.96(d，*J*=1.6Hz，1H)，4.66(d，*J*=1.2Hz，1H)，4.64(s，2H)，4.60(dd，*J*=6.4，8.0Hz，2H)，3.63-3.73(m，3H)，3.47-3.53(m，1H)，3.38(s，3H)，3.34(s，3H)，1.78-1.82(m，1H)，1.69-1.76(m，1H)，1.58-1.67(m，4H)，1.30(ddd，*J*=4.4，6.0，8.0Hz，1H)，0.81(s，3H)，0.65-0.69(m，1H)，0.61(td，*J*=5.2，8.0Hz，1H)；

^{13}C NMR(100MHz，$CDCl_3$): δ 155.0，103.0，96.6，96.4，67.6，65.4，55.4，55.3，43.1，42.0，38.0，28.1，27.1，23.3，20.9，9.7；

HRMS(ESI):m/z calcd for $C_{16}H_{28}O_4$ Na $[M+Na]^+$ 307.1880, found 307.1887

Method B: To a methanol(2.3 mL) solution of hydrazone 1f(115mg,0.23mmol) was added dropwise CH_3ONa (0.46 mL,0.46mmol,1.0M in CH_3OH) at 0℃ under argon. The resulting mixture was stired at 0℃ for 5 minutes and 15 minutes for ambient temperature, then concentrated. To the resulting solid was added $Pd_2(dba)_3$(32mg,0.034mmol) and dba(54mg,0.23mmol) and dry DMF(11.5 mL) successively under argon, and the mixture was stired at 60℃ for 5h and diluted with Et_2O. The resulting mixture was washed with water for two times, and the organic extract was dried over Na_2SO_4 and concentrated. The residue was purified on a silica gel column chromatography(petroluem ether/dichloromethane=3:1), which furnished the cyclopropanation product 2f(50mg,0.16mmol,69%) as a white solid.



2f

2f: white solid

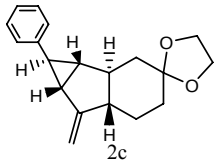
[α]$_D^{14}$=-3.9(c 0.54,$CHCl_3$)

IR(thin film):3435.60 cm^{-1}，2926.76 cm^{-1}，2879.42 cm^{-1}，1656.85 cm^{-1}，1070.13 cm^{-1}；

^{1}H NMR (400MHz , d_6-acetone): δ 7.26(dt，*J*=2.2，8.8Hz，2H)，7.05(d，*J*=8.4Hz，2H)，4.95(t，*J*=1.3Hz，1H)，4.77(s，1H)，3.88-3.92(m，4H)，2.19-2.26(m，2H)，2.11(dt，*J*=2.8，12.0Hz，1H)，1.78-1.84(m，2H)，1.71-1.77(m，1H)，1.62-1.65(m，1H)，1.60(t，12.6Hz，1H)，1.51(td，*J*=4.8，13.2Hz，1H)，1.35-1.43(m，1H)，1.22(ddd，*J*=3.8，12.8，24.6Hz，1H)；

^{13}C NMR(100MHz，d_6-acetone): δ 154.1，142.2，131.5，129.1，127.8，110.3，104.9，65.0，64.9，59.1，48.3，41.3，39.6，37.1，35.4，33.0，24.9；

HRMS(ESI):m/z calcd for $C_{19}H_{22}O_2Cl[M+H]^+$ 317.1303, found 317.1306



2c

2c: colourless liquid

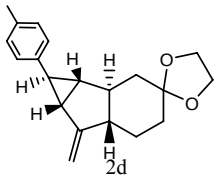
[α]$_D^{14}$=-7.7(c 0.94,$CHCl_3$)

IR(thin film):3387.98 cm^{-1}，3027.23 cm^{-1}，2941.46 cm^{-1}，2879.82 cm^{-1}，1657.10 cm^{-1}，1602.80 cm^{-1}，1140.37 cm^{-1}，1116.46 cm^{-1}；

^{1}H NMR (400MHz , d_6-acetone): δ 7.24(t，*J*=7.2Hz，2H)，7.13(t，*J*=7.6Hz，1H)，7.02(d，*J*=7.2Hz，2H)，4.95(s，1H)，4.77(s，1H)，3.90(s，4H)，2.20-2.27(m，2H)，2.12(dt，*J*=2.7，8.1Hz，1H)，1.73-1.85(m，3H)，1.61-1.64(m，1H)，1.61(t，*J*=12.6Hz，1H)，1.52(td，*J*=4.8，13.2，1H)，1.37-1.44(m，1H)，1.20-1.30(m，1H)；

^{13}C NMR(100MHz，d_6-acetone): δ 154.3，143.1，129.1，126.3，126.1，110.3，104.7，65.0，64.9，59.1，48.3，41.3，40.3，36.9，35.4，32.9，24.9；

HRMS(ESI):m/z calcd for $C_{19}H_{23}O_2[M+H]^+$ 283.1693, found 283.1695



2d

2d: colourless liquid

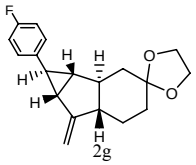
[α]$_D^{14}$=-8.3(c 0.30,$CHCl_3$)

IR(thin film):3019.44 cm^{-1}，2928.04 cm^{-1}，2878.68 cm^{-1}，1762.63 cm^{-1}，1656.44 cm^{-1}，1115.84 cm^{-1}，1069.60 cm^{-1}；

^{1}H NMR (400MHz , d_6-acetone): δ 7.05(d，*J*=8.0Hz，2H)，6.91(d，*J*=8.0Hz，2H)，4.93(d，*J*=1.6Hz，1H)，4.75(s，1H)，3.90(s，4H)，2.26(s，3H)，2.18-2.26(m，1H)，2.14-2.17(m，1H)，2.11(dt，*J*=2.7，12.1Hz，1H)，1.78-1.84(m，1H)，1.72-1.77(m，2H)，1.60(t，*J*=12.6Hz，1H)，1.57-1.60(m，1H)，1.51(td，*J*=4.8，13.2Hz，1H)，1.38(tt，*J*=3.3，12.8Hz，1H)，1.23(ddd，*J*=3.8，12.8，24.8Hz，1H)；

^{13}C NMR(100MHz，d_6-acetone): δ 154.5，140.1，135.6，129.8，126.1，110.3，104.6，65.0，64.9，59.1，48.3，41.4，40.2，36.7，35.4，32.6，24.9，21.0；

HRMS(ESI):m/z calcd for $C_{20}H_{25}O_2[M+H]^+$ 297.1849, found 297.1862



2g: colourless liquid

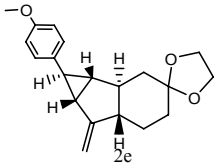
$[\alpha]_D^{14}$=-8.8(c 0.33,$CHCl_3$)

IR(thin film):3387.54 cm^{-1}，2932.22 cm^{-1}，2880.49 cm^{-1}，1116.88 cm^{-1}，1070.02 cm^{-1}；

^{1}H NMR (400MHz , d_6-acetone): δ 7.05-7.09(m，2H)，7.01(t，*J*=8.8Hz，2H)，4.95(s，1H)，4.77(s，1H)，3.90(s，4H)，2.17-2.26(m，2H)，2.11(d，*J*=12.8Hz，1H)，1.80-1.82(m，2H)，1.73-1.77(m，1H)，1.60(t，*J*=12.6，1H)，1.60-1.64(m，1H)，1.51(td，*J*=4.5，13.2Hz，1H)，1.35-1.42(m，1H)，1.22(ddd，*J*=3.6，12.8，24.8Hz，1H)；

^{13}C NMR(100MHz，d_6-acetone): δ 163.2，160.8，154.2，139.2，127.8，115.8，115.6，110.3，104.8，65.0，64.9，59.1，48.3，41.3，39.5，36.8，35.4，32.8，24.9;

HRMS(ESI):m/z calcd for $C_{19}H_{21}O_2F$ Na $[M+Na]^+$ 323.1418, found 323.1423



2e: white solid

$[\alpha]_D^{14}$=-5.7(c 0.65,$CHCl_3$)

IR(thin film):2932.88 cm^{-1}，2879.09 cm^{-1}，1656.46 cm^{-1}，1611.07 cm^{-1}，1514.32 cm^{-1}，1247.32 cm^{-1}；

^{1}H NMR (400MHz , d_6-acetone): δ 6.94-6.97(m，2H)，6.79-6.83(m，2H)，4.93(t，*J*=1.2Hz，1H)，4.75(s，1H)，3.88-3.92(m，4H)，3.74(s，3H)，2.21(tq，*J*=2.8，11.6Hz，1H)，2.08-2.13(m，2H)，1.78-1.84(m，1H)，1.71-1.77(m，2H)，1.60(t，*J*=12.6，1H)，1.53-1.57(m，1H)，1.51(td，*J*=4.8，13.2Hz，1H)，1.37(tt，*J*=3.2，12.8Hz，1H)，1.22(ddd，*J*=3.8，12.8，24.8Hz，1H)；

^{13}C NMR(100MHz，d_6-acetone): δ 158.9，154.5，135.1，127.2，114.6，110.3，104.5，65.0，64.9，59.1，55.5，48.3，41.4，39.8，36.5，35.4，32.4，25.0；

HRMS(ESI):m/z calcd for $C_{20}H_{24}O_3$ K $[M+K]^+$ 351.1357, found 351.1356

[1]B.Du,C.Yuan,T.Yu,L.Yang,Y.Yang,B.Liu and S.Qin, Chem,Eur.J. ,2014 , 20 , 2613.

Table S1

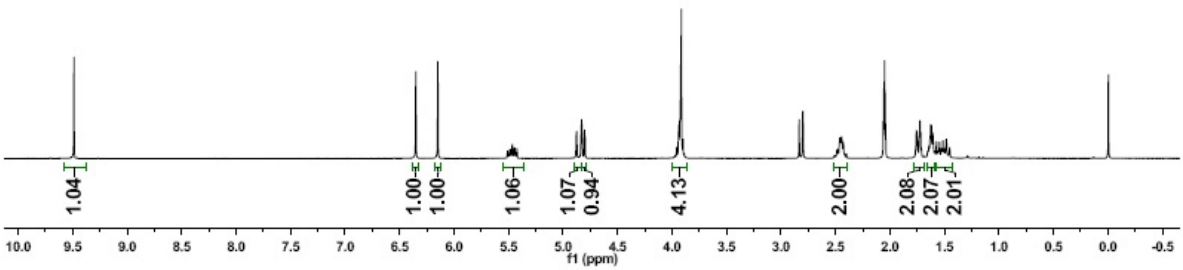
Condition / Entry	Base(n equiv)	Catalyst (mmol%)	T/℃	Solvent	c/(mol/L)	adducts	Yield(%)
1	CH_3ONa (1.5)	$Pd_2(dba)_3$ (15%)	35	DMF	0.02		81%
2	CH_3ONa (1.5)	**$Pd_2(dba)_3$ (0%)**	35	DMF	0.02		0%
3	CH_3ONa (1.5)	**$Pd_2(dba)_3$**	35	DMF	0.02		45%

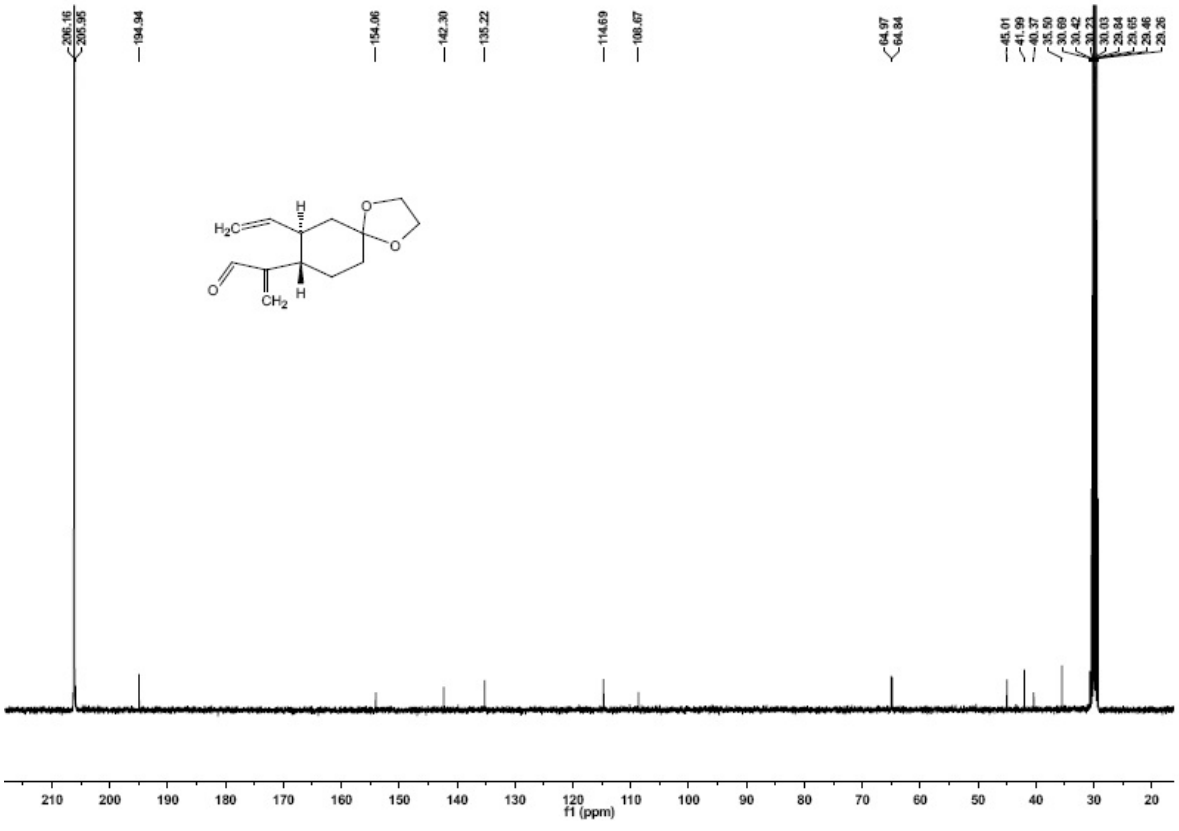
		(7%)					
4	CH_3ONa (1.5)	**$Pd_2(dba)_3$ (50%)**	35	DMF	0.02		88%
5	CH_3ONa (1.5)	**$Pd_2(dba)_3 \cdot CHCl_3$ (15%)**	35	DMF	0.02		73%
6	CH_3ONa (1.5)	**$Pd(MeCN)_2Cl_2$**	35	DMF	0.02		48%
7	CH_3ONa (1.5)	**$Pd(COD)Cl_2$(30%)**	35	DMF	0.02		55%
8	CH_3ONa (1.5)	**$Rh_2(OAc)_4$(15%)**	35	DMF	0.02		63%
9	CH_3ONa (1.5)	**Ir(COD)Cl(30%)**	35	DMF	0.02		37%
10	CH_3ONa (1.5)	**$Cu(OTf)_2$ (30%)**	35	DMF	0.02		0%
11	CH_3ONa (1.5)	**$Cu(acac)_2$ (30%)**	35	DMF	0.02		0%
12	CH_3ONa (1.5)	**AgOTf (30%)**	35	DMF	0.02		0%
13	CH_3ONa (1.5)	**$AgSbF_6$ (30%)**	35	DMF	0.02		0%
14	**CH_3ONa (3.0)**	$Pd_2(dba)_3$ (15%)	35	DMF	0.02		63%
15	**NaH(1.5)**	$Pd_2(dba)_3$ (15%)	35	DMF	0.02		65%
16	**NaHMDS(1.5)**	$Pd_2(dba)_3$ (15%)	35	DMF	0.02		49%
17	**LiHMDS (1.5)**	$Pd_2(dba)_3$ (15%)	35	DMF	0.02		52%
18	**KHMDS (1.5)**	$Pd_2(dba)_3$ (15%)	35	DMF	0.02		63%
19	**tBuOK (1.5)**	$Pd_2(dba)_3$ (15%)	35	DMF	0.02		33%
20	CH_3ONa (1.5)	$Pd_2(dba)_3$ (15%)	**55**	DMF	0.02		60%
21	CH_3ONa (1.5)	$Pd_2(dba)_3$ (15%)	**70**	DMF	0.02		54%
22	CH_3ONa (1.5)	$Pd_2(dba)_3$ (15%)	35	**DMA**	0.02		36%
23	CH_3ONa (1.5)	$Pd_2(dba)_3$ (15%)	35	**NMP**	0.02		55%
24	CH_3ONa (1.5)	$Pd_2(dba)_3$ (15%)	35	**THF**	0.02		63%

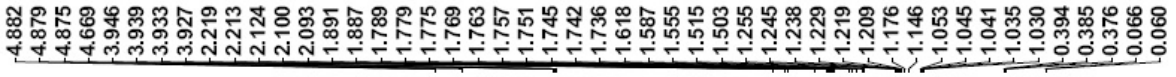
25	CH_3ONa (1.5)	$Pd_2(dba)_3$ (15%)	35	**DCM**	0.02		50%
26	CH_3ONa (1.5)	$Pd_2(dba)_3$ (15%)	35	**Toluene**	0.02		39%
27	CH_3ONa (1.5)	$Pd_2(dba)_3$ (15%)	35	DMF	**0.1**		46%
28	CH_3ONa (1.5)	$Pd_2(dba)_3$ (15%)	35	DMF	**0.01**		35%
29	CH_3ONa (1.5)	$Pd_2(dba)_3$ (15%)	35	DMF	**0.005**		17%
30	CH_3ONa (1.5)	**$Pd_2(dba)_3$ (0%)**	**150[1]**	DMF	0.02		40%
31	CH_3ONa (1.5)	$Pd_2(dba)_3$ (15%)	35	DMF	0.02	**4A MS**	61%
32	CH_3ONa (1.5)	$Pd_2(dba)_3$ (15%)	35	DMF	0.02	**2.0 equiv dba**	69%

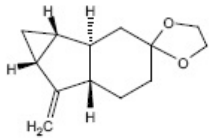
[1] seal tube

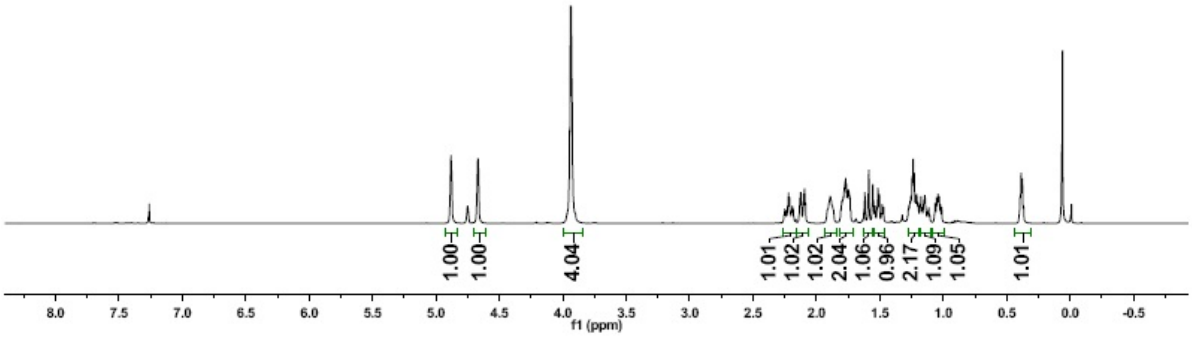
Spectra for compounds



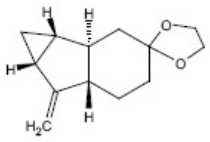


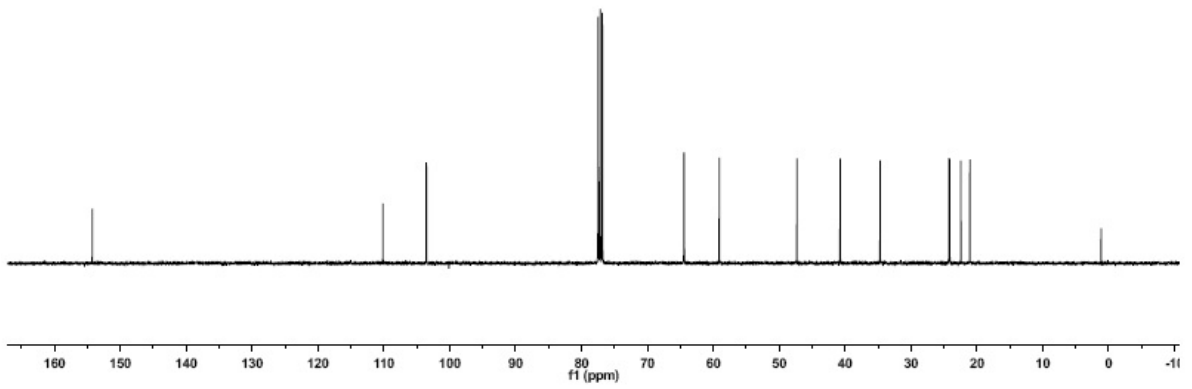

4.882
4.879
4.875
4.669
3.946
3.939
3.933
3.927
2.219
2.213
2.124
2.100
2.093
1.891
1.887
1.789
1.779
1.775
1.769
1.763
1.757
1.751
1.745
1.742
1.736
1.618
1.587
1.555
1.515
1.503
1.255
1.245
1.238
1.229
1.219
1.209
1.176
1.146
1.053
1.045
1.041
1.035
1.030
0.394
0.385
0.376
0.066
0.060

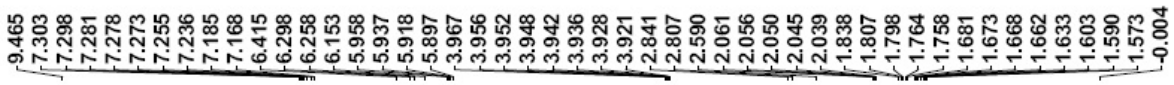


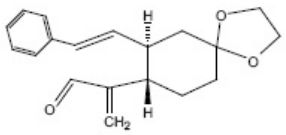

1.00
1.00
4.04
1.01
1.02
1.02
2.04
1.06
0.96
2.17
1.09
1.05
1.01
f1 (ppm)

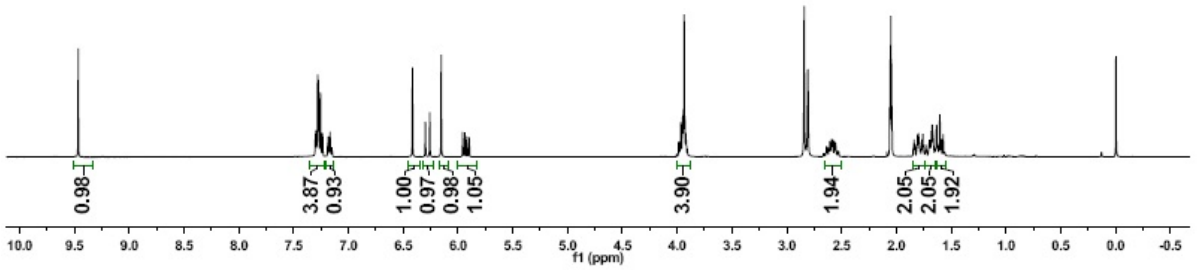

154.25
110.15
103.55
77.48
77.16
76.84
64.47
64.41
59.10
47.31
40.75
34.69
24.22
24.13
22.42
21.06
1.14



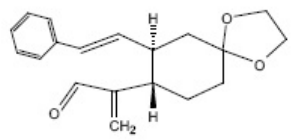

f1 (ppm)

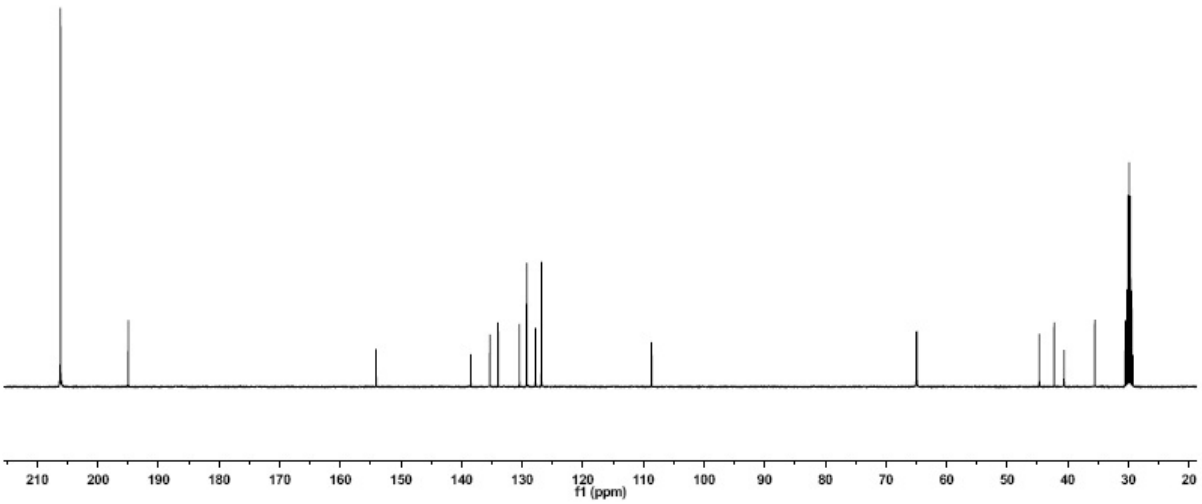

9.465
7.303
7.298
7.281
7.278
7.273
7.255
7.236
7.185
7.168
6.415
6.298
6.258
6.153
5.958
5.937
5.918
5.897
3.967
3.956
3.952
3.948
3.942
3.936
3.928
3.921
2.841
2.807
2.590
2.061
2.056
2.050
2.045
2.039
1.838
1.807
1.798
1.764
1.758
1.681
1.673
1.668
1.662
1.633
1.603
1.590
1.573
-0.004

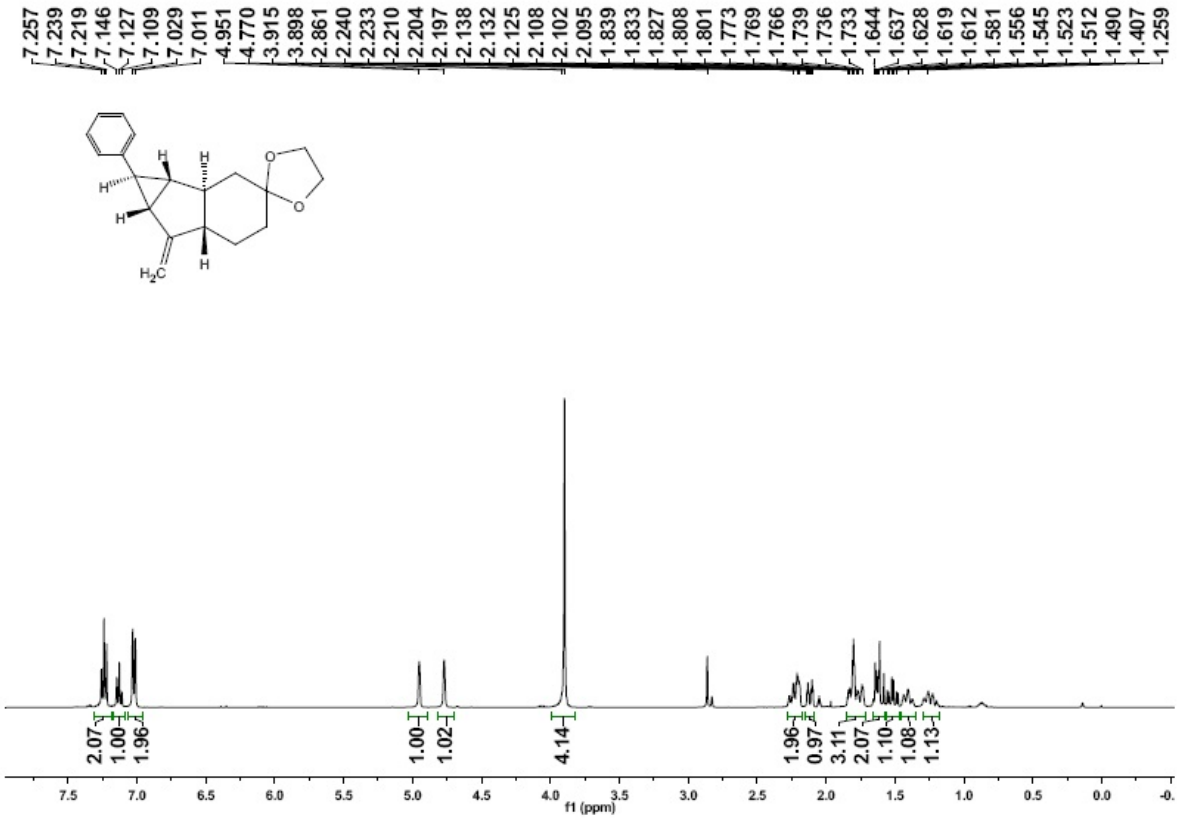

H
O
O
O
CH2
H

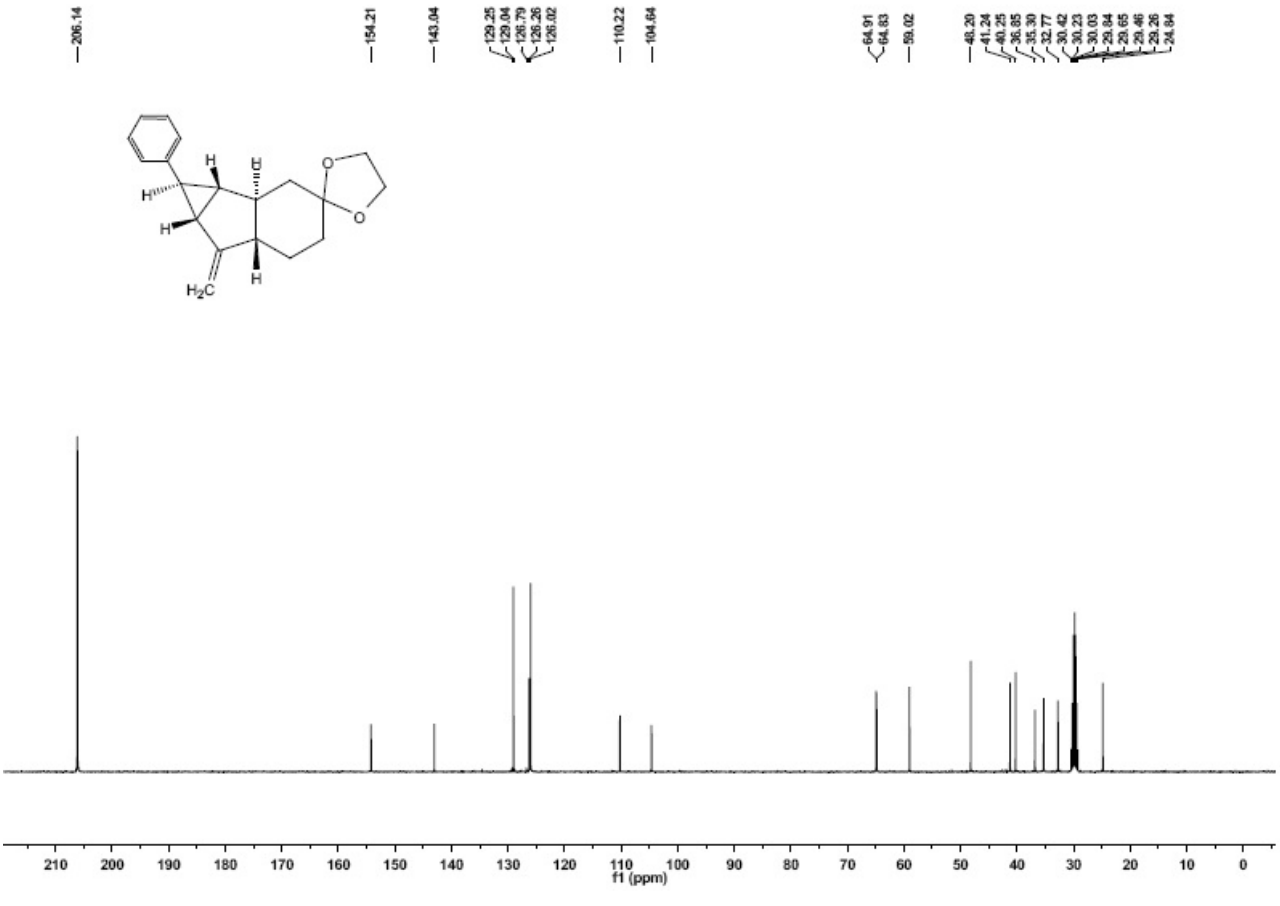

0.98
3.87
0.93
1.00
0.97
0.98
1.05
3.90
1.94
2.05
2.05
1.92
f1 (ppm)

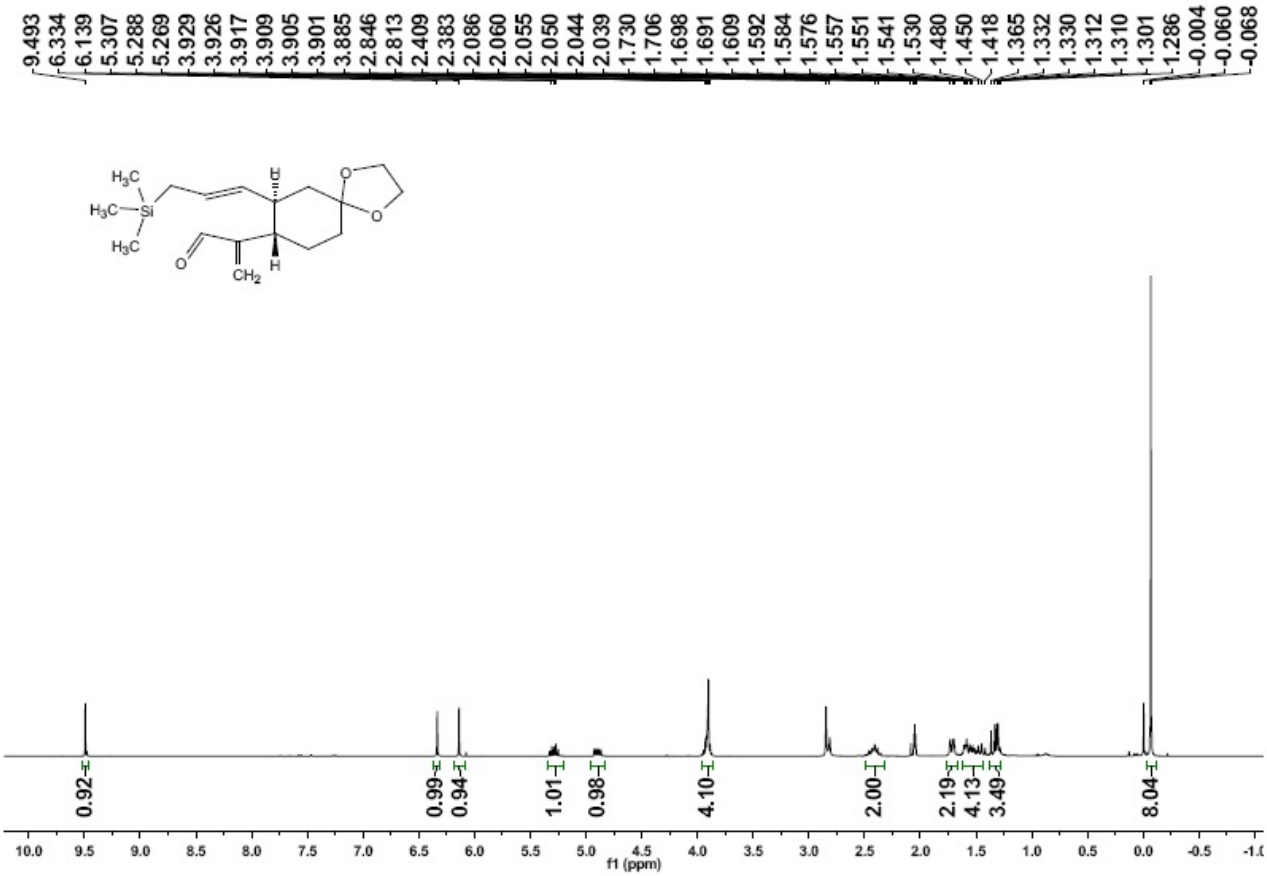

206.37
206.17
205.98
194.99
154.10
138.46
135.34
133.98
130.46
129.25
127.80
126.82
108.66
64.98
64.85
44.68
42.23
40.39
35.53
30.50
30.22
30.03
29.84
29.65

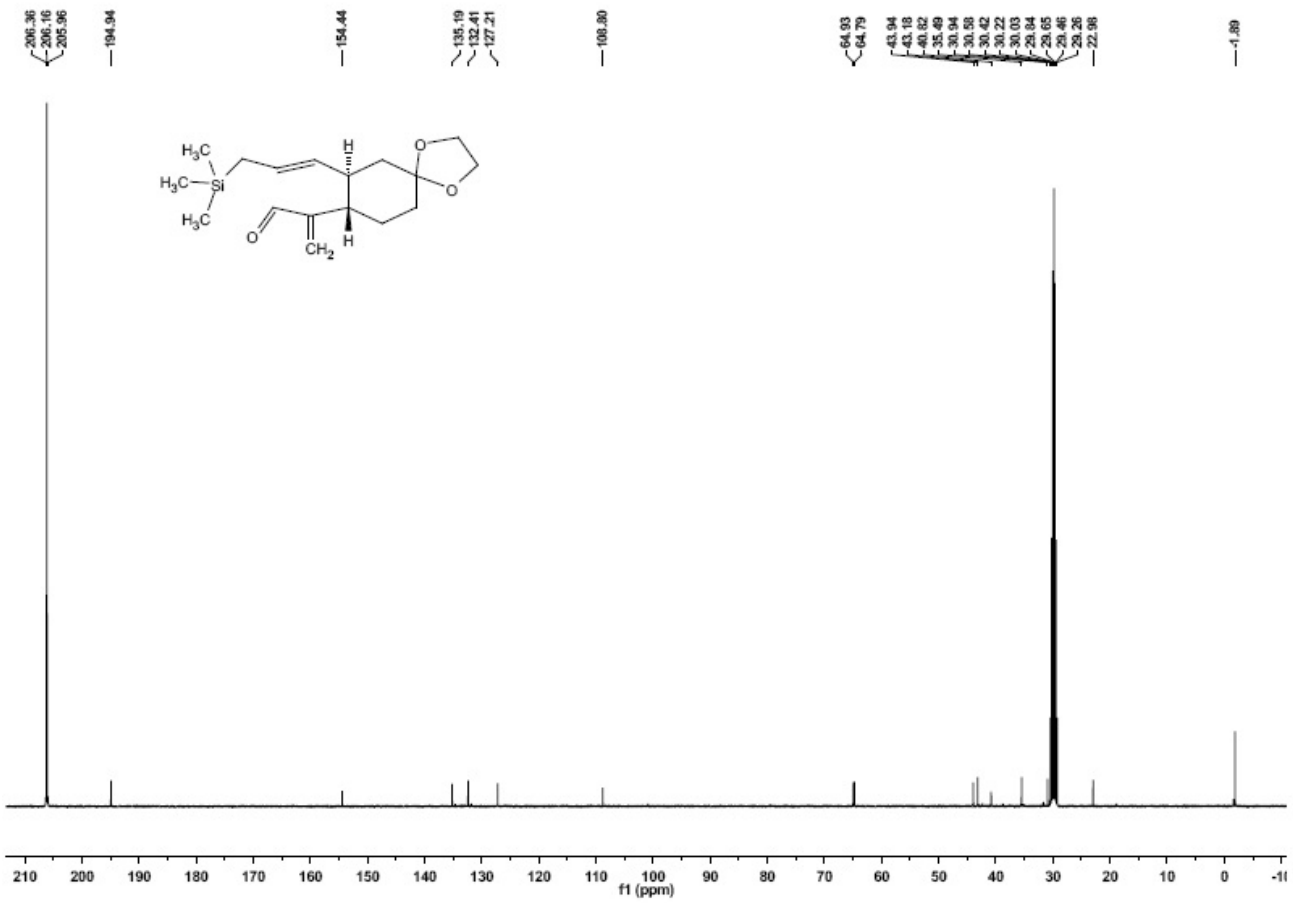

H
O
O
O
CH2
H

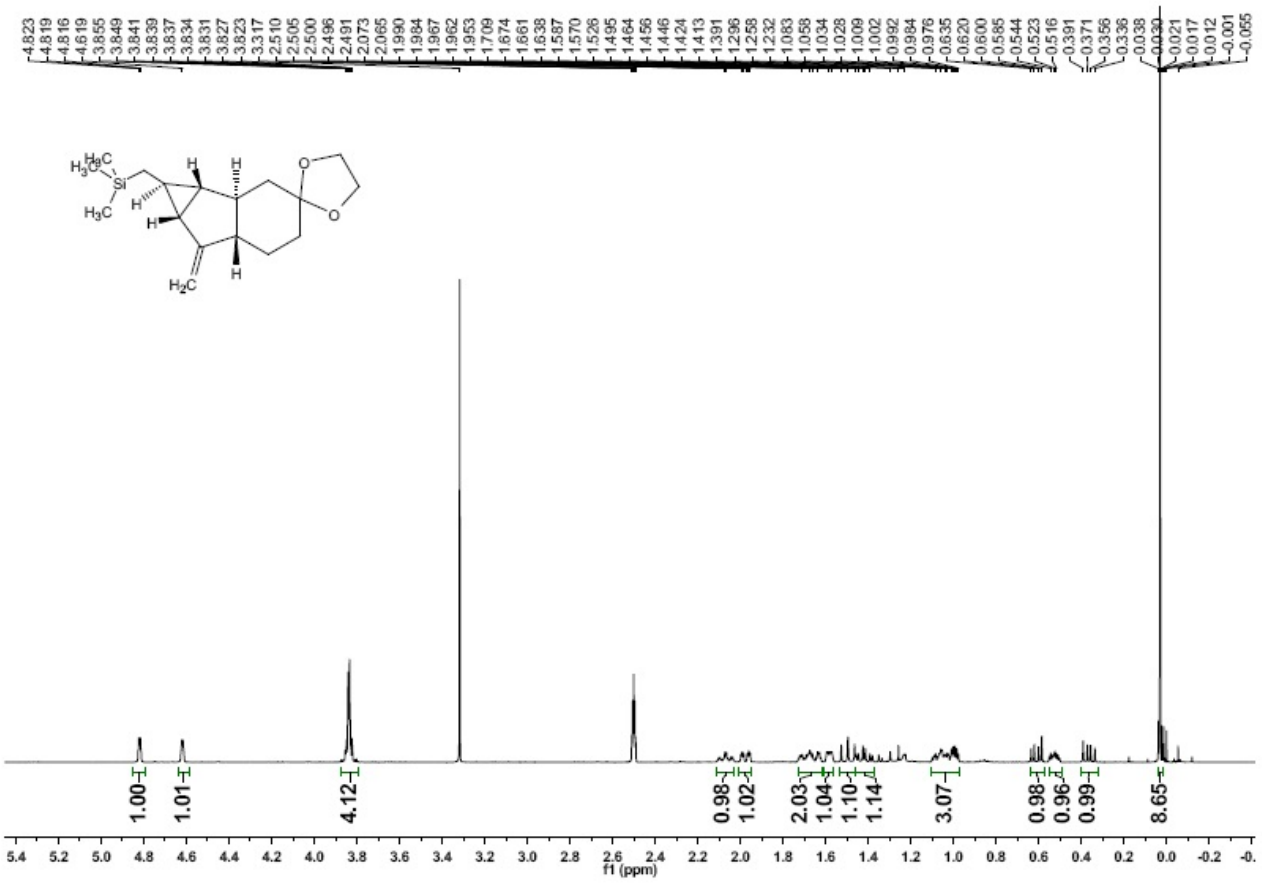

f1 (ppm)

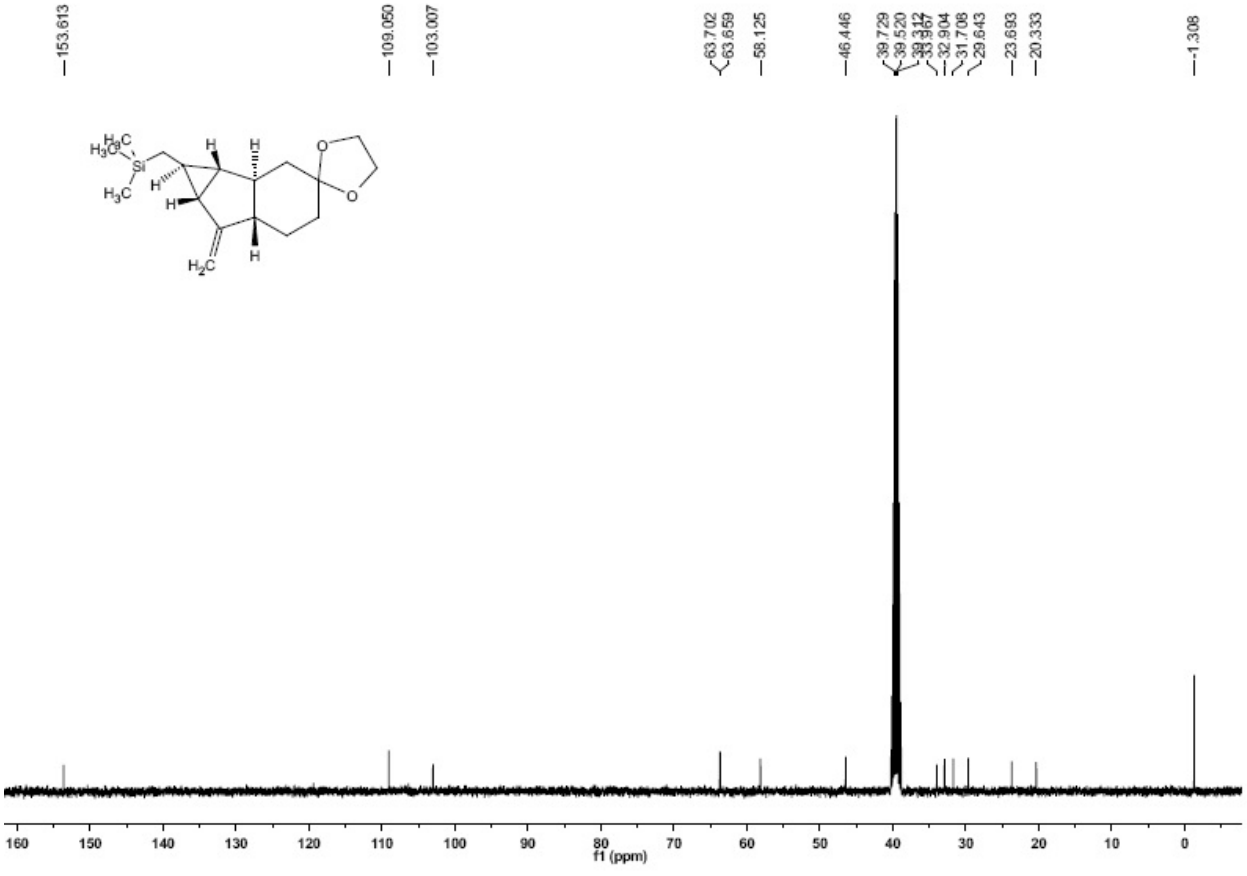

7.257
7.239
7.219
7.146
7.127
7.109
7.029
7.011
4.951
4.770
3.915
3.898
2.861
2.240
2.233
2.210
2.204
2.197
2.138
2.132
2.125
2.108
2.102
2.095
1.839
1.833
1.827
1.808
1.801
1.773
1.769
1.766
1.739
1.736
1.733
1.644
1.637
1.628
1.619
1.612
1.581
1.556
1.545
1.523
1.512
1.490
1.407
1.259
2.07
1.00
1.96
1.00
1.02
4.14
1.96
0.97
3.11
2.07
1.10
1.08
1.13
f1 (ppm)

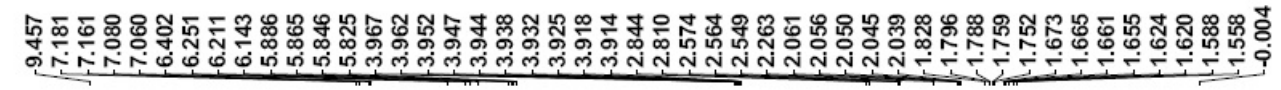

206.14
154.21
143.04
129.25
129.04
126.79
126.26
126.02
110.22
104.64
64.91
64.83
59.02
48.20
41.24
40.25
36.85
35.30
32.77
30.42
30.23
30.03
29.84
29.65
29.46
29.26
24.84
f1 (ppm)

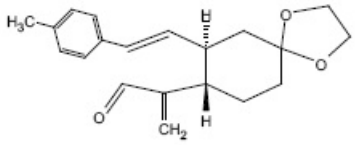

9.493
6.334
6.139
5.307
5.288
5.269
3.929
3.926
3.917
3.909
3.905
3.901
3.885
2.846
2.813
2.409
2.383
2.086
2.060
2.055
2.050
2.044
2.039
1.730
1.706
1.698
1.691
1.609
1.592
1.584
1.576
1.557
1.551
1.541
1.530
1.480
1.450
1.418
1.365
1.332
1.330
1.312
1.310
1.301
1.286
-0.004
-0.060
-0.068
0.92
0.99
0.94
1.01
0.98
4.10
2.00
2.19
4.13
3.49
8.04
f1 (ppm)

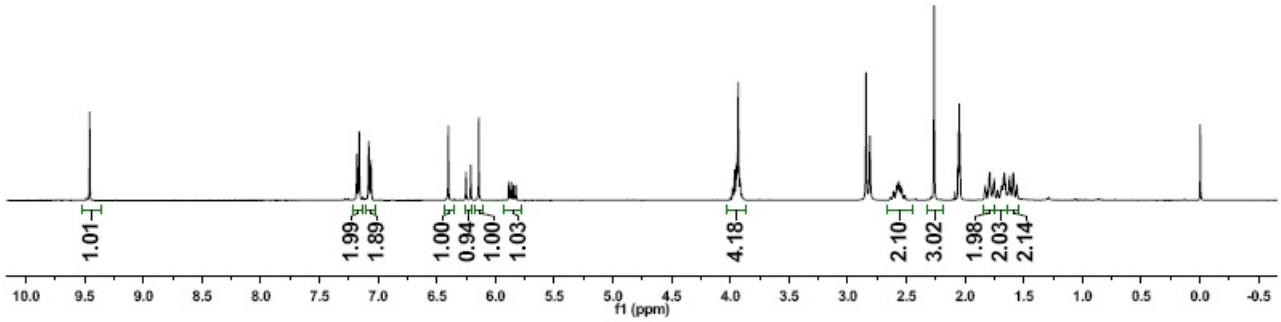

206.36
206.16
205.96
194.94
154.44
135.19
132.41
127.21
108.80
64.93
64.79
43.94
43.18
40.82
35.49
30.94
30.58
30.42
30.22
30.03
29.84
29.65
29.46
29.26
22.98
-1.89
f1 (ppm)


-4.823
-4.819
-4.816
-4.619
3.855
3.849
3.841
3.839
3.837
3.834
3.831
3.827
3.823
3.317
2.510
2.505
2.500
2.496
2.491
2.073
2.065
1.990
1.984
1.967
1.962
1.953
1.709
1.674
1.661
1.638
1.587
1.570
1.526
1.495
1.464
1.456
1.446
1.424
1.413
1.391
1.296
1.258
1.232
1.083
1.058
1.034
1.028
1.009
1.002
0.992
0.984
0.976
0.635
0.620
0.600
0.585
0.544
0.523
0.516
0.391
0.371
0.356
0.336
0.038
0.030
0.021
0.017
0.012
-0.001
-0.055
1.00
1.01
4.12
0.98
1.02
2.03
1.04
1.10
1.14
3.07
0.98
0.96
0.99
8.65
f1 (ppm)

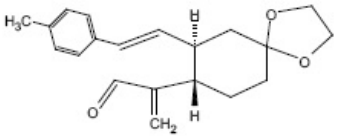

153.613
109.050
103.007
63.702
63.659
58.125
46.446
39.729
39.520
32.904
31.708
29.643
23.693
20.333
1.308
f1 (ppm)

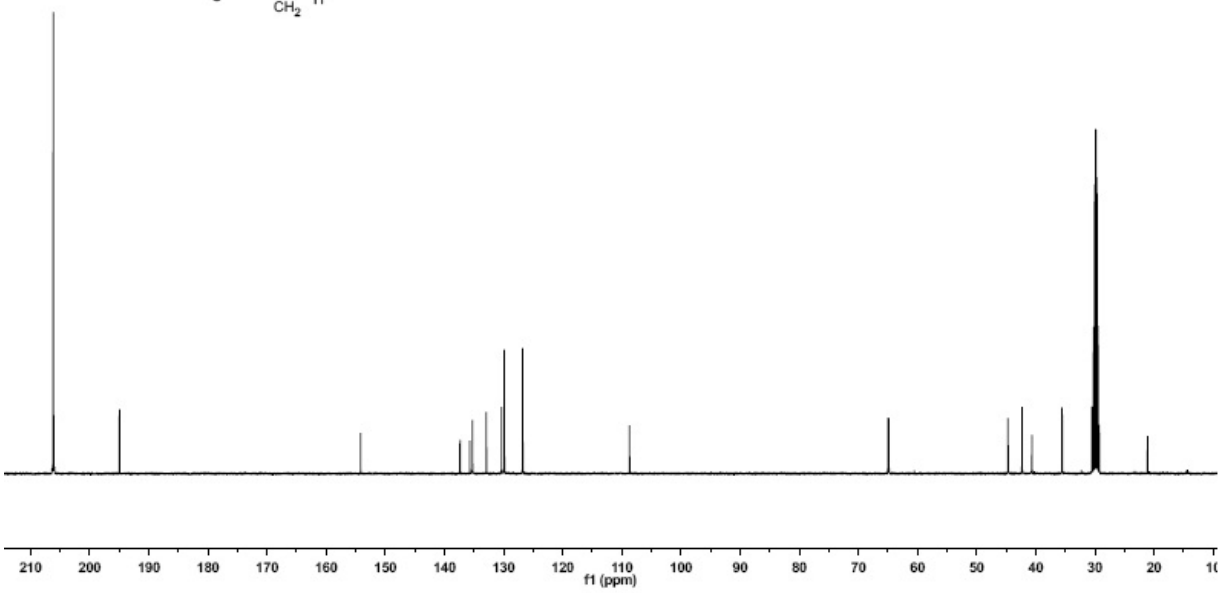

9.457
7.181
7.161
7.080
7.060
6.402
6.251
6.211
6.143
5.886
5.865
5.846
5.825
3.967
3.962
3.952
3.947
3.944
3.938
3.932
3.925
3.918
3.914
2.844
2.810
2.574
2.564
2.549
2.263
2.061
2.056
2.050
2.045
2.039
1.828
1.796
1.788
1.759
1.752
1.673
1.665
1.661
1.655
1.624
1.620
1.588
1.558
-0.004

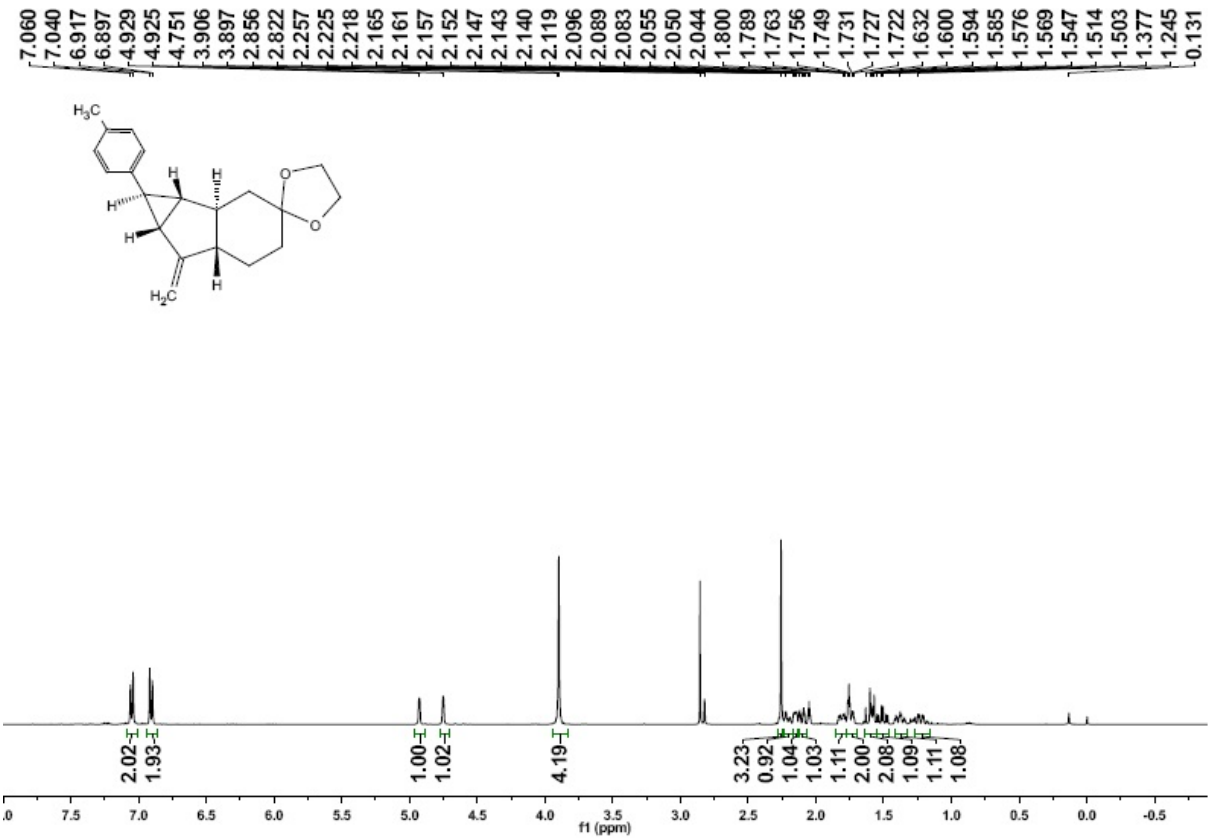

H3C
O
O
O
CH2
H

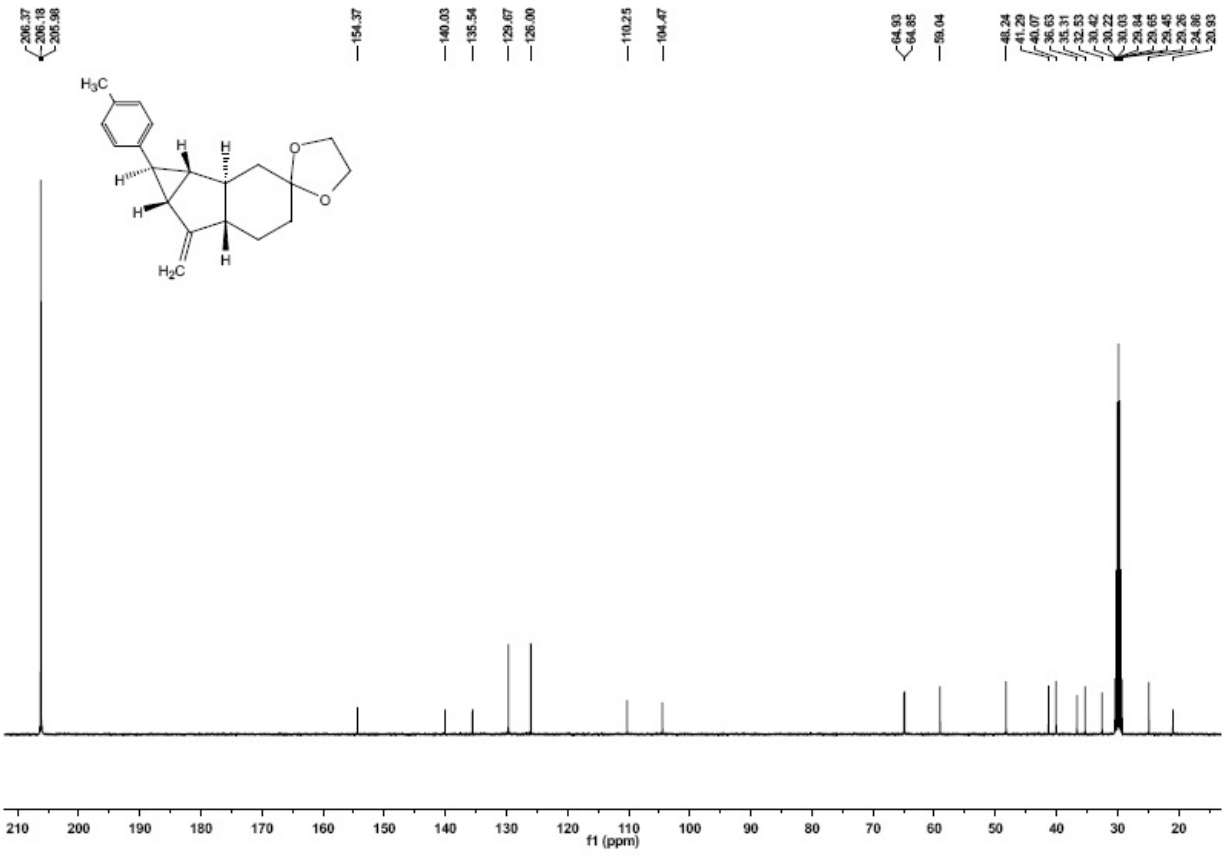

1.01
1.99
1.89
1.00
0.94
1.00
1.03
4.18
2.10
3.02
1.98
2.03
2.14
f1 (ppm)

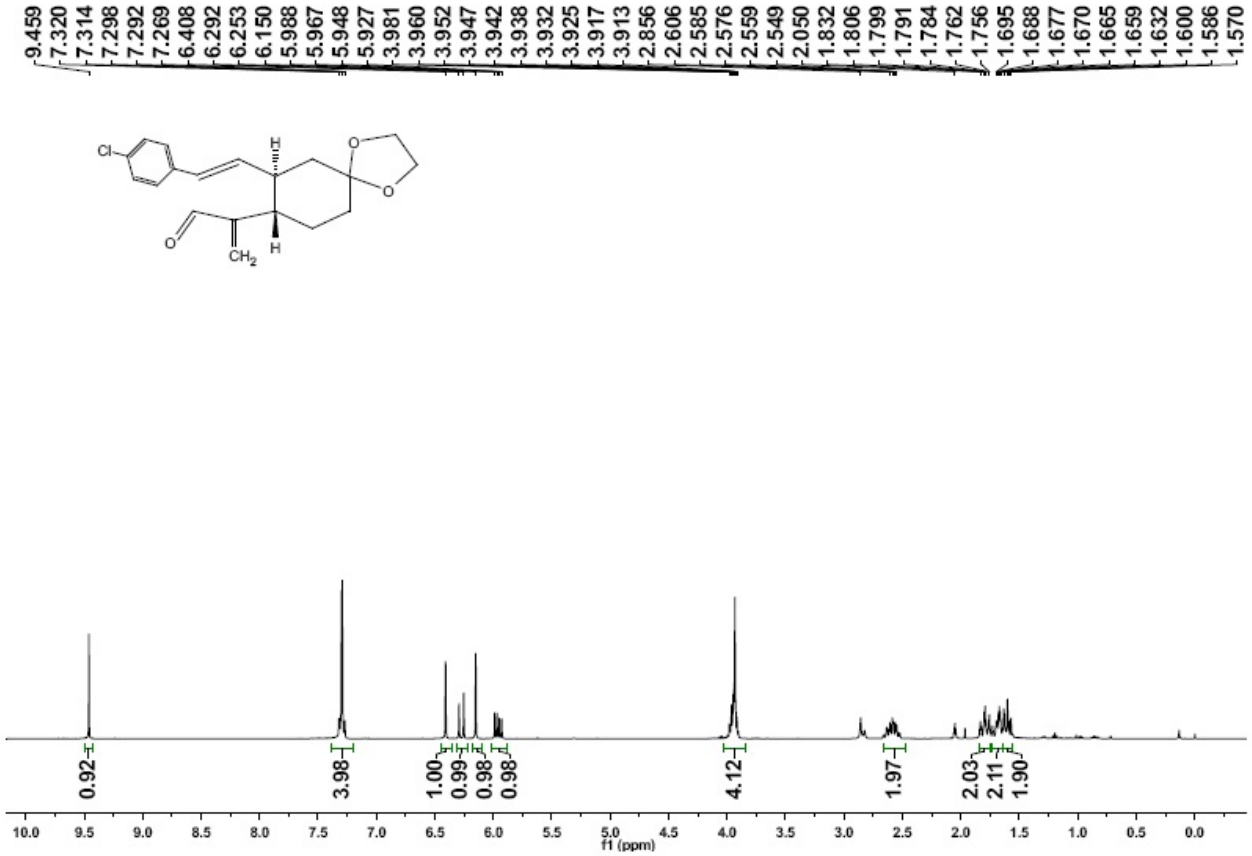

206.15
205.95
194.96
154.17
137.37
135.70
135.25
132.91
130.34
129.88
126.76
108.68
64.98
64.85
44.69
42.32
40.64
35.54
30.03
29.84
29.65
21.66

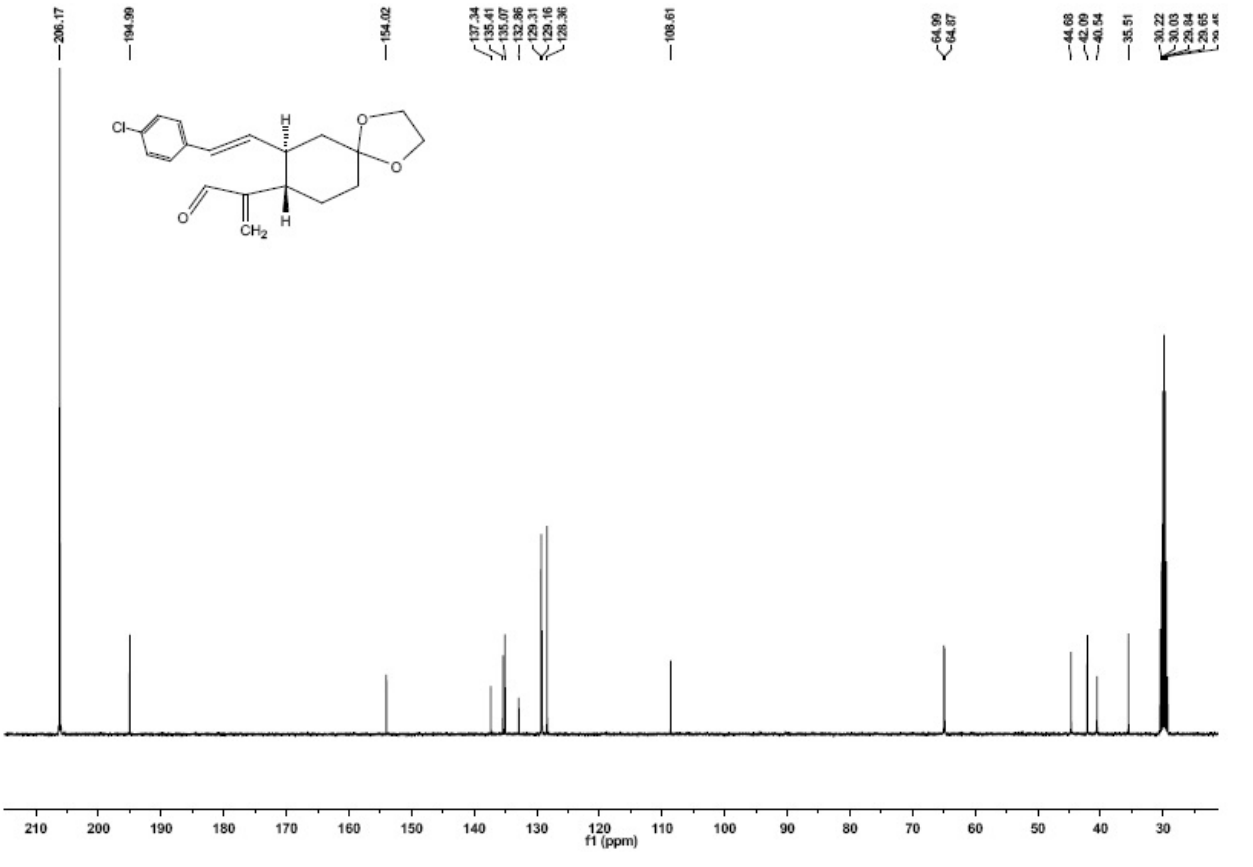

H3C
O
O
O
CH2
H

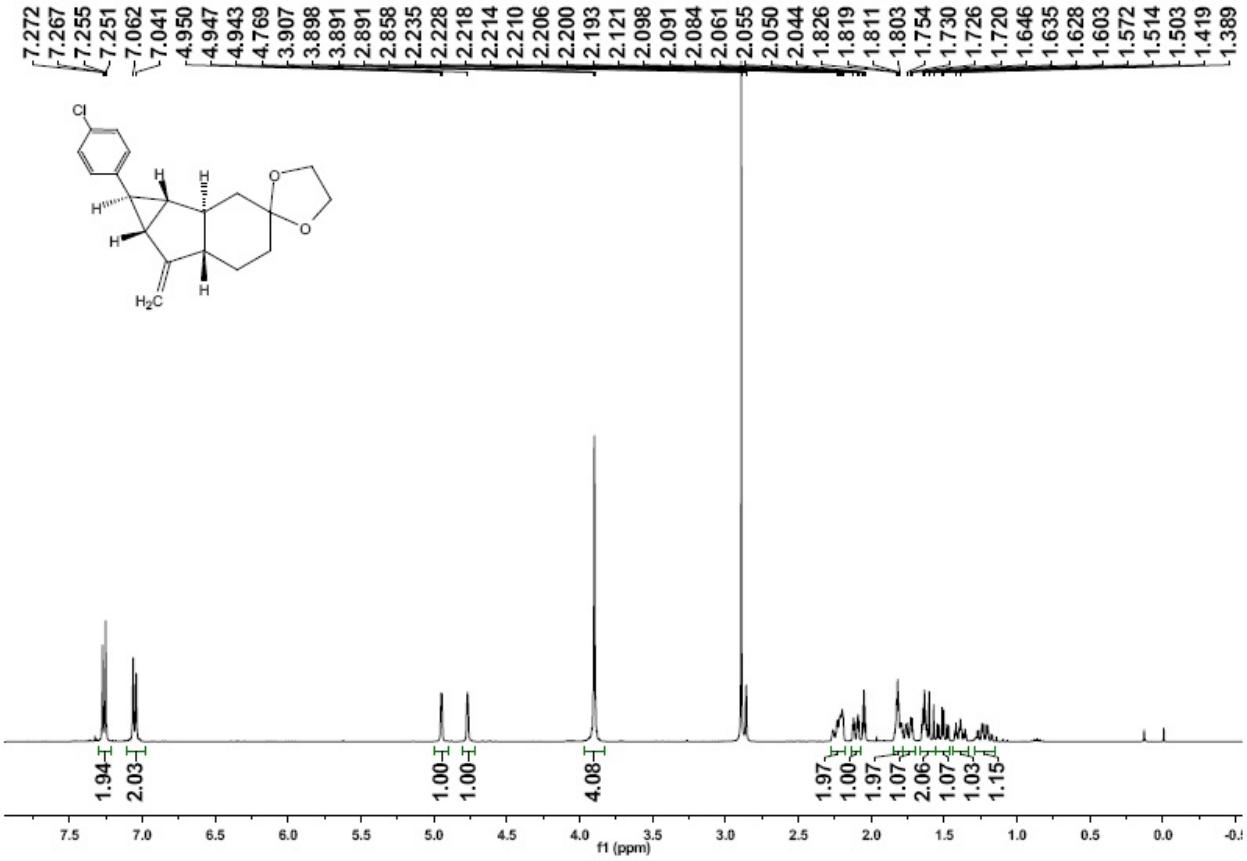

f1 (ppm)

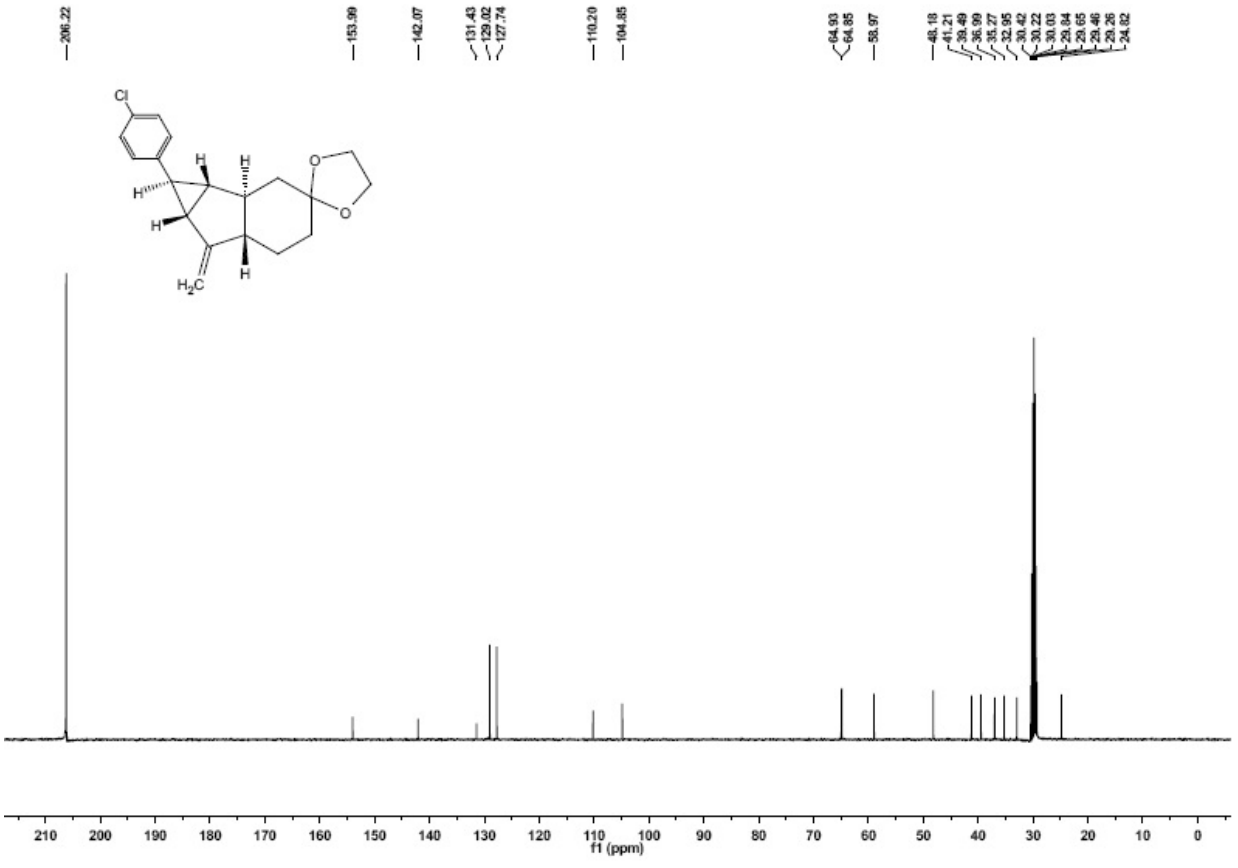

7.060
7.040
6.917
6.897
4.929
4.925
4.751
3.906
3.897
2.856
2.822
2.257
2.225
2.218
2.165
2.161
2.157
2.152
2.147
2.143
2.140
2.119
2.096
2.089
2.083
2.055
2.050
2.044
1.800
1.789
1.763
1.756
1.749
1.731
1.727
1.722
1.632
1.600
1.594
1.585
1.576
1.569
1.547
1.514
1.503
1.377
1.245
0.131
H3C
H
H
H
O
O
H
H2C
2.02
1.93
1.00
1.02
4.19
3.23
0.92
1.04
1.03
1.11
2.00
2.08
1.09
1.11
1.08
f1 (ppm)

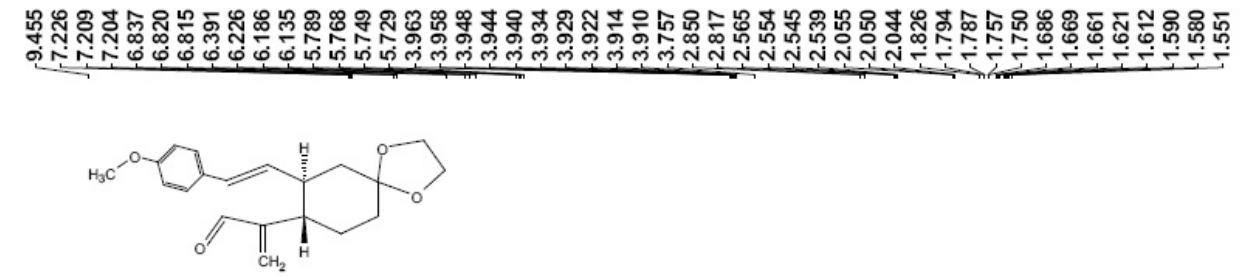

206.37
206.18
205.98
154.37
140.03
135.54
129.67
126.00
110.25
104.47
64.93
64.85
59.04
48.24
41.29
40.07
36.63
35.31
32.53
30.42
30.22
30.03
29.84
29.65
29.45
29.26
24.86
20.93
H3C
H
H
H
O
O
H
H2C
f1 (ppm)

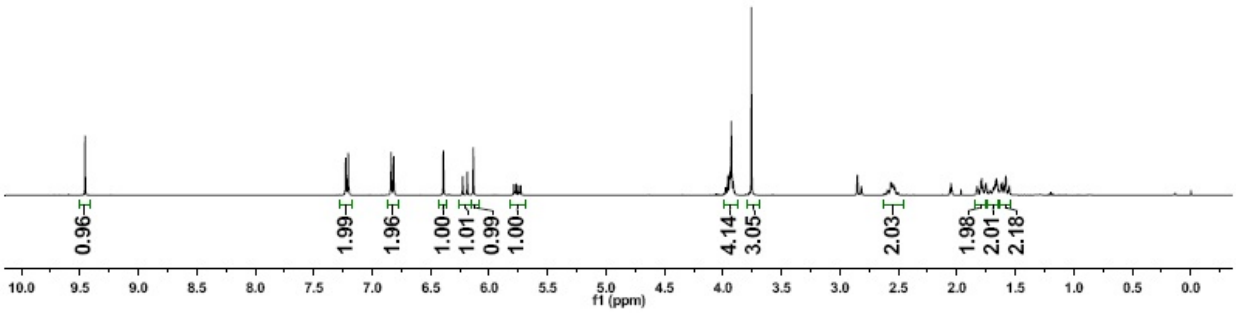

9.459
7.320
7.314
7.298
7.292
7.269
6.408
6.292
6.253
6.150
5.988
5.967
5.948
5.927
3.981
3.960
3.952
3.947
3.942
3.938
3.932
3.925
3.917
3.913
2.856
2.606
2.585
2.576
2.559
2.549
2.050
1.832
1.806
1.799
1.791
1.784
1.762
1.756
1.695
1.688
1.677
1.670
1.665
1.659
1.632
1.600
1.586
1.570
Cl
H
O
O
O
H
CH2
0.92
3.98
1.00
0.99
0.98
0.98
4.12
1.97
2.03
2.11
1.90
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

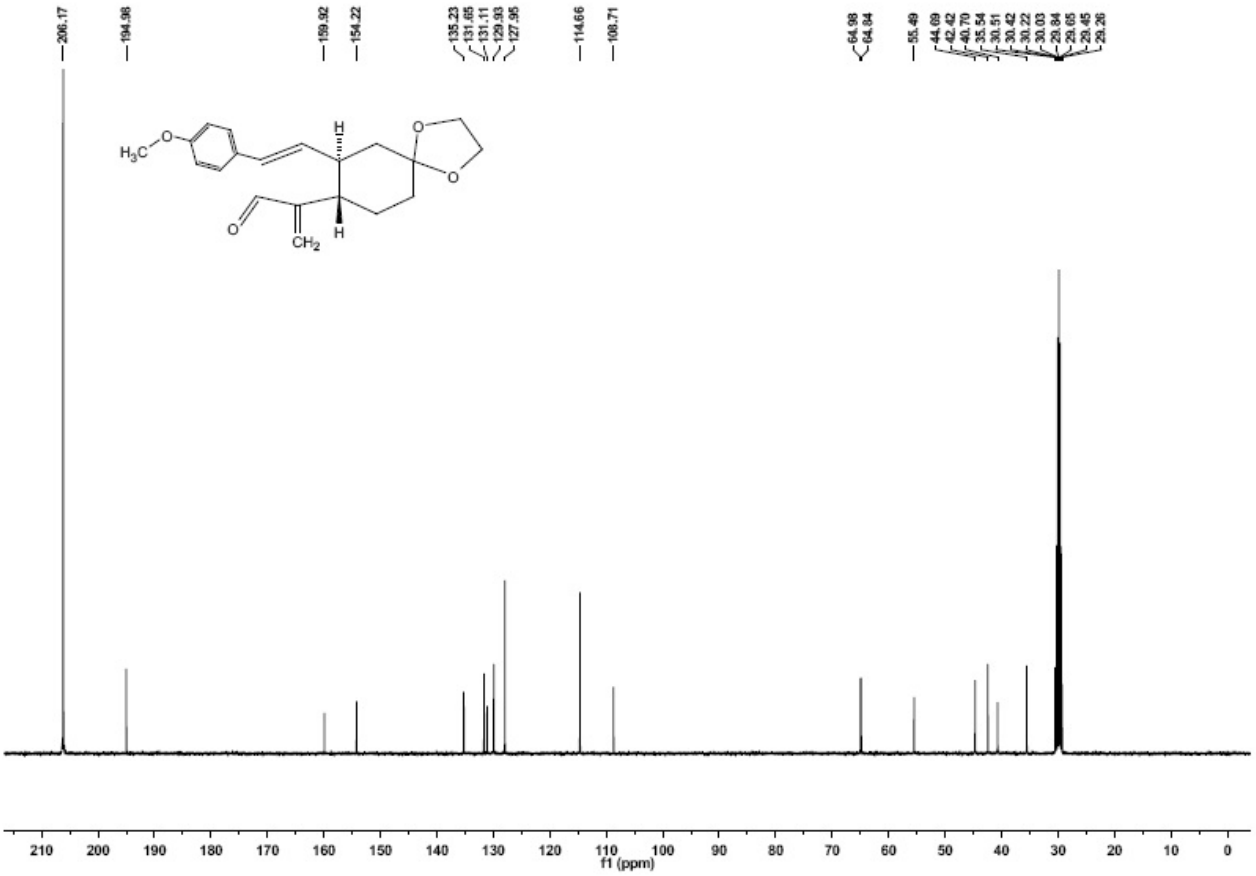

206.17
194.99
154.02
137.34
135.41
135.07
132.86
129.31
129.16
128.36
108.61
64.99
64.67
44.68
42.09
40.54
35.51
30.22
30.03
29.84
29.65
Cl
H
O
O
O
H
CH2
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
f1 (ppm)

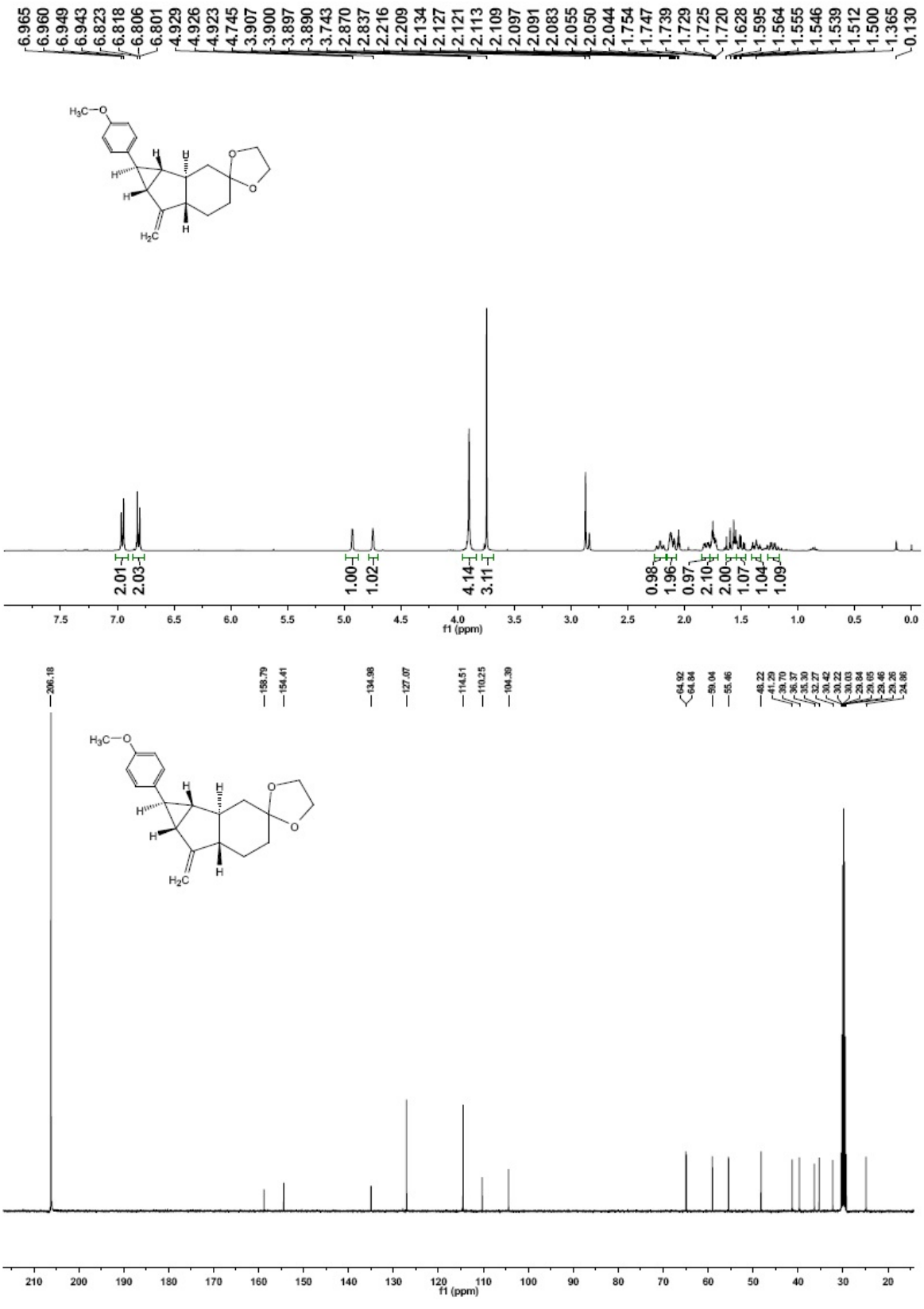

7.272
7.267
7.255
7.251
7.062
7.041
4.950
4.947
4.943
4.769
3.907
3.898
3.891
2.891
2.858
2.235
2.228
2.218
2.214
2.210
2.206
2.200
2.193
2.121
2.098
2.091
2.084
2.061
2.055
2.050
2.044
1.826
1.819
1.811
1.803
1.754
1.730
1.726
1.720
1.646
1.635
1.628
1.603
1.572
1.514
1.503
1.419
1.389
Cl
H
H
H
H
O
O
H2C
1.94
2.03
1.00
1.00
4.08
1.97
1.00
1.97
1.07
2.06
1.07
1.03
1.15
f1 (ppm)

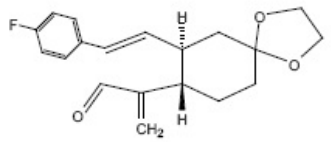

206.22
153.99
142.07
131.43
129.02
127.74
110.20
104.85
64.93
64.85
58.97
48.18
41.21
39.49
36.99
35.27
32.95
30.42
30.22
30.03
29.84
29.65
29.46
29.26
24.82
Cl
H
H
H
H
O
O
H2C
f1 (ppm)

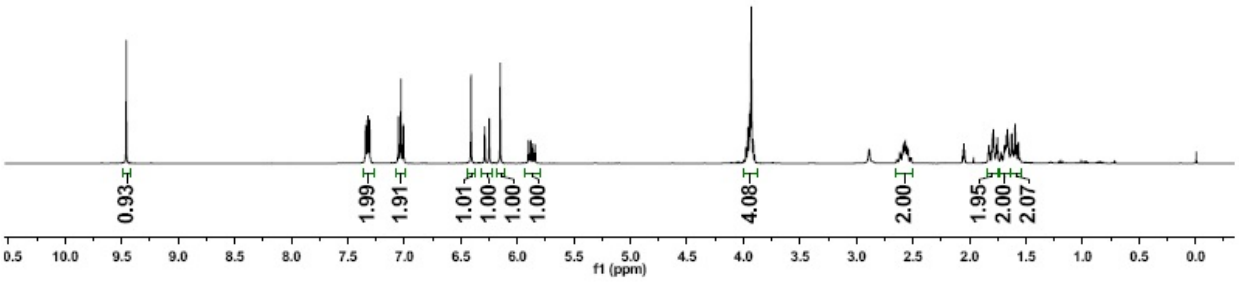

9.455
7.226
7.209
7.204
6.837
6.820
6.815
6.391
6.226
6.186
6.135
5.789
5.768
5.749
5.729
3.963
3.958
3.948
3.944
3.940
3.934
3.929
3.922
3.914
3.910
3.757
2.850
2.817
2.565
2.554
2.545
2.539
2.055
2.050
2.044
1.826
1.794
1.787
1.757
1.750
1.686
1.669
1.661
1.621
1.612
1.590
1.580
1.551

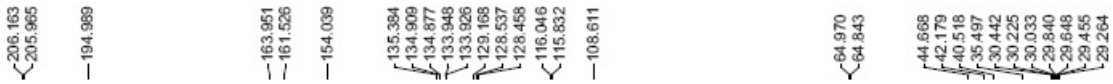

0.96
1.99
1.96
1.00
1.01
0.99
1.00
4.14
3.05
2.03
1.98
2.01
2.18
f1 (ppm)

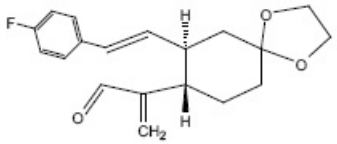

206.17
194.98
159.92
154.22
135.23
131.65
131.11
129.93
127.95
114.66
108.71
64.98
64.84
55.49
44.69
42.42
40.70
35.54
30.51
30.42
30.22
30.03
29.84
29.65
29.45
29.26
f1 (ppm)

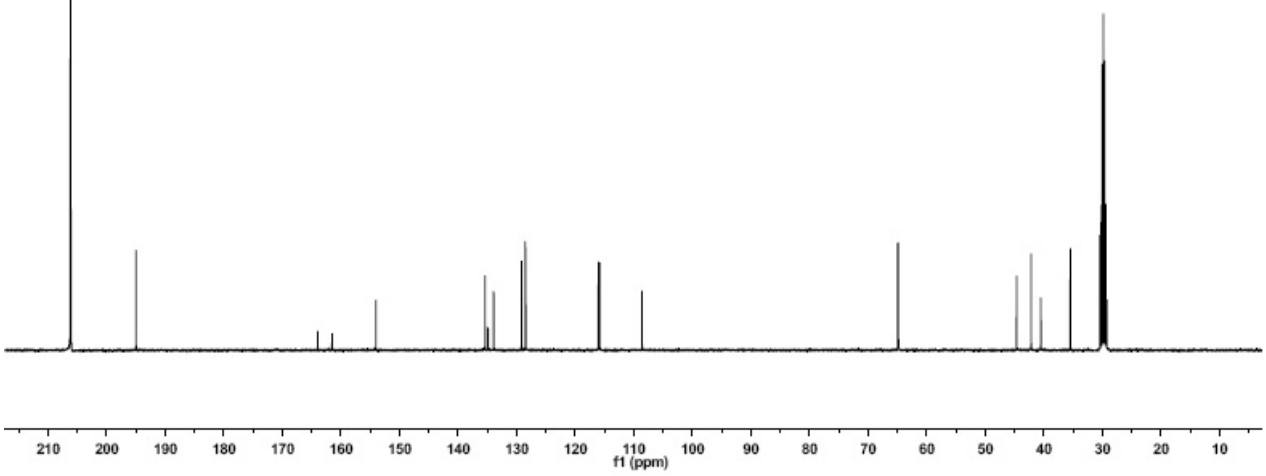

6.965
6.960
6.949
6.943
6.823
6.818
6.806
6.801
4.929
4.926
4.923
4.745
3.907
3.900
3.897
3.890
3.743
2.870
2.837
2.216
2.209
2.134
2.127
2.121
2.113
2.109
2.097
2.091
2.083
2.055
2.050
2.044
1.754
1.747
1.739
1.729
1.725
1.720
1.628
1.595
1.564
1.555
1.546
1.539
1.512
1.500
1.365
0.130
H3C—O
H
H
H
H
H2C
O
O
2.01
2.03
1.00
1.02
4.14
3.11
0.98
1.96
0.97
2.10
2.00
1.07
1.04
1.09
f1 (ppm)
206.18
159.79
154.41
134.98
127.07
114.51
110.25
104.39
64.92
64.84
59.04
55.46
48.22
41.29
39.70
36.37
35.30
32.27
30.42
30.22
30.03
29.84
29.65
29.46
29.26
24.86
f1 (ppm)

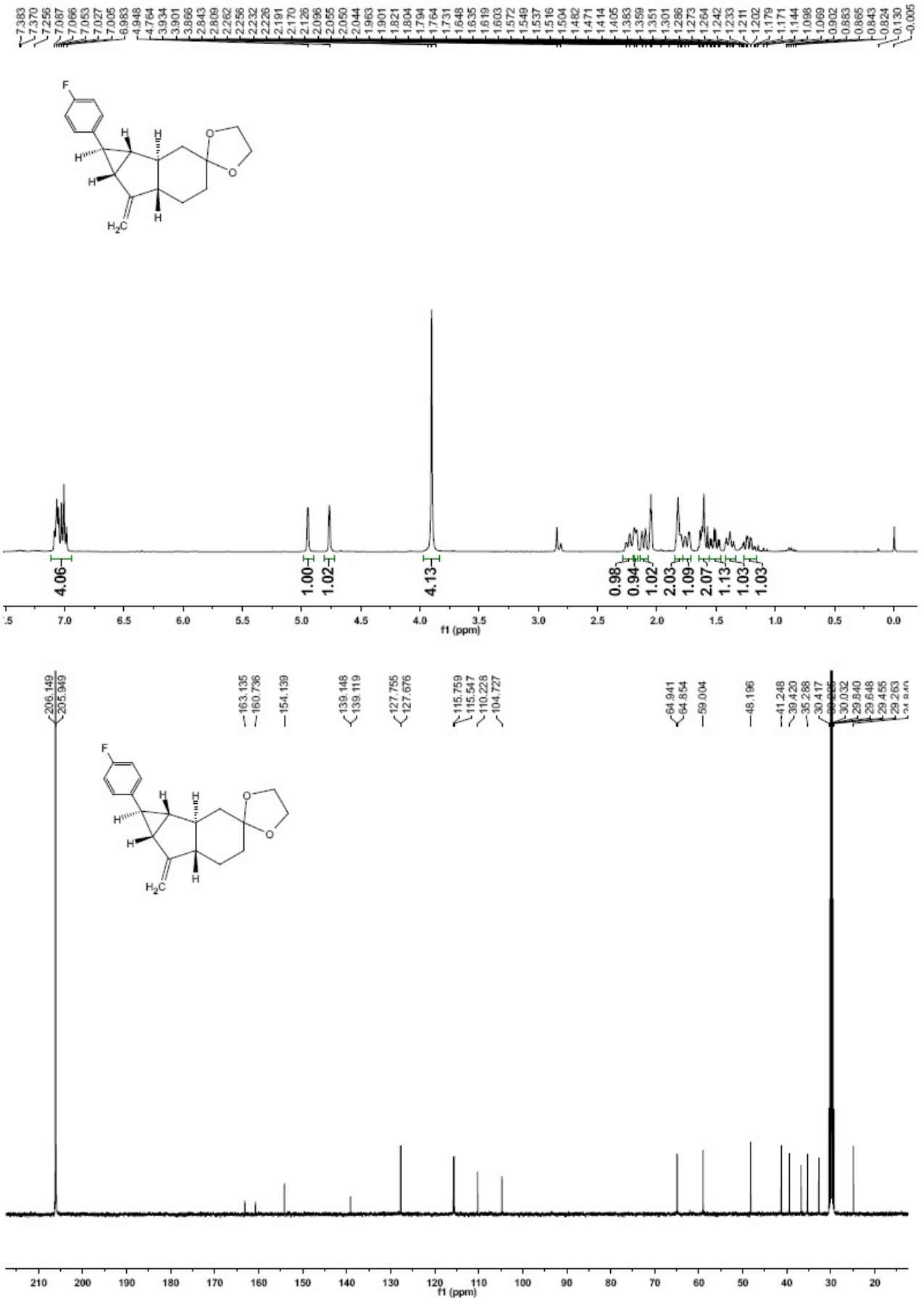

F
O
O
H
O
H
CH2

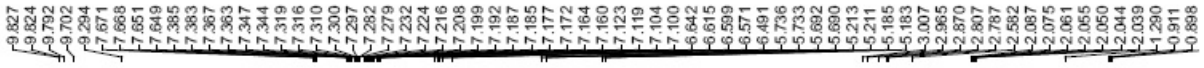

0.93
1.99
1.91
1.01
1.00
1.00
1.00
4.08
2.00
1.95
2.00
2.07
f1 (ppm)

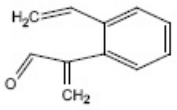


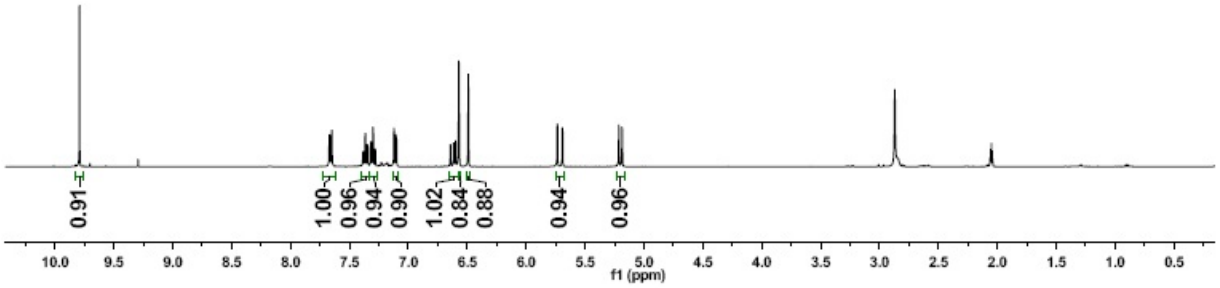

F
O
O
H
O
H
CH2

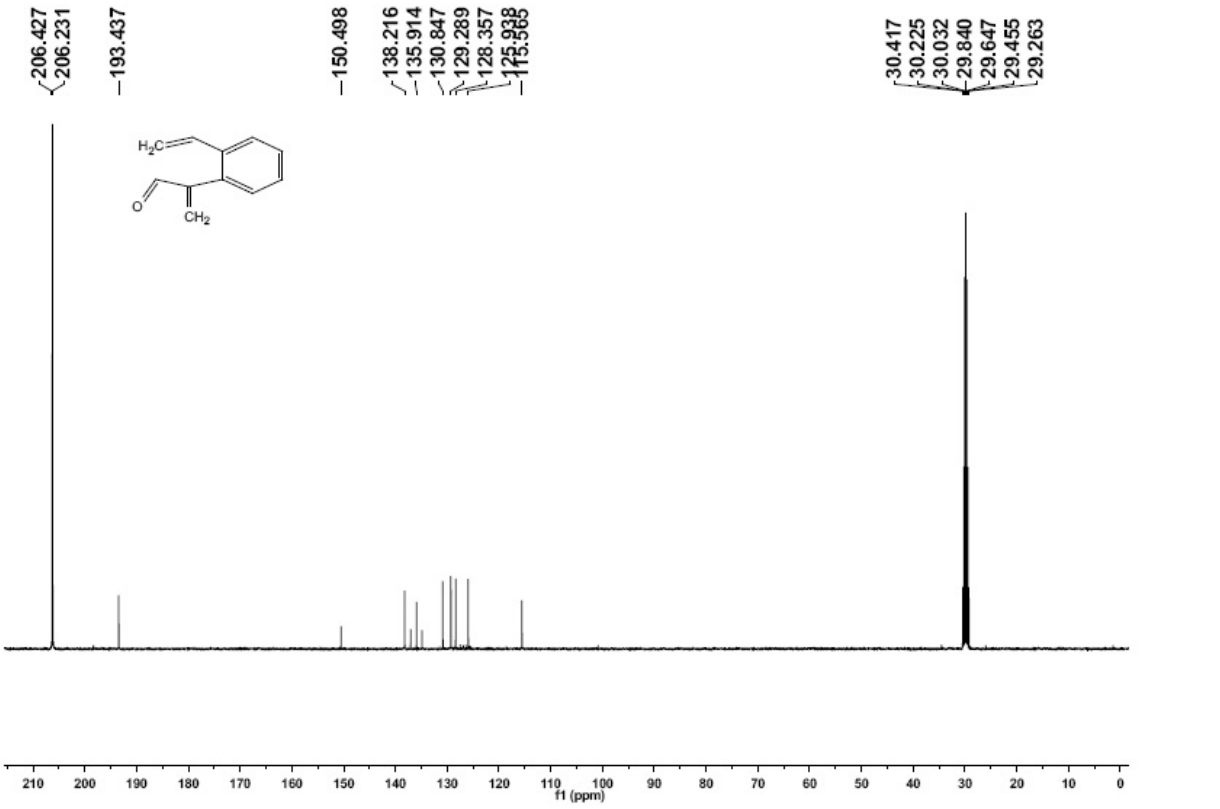

f1 (ppm)

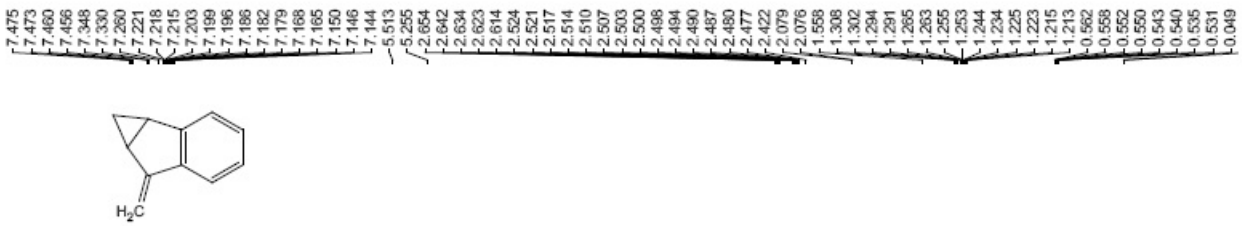

7.383
7.370
7.256
7.087
7.066
7.053
7.027
7.005
6.983
4.948
4.764
3.934
3.901
3.866
2.843
2.809
2.262
2.256
2.232
2.226
2.191
2.170
2.126
2.096
2.055
2.050
2.044
1.963
1.901
1.821
1.804
1.794
1.764
1.731
1.648
1.635
1.619
1.603
1.572
1.549
1.537
1.516
1.504
1.482
1.471
1.414
1.405
1.383
1.359
1.351
1.301
1.286
1.273
1.264
1.242
1.233
1.211
1.202
1.179
1.171
1.144
1.098
1.069
0.902
0.883
0.865
0.843
0.824
0.130
-0.005
F
H
H
H
H
O
O
H2C
4.06
1.00
1.02
4.13
0.98
0.94
1.02
2.03
1.09
2.07
1.13
1.03
1.03
f1 (ppm)
206.149
205.949
163.135
160.736
154.139
139.148
139.119
127.755
127.676
115.759
115.547
110.228
104.727
64.941
64.854
59.004
48.196
41.248
39.420
35.288
30.417
30.032
29.840
29.648
29.455
29.263
f1 (ppm)


9.827
9.824
9.792
9.702
9.294
7.671
7.668
7.651
7.649
7.385
7.383
7.367
7.363
7.347
7.344
7.319
7.316
7.310
7.300
7.297
7.282
7.279
7.232
7.224
7.216
7.208
7.199
7.192
7.187
7.185
7.177
7.172
7.164
7.160
7.123
7.119
7.104
7.100
6.642
6.615
6.599
6.571
6.491
5.736
5.733
5.692
5.690
5.213
5.211
5.185
5.183
3.007
2.965
2.870
2.807
2.787
2.582
2.087
2.075
2.061
2.055
2.050
2.044
2.039
1.290
0.911
0.898

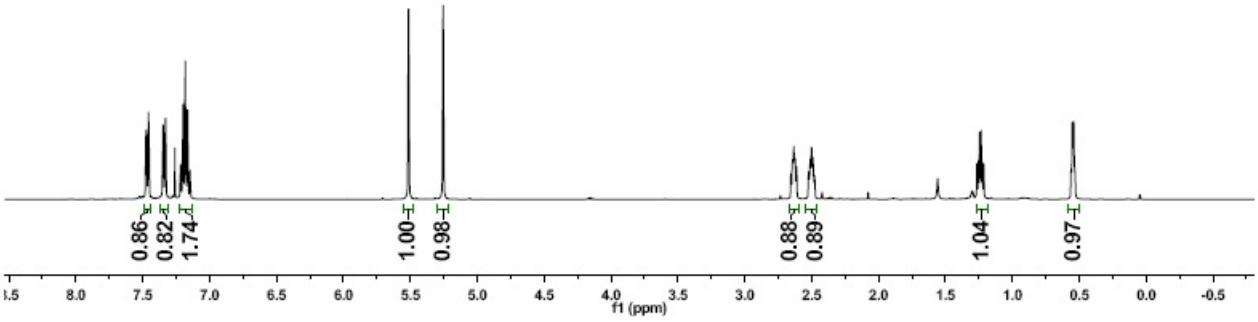

H2C
O
CH2


0.91
1.00
0.96
0.94
0.90
1.02
0.84
0.88
0.94
0.96
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

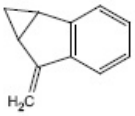

206.427
206.231
193.437
150.498
138.216
135.914
130.847
129.289
128.357
125.938
115.565
30.417
30.225
30.032
29.840
29.647
29.455
29.263
H2C
O
CH2
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

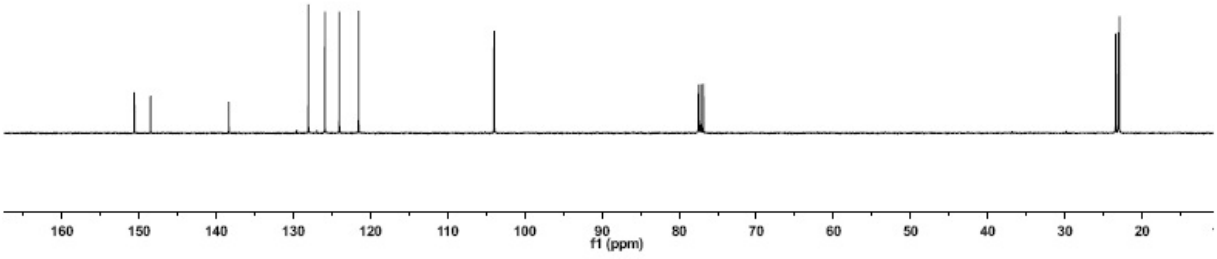

7.475
7.473
7.460
7.456
7.348
7.330
7.260
7.221
7.218
7.215
7.203
7.199
7.196
7.186
7.182
7.179
7.168
7.165
7.150
7.146
7.144
5.513
5.255
2.654
2.642
2.634
2.623
2.614
2.524
2.521
2.517
2.514
2.510
2.507
2.503
2.500
2.498
2.494
2.490
2.487
2.480
2.477
2.422
2.079
2.076
1.558
1.308
1.302
1.294
1.291
1.265
1.263
1.255
1.253
1.244
1.234
1.225
1.223
1.215
1.213
0.562
0.558
0.552
0.550
0.543
0.540
0.535
0.531
0.049

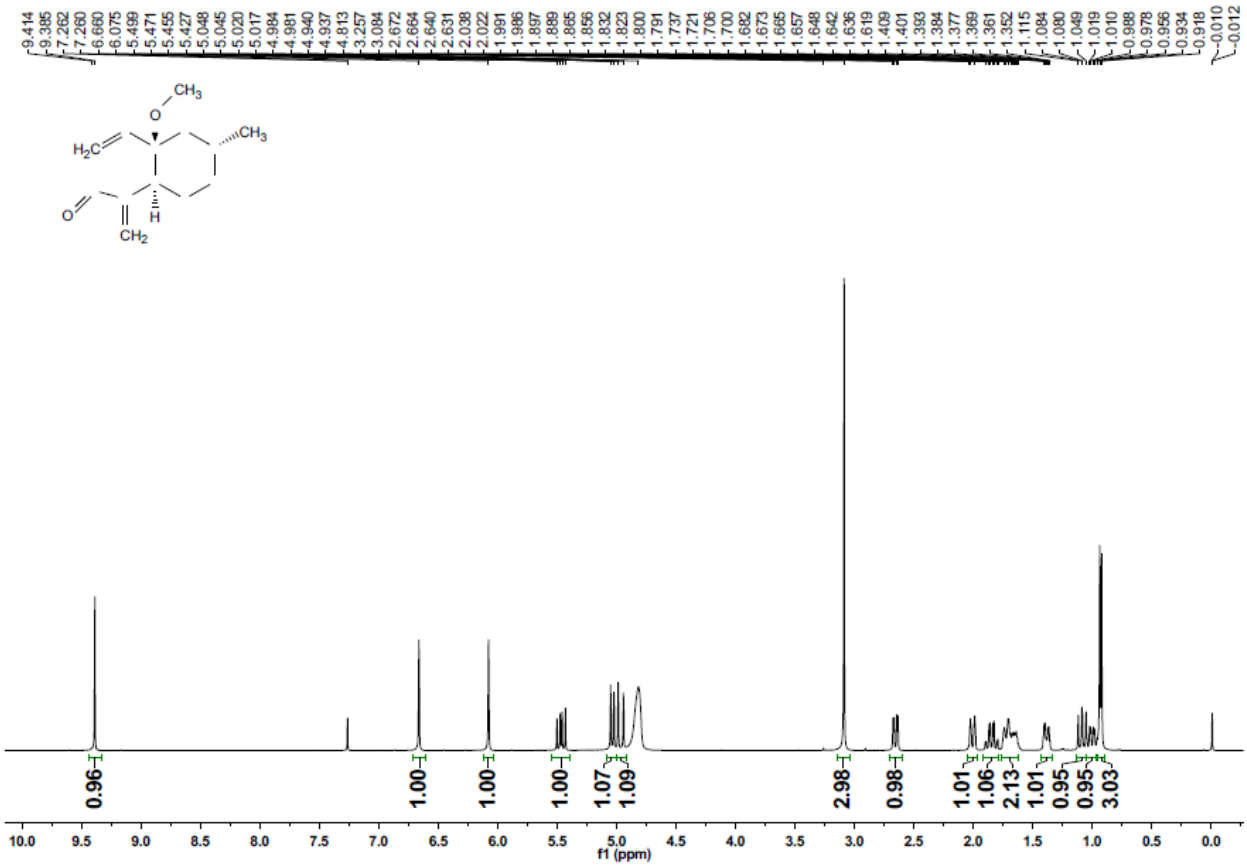
H2C

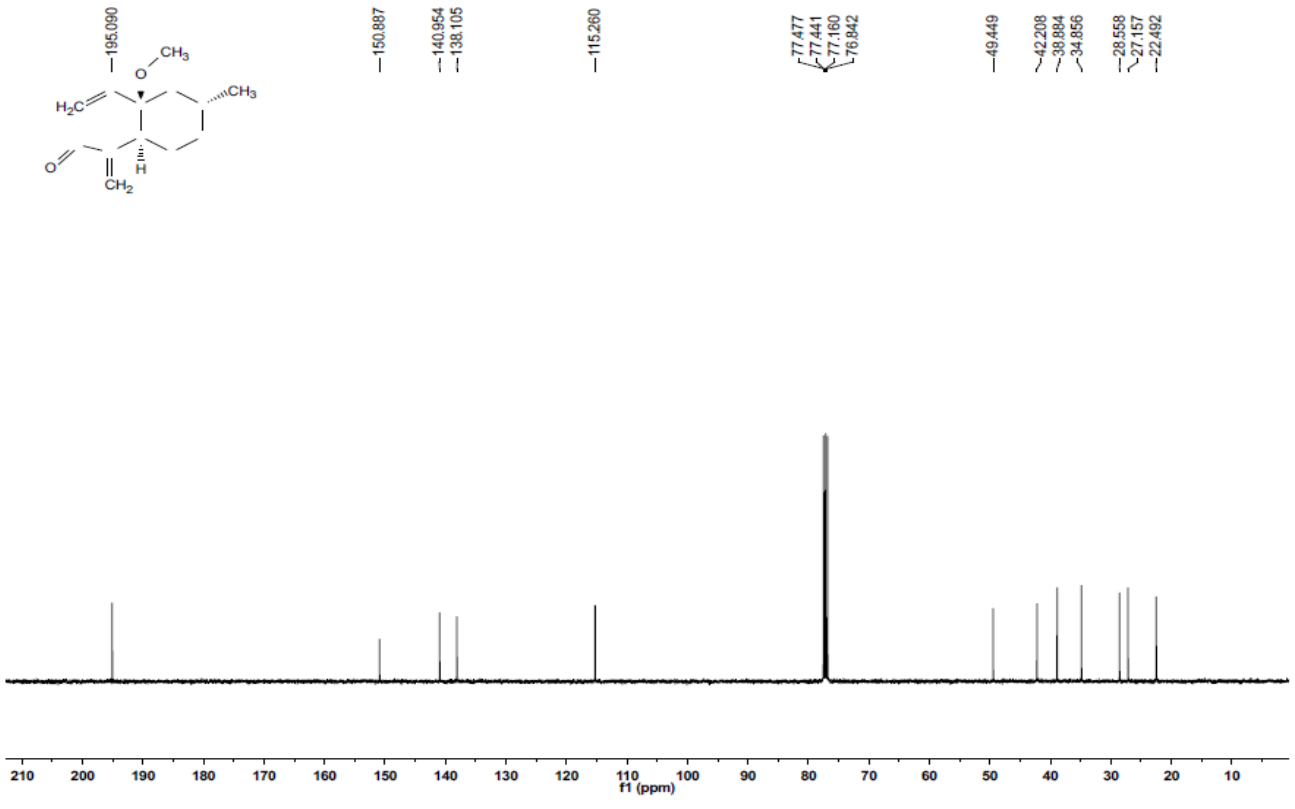

0.86
0.82
1.74
1.00
0.98
0.88
0.89
1.04
0.97
f1 (ppm)

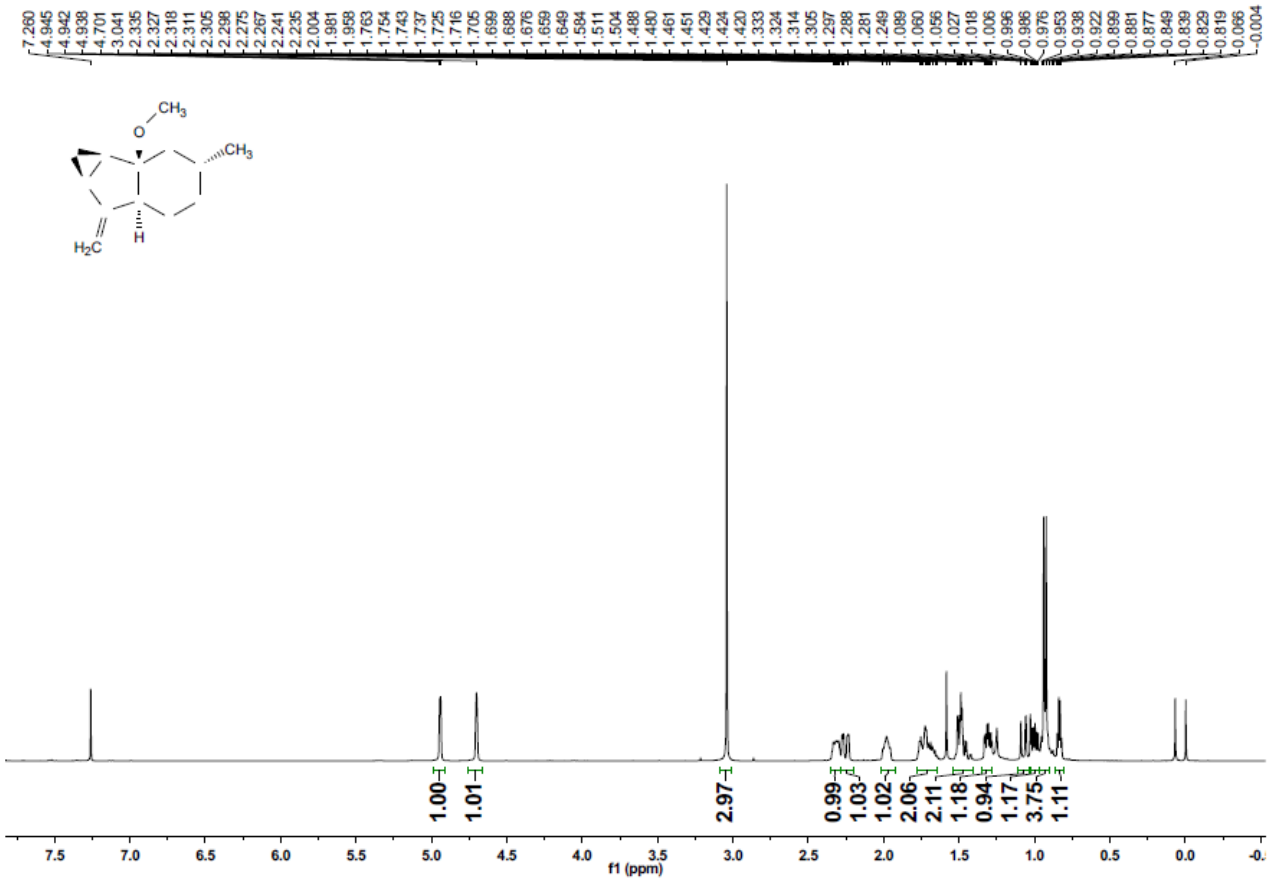

150.605
148.495
138.345
129.559
128.048
126.926
125.906
124.036
121.532
103.972
77.478
77.160
76.842
23.407
23.060
22.946

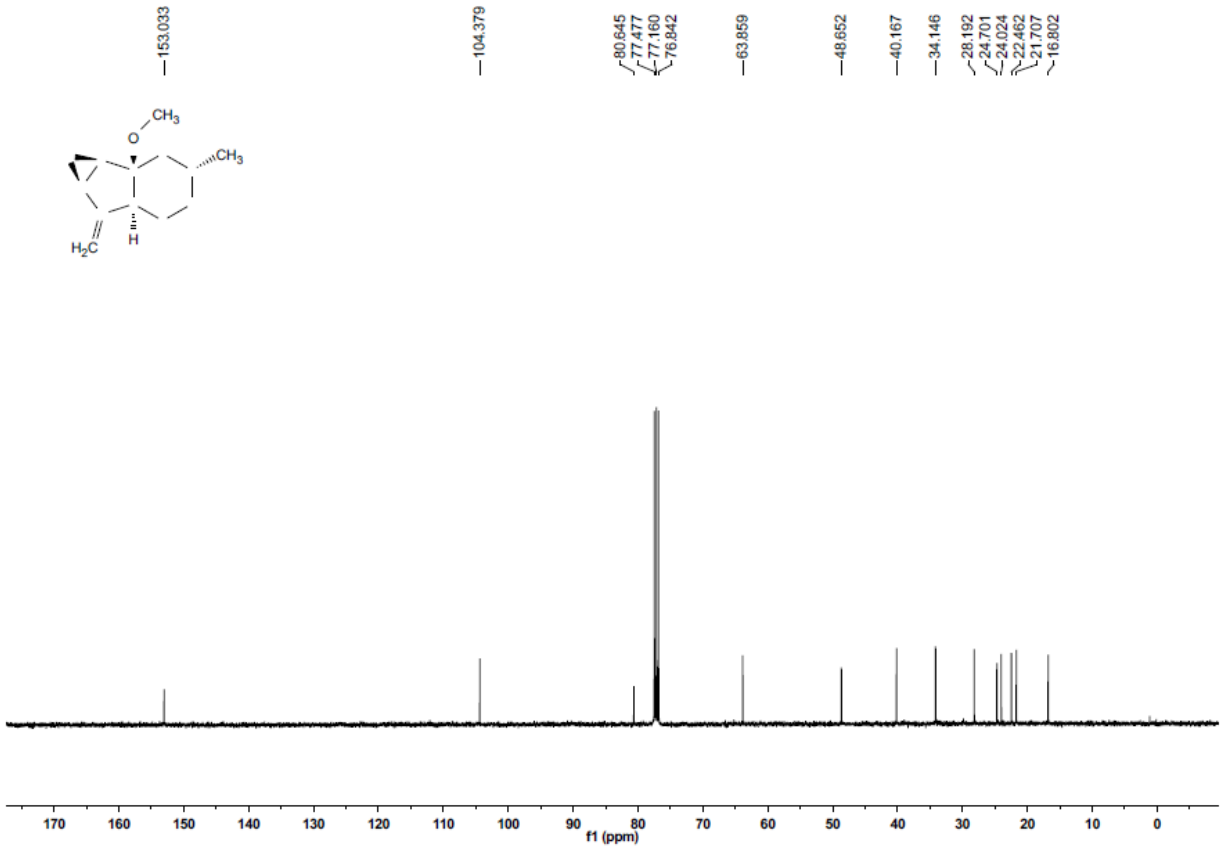

H2C

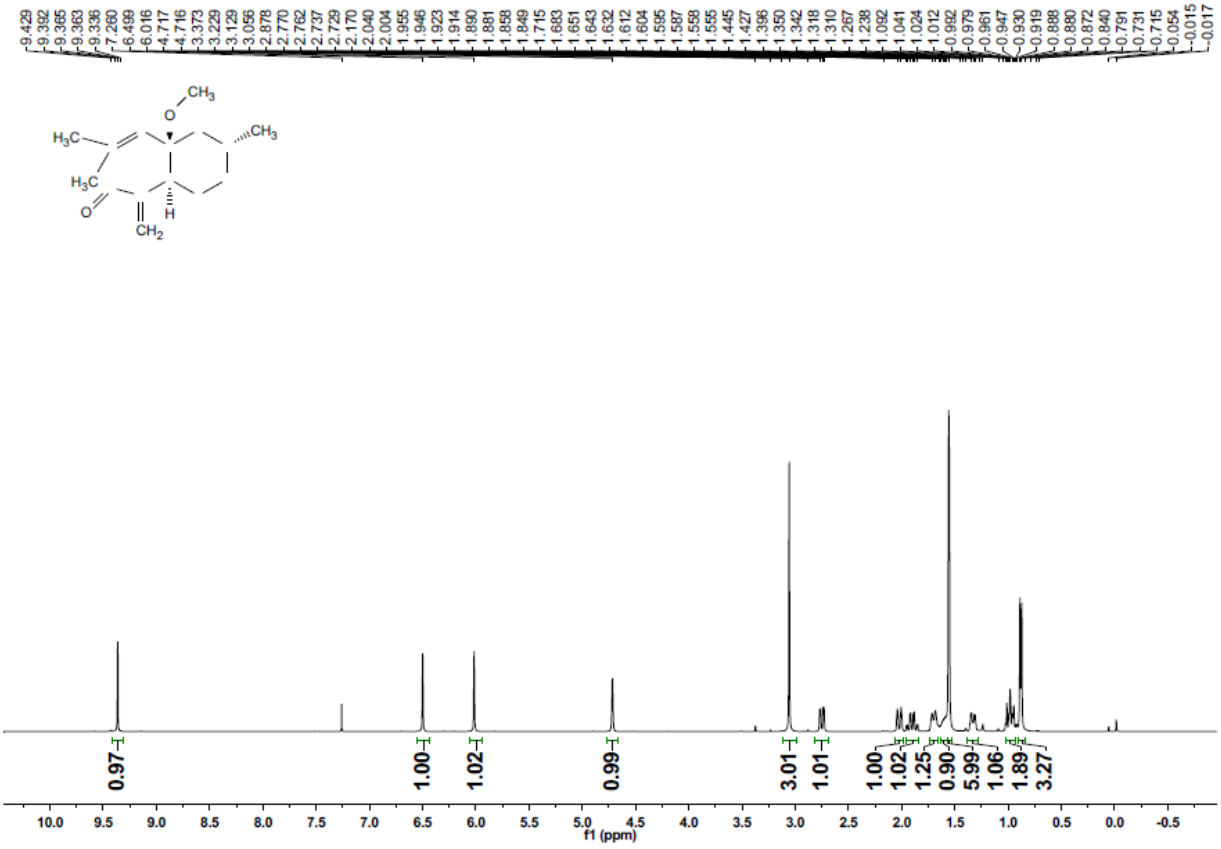

f1 (ppm)

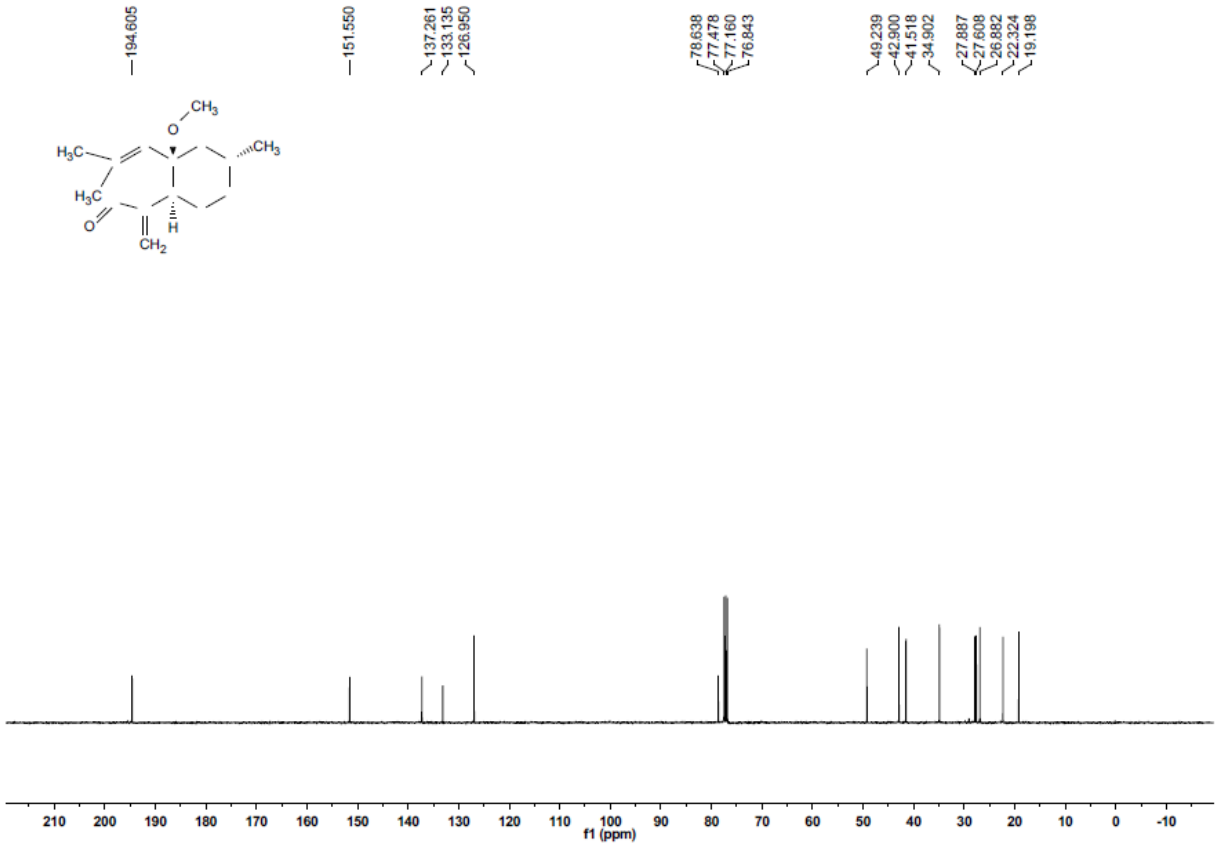

9.414
9.385
7.262
7.260
6.660
6.075
5.499
5.471
5.455
5.427
5.048
5.045
5.020
5.017
4.984
4.981
4.940
4.937
4.813
3.257
3.084
2.672
2.664
2.640
2.631
2.038
2.022
1.991
1.986
1.897
1.889
1.865
1.856
1.832
1.823
1.800
1.791
1.737
1.721
1.706
1.700
1.682
1.673
1.665
1.657
1.648
1.642
1.636
1.619
1.409
1.401
1.393
1.384
1.377
1.369
1.361
1.352
1.115
1.084
1.080
1.049
1.019
1.010
0.988
0.978
0.956
0.934
0.918
-0.010
-0.012
CH3
O
H2C
CH3
O
H
CH2
0.96
1.00
1.00
1.00
1.07
1.09
2.98
0.98
1.01
1.06
2.13
1.01
0.95
0.95
3.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

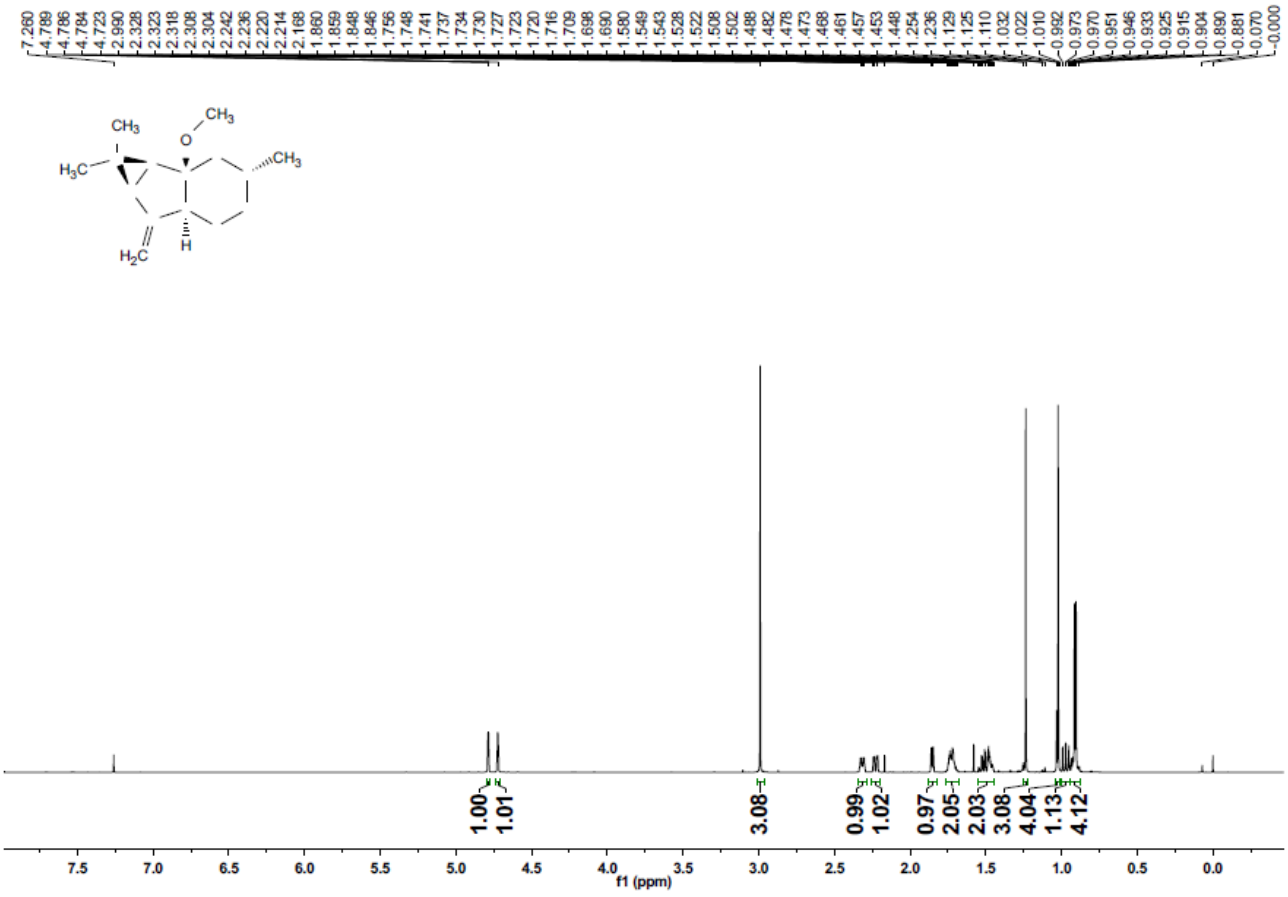

195.090
150.887
140.954
138.105
115.260
77.477
77.441
77.160
76.842
49.449
42.208
38.884
34.856
28.558
27.157
22.492
CH3
O
H2C
CH3
O
H
CH2
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

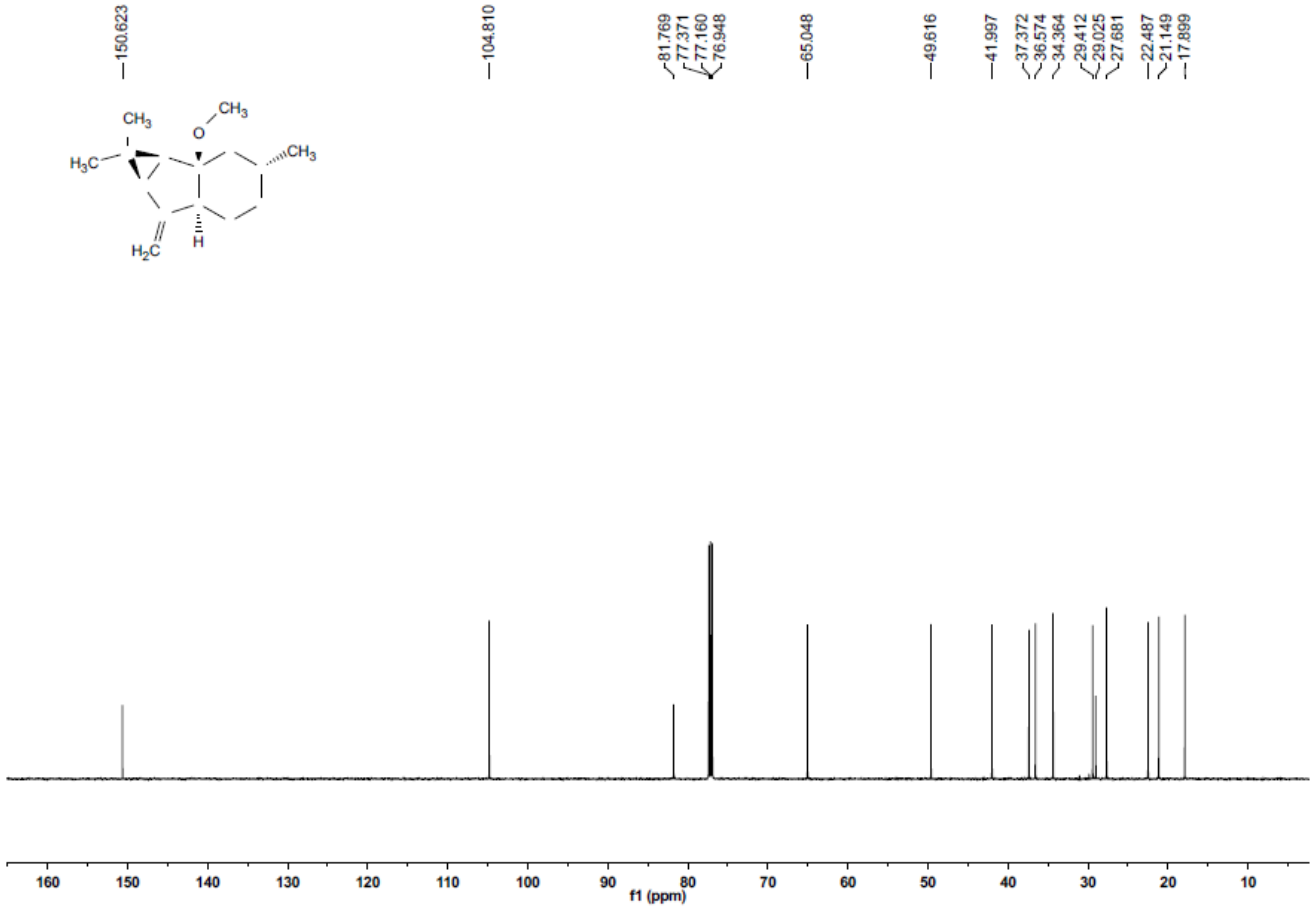

7.260
4.945
4.942
4.938
4.701
3.041
2.335
2.327
2.318
2.311
2.305
2.298
2.275
2.267
2.241
2.235
2.004
1.981
1.958
1.763
1.754
1.743
1.737
1.725
1.716
1.705
1.699
1.688
1.676
1.659
1.649
1.584
1.511
1.504
1.488
1.480
1.461
1.451
1.429
1.424
1.420
1.333
1.324
1.314
1.305
1.297
1.288
1.281
1.249
1.089
1.060
1.056
1.027
1.018
1.006
0.996
0.986
0.976
0.953
0.938
0.922
0.899
0.881
0.877
0.849
0.839
0.829
0.819
0.066
-0.004
CH3
O
CH3
H
H2C
1.00
1.01
2.97
0.99
1.03
1.02
2.06
2.11
1.18
0.94
1.17
3.75
1.11
f1 (ppm)


153.033
104.379
80.645
77.477
77.160
76.842
63.859
48.652
40.167
34.146
28.192
24.701
24.024
22.462
21.707
16.802
CH3
O
CH3
H
H2C
f1 (ppm)

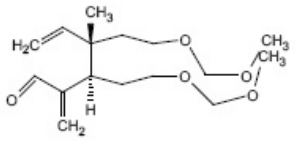

9.429
9.392
9.385
9.363
9.336
7.260
6.499
6.016
4.717
4.716
3.373
3.229
3.129
3.056
2.878
2.770
2.762
2.737
2.729
2.170
2.040
2.004
1.955
1.946
1.923
1.914
1.890
1.881
1.858
1.849
1.715
1.683
1.651
1.643
1.632
1.612
1.604
1.595
1.587
1.558
1.555
1.445
1.427
1.396
1.350
1.342
1.318
1.310
1.267
1.238
1.092
1.041
1.024
1.012
0.992
0.979
0.961
0.947
0.930
0.919
0.888
0.880
0.872
0.840
0.791
0.731
0.715
0.054
-0.015
-0.017
O
CH3
H3C
CH3
H3C
O
H
CH2
0.97
1.00
1.02
0.99
3.01
1.01
1.00
1.02
1.25
0.90
5.99
1.06
1.89
3.27
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

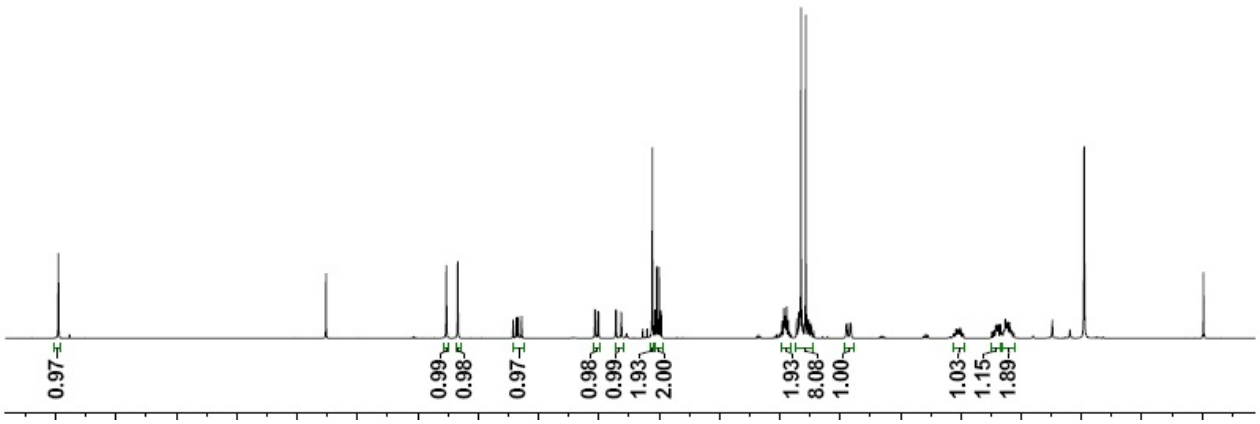

194.605
151.550
137.261
133.135
126.950
78.638
77.478
77.160
76.843
49.239
42.900
41.518
34.902
27.887
27.608
26.882
22.324
19.198
O
CH3
H3C
CH3
H3C
O
H
CH2
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.260
4.789
4.786
4.784
4.723
2.990
2.328
2.323
2.318
2.308
2.304
2.242
2.236
2.220
2.214
2.168
1.860
1.859
1.848
1.846
1.756
1.748
1.741
1.737
1.734
1.730
1.727
1.723
1.720
1.716
1.709
1.698
1.690
1.580
1.549
1.543
1.528
1.522
1.508
1.502
1.488
1.482
1.478
1.473
1.468
1.461
1.457
1.453
1.448
1.254
1.236
1.129
1.125
1.110
1.032
1.022
1.010
0.992
0.973
0.970
0.951
0.946
0.933
0.925
0.915
0.904
0.890
0.881
0.070
-0.000
CH3
O
CH3
H3C
CH3
H2C
H
1.00
1.01
3.08
0.99
1.02
0.97
2.05
2.03
3.08
4.04
1.13
4.12
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


150.623
104.810
81.769
77.371
77.160
76.948
65.048
49.616
41.997
37.372
36.574
34.364
29.412
29.025
27.681
22.487
21.149
17.899
CH3
O
CH3
H3C
CH3
H2C
H
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

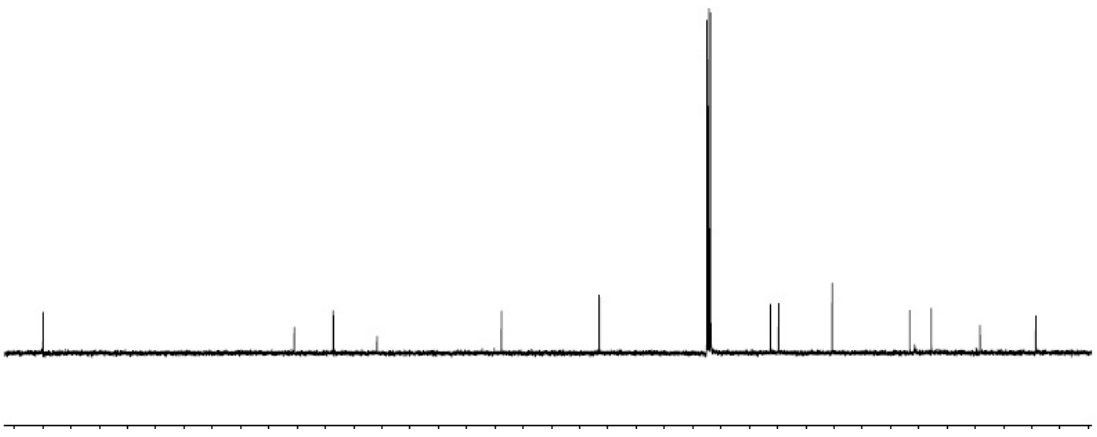

9.478
7.260
6.263
6.168
5.709
5.682
5.665
5.638
5.032
5.030
5.005
5.003
4.858
4.855
4.814
4.811
4.635
4.600
4.556
4.534
4.518
4.499
4.483
3.481
3.466
3.459
3.452
3.443
3.429
3.360
3.351
3.342
3.338
3.325
3.307
3.285
3.263
3.261
3.243
3.240
3.219
2.949
2.943
2.918
2.912
2.040
2.034
2.026
2.020
2.006
2.000
1.744
1.727
1.721
1.710
1.704
1.694
1.687
1.671
1.642
1.631
1.618
1.610
1.596
1.584
1.577
1.242
1.096
0.978
-0.011

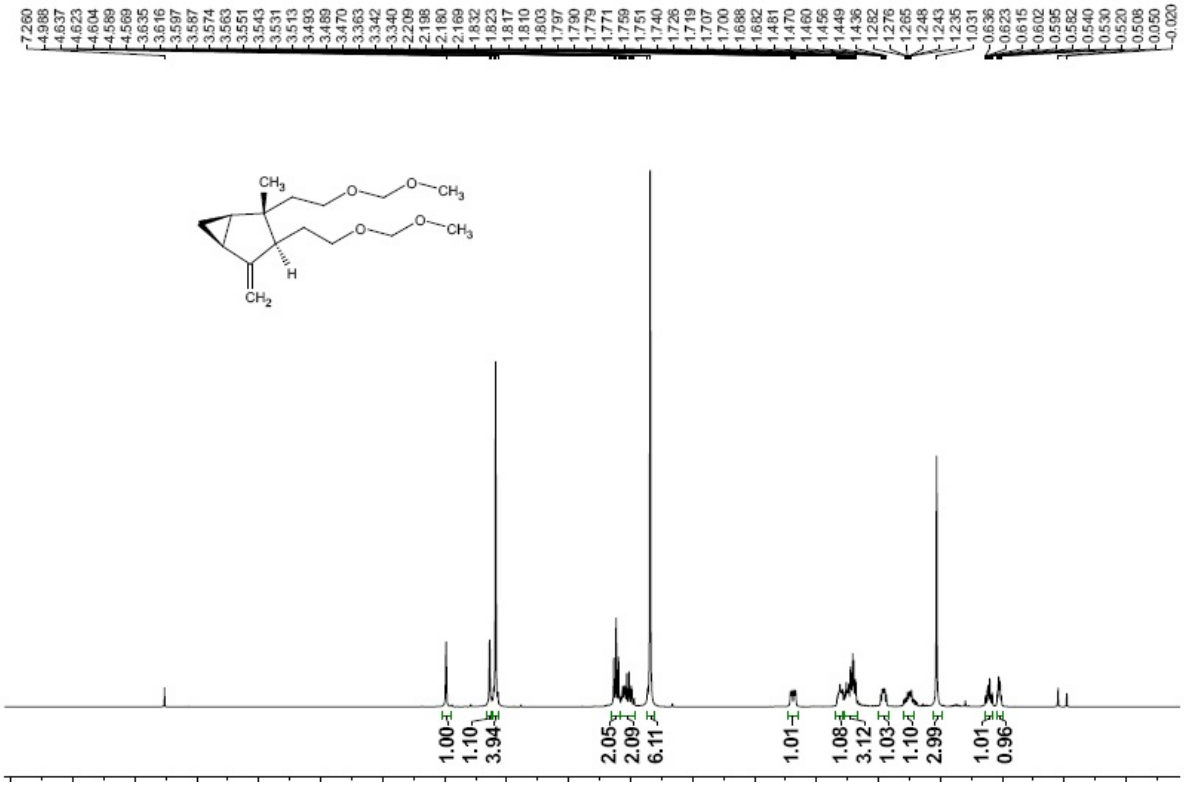

CH3
H2C
O
CH3
CH3
O
O
O
O
H
CH2

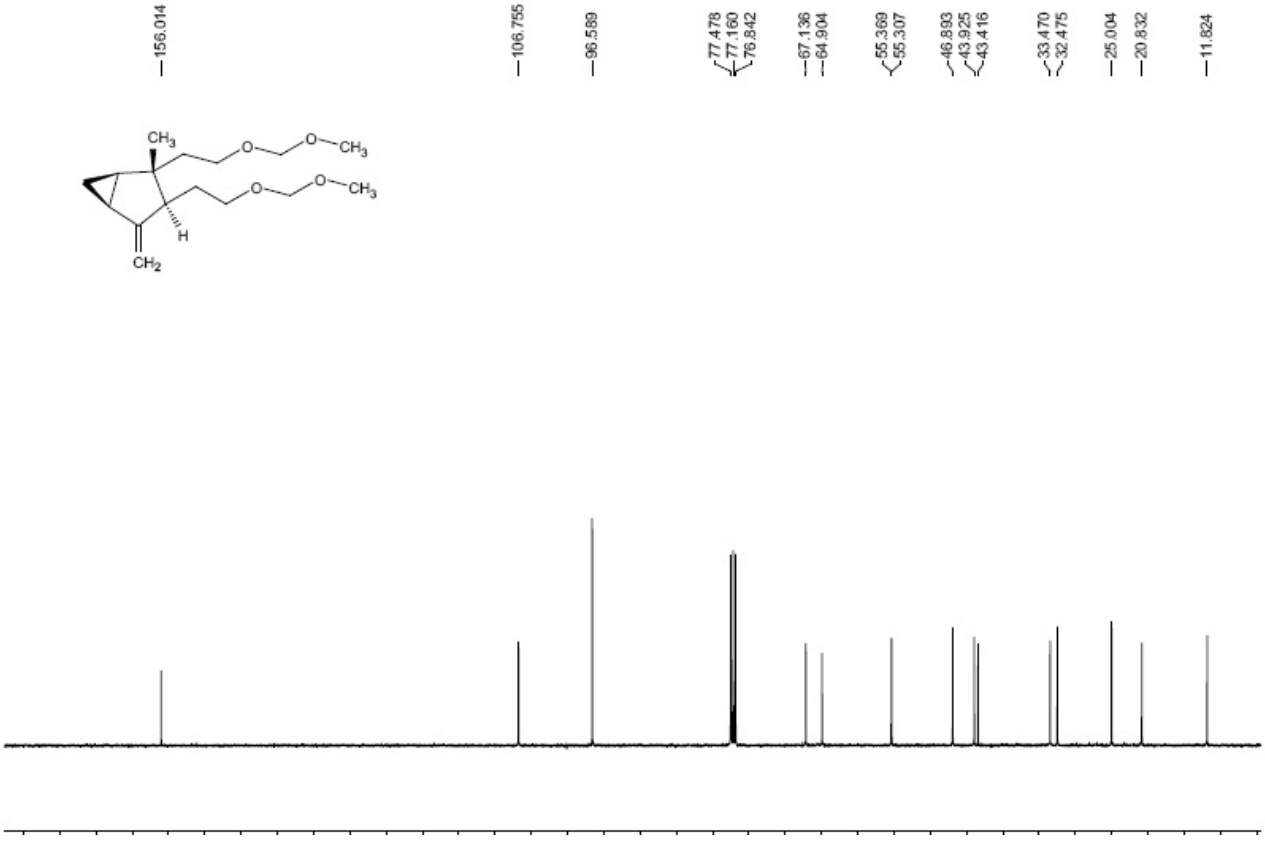

0.97
0.99
0.98
0.97
0.98
0.99
1.93
2.00
1.93
8.08
1.00
1.03
1.15
1.89


194.935
150.488
143.594
135.855
113.849
96.567
96.516
66.255
64.803
41.602
37.805
29.168
19.301

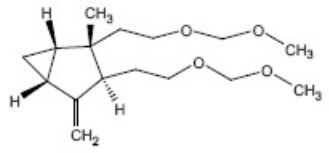
CH3
H2C
O
CH3
CH3
O
O
O
O
H
CH2

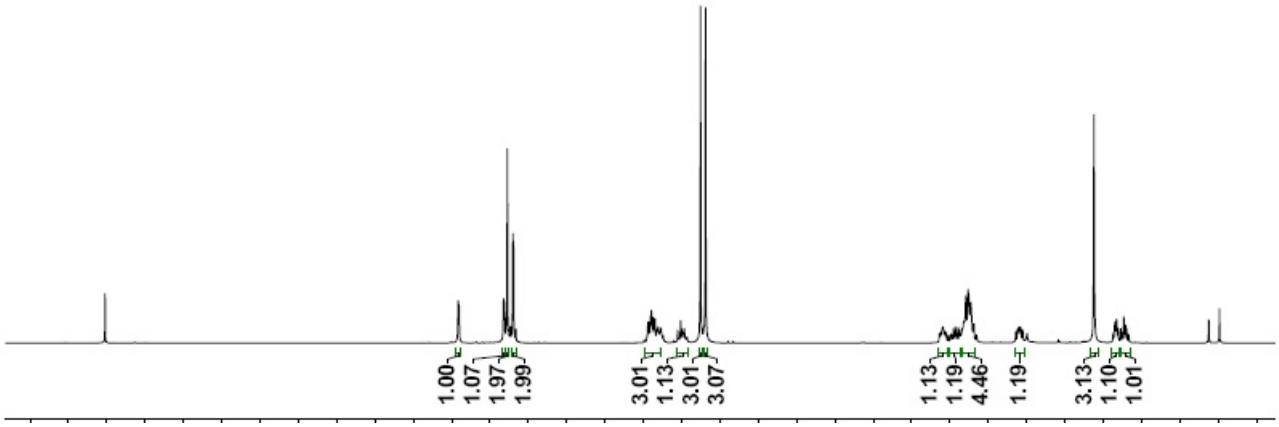



7.260
4.988
4.637
4.623
4.604
4.589
4.569
3.635
3.616
3.597
3.587
3.574
3.563
3.551
3.543
3.531
3.513
3.493
3.489
3.470
3.363
3.342
3.340
2.209
2.198
2.180
2.169
1.832
1.823
1.817
1.810
1.803
1.797
1.790
1.779
1.771
1.759
1.751
1.740
1.726
1.719
1.707
1.700
1.688
1.682
1.481
1.470
1.460
1.456
1.449
1.436
1.282
1.276
1.265
1.248
1.243
1.235
1.031
0.636
0.623
0.615
0.602
0.595
0.582
0.540
0.530
0.520
0.506
0.050
-0.020
CH3
O
O
CH3
O
O
CH3
H
CH2
1.00
1.10
3.94
2.05
2.09
6.11
1.01
1.08
3.12
1.03
1.10
2.99
1.01
0.96


156.014
106.755
96.589
77.478
77.160
76.842
67.136
64.904
55.369
55.307
46.893
43.925
43.416
33.470
32.475
25.004
20.832
11.824
CH3
O
O
CH3
O
O
CH3
H
CH2

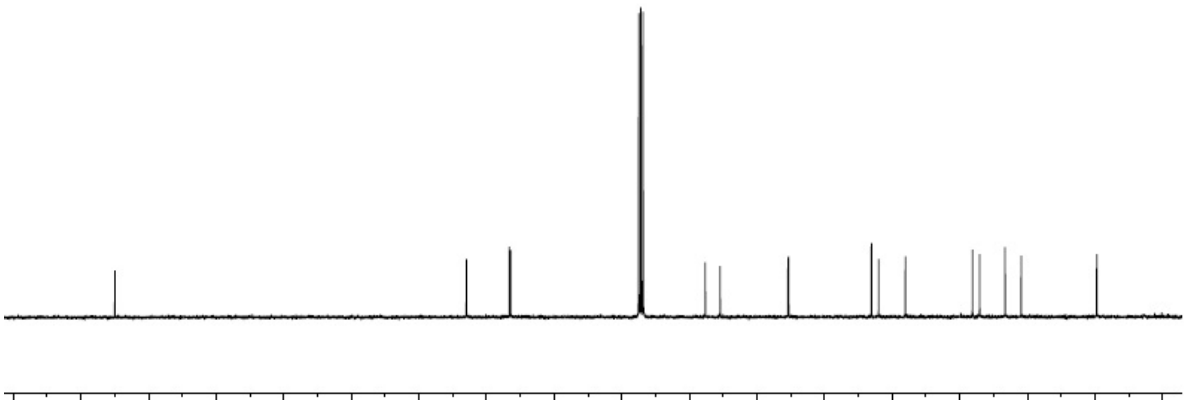

7.260
4.957
4.953
4.661
4.637
4.629
4.617
4.601
4.597
4.581
3.720
3.712
3.703
3.698
3.696
3.690
3.681
3.674
3.666
3.658
3.653
3.644
3.640
3.634
3.526
3.507
3.502
3.488
3.483
3.377
3.356
3.353
3.344
1.818
1.810
1.797
1.783
1.775
1.726
1.710
1.705
1.689
1.657
1.646
1.632
1.628
1.614
1.598
1.593
1.321
1.310
1.305
1.301
1.295
1.290
1.286
1.275
1.247
0.810
0.685
0.673
0.664
0.654
0.636
0.623
0.616
0.603
0.596
0.062
-0.008

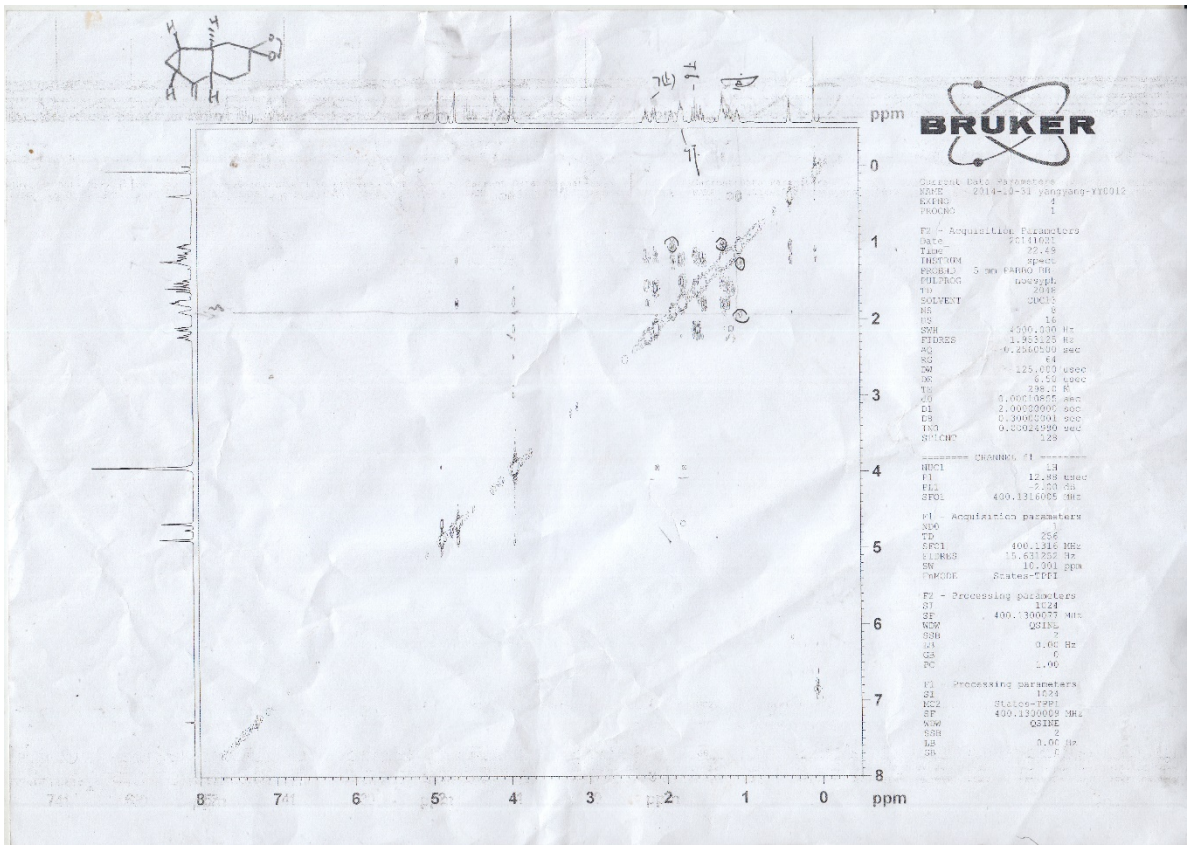

H
CH3
O
O
CH3
O
O
CH3
H
H
CH2

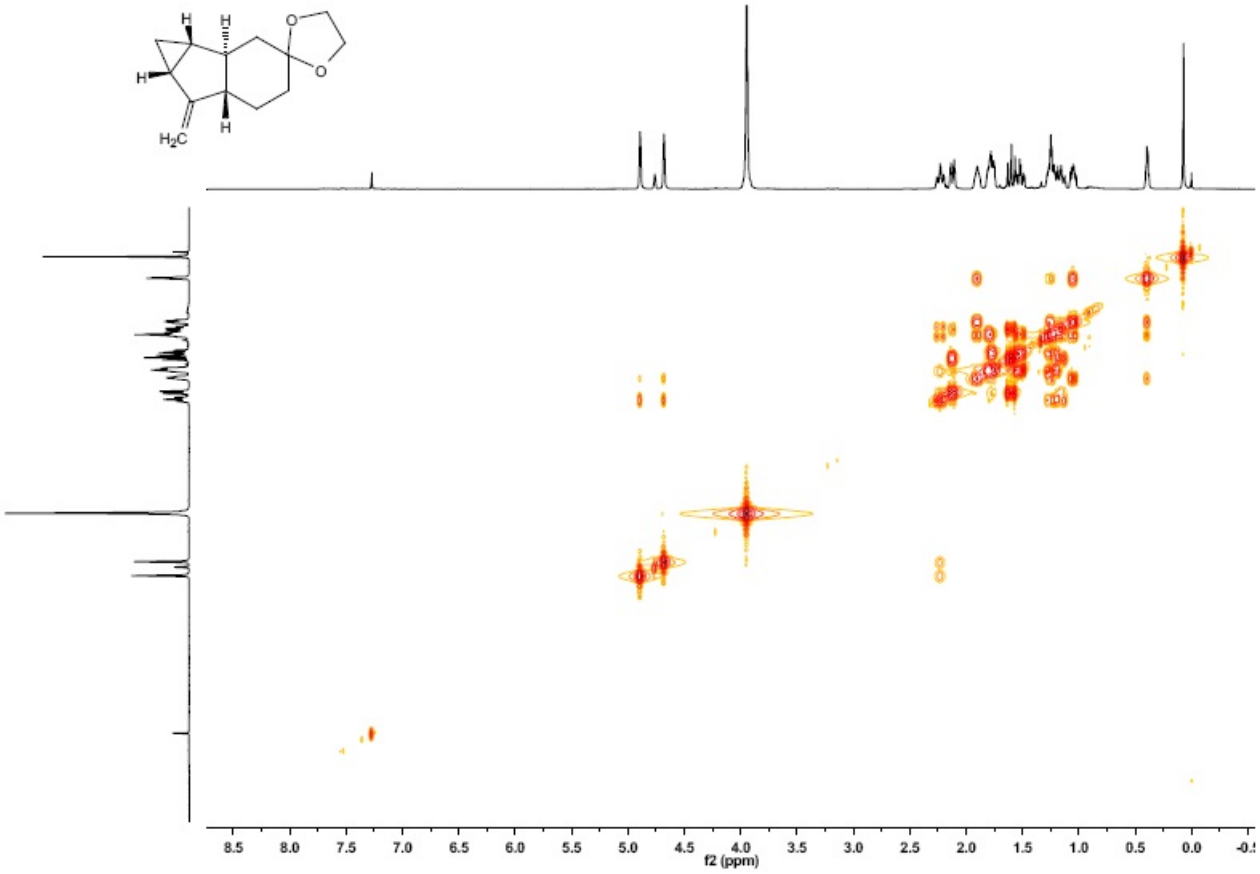

1.00
1.07
1.97
1.99
3.01
1.13
3.01
3.07
1.13
1.19
4.46
1.19
3.13
1.10
1.01

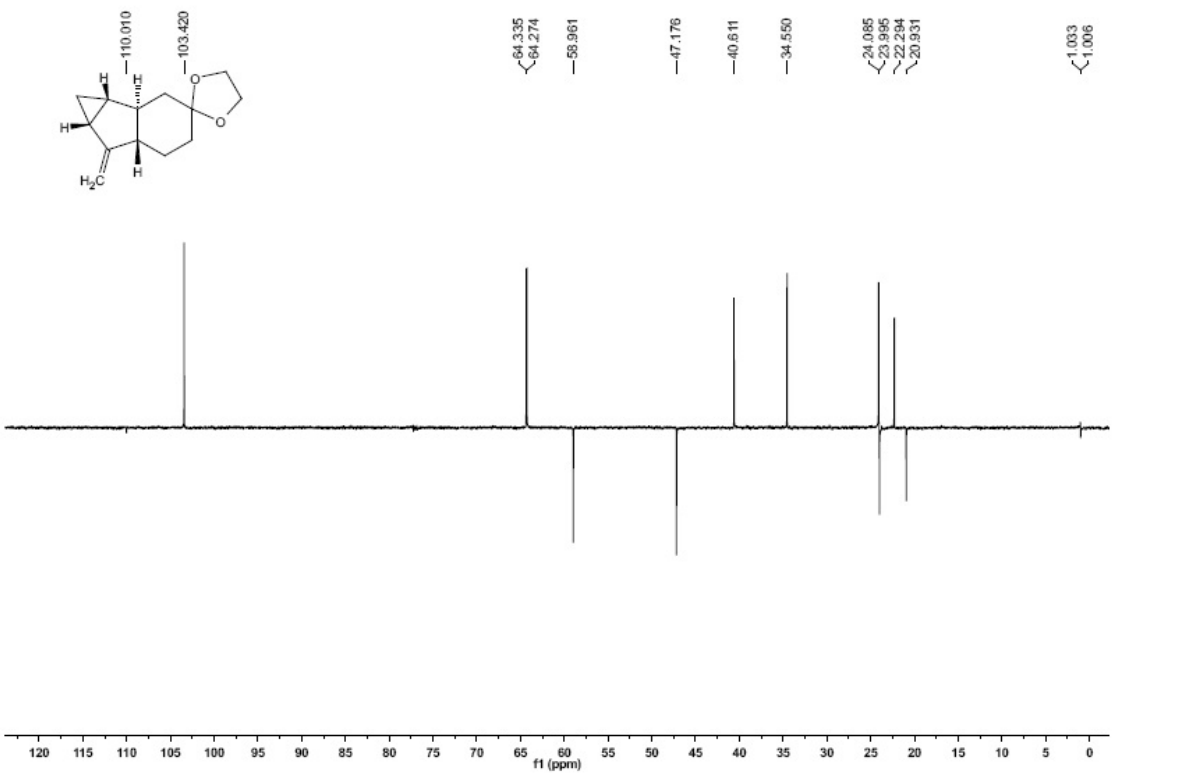

154.986
102.976
96.607
96.429
77.477
77.160
76.842
67.638
65.438
55.392
55.303
43.056
41.985
38.037
28.101
27.052
23.285
20.903
9.721

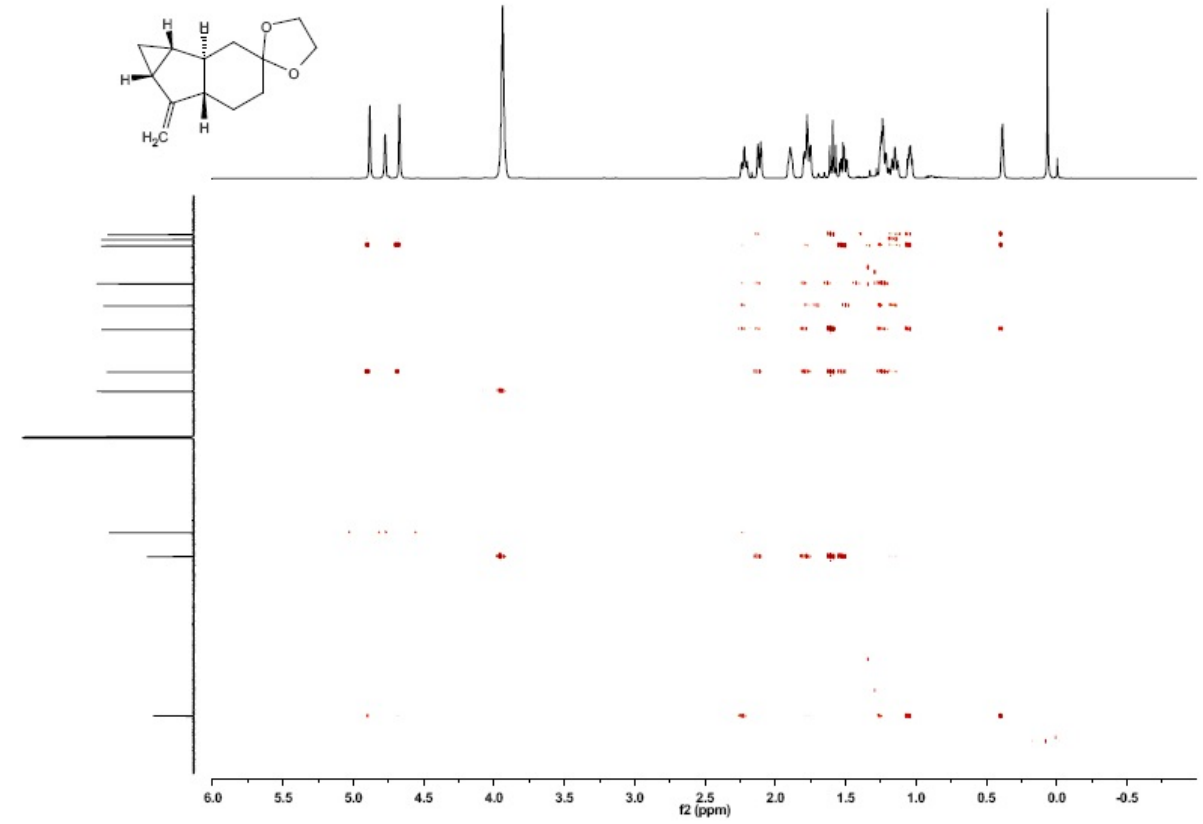
H
CH3
O
O
CH3
O
O
CH3
H
H
CH2

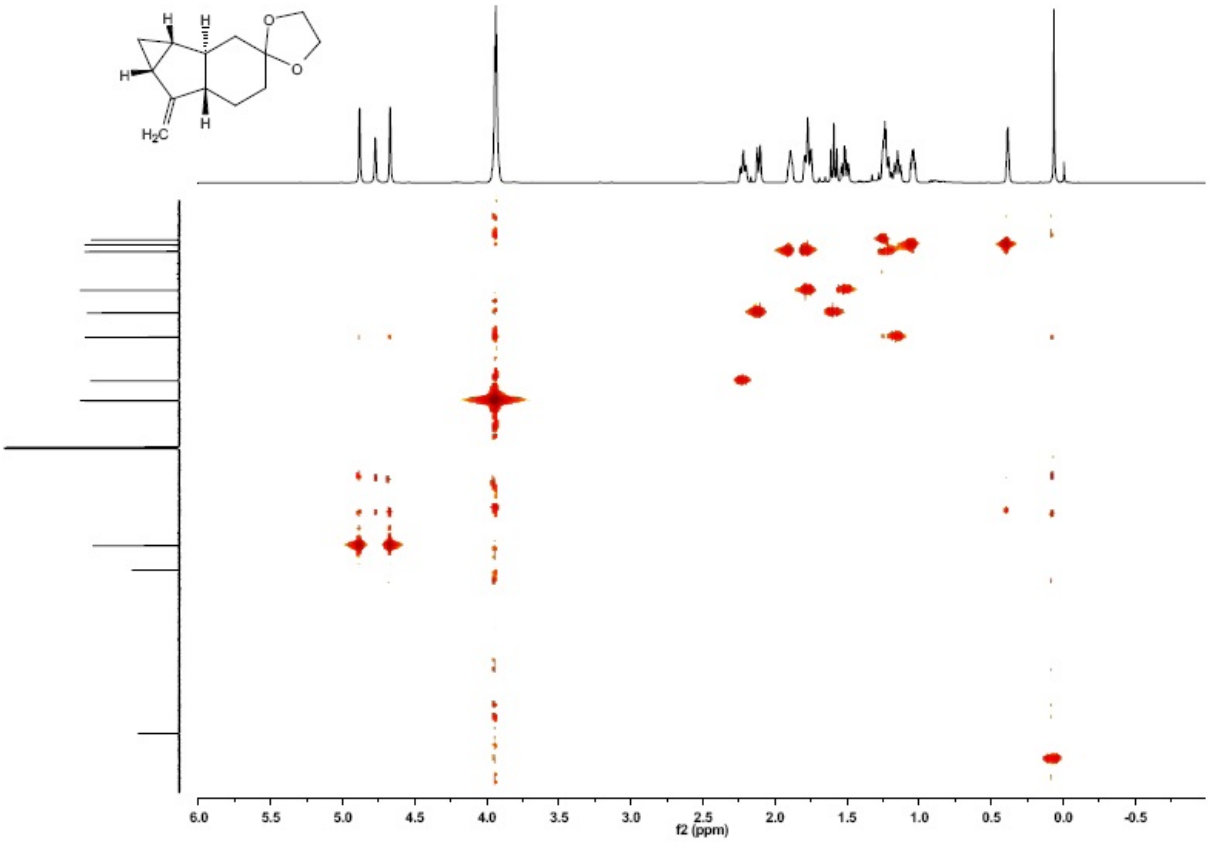


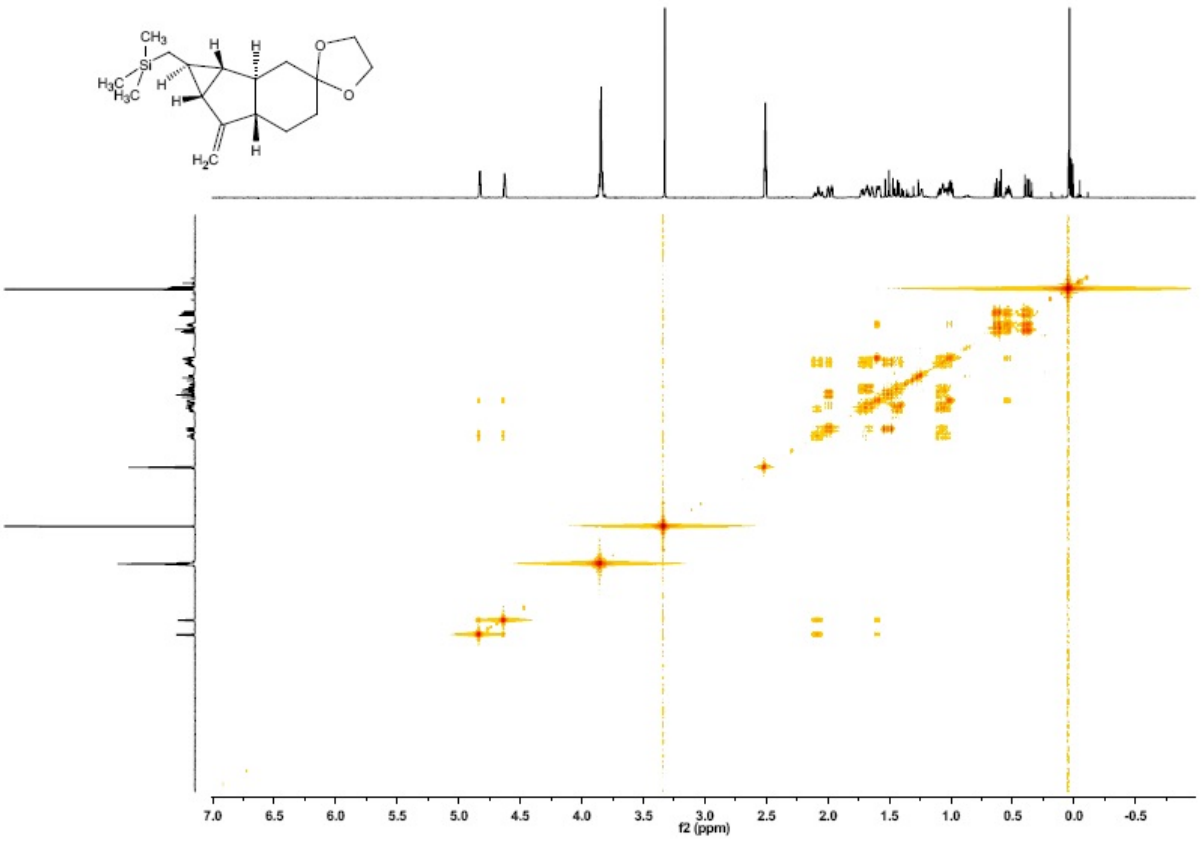

BRUKER
ppm
0
1
2
3
4
5
6
7
8
8
7
6
5
4
3
2
1
0
ppm

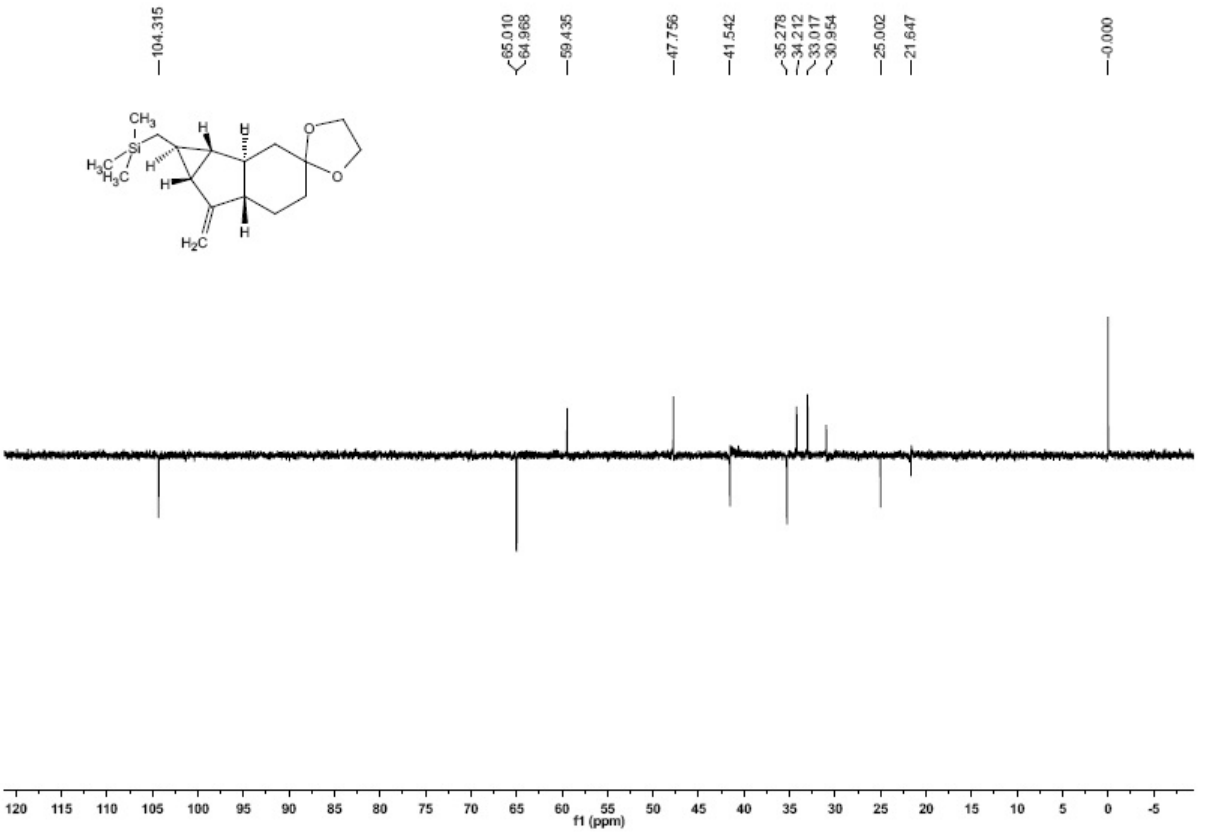

H
H
O
O
H
H
H2C
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)

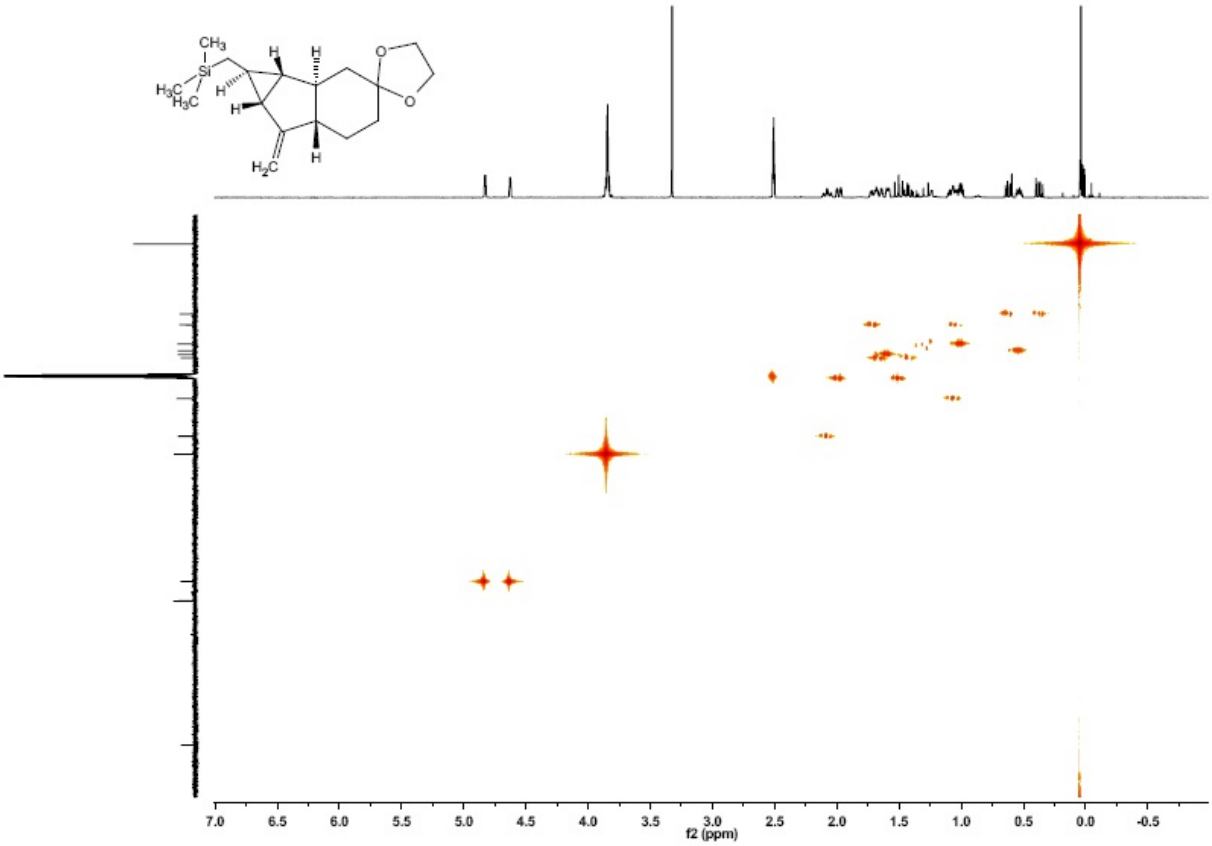

110.010
103.420
64.335
64.274
58.961
47.176
40.611
34.550
24.085
23.995
22.294
20.931
1.033
1.006
f1 (ppm)

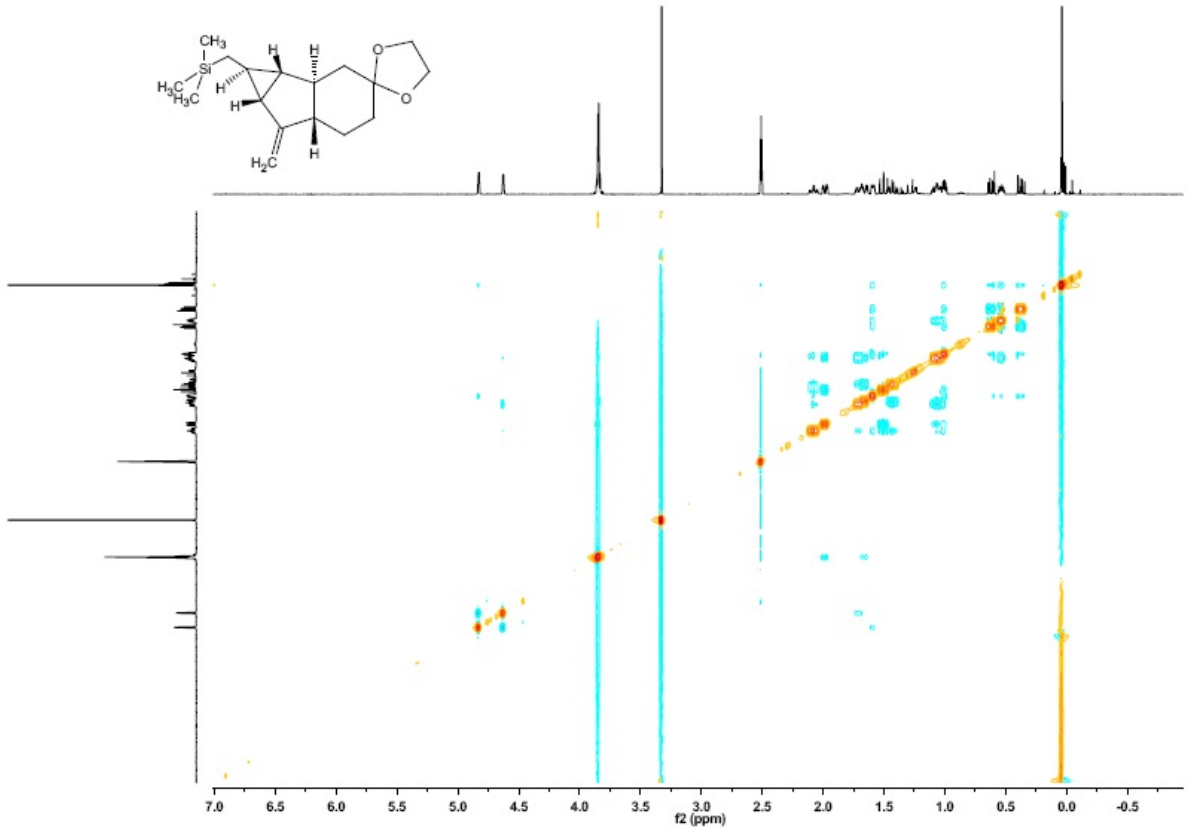

f2 (ppm)

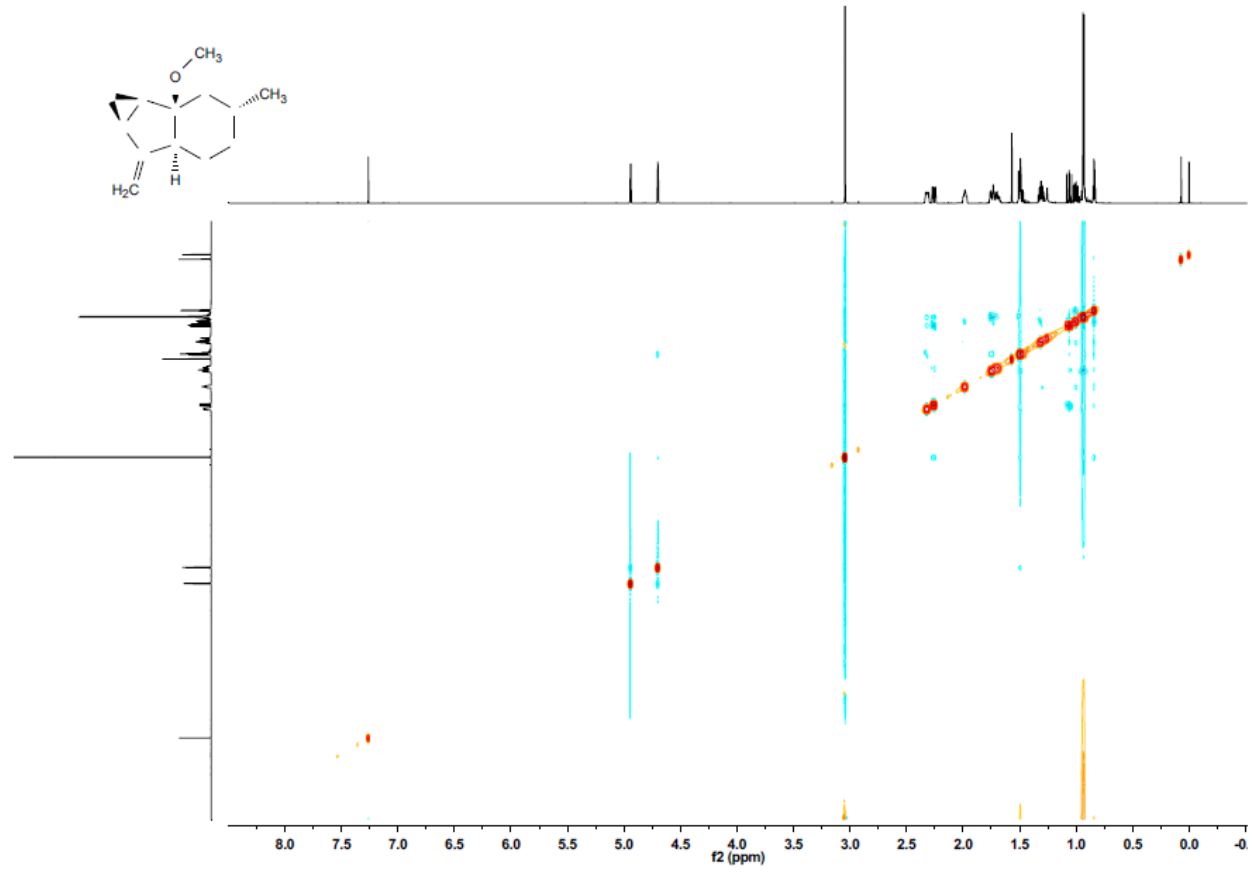

H
H
H
O
O
H2C
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f2 (ppm)

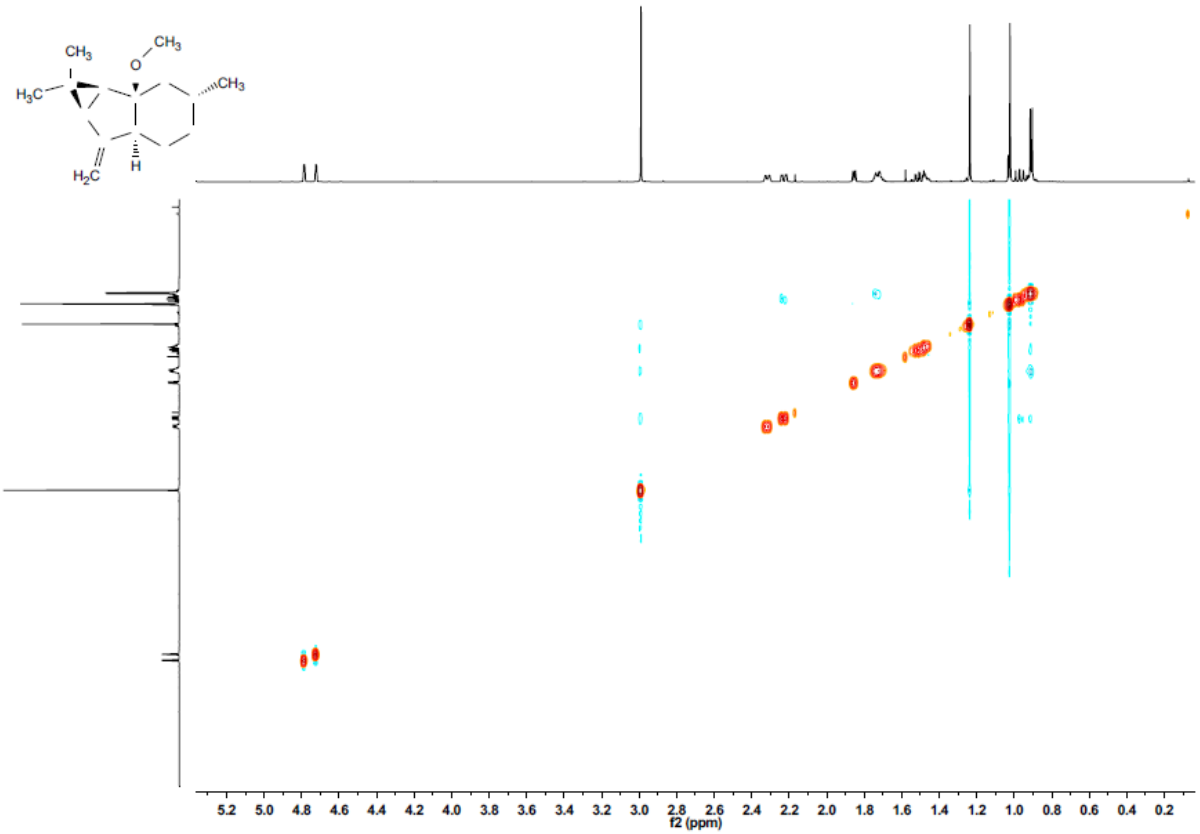

CH3
Si
H3C
H3C
H
H
H
O
O
H2C
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f2 (ppm)

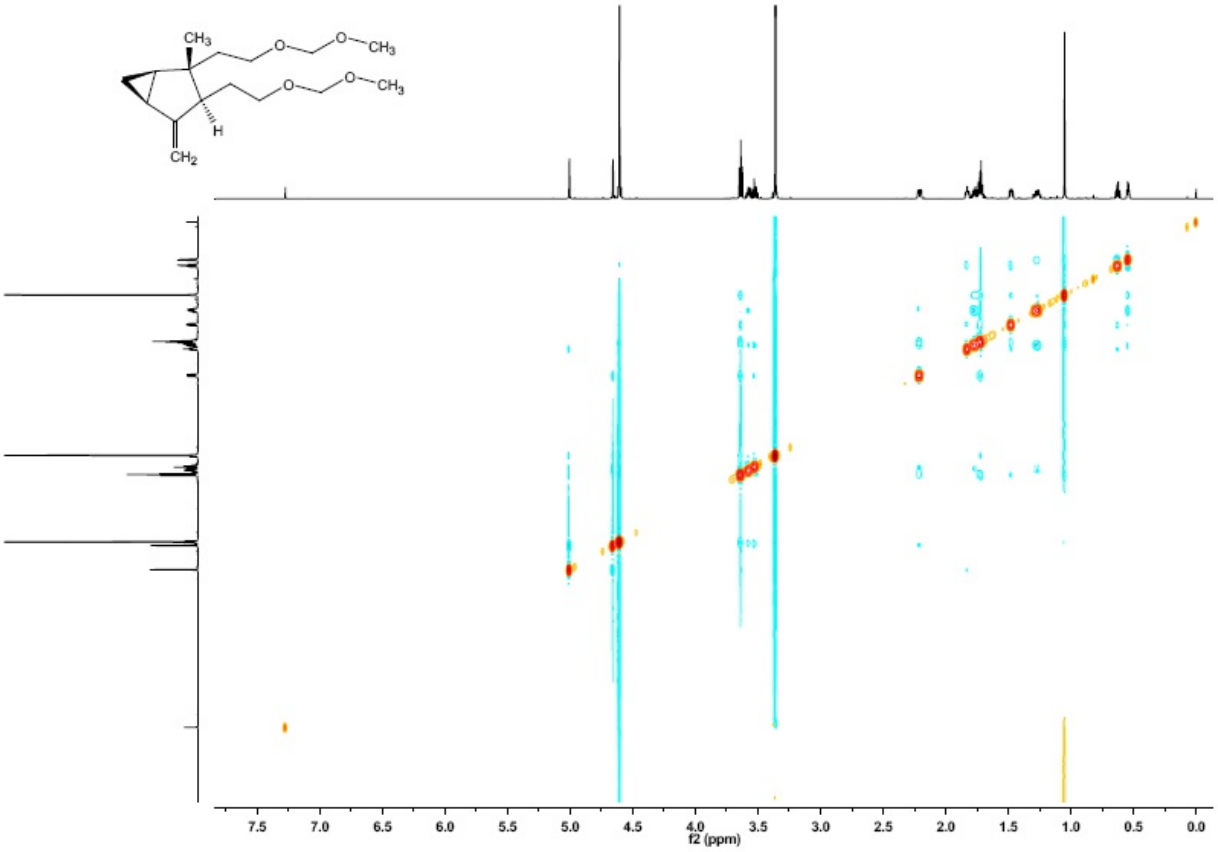

104.315
65.010
64.968
59.435
47.756
41.542
35.278
34.212
33.017
30.954
25.002
21.647
0.000
f1 (ppm)

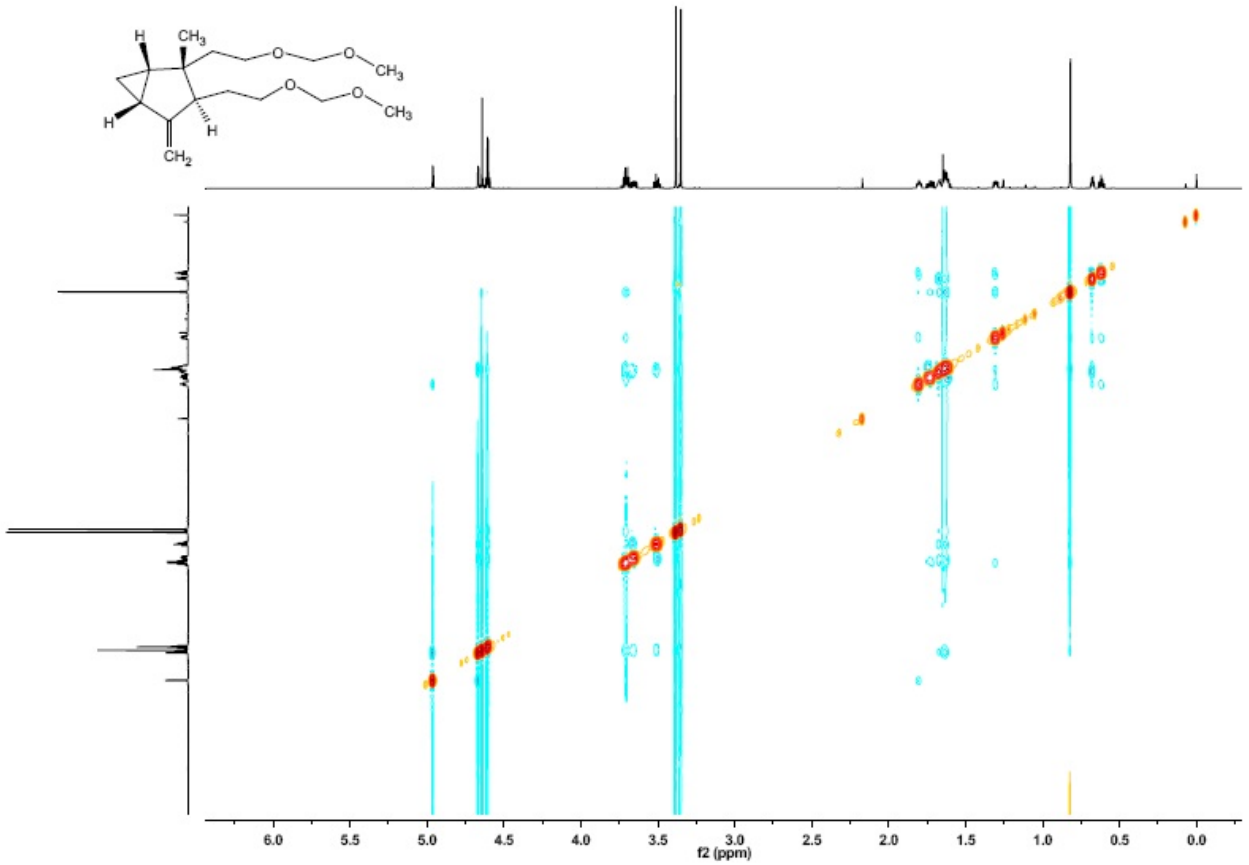

f2 (ppm)


CH3
Si
H3C
H3C
H
H
H
H
O
O
H2C
H
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f2 (ppm)

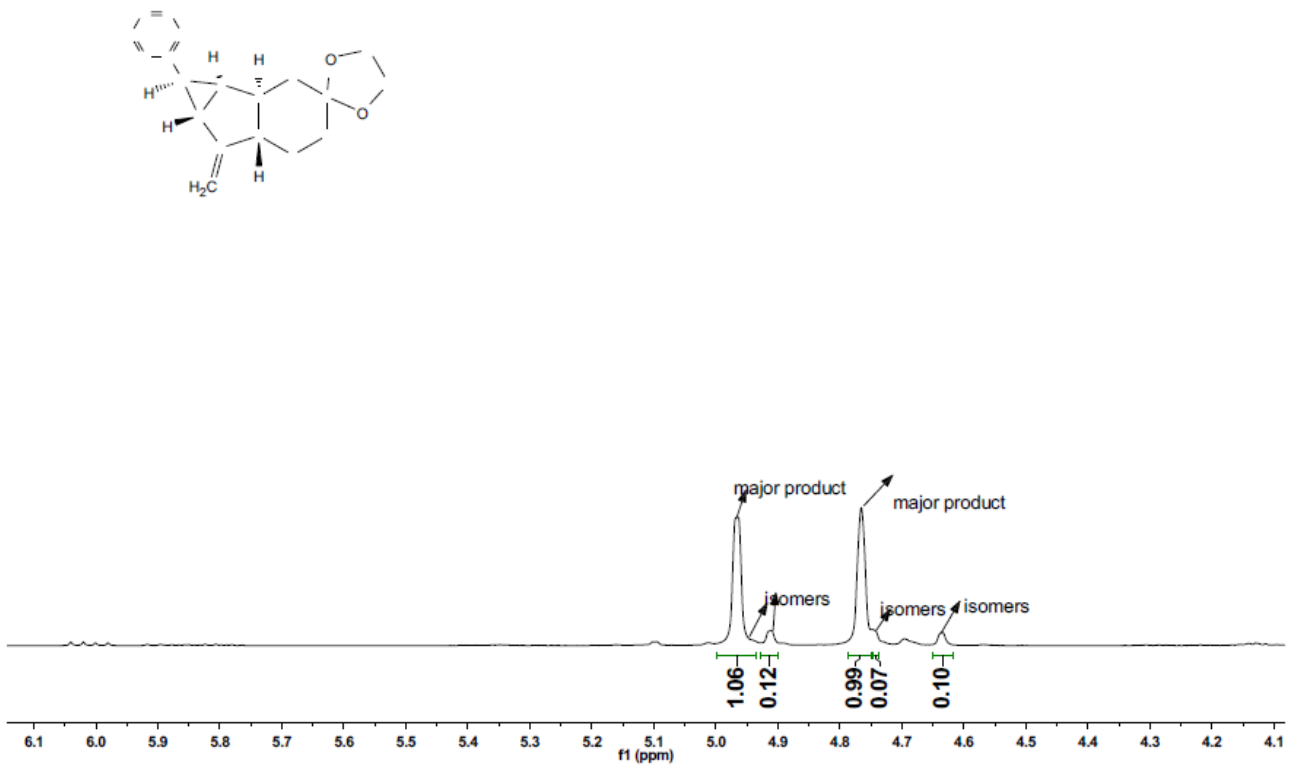

CH3
O
CH3
H2C
H
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)

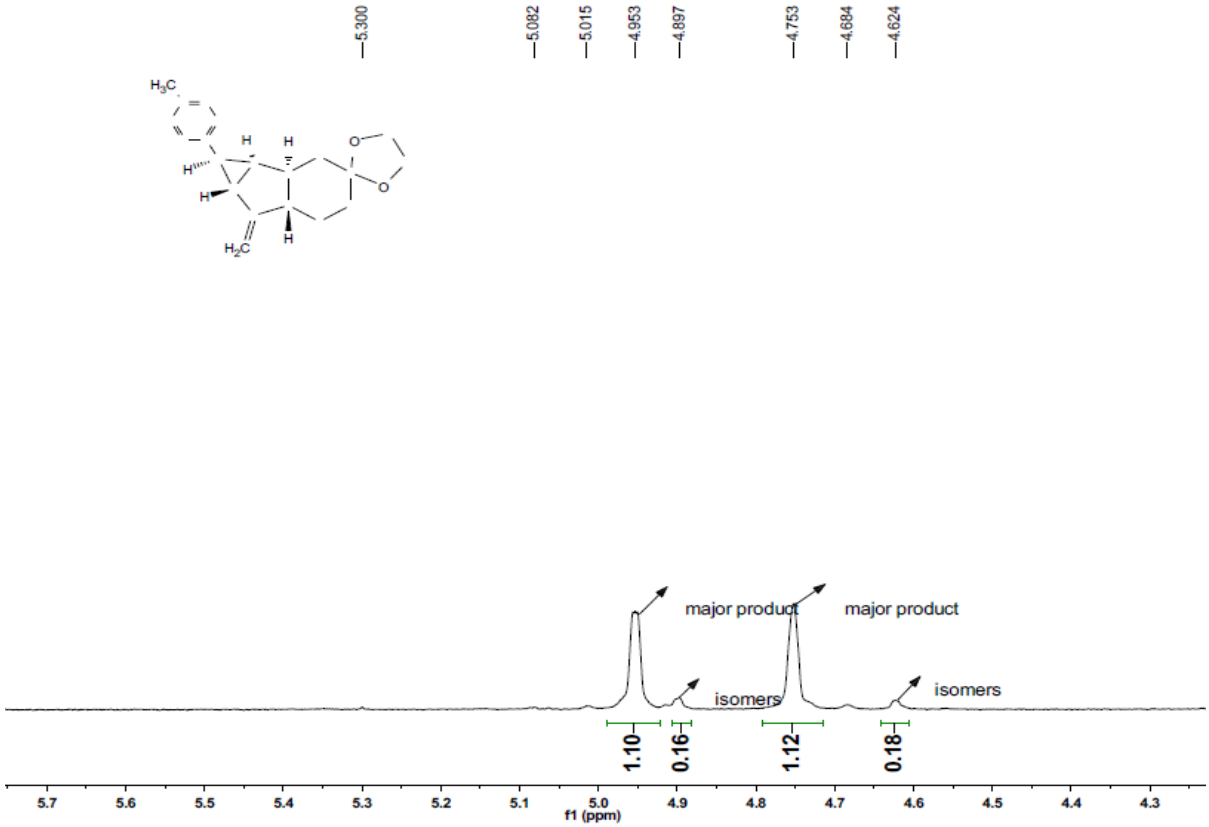

CH3
O
CH3
H3C
CH3
H2C
H
5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6 0.4 0.2
f2 (ppm)

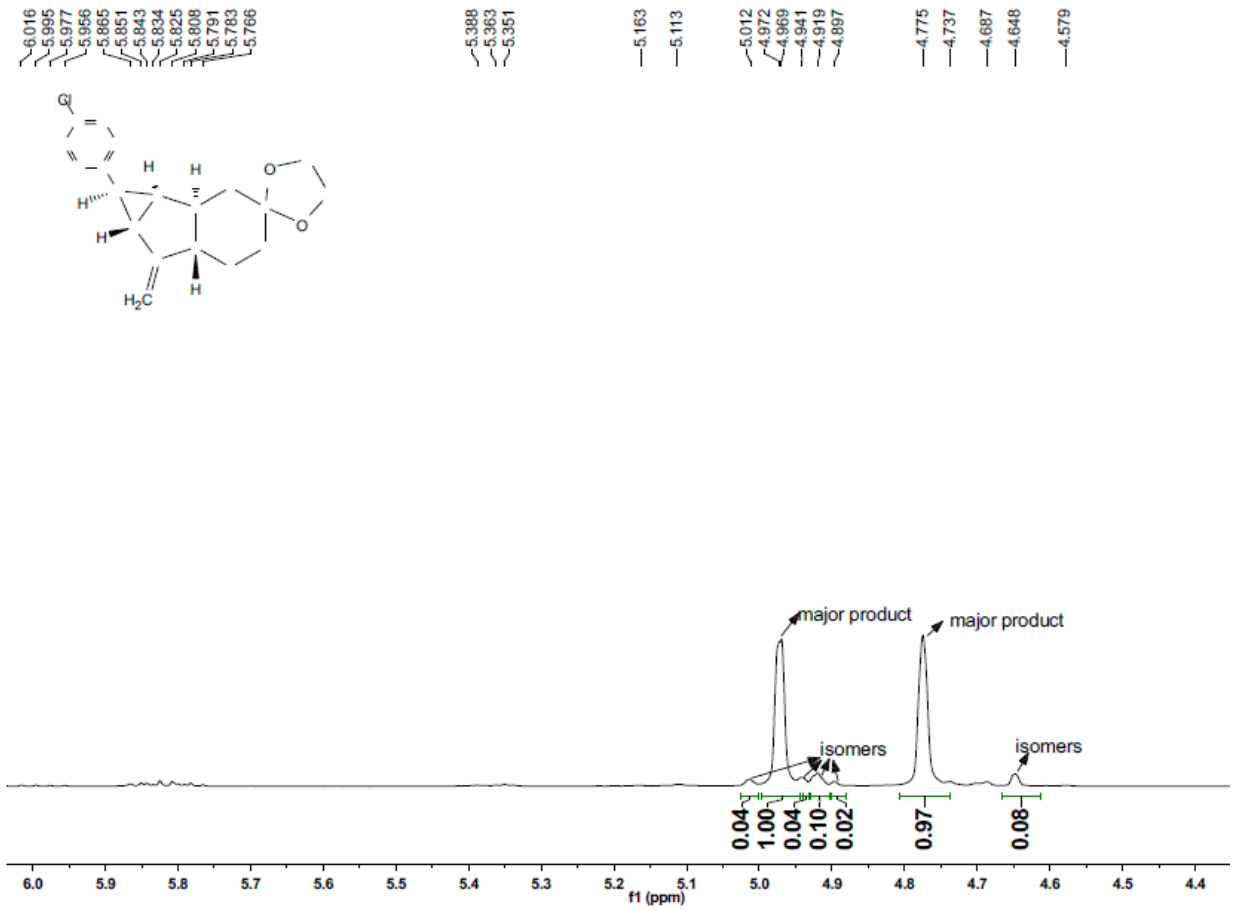

CH3
O
O
CH3
O
O
CH3
H
CH2
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f2 (ppm)

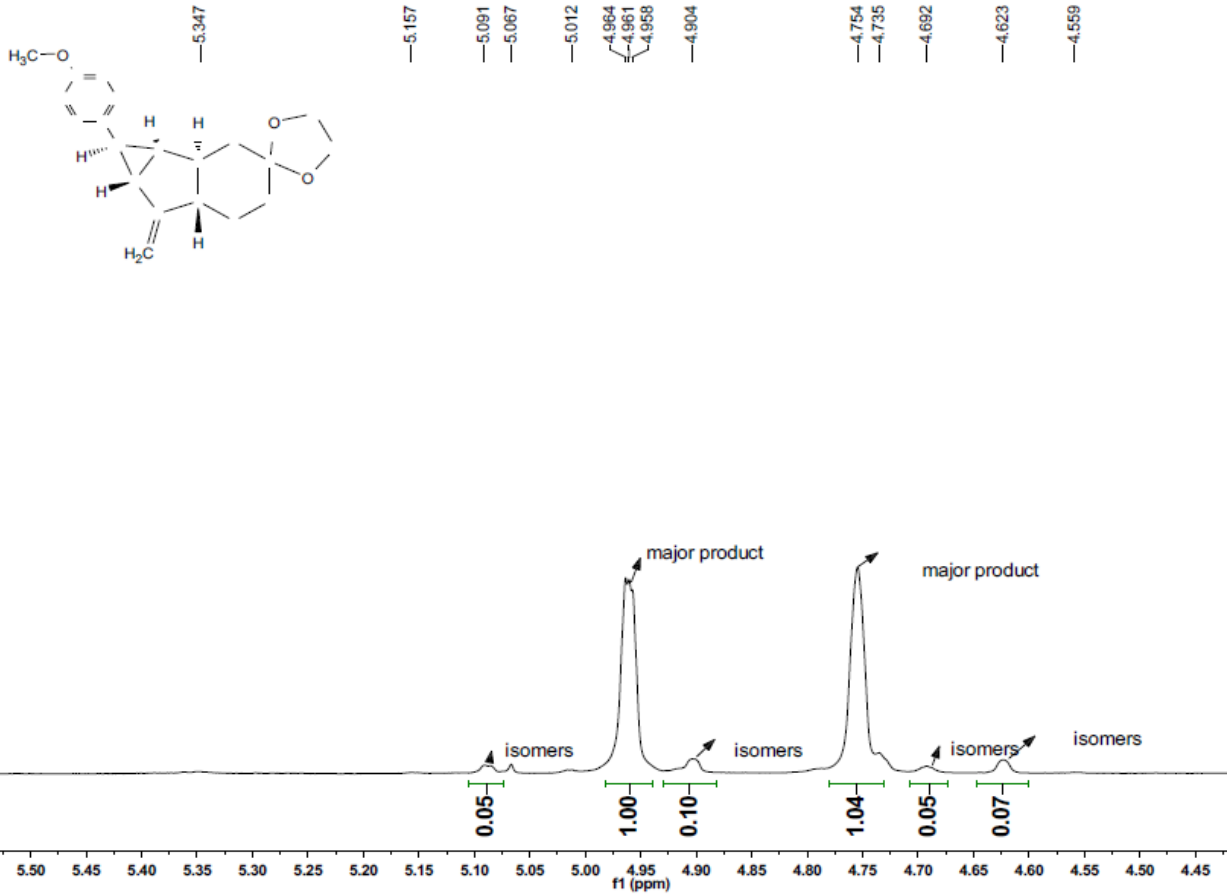


6.040
6.020
6.001
5.981
5.917
5.896
5.877
5.849
5.824
5.807
5.780
5.347
5.160
5.095
5.011
4.966
4.910
4.765
4.696
4.635
4.569
4.306
4.285
4.218
4.140
4.129
4.113

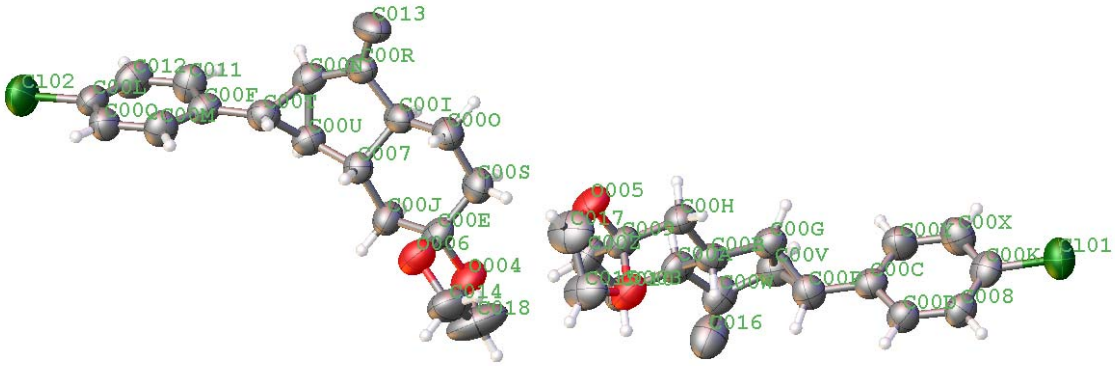



5.300
5.082
5.015
4.953
4.897
4.753
4.684
4.624
major product
major product
isomers
isomers
1.10
0.16
1.12
0.18
f1 (ppm)


6.016
5.995
5.977
5.956
5.865
5.851
5.843
5.834
5.825
5.808
5.791
5.783
5.766
5.388
5.363
5.351
5.163
5.113
5.012
4.972
4.969
4.941
4.919
4.897
4.775
4.737
4.687
4.648
4.579
major product
major product
isomers
isomers
0.04
1.00
0.04
0.10
0.02
0.97
0.08
f1 (ppm)


5.347
5.157
5.091
5.067
5.012
4.964
4.961
4.958
4.904
4.754
4.735
4.692
4.623
4.559
major product
major product
isomers
isomers
isomers
isomers
0.05
1.00
0.10
1.04
0.05
0.07
f1 (ppm)
4.945
4.900
4.881
4.763
4.616
major product
major product
isomers
isomers
0.93
0.31
1.00
0.29
f1 (ppm)

Crystal data of compound 2f



The crystal data has been deposited at the Cambridge Crystallographic Data Centre (CCDC 1042883).

Table 1 Crystal data and structure refinement for 2f

Identification code	lb-h0003-w6
Empirical formula	$C_{38}H_{35}Cl_2O_4$
Formula weight	626.56
Temperature/K	292.23(10)
Crystal system	tetragonal
Space group	$P4_32_12$
a/Å	11.6351(6)
b/Å	11.6351(6)
c/Å	48.952(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	6626.9(8)
Z	8
ρ_{calc}mg/mm^3	1.256
m/mm^{-1}	2.069
F(000)	2632.0
Crystal size/mm^3	0.8 × 0.6 × 0.5
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection	9.336 to 146.212°
Index ranges	-11 ≤ h ≤ 14, -14 ≤ k ≤ 7, -44 ≤ l ≤ 60
Reflections collected	19825
Independent reflections	6436 [R_{int} = 0.0740, R_{sigma} = 0.0605]
Data/restraints/parameters	6436/0/398
Goodness-of-fit on F^2	1.047
Final R indexes [I>=2σ (I)]	R_1 = 0.0954, wR_2 = 0.2674

Final R indexes [all data]	R_1 = 0.1264, wR_2 = 0.2926
Largest diff. peak/hole / e Å^{-3}	0.38/-0.29
Flack parameter	0.06(2)

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 2f. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Cl01	9612(2)	6894(2)	9924.1(5)	88.0(8)
Cl02	3107(3)	5451(2)	5014.2(5)	94.7(8)
O003	5022(6)	6707(6)	8082.3(11)	78.3(17)
O004	3580(6)	8607(6)	7239.2(11)	84.4(19)
O005	6301(7)	6504(6)	7734.4(11)	88(2)
O006	3364(6)	9893(6)	6894.9(12)	84.1(19)
C007	4604(7)	8374(6)	6519.3(14)	56.8(16)
C008	7761(8)	6851(7)	9597.3(16)	63.7(19)
C009	5942(8)	6003(7)	7984.0(15)	65(2)
C00A	6190(8)	4157(7)	8380.8(16)	66(2)
C00B	6551(7)	5401(7)	8446.7(16)	60.7(18)
C00C	7545(7)	5582(7)	9203.4(15)	61.1(19)
C00D	7153(7)	6475(7)	9372.5(16)	66(2)
C00E	4071(8)	8969(8)	6986.7(15)	67(2)
C00F	4359(7)	7407(7)	5755.5(16)	64.3(19)
C00G	7384(7)	5249(8)	8683.1(15)	64.3(19)
C00H	6904(8)	6038(8)	8191.2(16)	67(2)
C00I	5853(7)	8728(8)	6578.4(14)	61.9(18)
C00J	3997(8)	8009(8)	6779.5(15)	68(2)
C00K	8797(9)	6360(8)	9648.2(16)	70(2)
C00L	3591(8)	6218(8)	5300.8(16)	68(2)
C00M	3541(8)	7871(8)	5579.6(17)	72(2)
C00N	5839(8)	7845(8)	6138.3(16)	69(2)
C00O	5921(8)	9711(9)	6777.0(16)	72(2)
C00P	6851(8)	5240(8)	8963.0(17)	70(2)
C00Q	3162(8)	7292(8)	5348.9(17)	69(2)
C00R	6396(7)	8784(9)	6299.5(15)	72(2)
C00S	5285(8)	9394(9)	7038.4(16)	75(2)
C00T	4715(7)	8091(8)	5999.8(16)	67.5(19)
C00U	4741(8)	7545(8)	6281.4(15)	66.1(19)
C00V	7069(9)	4119(8)	8819.4(18)	74(2)
C00W	6124(9)	3611(7)	8657.2(17)	72(2)
C00X	9222(9)	5502(9)	9495.0(19)	79(2)

C00Y	8597(8)	5094(9)	9272.8(19)	81(3)
C00Z	5498(9)	4793(8)	7923.8(16)	78(2)
C010	5204(9)	4125(8)	8185.1(17)	76(2)
C011	4785(9)	6322(8)	5692.9(18)	76(2)
C012	4405(10)	5733(9)	5465(2)	85(3)
C013	7173(8)	9540(12)	6220(2)	95(3)
C014	2746(10)	10313(12)	7123(2)	107(4)
C015	4573(10)	7303(10)	7857(2)	98(3)
C016	5368(12)	2824(9)	8739(2)	100(3)
C017	5513(12)	7345(10)	7662(2)	106(4)
C018	2787(14)	9416(13)	7328(3)	141(6)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for 2f. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl01	95.5(17)	94.8(16)	73.7(12)	-4.2(11)	-21.6(11)	-2.2(14)
Cl02	102.9(18)	93.4(17)	87.8(14)	-32.8(13)	-6.6(13)	-5.7(15)
O003	90(4)	83(4)	61(3)	0(3)	9(3)	17(4)
O004	101(5)	98(5)	54(3)	5(3)	16(3)	-8(4)
O005	104(5)	105(5)	55(3)	8(3)	22(3)	1(4)
O006	89(4)	97(5)	66(3)	1(3)	9(3)	21(4)
C007	61(4)	56(4)	54(3)	6(3)	-3(3)	2(4)
C008	79(5)	52(4)	60(4)	-5(3)	3(4)	1(4)
C009	74(5)	66(5)	54(4)	-2(3)	8(4)	10(4)
C00A	74(5)	59(4)	64(4)	-11(3)	8(4)	3(4)
C00B	58(4)	55(4)	69(4)	-8(3)	8(3)	3(4)
C00C	64(4)	59(4)	61(4)	6(3)	7(3)	2(4)
C00D	66(5)	68(5)	63(4)	2(4)	0(4)	11(4)
C00E	81(5)	71(5)	48(3)	10(3)	6(4)	9(4)
C00F	69(5)	62(5)	62(4)	1(3)	11(4)	0(4)
C00G	66(5)	66(5)	61(4)	3(3)	5(3)	10(4)
C00H	64(5)	75(5)	62(4)	2(4)	8(4)	-6(4)
C00I	53(4)	78(5)	54(4)	11(4)	-3(3)	0(4)
C00J	79(5)	72(5)	54(4)	-4(4)	3(4)	-12(5)
C00K	89(6)	63(5)	56(4)	12(4)	-2(4)	-2(5)
C00L	66(5)	77(5)	61(4)	-10(4)	7(4)	-6(4)
C00M	80(6)	63(5)	73(5)	-7(4)	-2(4)	10(5)
C00N	70(5)	75(5)	63(4)	5(4)	10(4)	4(4)
C00O	67(5)	85(6)	65(4)	6(4)	-4(4)	-9(5)

C00P	71(5)	65(5)	76(5)	-3(4)	-6(4)	5(4)
C00Q	67(5)	71(5)	68(4)	-8(4)	-3(4)	-4(4)
C00R	52(4)	109(7)	55(4)	15(4)	-1(3)	7(5)
C00S	78(6)	90(6)	57(4)	7(4)	-8(4)	-3(5)
C00T	64(5)	71(5)	68(4)	1(4)	2(4)	6(4)
C00U	66(5)	68(5)	64(4)	-2(4)	8(4)	2(4)
C00V	77(6)	66(5)	79(5)	8(4)	0(4)	8(5)
C00W	99(7)	46(4)	71(4)	-5(3)	5(4)	-1(4)
C00X	76(6)	76(6)	87(6)	5(5)	-15(5)	11(5)
C00Y	71(5)	89(7)	84(6)	-11(5)	1(4)	6(5)
C00Z	101(7)	77(6)	55(4)	-8(4)	5(4)	2(5)
C010	90(6)	67(5)	70(5)	-14(4)	9(4)	-13(5)
C011	89(6)	66(5)	72(5)	-1(4)	-9(4)	14(5)
C012	101(8)	67(5)	86(6)	-10(5)	13(6)	5(5)
C013	60(5)	141(10)	83(6)	16(6)	7(4)	-16(6)
C014	95(8)	122(10)	104(7)	-19(7)	34(6)	9(7)
C015	93(7)	113(8)	87(6)	42(6)	9(6)	24(7)
C016	140(10)	79(7)	81(6)	2(5)	4(7)	-24(7)
C017	122(10)	98(8)	99(7)	49(6)	5(7)	12(7)
C018	160(14)	126(11)	138(11)	23(9)	91(10)	35(10)

Table 4 Bond Lengths for 2f.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cl01	C00K	1.763(9)	C00E	C00S	1.518(13)
Cl02	C00L	1.755(8)	C00F	C00M	1.392(12)
O003	C009	1.431(10)	C00F	C00T	1.496(12)
O003	C015	1.406(11)	C00F	C011	1.390(12)
O004	C00E	1.425(9)	C00G	C00P	1.504(11)
O004	C018	1.389(14)	C00G	C00V	1.519(12)
O005	C009	1.417(10)	C00I	C00O	1.503(12)
O005	C017	1.387(13)	C00I	C00R	1.506(10)
O006	C00E	1.426(10)	C00K	C00X	1.343(13)
O006	C014	1.416(11)	C00L	C00Q	1.366(13)
C007	C00I	1.538(11)	C00L	C012	1.365(14)
C007	C00J	1.517(10)	C00M	C00Q	1.387(11)
C007	C00U	1.520(10)	C00N	C00R	1.495(13)
C008	C00D	1.379(11)	C00N	C00T	1.500(12)
C008	C00K	1.357(13)	C00N	C00U	1.498(12)
C009	C00H	1.511(12)	C00O	C00S	1.523(11)

C009	C00Z	1.528(13)	C00P	C00V	1.503(13)
C00A	C00B	1.541(11)	C00R	C013	1.320(14)
C00A	C00W	1.497(11)	C00T	C00U	1.518(11)
C00A	C010	1.494(12)	C00V	C00W	1.480(13)
C00B	C00G	1.520(11)	C00W	C016	1.331(15)
C00B	C00H	1.511(11)	C00X	C00Y	1.392(13)
C00C	C00D	1.404(11)	C00Z	C010	1.536(12)
C00C	C00P	1.481(12)	C011	C012	1.381(13)
C00C	C00Y	1.391(13)	C014	C018	1.448(18)
C00E	C00J	1.512(11)	C015	C017	1.451(16)

Table 5 Bond Angles for 2f.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C015	O003	C009	107.2(7)	C008	C00K	Cl01	118.0(7)
C018	O004	C00E	109.8(8)	C00X	C00K	Cl01	119.4(8)
C017	O005	C009	108.4(7)	C00X	C00K	C008	122.5(9)
C014	O006	C00E	107.7(7)	C00Q	C00L	Cl02	119.0(7)
C00J	C007	C00I	110.9(6)	C012	C00L	Cl02	119.0(7)
C00J	C007	C00U	120.9(7)	C012	C00L	C00Q	122.0(8)
C00U	C007	C00I	102.4(7)	C00Q	C00M	C00F	122.2(8)
C00K	C008	C00D	117.9(8)	C00R	C00N	C00T	118.5(8)
O003	C009	C00H	108.3(6)	C00R	C00N	C00U	107.1(7)
O003	C009	C00Z	109.8(8)	C00U	C00N	C00T	60.8(6)
O005	C009	O003	106.0(7)	C00I	C00O	C00S	109.5(8)
O005	C009	C00H	110.4(7)	C00C	C00P	C00G	119.8(8)
O005	C009	C00Z	108.2(7)	C00C	C00P	C00V	120.8(8)
C00H	C009	C00Z	113.9(7)	C00V	C00P	C00G	60.7(6)
C00W	C00A	C00B	102.9(6)	C00L	C00Q	C00M	117.9(8)
C010	C00A	C00B	111.5(7)	C00N	C00R	C00I	105.4(7)
C010	C00A	C00W	122.0(8)	C013	C00R	C00I	125.6(10)
C00G	C00B	C00A	103.0(7)	C013	C00R	C00N	129.0(8)
C00H	C00B	C00A	111.2(7)	C00E	C00S	C00O	113.0(7)
C00H	C00B	C00G	120.9(7)	C00F	C00T	C00N	120.1(8)
C00D	C00C	C00P	119.4(8)	C00F	C00T	C00U	120.6(8)
C00Y	C00C	C00D	116.3(8)	C00N	C00T	C00U	59.5(6)
C00Y	C00C	C00P	124.3(8)	C00N	C00U	C007	107.4(7)
C008	C00D	C00C	122.6(8)	C00N	C00U	C00T	59.6(5)
O004	C00E	O006	105.4(7)	C00T	C00U	C007	115.3(7)
O004	C00E	C00J	109.9(7)	C00P	C00V	C00G	59.7(6)

O004	C00E	C00S	108.9(7)	C00W	C00V	C00G	106.9(7)
O006	C00E	C00J	108.2(7)	C00W	C00V	C00P	118.2(8)
O006	C00E	C00S	110.1(8)	C00V	C00W	C00A	106.1(8)
C00J	C00E	C00S	113.9(8)	C016	C00W	C00A	126.6(9)
C00M	C00F	C00T	118.5(8)	C016	C00W	C00V	127.3(9)
C011	C00F	C00M	117.4(8)	C00K	C00X	C00Y	119.8(9)
C011	C00F	C00T	124.1(8)	C00C	C00Y	C00X	120.8(9)
C00P	C00G	C00B	115.6(7)	C009	C00Z	C010	112.4(7)
C00P	C00G	C00V	59.6(6)	C00A	C010	C00Z	110.5(8)
C00V	C00G	C00B	106.3(8)	C012	C011	C00F	120.9(9)
C00B	C00H	C009	109.9(7)	C00L	C012	C011	119.6(9)
C00O	C00I	C007	112.1(7)	O006	C014	C018	106.4(10)
C00O	C00I	C00R	122.1(8)	O003	C015	C017	104.6(9)
C00R	C00I	C007	103.7(6)	O005	C017	C015	107.9(8)
C00E	C00J	C007	109.3(7)	O004	C018	C014	107.0(9)

Table 6 Torsion Angles for 2f.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Cl01	C00K	C00X	C00Y	-178.5(8)	C00K	C008	C00D	C00C	2.6(13)
Cl02	C00L	C00Q	C00M	178.7(7)	C00K	C00X	C00Y	C00C	1.4(16)
Cl02	C00L	C012	C011	-179.3(8)	C00M	C00F	C00T	C00N	-159.0(8)
O003	C009	C00H	C00B	69.8(9)	C00M	C00F	C00T	C00U	130.8(9)
O003	C009	C00Z	C010	-70.8(10)	C00M	C00F	C011	C012	-0.2(14)
O003	C015	C017	O005	18.8(14)	C00N	C00T	C00U	C007	96.1(8)
O004	C00E	C00J	C007	-175.6(7)	C00O	C00I	C00R	C00N	-162.5(8)
O004	C00E	C00S	C00O	175.3(8)	C00O	C00I	C00R	C013	15.7(14)
O005	C009	C00H	C00B	-174.5(7)	C00P	C00C	C00D	C008	-179.0(8)
O005	C009	C00Z	C010	174.0(8)	C00P	C00C	C00Y	C00X	176.9(9)
O006	C00E	C00J	C007	69.7(9)	C00P	C00G	C00V	C00W	113.3(9)
O006	C00E	C00S	C00O	-69.6(10)	C00P	C00V	C00W	C00A	85.4(10)
O006	C014	C018	O004	10.7(17)	C00P	C00V	C00W	C016	-94.8(13)
C007	C00I	C00O	C00S	55.8(9)	C00Q	C00L	C012	C011	2.2(16)
C007	C00I	C00R	C00N	-34.9(9)	C00R	C00I	C00O	C00S	179.7(7)
C007	C00I	C00R	C013	143.3(10)	C00R	C00N	C00T	C00F	155.5(7)
C008	C00K	C00X	C00Y	0.7(16)	C00R	C00N	C00T	C00U	-94.6(8)
C009	O003	C015	C017	-24.7(12)	C00R	C00N	C00U	C007	4.0(9)
C009	O005	C017	C015	-5.6(13)	C00R	C00N	C00U	C00T	113.6(8)
C009	C00Z	C010	C00A	-51.5(11)	C00S	C00E	C00J	C007	-53.1(10)
C00A	C00B	C00G	C00P	-88.4(8)	C00T	C00F	C00M	C00Q	-179.9(8)

C00A	C00B	C00G	C00V	-24.7(8)	C00T	C00F	C011	C012	179.2(9)
C00A	C00B	C00H	C009	55.9(9)	C00T	C00N	C00R	C00I	85.0(9)
C00B	C00A	C00W	C00V	-36.5(9)	C00T	C00N	C00R	C013	-93.1(13)
C00B	C00A	C00W	C016	143.6(11)	C00T	C00N	C00U	C007	-109.6(8)
C00B	C00A	C010	C00Z	55.8(9)	C00U	C007	C00I	C00O	170.1(7)
C00B	C00G	C00P	C00C	-154.6(8)	C00U	C007	C00I	C00R	36.5(8)
C00B	C00G	C00P	C00V	94.6(9)	C00U	C007	C00J	C00E	175.6(7)
C00B	C00G	C00V	C00P	-110.5(7)	C00U	C00N	C00R	C00I	19.4(9)
C00B	C00G	C00V	C00W	2.8(9)	C00U	C00N	C00R	C013	-158.7(11)
C00C	C00P	C00V	C00G	-109.2(9)	C00U	C00N	C00T	C00F	-109.9(9)
C00C	C00P	C00V	C00W	156.9(8)	C00V	C00G	C00P	C00C	110.8(9)
C00D	C008	C00K	Cl01	176.6(6)	C00W	C00A	C00B	C00G	37.4(8)
C00D	C008	C00K	C00X	-2.6(14)	C00W	C00A	C00B	C00H	168.3(7)
C00D	C00C	C00P	C00G	123.9(9)	C00W	C00A	C010	C00Z	177.7(8)
C00D	C00C	C00P	C00V	-164.5(8)	C00Y	C00C	C00D	C008	-0.6(13)
C00D	C00C	C00Y	C00X	-1.3(14)	C00Y	C00C	C00P	C00G	-54.3(12)
C00E	O004	C018	C014	1.4(16)	C00Y	C00C	C00P	C00V	17.4(14)
C00E	O006	C014	C018	-18.7(15)	C00Z	C009	C00H	C00B	-52.6(9)
C00F	C00M	C00Q	C00L	1.9(14)	C010	C00A	C00B	C00G	169.7(7)
C00F	C00T	C00U	C007	-154.7(8)	C010	C00A	C00B	C00H	-59.4(9)
C00F	C00T	C00U	C00N	109.2(9)	C010	C00A	C00W	C00V	-162.4(8)
C00F	C011	C012	C00L	-0.7(16)	C010	C00A	C00W	C016	17.7(15)
C00G	C00B	C00H	C009	176.8(7)	C011	C00F	C00M	C00Q	-0.5(14)
C00G	C00P	C00V	C00W	-93.9(9)	C011	C00F	C00T	C00N	21.7(13)
C00G	C00V	C00W	C00A	21.2(9)	C011	C00F	C00T	C00U	-48.5(12)
C00G	C00V	C00W	C016	-158.9(11)	C012	C00L	C00Q	C00M	-2.8(14)
C00H	C009	C00Z	C010	50.8(11)	C014	O006	C00E	O004	19.3(11)
C00H	C00B	C00G	C00P	146.8(8)	C014	O006	C00E	C00J	136.9(9)
C00H	C00B	C00G	C00V	-149.5(7)	C014	O006	C00E	C00S	-98.0(9)
C00I	C007	C00J	C00E	55.8(10)	C015	O003	C009	O005	21.7(10)
C00I	C007	C00U	C00N	-25.0(8)	C015	O003	C009	C00H	140.2(8)
C00I	C007	C00U	C00T	-89.0(8)	C015	O003	C009	C00Z	-94.9(9)
C00I	C00O	C00S	C00E	-52.0(11)	C017	O005	C009	O003	-9.7(11)
C00J	C007	C00I	C00O	-59.5(9)	C017	O005	C009	C00H	-126.7(9)
C00J	C007	C00I	C00R	166.9(8)	C017	O005	C009	C00Z	108.1(10)
C00J	C007	C00U	C00N	-148.9(8)	C018	O004	C00E	O006	-12.7(12)
C00J	C007	C00U	C00T	147.0(8)	C018	O004	C00E	C00J	-129.2(11)
C00J	C00E	C00S	C00O	52.2(10)	C018	O004	C00E	C00S	105.4(12)

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 2f.

Atom	*x*	*y*	*z*	U(eq)
H007	4204	9055	6450	68
H008	7470	7424	9710	76
H00G	6843	3801	8287	79
H00H	5871	5792	8519	73
H00J	6457	6826	9331	79
H00K	8194	5462	8661	77
H00L	7588	5687	8114	81
H00O	7083	6830	8236	81
H00I	6207	8070	6671	74
H00A	3198	7836	6741	82
H00B	4355	7321	6852	82
H00M	3239	8593	5618	86
H00N	6320	7221	6068	83
H00C	5579	10392	6697	86
H00D	6719	9879	6818	86
H00P	6044	5479	8969	85
H00Q	2632	7625	5231	82
H00E	5713	8800	7133	90
H00F	5254	10062	7157	90
H00T	4490	8903	5996	81
H00U	4522	6737	6304	79
H00V	7685	3618	8886	88
H00X	9932	5181	9537	95
H00Y	8886	4489	9169	98
H00R	6078	4374	7822	93
H00S	4817	4846	7810	93
H01C	4531	4460	8270	91
H01D	5028	3333	8139	91
H011	5333	5988	5806	91
H012	4701	5012	5424	102
H01A	1957	10478	7073	129
H01B	3097	11012	7192	129
H015	3837	7604	7836	117
H017	5577	7848	7515	128
H018	2362	9388	7489	170

Experimental

A suitable crystal was selected on a **New Gemini, Dual, Cu at zero, EosS2** diffractometer. The crystal was kept at 292.23(10) K during data collection. Using Olex2 [1], the structure was solved with the ShelXT [2] structure solution program using Direct Methods and refined with the ShelXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.
3. Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.

Crystal structure determination of 2f

Crystal Data for $C_{38}H_{35}Cl_2O_4$ (M =626.56): tetragonal, space group $P4_32_12$ (no. 96), a = 11.6351(6) Å, c = 48.952(3) Å, V = 6626.9(8) Å^3, Z = 8, T = 292.23(10) K, μ(CuKα) = 2.069 mm^{-1}, *Dcalc* = 1.256 g/mm^3, 19825 reflections measured (9.336 ≤ 2Θ ≤ 146.212), 6436 unique (R_{int} = 0.0740, R_{sigma} = 0.0605) which were used in all calculations. The final R_1 was 0.0954 (I > 2σ(I)) and wR_2 was 0.2926 (all data).

Refinement model description

Number of restraints - 0, number of constraints - unknown.

Details:

Others

Fixed Uiso: H007(0.068) H008(0.076) H00G(0.079) H00H(0.073) H00J(0.079) H00K(0.077) H00L(0.081) H00O(0.081) H00I(0.074) H00A(0.082) H00B(0.082) H00M(0.086) H00N(0.083) H00C(0.086) H00D(0.086) H00P(0.085) H00Q(0.082) H00E(0.09) H00F(0.09) H00T(0.081) H00U(0.079) H00V(0.088) H00X(0.095) H00Y(0.098) H00R(0.093) H00S(0.093) H01C(0.091) H01D(0.091) H011(0.091) H012(0.102) H01A(0.129) H01B(0.129) H015(0.117) H017(0.128) H018(0.17)

Fixed X: H007(0.4204) H008(0.747) H00G(0.6843) H00H(0.5871) H00J(0.6457) H00K(0.8194) H00L(0.7588) H00O(0.7083) H00I(0.6207) H00A(0.3198) H00B(0.4355) H00M(0.3239) H00N(0.632) H00C(0.5579) H00D(0.6719) H00P(0.6044) H00Q(0.2632) H00E(0.5713) H00F(0.5254) H00T(0.449) H00U(0.4522) H00V(0.7685) H00X(0.9932) H00Y(0.8886) H00R(0.6078) H00S(0.4817) H01C(0.4531) H01D(0.5028) H011(0.5333) H012(0.4701) H01A(0.1957) H01B(0.3097) H015(0.3837) H017(0.5577) H018(0.2362)

Fixed Y: H007(0.9055) H008(0.7424) H00G(0.3801) H00H(0.5792) H00J(0.6826) H00K(0.5462) H00L(0.5687) H00O(0.683) H00I(0.807) H00A(0.7836) H00B(0.7321) H00M(0.8593) H00N(0.7221) H00C(1.0392) H00D(0.9879) H00P(0.5479) H00Q(0.7625) H00E(0.88) H00F(1.0062) H00T(0.8903) H00U(0.6737) H00V(0.3618) H00X(0.5181) H00Y(0.4489) H00R(0.4374) H00S(0.4846) H01C(0.446) H01D(0.3333) H011(0.5988) H012(0.5012) H01A(1.0478) H01B(1.1012) H015(0.7604) H017(0.7848) H018(0.9388)

Fixed Z: H007(0.645) H008(0.971) H00G(0.8287) H00H(0.8519) H00J(0.9331) H00K(0.8661) H00L(0.8114) H00O(0.8236) H00I(0.6671) H00A(0.6741) H00B(0.6852) H00M(0.5618) H00N(0.6068) H00C(0.6697) H00D(0.6818) H00P(0.8969) H00Q(0.5231) H00E(0.7133) H00F(0.7157) H00T(0.5996) H00U(0.6304) H00V(0.8886) H00X(0.9537) H00Y(0.9169) H00R(0.7822) H00S(0.781) H01C(0.827) H01D(0.8139) H011(0.5806) H012(0.5424) H01A(0.7073) H01B(0.7192) H015(0.7836) H017(0.7515) H018(0.7489)

Computational Part

1. Models and Computational Details

In order to obtain insightful information on the mechanism of the Pd-catalyzed reaction, the DFT calculation with the emphasis on the diastereoselectivity of the transformation from **1a** to **2a** was performed at the M06(PCM, DMF)//M06/6-31+G**, LanL2DZ level.

M06[1] method combined with the Lanl2DZ basis set[2] for Pd and 6-31+G** basis set[3] for the rest atoms was employed in the gas-phase simulation. To take the entropy effects in solvents into account, single-point self-consistent reaction field (SCRF) calculations based on the polarized continuum model (PCM)[4] were carried out on the gas-phase optimized geometries for all species in the above system. The free energy was calculated at the same level and added to the gas-phase free energy to obtain the Gibbs energy in DMF (G_{solv}) at 298.15 K, with *radii*=UAHF. Unless otherwise stated, the G_{solv} is used in the discussion and the energy curves refer to the G_{solv} scale. All calculations were performed with the Gaussian 09 programs.[5]

Since dba might participate in the reaction by coordination to Pd-end, this ligand is initially considered in theoretical simulation. The calculation, however, failed to locate a converged result under dba involved. The dba moiety is liable to leave the Pd-end in M06 geometric optimization. Therefore, combined with the experimental findings, it is reasonable to consider that dba has no or little impact on the reaction mechanism and the following calculation will focus on the interaction between Pd and the substrate.

2. Reaction Mechanism

The schematic reaction path is shown in Figure S1 and the energies of various species are summarized in Table S3.

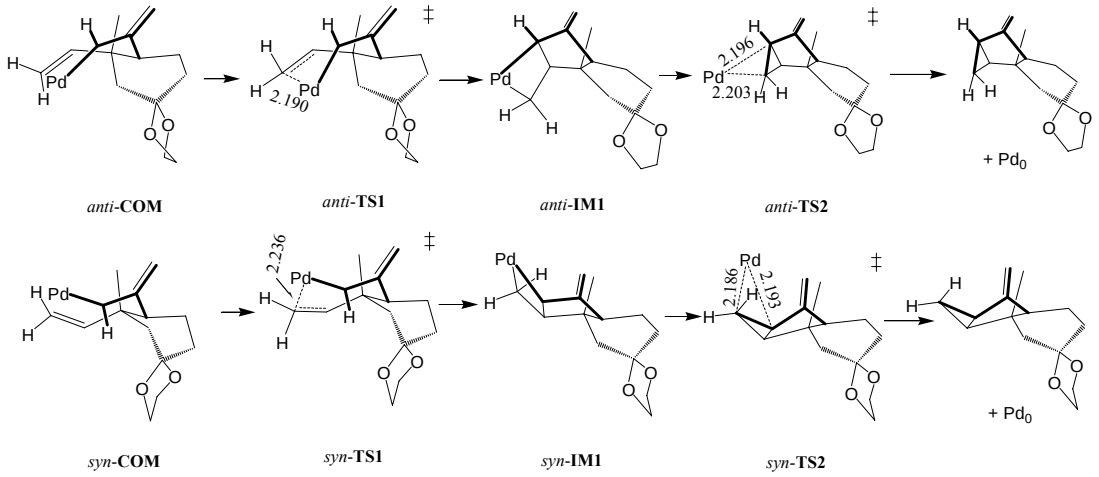


Fig. S1. Schematic structures along the reaction paths obtained by the DFT calculations. (Selected bond lengths are marked in Å)

Table S3. Total and realtvie Gibbs free energis for the various species calcualted at the M06(PCM, DMF)//M06/6-31+G**, LanL2DZ level

Species	ZPG(a.u)	G(a.u.)	ΔG(kJ/mol)
syn-COM	0.268068	-822.1834551	0.0
syn-TS1	0.267329	-822.1768538	15.3
syn-IM	0.270918	-822.2305476	-116.1
syn-TS2	0.270204	-822.2105161	-65.4
syn-pro + Pd			-88.8
anti-COM	0.269326	-822.191593	-18.2
anti-TS1	0.266499	-822.1740559	20.5
anti-IM	0.271380	-822.2407182	-142.1
anti-TS2	0.270580	-822.2223676	-95.5
anti-pro + Pd			-110.0

As shown in Figure S1, the entire reaction can be generally divided into two subsequent stages: (1) the addition of Pd-end into the unsaturated bond of the substrate via a [2+2] cyclization; (2) the release of Pd accompanied by the construction of final products. The entire reaction mechanism could generated two products with different configuration (*syn- and anti-*), and this is originated from the initial step in which two conformations of the unsaturated bond adjacent to the tertiary CH_3 of the substrate are available.

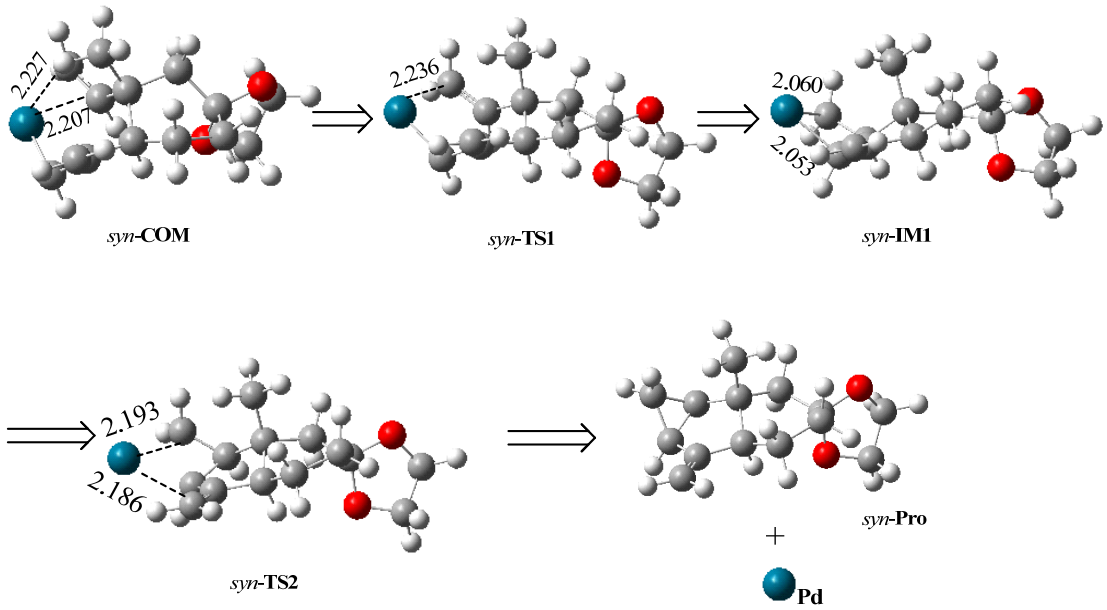


Fig. S3. 3D models along *syn*-path optimized at M06/6-31+G**, LanL2DZ level (Selected bond lengths are marked in Å)

To give a brief expression, *syn*-path is selected to illustrate the reaction mechanism. As shown in 3D model in Figure S2, *syn*-path is initialed form *syn*-**COM** species. This species is featured by the shorter distance of Pd and unsaturated C=C bond (2.227 and 2.207 Å), which indicated that the η^2-type Pd···C=C structure forms in *syn*-**COM**. From *syn*-**COM**, the addition of Pd-end to the unsaturated bond occurs via *syn*-**TS1** and leads to the formation of *syn*-**IM1**. As shown in Figure S2, an obvious geometric property of *syn*-**TS1** is the almost parallel Pd−C and C=C bond. As a result, 2+2 cyclization takes place and generates the *syn*-**IM1** with Pd-containing four-membered ring. The Gibbs free energy barrier in this step is calculated to be 15.3 kJ/mol in DMF.

Form *syn*-**I**M1, the reaction underdoes the release of Pd and yields the final product via *syn*-**TS2**. As shown in Figure S2, the Pd-containing ring is obviously distorted and the corresponding Pd−C bonds are also remarkably stretched (2.186 and 2.193 Å). Consequently, final product of *syn*-**Pro** results by the recovery of Pd(0) species. DFT calculation places the Gibbs free energy barrier in this step to be 50.7 kJ/mol in DMF.

NBO analysis along *syn*-path in Figure S3 indicates that the positive charge at Pd atom gradually decreases from 0.27 to 0.0 along the reaction path, identifying the practical catalyst should be Pd(0).

3. Distribution of Products

PCM calculation predicts that two summits emerge along the energy-surface at **TS1** and **TS2**, respectively. Therefore, the system must successively overcome these two energy summits to complete the reaction. It should be noted that, according to Curtin-Hammett principle,[6] the evolution of the most stable intermediate **IM** is vital for the distribution of the final product. Here, along the two paths, the reverse energy barrier via **TS1** from **IM** to **COM** is much greater than the forward one via **TS2** to the product, meaning that the first reaction step should be irreversible and account for the distribution and the diastereoselectivity of final products.

As shown in Figure S3, the *syn*-**TS1** to *syn*-configuration products is 5.2kJ/mol lower than *anti*-**TS1** in Gibbs free energies. According to Boltzmann distribution, the calculation predicts theoretical ratio of product in *syn*-configuration should be ca. 89%, according well with the experimental result (>20:1 dr).

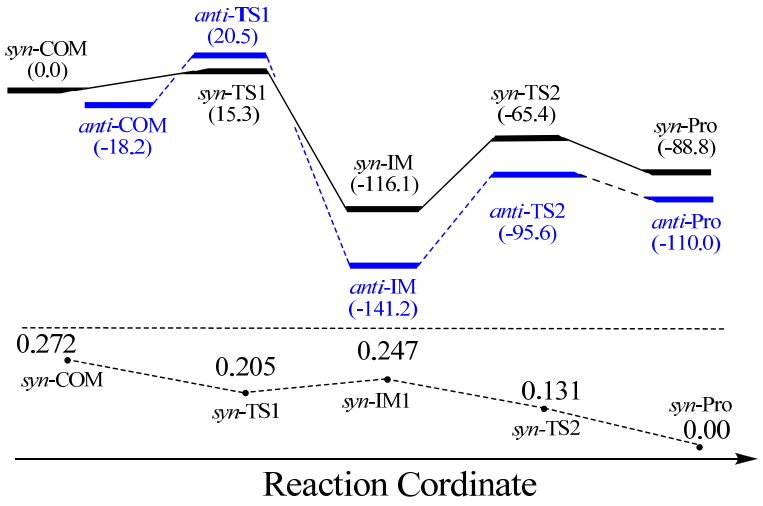


Fig. S3. Potential Gibbs energy surface calculated at the M06/6-31+G**,Lanl2DZ level in DMF. Relative Gibbs energies in kJ/mol are listed in parentheses. The lower part shows the evolution of the positive charge accumulated at Pd center along the reaction *syn*-path

It should be noted that, the curve of *anti*-path is generally lower than *syn*-path in Gibbs free energies. This could be explained by the reason that *syn*-configuration suffers from the hindrance between reaction site and CH_3 of substrate. However, *syn*-**TS1** is unexpected lower than its completing *anti*-**TS1** on the energy surface. Molecular orbital analysis predicts that there might exists remarkeble interaction of the *d* orbital of Pd and π orbtial of double bond in *syn*-**TS1** (in Figure S4). This orbital rearrangement could make thte *syn*-**TS1** more stable and therefore the *syn*-**Pro** becomes the major product.

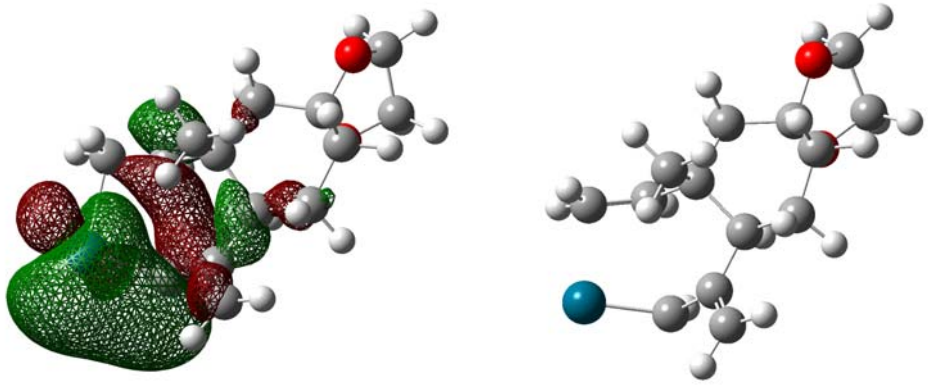


Fig. S4. Visualization of HOMO in *syn*-**TS1** (orbital in the left, and the corresponding skeleton structure in the right). The overlap of MO could be ascribed as the remarkble interaction of the d orbital of Pd and π orbtial of double bond.

Ref.

1 Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.*, 2008, 120, 215.

2 M. Dupuis, J. Rys, H.-F. King, *J. Chem. Phys.*, 1976, 65, 111.

3 G.-A. Petersson, A. Bennett, T.-G. Tensfeldt, M.-A. Al-Laham, W.-A. Shirley, J. Mantzaris, *J. Chem. Phys.*, 1988, 89, 2193.

4 M. Cossi, G. Scalmani, N. Rega, V. Barone, *J. Chem. Phys*., 2002, 117, 43.

5 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant,

S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, 2009. *Gaussian 09* (Revision A.02).

6 (a) J. I. Seeman, *J. Chem. Educ*., 1986, **63**, 42; (b) J. I. Seeman, *Chem. Rev*., 1983, **83**, 84.

M06-optimized orientation of various species

syn-COM

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	46	0	2.618068	-0.752686	-0.241833
2	6	0	2.150130	0.869175	-1.228554
3	6	0	0.495846	-1.137799	0.227118
4	6	0	1.281792	1.806739	-0.525578
5	6	0	-0.113476	1.243944	-0.289999
6	6	0	-0.110201	0.126980	0.814350
7	6	0	-1.200977	2.276281	-0.002218
8	6	0	-2.592696	1.649665	-0.162588
9	6	0	-2.610830	0.158237	0.162652
10	6	0	-1.582718	-0.181532	1.222250
11	8	0	-3.920536	-0.189326	0.594076
12	6	0	-4.307090	-1.365172	-0.090709
13	6	0	-3.589599	-1.197890	-1.410935
14	8	0	-2.356377	-0.643950	-0.995055
15	1	0	-1.094510	3.130080	-0.681601
16	1	0	-1.082442	2.681019	1.013942
17	1	0	-2.964333	1.768054	-1.189700
18	1	0	-3.316728	2.139238	0.499994
19	1	0	-1.690245	-1.237327	1.506797
20	1	0	-1.846202	0.415021	2.107853
21	1	0	-5.398609	-1.382961	-0.161648
22	1	0	-3.960285	-2.267352	0.439759
23	1	0	-4.132656	-0.503857	-2.074028
24	1	0	-3.390301	-2.130579	-1.947246
25	6	0	0.626513	0.576578	2.074588
26	1	0	0.231495	1.532752	2.439529
27	1	0	0.490109	-0.159217	2.877998

28	1	0	1.701220	0.701846	1.896537
29	1	0	-0.405166	0.741680	-1.227740
30	6	0	1.684106	3.025643	-0.129847
31	1	0	2.708690	3.351517	-0.292925
32	1	0	0.998860	3.739062	0.322837
33	6	0	1.250172	-2.091594	0.896960
34	1	0	1.757667	0.722140	-2.254166
35	1	0	0.036298	-1.435354	-0.720006
36	1	0	1.513124	-1.977349	1.949005
37	1	0	1.342378	-3.094178	0.482043

syn-**TS1**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	46	0	3.302276	-0.356969	-0.206738
2	6	0	1.974248	0.768969	-1.119669
3	6	0	0.651555	-1.280615	-0.122861
4	6	0	0.996135	1.552838	-0.367008
5	6	0	-0.395739	0.979429	-0.202976
6	6	0	-0.310878	-0.366264	0.585772
7	6	0	-1.431225	1.932098	0.399539
8	6	0	-2.723245	1.235588	0.854027
9	6	0	-2.885904	-0.134824	0.231542
10	6	0	-1.710210	-1.052388	0.548895
11	8	0	-4.093536	-0.720795	0.709664
12	6	0	-4.878806	-1.102854	-0.404043
13	6	0	-4.416341	-0.131820	-1.468130
14	8	0	-3.034514	-0.032614	-1.184022
15	1	0	-1.660990	2.697018	-0.353055
16	1	0	-0.992765	2.466378	1.253005
17	1	0	-3.608009	1.836326	0.608183
18	1	0	-2.743419	1.094741	1.943555
19	1	0	-1.736454	-1.866758	-0.187638
20	1	0	-1.911952	-1.505260	1.528270
21	1	0	-5.936258	-1.011650	-0.136552
22	1	0	-4.665882	-2.144556	-0.694379
23	1	0	-4.915589	0.845929	-1.364278
24	1	0	-4.535530	-0.489302	-2.495076
25	6	0	0.111256	-0.109728	2.031871
26	1	0	-0.620712	0.519409	2.550587
27	1	0	0.176083	-1.051608	2.591055

28	1	0	1.083637	0.394798	2.087170
29	1	0	-0.736637	0.706884	-1.215573
30	6	0	1.372651	2.771131	0.066886
31	1	0	2.401448	3.093233	-0.073805
32	1	0	0.678028	3.483456	0.508343
33	6	0	1.773680	-1.872812	0.397920
34	1	0	1.519240	0.325422	-2.023573
35	1	0	0.352466	-1.556479	-1.138019
36	1	0	1.979230	-1.818674	1.469733
37	1	0	2.230708	-2.703960	-0.143743

syn-**IM**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	46	0	3.280401	-0.281509	0.036482
2	6	0	1.643593	0.340316	-1.035381
3	6	0	0.784169	-0.901364	-0.780046
4	6	0	0.944995	1.516227	-0.459994
5	6	0	-0.456027	1.044126	-0.182520
6	6	0	-0.278802	-0.423789	0.255201
7	6	0	-1.375709	1.847972	0.722107
8	6	0	-2.595874	1.012138	1.156697
9	6	0	-2.843340	-0.194383	0.260311
10	6	0	-1.639435	-1.139822	0.154925
11	8	0	-3.974736	-0.901442	0.763185
12	6	0	-4.915301	-1.045736	-0.283227
13	6	0	-4.616030	0.158864	-1.148115
14	8	0	-3.208547	0.238985	-1.052610
15	1	0	-1.708076	2.748362	0.189468
16	1	0	-0.823520	2.198640	1.605963
17	1	0	-3.512430	1.615603	1.163539
18	1	0	-2.477479	0.631529	2.179974
19	1	0	-1.742585	-1.678773	-0.797139
20	1	0	-1.743979	-1.880371	0.959337
21	1	0	-5.921734	-1.055289	0.147304
22	1	0	-4.747504	-1.985095	-0.835345
23	1	0	-5.096773	1.068269	-0.749974
24	1	0	-4.886993	0.042014	-2.201745
25	6	0	0.225340	-0.494446	1.700485
26	1	0	-0.522320	-0.105060	2.400184
27	1	0	0.418513	-1.532475	1.997190

28	1	0	1.151483	0.075968	1.846394
29	1	0	-0.935748	0.990649	-1.177632
30	6	0	1.430011	2.753982	-0.296522
31	1	0	2.461485	2.992406	-0.551845
32	1	0	0.814560	3.566890	0.084674
33	6	0	1.918251	-1.788395	-0.310014
34	1	0	2.068746	0.446932	-2.038971
35	1	0	0.264531	-1.274766	-1.677682
36	1	0	1.810598	-2.295462	0.653117
37	1	0	2.341983	-2.435069	-1.083009

syn-**TS2**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	46	0	3.605423	-0.149897	-0.119160
2	6	0	1.545951	-0.039463	-0.863511
3	6	0	0.612027	-1.167608	-0.493527
4	6	0	0.931125	1.219471	-0.318381
5	6	0	-0.520097	0.888176	-0.112954
6	6	0	-0.491098	-0.562767	0.408487
7	6	0	-1.424710	1.803259	0.692197
8	6	0	-2.736870	1.085039	1.067314
9	6	0	-3.020201	-0.142175	0.209533
10	6	0	-1.885871	-1.179130	0.206352
11	8	0	-4.225117	-0.743450	0.677740
12	6	0	-5.116420	-0.871021	-0.413323
13	6	0	-4.685741	0.268435	-1.310395
14	8	0	-3.282825	0.255714	-1.138228
15	1	0	-1.643952	2.704936	0.105819
16	1	0	-0.906879	2.143892	1.600494
17	1	0	-3.599915	1.756609	0.976553
18	1	0	-2.725716	0.751260	2.113037
19	1	0	-1.952881	-1.715127	-0.750531
20	1	0	-2.106006	-1.903501	1.001954
21	1	0	-6.142252	-0.790608	-0.039836
22	1	0	-4.987489	-1.844747	-0.914017
23	1	0	-5.120845	1.226144	-0.978937
24	1	0	-4.906978	0.121521	-2.371824
25	6	0	-0.117913	-0.608813	1.892639
26	1	0	-0.919188	-0.199261	2.516837
27	1	0	0.041516	-1.645159	2.217152

28	1	0	0.791574	-0.034462	2.112279
29	1	0	-0.942540	0.813815	-1.132283
30	6	0	1.508507	2.410232	-0.139742
31	1	0	2.572137	2.556943	-0.319208
32	1	0	0.931252	3.275311	0.183574
33	6	0	1.936523	-1.548912	0.068894
34	1	0	1.892937	-0.016146	-1.900754
35	1	0	0.238868	-1.797155	-1.305049
36	1	0	2.038542	-1.585066	1.154706
37	1	0	2.450639	-2.350371	-0.466175

---

anti-**COM**

Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.696296	-1.811987	1.165337
2	6	0	2.848732	1.442029	-0.253499
3	6	0	1.351761	-0.467117	1.271159
4	6	0	1.550824	2.078196	-0.193331
5	6	0	0.355560	1.183742	-0.433492
6	6	0	0.079188	0.235290	0.785756
7	6	0	-0.926018	1.872700	-0.893148
8	6	0	-2.231814	-0.208209	-0.277069
9	6	0	-0.962977	-0.795231	0.330372
10	8	0	-3.077146	0.381075	0.708687
11	8	0	-2.976522	-1.292011	-0.830049
12	1	0	2.416446	-2.238886	1.861391
13	1	0	1.077807	-2.523581	0.619108
14	6	0	-0.421713	1.028418	2.002301
15	1	0	-1.386988	1.508442	1.824853
16	1	0	-0.550832	0.352308	2.858516
17	1	0	0.309442	1.796169	2.287126
18	1	0	0.666468	0.511639	-1.252792
19	6	0	1.464337	3.422523	-0.042015
20	1	0	2.352605	4.011804	0.179695
21	1	0	0.539956	3.975168	-0.202057
22	46	0	2.881642	-0.538819	-0.255225
23	1	0	1.866957	0.097916	2.056188
24	1	0	3.597411	2.018418	0.317814
25	6	0	-4.301314	-1.215691	-0.342089
26	6	0	-4.102881	-0.547155	1.000418
27	1	0	-0.696117	2.543884	-1.731423

28	1	0	-1.358038	2.498953	-0.099235
29	1	0	-1.251275	-1.446924	1.169104
30	1	0	-0.527381	-1.442554	-0.445473
31	1	0	-4.713557	-2.228311	-0.289085
32	1	0	-4.932551	-0.600607	-1.004259
33	1	0	-3.777355	-1.272350	1.765095
34	1	0	-4.973253	0.001754	1.372028
35	6	0	-1.938072	0.827131	-1.347742
36	1	0	-1.536483	0.283353	-2.215102
37	1	0	-2.889046	1.281320	-1.654963

anti-**TS1**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.155026	-1.157288	1.488387
2	6	0	2.486373	0.761846	-0.309999
3	6	0	0.905284	0.187545	1.666360
4	6	0	1.386897	1.629184	-0.671925
5	6	0	-0.000431	1.065194	-0.484816
6	6	0	-0.257430	0.939522	1.054694
7	6	0	-1.128182	1.795067	-1.208286
8	6	0	-2.525382	1.333094	-0.759588
9	6	0	-2.492331	0.057982	0.060809
10	6	0	-1.605851	0.197348	1.289310
11	8	0	-3.822522	-0.259131	0.465181
12	6	0	-4.115089	-1.581006	0.054361
13	6	0	-3.199599	-1.755373	-1.137822
14	8	0	-2.047542	-1.050566	-0.719222
15	1	0	1.854770	-1.654918	2.165275
16	1	0	0.378890	-1.788815	1.041104
17	1	0	-1.001677	1.627708	-2.285245
18	1	0	-1.044930	2.879045	-1.058236
19	1	0	-3.190740	1.174508	-1.617621
20	1	0	-3.013887	2.092258	-0.132781
21	1	0	-1.456070	-0.808806	1.699160
22	1	0	-2.196155	0.751827	2.031044
23	1	0	-5.182099	-1.647991	-0.180817
24	1	0	-3.873300	-2.302200	0.852068
25	1	0	-3.632834	-1.306499	-2.047050
26	1	0	-2.917031	-2.790801	-1.349459
27	6	0	-0.322689	2.323474	1.706413
28	1	0	-1.158819	2.915322	1.314327

29	1	0	-0.468394	2.220181	2.790028
30	1	0	0.600640	2.890426	1.537178
31	1	0	0.028178	0.034840	-0.870580
32	6	0	1.645020	2.859585	-1.167287
33	1	0	2.665760	3.231820	-1.237214
34	1	0	0.866917	3.490280	-1.588777
35	46	0	2.471574	-1.194054	-0.260694
36	1	0	1.546865	0.744704	2.352388
37	1	0	3.256056	1.235553	0.318683

anti-**IM1**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.227940	-1.262460	1.071233
2	6	0	2.011644	0.799171	0.507004
3	6	0	0.973090	0.182707	1.451418
4	6	0	1.283845	1.459341	-0.597552
5	6	0	-0.142751	0.986627	-0.511245
6	6	0	-0.362978	0.816390	1.008450
7	6	0	-1.253233	1.772041	-1.190349
8	6	0	-2.636609	1.341921	-0.657012
9	6	0	-2.613911	0.012109	0.086529
10	6	0	-1.639122	-0.000062	1.266514
11	8	0	-3.935446	-0.264548	0.542615
12	6	0	-4.284558	-1.569175	0.124481
13	6	0	-3.481273	-1.716384	-1.148739
14	8	0	-2.280312	-1.053114	-0.808653
15	1	0	1.623592	-1.903662	1.863396
16	1	0	0.456688	-1.748752	0.463019
17	1	0	-1.200865	1.608250	-2.274429
18	1	0	-1.111620	2.851121	-1.035320
19	1	0	-3.372046	1.256609	-1.467008
20	1	0	-3.040227	2.086245	0.043294
21	1	0	-1.416005	-1.051050	1.497198
22	1	0	-2.183267	0.410607	2.127556
23	1	0	-5.369203	-1.614552	-0.014637
24	1	0	-3.982024	-2.318443	0.874678
25	1	0	-3.982675	-1.222695	-1.998157
26	1	0	-3.243778	-2.749092	-1.422057
27	6	0	-0.467694	2.181505	1.697486
28	1	0	-1.357553	2.738742	1.381097

29	1	0	-0.535475	2.045701	2.785026
30	1	0	0.407573	2.810495	1.490667
31	1	0	-0.156891	-0.025889	-0.945471
32	6	0	1.783892	2.372455	-1.443233
33	1	0	2.833843	2.658606	-1.406605
34	1	0	1.163652	2.859071	-2.193253
35	46	0	2.776756	-0.958113	-0.240715
36	1	0	1.180436	0.370001	2.514047
37	1	0	2.891424	1.296083	0.928263

---

anti-**TS2**

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.329659	-0.796468	1.288433
2	6	0	1.881345	0.797735	0.611036
3	6	0	0.776169	0.547118	1.603687
4	6	0	1.241429	1.269382	-0.648378
5	6	0	-0.197562	0.848335	-0.564785
6	6	0	-0.525046	0.999668	0.936553
7	6	0	-1.253716	1.474592	-1.458276
8	6	0	-2.667941	1.132058	-0.940739
9	6	0	-2.693827	-0.029905	0.047787
10	6	0	-1.783648	0.183435	1.264004
11	8	0	-4.040848	-0.217833	0.473696
12	6	0	-4.395299	-1.569412	0.254748
13	6	0	-3.508849	-1.945686	-0.911818
14	8	0	-2.319511	-1.245143	-0.605603
15	1	0	1.904037	-1.260565	2.091568
16	1	0	0.688657	-1.477040	0.719355
17	1	0	-1.127138	1.103595	-2.483350
18	1	0	-1.124851	2.564995	-1.505890
19	1	0	-3.344073	0.878215	-1.766834
20	1	0	-3.125478	1.990655	-0.431018
21	1	0	-1.527153	-0.809662	1.658907
22	1	0	-2.384023	0.693896	2.028835
23	1	0	-5.468024	-1.621198	0.043235
24	1	0	-4.169333	-2.183984	1.141636
25	1	0	-3.937128	-1.604155	-1.869000
26	1	0	-3.275632	-3.012290	-0.982283
27	6	0	-0.718073	2.471041	1.318816

28	1	0	-1.625277	2.905104	0.883517
29	1	0	-0.807598	2.560801	2.409726
30	1	0	0.134939	3.083414	0.998360
31	1	0	-0.210515	-0.231805	-0.780600
32	6	0	1.812485	2.032987	-1.587307
33	1	0	2.868318	2.293219	-1.539403
34	1	0	1.244046	2.410770	-2.434735
35	46	0	2.970740	-0.939791	-0.173853
36	1	0	0.925844	0.896588	2.628259
37	1	0	2.806468	1.264345	0.959624
