Supporting Information for

Non-Cp Titanium Alkoxide-Based Homolytic Ring-Opening of Epoxides by An Intramolecular Hydrogen Abstraction in β-Titanoxy Radical Intermediates

Tsuyoshi Kawaji, Noriaki Shohji, Kenji Miyashita, and Sentaro Okamoto*

Department of Material & Life Chemistry, Kanagawa University, 3-27-1 Rokkakubashi, Kanagawa-ku, Yokohama 221-8686, Japan

E-mail: okamos10@kanagawa-u.ac.jp

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General. NMR spectra were recorded in $CDCl_3$ at 600 and 500 MHz for ^1H and 150 and 125 MHz for ^{13}C, respectively, on JEOL JNM-ECA600 and 500 spectrometers. Chemical shifts are reported in parts per million (ppm, δ) relative to Me_4Si (δ 0.00), residual $CHCl_3$ (δ 7.26 for ^1H NMR), or a center peak of $CDCl_3$ (δ 77.0 for ^{13}C NMR). IR spectra were recorded on an FT-IR spectrometer (JASCO FT/IR-4100). High-resolution mass spectra (HR-MS) were measured on JEOL Accu TOF T-100 equipped with ESI ionization. All reactions sensitive to oxygen and/or moisture were performed under an argon atmosphere.

Dry solvents was purchased from Kanto Chemical Co., Inc. and used as received. $Ti(O\text{-}i\text{-}Pr)_4$ was distilled and stored under an Ar atmosphere. Me_3SiCl was stored over CaH_2 to remove HCl. Ti(4-*tert*-butylcyclohexan-1-yloxy)$_4$ (**4**)[1] was prepared by azeotropic removal of *i*-PrOH form a 1:4 mixture of $Ti(O\text{-}i\text{-}Pr)_4$ and 4-*tert*-butylcyclohexan-1-ol in toluene followed by concentration in *vacuo*.

Room temperature refers to 20-25 °C.

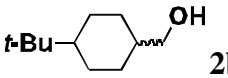
General Procedure for Reductive Cleavage of Epoxides Mediated by $Ti(O\text{-}i\text{-}Pr)_4/Me_3SiCl/Mg$. To a mixture of Mg powder (73 mg, 3.0 mmol), $Ti(O\text{-}i\text{-}Pr)_4$ (356 μL, 1.2 mmol) and epoxide **1** (1.0 mmol) in THF (5 mL) was added Me_3SiCl (153 μL, 1.2 mmol) at room temperature. The resulting mixture was stirred at ambient temperature. After completion of the reaction checked by TLC analysis, aqueous saturate $NaHCO_3$ (0.5 mL), NaF (1 g) and Celite (1 g) were sequentially added. After being stirred for 1 h, the mixture was filtered through a pad of Celite with ether. The filtrate was washed with 0.5 M aqueous HCl and saturated aqueous $NaHCO_3$, dried over $MgSO_4$, concentrated *in vacuo* and chromatographed on silica gel to give the corresponding alcohol(s) **2, 2'** and alkene **3**.

General Procedure for Reductive Cleavage of Epoxide Mediated by $Cp_2TiCl_2/Zn/1,4\text{-Cyclohexadiene}$. To a solution of epoxide **1** (1.0 mmol) and 1,4-cyclohexadiene (10~18 mmol) in THF (30 mL) was added a solution of 1.2 mmol of Cp_2TiCl in THF (5 mL), which was prepared from Cp_2TiCl_2 and Mn powder, over 15 min at room temperature under an Ar atmosphere. The resulting mixture was stirred at room temperature for 40 min. The mixture was quenched with saturated aqueous KH_2PO_4, extracted ether, washed with saturated aqueous $NaHCO_3$ and brine, dried over Na_2SO_4 and filtered through a pad of Celite with ether. The filtrate was concentrated and chromatography on silica gel to give the alcohol.

1) Jaggers, B. G.; Ufton, K. F.; Wagner, H. R. Brit. (1974), GB 1365064 A 19740829.

Characterization of Products

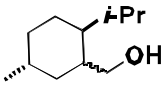
The structure of the products **2a**, **2a'**, **2b**, **2c**, **2d**, **2d"**, **2g**, **2g'**, **2h**, **2i** and **3f** was confirmed by comparison of their spectroscopic data with those of commercially available authentic samples and/or with those reported.



2b[2] (a daistereomeric mixture)

For a major isomer: ^{1}H NMR ($CDCl_3$, 600 MHz) δ 3.44 (d, *J* = 5.7 Hz, 1.8H), 1.78-1.85 (m, 4H) 1.38-1.48 (m, 1H), 1.22-1.27 (m, 1H), 0.87-1.05 (m, 4H), 0.85 (s, 9H); ^{13}C NMR($CDCl_3$, 125 MHz) δ 68.8, 48.2, 40.5, 29.9, 27.4, 26.7, 22.0.

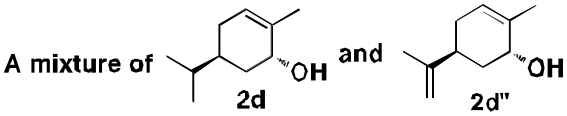
For a minor isomer (selected): ^{1}H NMR ($CDCl_3$, 600 MHz) δ 3.64 (d, *J* = 7.5 Hz, 0.2H), 0.83 (s, 9H, $C(CH_3)_3$).



2c[3] (a daistereomeric mixture)

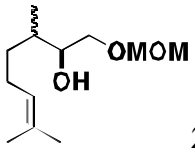
For a major isomer (selected): ^{1}H NMR ($CDCl_3$, 600 MHz) δ 3.63-3.69 (m, 2H), 0.77 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR($CDCl_3$, 125 MHz) δ 65.4, 46.8, 39.0, 38.1, 36.5, 32.5, 25.9, 24.1, 22.7, 21.4, 15.5.

For a minor isomer (selected): ^{1}H NMR ($CDCl_3$, 600 MHz) δ 3.52-3.56 (m, 2H); ^{13}C NMR($CDCl_3$, 125 MHz) δ 60.2, 43.7, 41.4, 35.7, 35.2, 29.5, 26.8, 26.2, 21.7, 20.9.



Alcohol 2d[2,4a]: ^{1}H NMR ($CDCl_3$, 600 MHz) δ5.57 (dd, *J* = 1.5, 6.6 Hz, 1H), 3.98 (br, 1H), 1.78 (s, 3H), 1.25-2.10 (m, 6H), 0.91 (d, *J* = 6.0 Hz, 3H), 0.89 (d, *J* = 6.6 Hz, 3H).

Alcohol 2d" [4b] (selected): ^{1}H NMR ($CDCl_3$, 600 MHz) δ5.59 (d, *J* = 5.4 Hz, 1H), 4.74 (m, 2H), 4.03 (br, 1H).



2e (a daistereomeric mixture) [new compound]

D.r. = 60:40. ^{1}H NMR ($CDCl_3$, 600 MHz, selected peaks for a major isomer) δ 5.10 (dd, *J* = 6.6, 7.8Hz, 1H), 4.69 (s, 2H), 3.38 (s, 3H), 3.42-3.68 (m, 3H), 2.50 and 2.39 (d, *J* = 3.6 Hz and d, *J* = 3.0 Hz, 1H, OH), 1.92-2.11 (m, 2H), 1.68 (s, 3H), 1.61 (s, 3H), 1.48-1.62 (m, 3H) 0.94 (d, *J* = 6.6 Hz, 3H), 0.91 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR($CDCl_3$, 125 MHz, measured for a mixture) δ 131.4, 124.5, 124.4, 96.9, 96.9, 74.3, 73.6, 71.4, 70.9, 55.3, 35.5, 35.2, 33.0, 32.4, 25.6, 25.5, 25.4,17.6, 15.0, 14.3; IR (neat, measured for a mixture) 3459, 2926, 1152, 1112, 1042 cm^{-1}. HR-MS: *m/z*= calcd For $C_{12}H_{24}NaO_2$ $[M+Na]^+$: 239.1623, found 239.1620.

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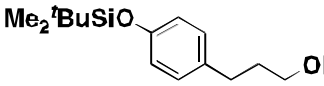
2) Jiménez, T.; Campaña, A. G.; Bazdi, B.; Paradas, M.; Arráez-Román, D.; Segura-Carretero, A.; Fernández-Gutiérrez, A.; Oltra, J. E.; Robles, R.; Justicia, J.; Cuerva, J. M. *Eur. J. Org. Chem.* **2010**, 4288.

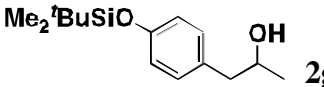
3) Torii, S.; Oie, T.; Tanaka, H.; White, J. D.; Furuta, T. *Tetrahedron Lett.* **1973**, 2471. Falorni, M.; Lardicci, L.; Giacomelli, G. *J. Org. Chem.* **1989**, *54*, 2383.

4) (a) Shull, B. K.; Sakai, T.; Nichols, J. B.; Koreeda, M. *J. Org. Chem.* **1997**, *62*, 8294. (b) Bermejo, F.; Sandoval, C. *J. Org. Chem.* **2004**, *69*, 5275.



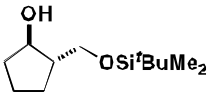
2g[5]

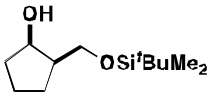
^{1}H NMR ($CDCl_3$, 500MHz) δ 7.04 (d, *J* = 8.0 Hz, 2H), 6.76 (d, *J* = 8.0 Hz, 2H), 3.66 (t, *J* = 6.5 Hz, 2H), 2.64 (t, *J* = 7.8 Hz, 2H), 1.82-1.90 (m, 2H), 0.98 (s, 9H), 0.18 (s, 6H).



2g'[6]

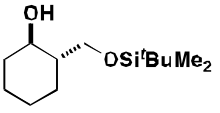
^{1}H NMR ($CDCl_3$, 500MHz) δ 7.06 (d, *J* = 8.0 Hz, 2H), 6.79 (d, *J* = 8.0 Hz, 2H), 3.93-4.01 (m, 1H), 2.73 (dd, *J* = 4.8, 13.5 Hz, 1H), 2.61 (dd, *J* = 8.0, 13.5 Hz, 1H), 1.23 (d, *J* = 6.5 Hz, 3H), 0.98 (s, 9H), 0.19 (s, 6H).

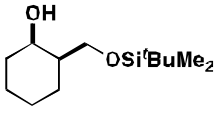


anti-**2h**[7] and 

syn-**2h**[7]

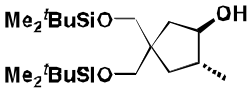
anti-**2h**[7]: ^{1}H-NMR ($CDCl_3$, 600 MHz) ™ 3.98 (dq, *J* = 1.7, 12.6 Hz, 1H), 3.80 (dd, *J* = 4.8, 9.6 Hz, 1H), 3.48 (t, *J* = 9.3 Hz, 1H) 2.56 (d, *J* = 1.8 Hz, 1H, O*H*), 1.99-1.91 (*m*, 2H), 1.80-1.69 (*m*, 2H), 1.63-1.54 (*m*, 2H), 1.20-1.12 (m, 1H), 0.90 (s, 9H), 0.07 (s, 6H); ^{13}C-NMR ($CDCl_3$, 150 MHz) ™ 78.20, 66.77, 49.20, 33.78, 25.83, 25.75, 21.54, 18.14, -5.53, -5.60.
syn-**2h**[7]: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.34 (brs, 1H), 3.92 (dd, *J* = 4.0, 10.0 Hz, 1H), 3.78 (dd, *J* = 7.0, 10.0 Hz, 1H), 3.17 (d, *J* = 2.5 Hz, 1H), 1.54-2.00 (m, 6H), 1.24-1.26 (m, 1H), 0.90 (s, 9H), 0.07 (s, 6H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 77.8, 63.6, 45.7, 35.0, 25.8, 25.5, 22.4, 18.1, -5.40, -5.43.
IR (neat, measured for a mixture of isomers) 3734, 2954, 2857, 1471, 1255, 838, 774, 671 cm^{-1}.

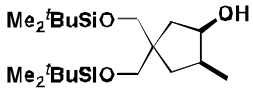


anti-**2i**[8] and 

syn-**2i**[8]

anti-**2i**[8]: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.35 (s, 1H), 3.72 (dd, *J* = 4.0, 10.0 Hz, 1H) 3.58 (t, *J* = 10.0 Hz, 1H), 3.46-3.50 (m, 1H), 1.95-2.00 (m, 1H), 1.52-1.73 (m, 4H), 1.18-1.27 (m, 4H), 0.90 (s, 9H), 0.09 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 76.0, 69.7, 45.5, 34.5, 26.8, 25.8, 25.1, 24.2, 18.1, -5.58, -5.68; IR (neat) 3366, 2929, 2857, 1739, 1449, 1255, 1106, 837, 776 cm^{-1}.
syn-**2i**[8]: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.12 (s, 1H), 3.81 (dd, *J* = 3.5, 10.0 Hz, 1H) 3.70-3.74 (m, 1H), 3.46-3.50 (m, 1H), 1.20-1.76 (m, 9H), 0.91 (s, 9H), 0.07 (s, 6H); IR (neat) 3445, 2929, 2857, 1471, 1255, 1106, 837, 776 cm^{-1}.



anti-**2j** and 

syn-**2j** [new compounds]

anti-**2j**: ^{1}H NMR ($CDCl_3$, 600 MHz) δ 3.66 (q, *J* = 6.3 Hz, 1H), 3.45 (s, 2H), 3.36 (s, 2H), 2.58 (br, 1H), 1.87-1.92 (m, 2H), 1.78-1.81 (m, 1H), 1.38-1.41 (m, 1H), 1.05-1.09 (m, 1H), 0.96 (d, *J* = 6.6Hz, 3H), 0.90 (s, 9H), 0.88 (s, 9H), 0.06 (s, 6H), 0.03 (s, 6H); ^{13}C NMR

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5) Cena, C.; Boschi, D.; Tron, G. C.; Chegaev, K.; Lazzarato, L.; Di Stilo, A.; Aragno, M.; Fruttero, R.; Gasco, A. *Bioorg. Med. Chem. Lett.* **2004**, *14*, 5971.
6) Nakajima, R.; Ono, M.; Aiso, S.; Akita, H. *Chem. Pharm. Bull.* **2005**, *53*, 684.
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8) Kanno, O.; Kawamoto, I. *Tetrahedron* **2000**, *56*, 5639. Vina, D.; Santana, L.; Uriarte, E.; Teran, C. *Tetrahedron* **2005**, *61*, 473.

($CDCl_3$, 150 MHz) δ 79.3, 68.4, 68.2, 47.1, 42.3, 40.3, 36.4, 25.9, 25.8, 18.4, 18.3, 18.2, -5.56.

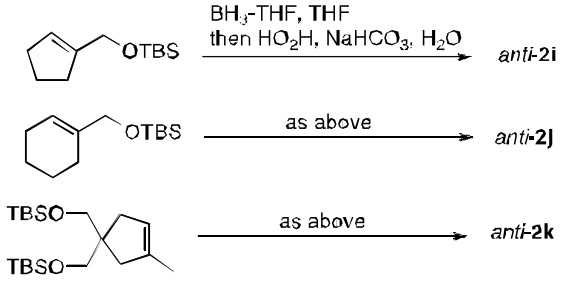
syn-**2j**: ^{1}H NMR ($CDCl_3$, 600 MHz) δ 3.80 (m, 1H), 3.47 (s, 2H), 3.34 (s, 2H), 1.77-1.92 (m, 2H), 1.69-1.72 (m, 1H), 1.50-1.54 (m, 1H), 1.34-1.39 (m, 1H), 1.01 (d, J = 6.0Hz, 3H), 0.93 (s, 9H), 0.88 (s, 9H), 0.10 (s, 6H), 0.02 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 76.0, 68.9, 68.7, 48.9, 42.2, 40.3, 35.3, 25.9, 25.8, 18.4, 18.2, 13.7, -5.57.

IR (neat, measured for a mixture of isomers) 3336, 2954, 2857, 1471, 1387, 1255, 1085, 837, 774 cm^{-1}.

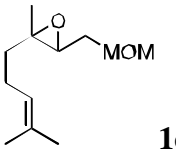
HR-MS: m/z= calcd For $C_{20}H_{44}NaO_3Si_2$ $[M+Na]^+$: 411.2727, found 411.2711.

Synthesis of Authentic Samples of *anti*-Stereoisomers for 2h, 2i and 2j

The authentic samples of *anti*-**2i**, -**2j** and -**2k** were prepared from the corresponding cyclic alkenes by hydroboration/oxidation method as illustrated below.

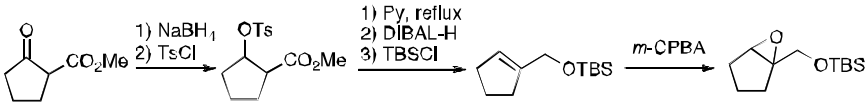


Synthesis of Epoxides



1e[9]

Epoxide 1e[9]: Epoxide **1e** was synthesized by epoxidation of geraniol with $VO(acac)_2$ catalyst/*t*-BuOOH in CH_2Cl_2 and then etheration with MOMCl/NaH/DMF. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.09 (t, *J* = 6.3Hz, 1H), 4.67 (q, *J* = 6.3 Hz, 2H), 3.60-3.72 (m, 2H), 3.39 (s, 3H), 2.98 (t, *J* = 5.5 Hz, 1H), 2.09 (q, *J* = 8.0 Hz, 2H), 1.69 (s, 3H), 1.61 (s, 3H), 1.42-2.10(m, 2H), 1.29 (s, 3H); ^{13}C NMR($CDCl_3$, 125 MHz,) δ 131.94, 123.37, 96.46, 66.29, 66.24, 60.93, 60.14, 55.20, 38.32, 25.58, 23.56, 17.55, 16.65; IR (Neat) 2928, 1154, 1108, 1044 cm^{-1}.



1h [new compound]

To methyl cyclopentanone-2-carboxylate (5.0 mL, 40 mmol) in MeOH (55 mL) was added portionwise $NaBH_4$ (1.51 g, 40 mmol). After 1 h, the mixture was quenched by addition of saturated aqueous NH_4Cl, extracted with AcOEt, washed with saturated aqueous $NaHCO_3$, dried over Na_2SO_4 and concentrated to give the alcohol (4.2g, 29 mmol). To the alcohol (4.2g, 29 mmol) in pyridine (150 mL) was added *p*-TsCl (8.3 g, 44 mmol). After 20 h, the mixture was quenched by addition of aqueous 1M HCl, extracted with AcOEt, washed with brine, dried over $MgSO_4$ and concentrated to give the tosylate (5.7 g, 19 mmol): ^{1}H NMR ($CDCl_3$, 500 MHz, a diastereomeric mixture) δ 7.79 and 7.76 (2d, *J* = 7.5 Hz and J = 8.5 Hz, total 2H), 7.34 (br s, 2H), 5.20 and 5.09 (2br s, total 1H) 3.60 and 3.51 (2s, total 3H), 2.97 and 2.86 (2br s, total 1H), 2.45 (s, 3H), 1.64-2.15 (m, 6H).

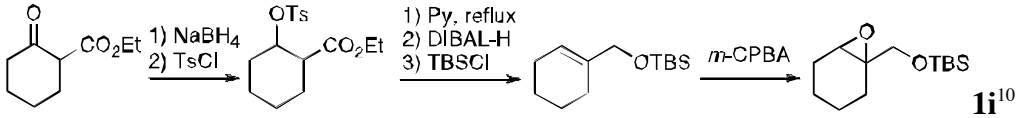
The tosylate in 95 mL of pyridine was heated to reflux. After being stirred for 36 h and then cooled to room temperature, the mixture was quenched by addition of aqueous 1M HCl, extracted with ether, washed with brine, dried over $MgSO_4$ and concentrated (>200 mmHg) to give methyl cyclopentene-2-carboxylate (18.9 mmol). To a solution of methyl cyclopentene-2-carboxylate in dry ether (52 mL) was added DIBAL (43.9 mmol, 1.02 M in ether, 43 mL) at -20 ºC. After 1.5 h, the mixture was quenched by careful addition of water (1.5 mL). After sequential addition of Celite and NaF, the mixture was filtered through a pad of Celite with ether and the filtrate was concentrated (>200 mmHg) to give the allylic alcohol (18.9 mmol). To a stirred solution of the allylic alcohol (18.9 mmol) in DMF (38 mL) were added imidazole (1.9g, 28.4 mmol) and *tert*-buthyldimethylsilyl chloride (4.3g, 28.4 mmol). After 12 h, the mixture was quenched by addition of saturated aqueous NH_4Cl, extracted with ether, washed with water, dried over $MgSO_4$ and concentrated to give the silyl ether (2.23g, 10.5 mmol): ^{1}H NMR ($CDCl_3$, 600 MHz) δ 5.58 (br s, 1H), 4.20 (s, 2H), 2.33 (br s, 2H), 2.27 (br s, 2H), 1.90 (q, *J* = 7.2 Hz, 2H), 0.20 (s, 9H), 0.07 (s, 6H).

m-Chloroperbenzoic acid (65 wt%, 3.3 g, 12.6 mmol) was added to a stirred solution of the silyl ether (2.23 g, 10.5 mmol) and $NaHCO_3$ (20 mg) in CH_2Cl_2 (26 mL). After 1 h, the mixture was quenched by addition of water, washed with aqueous 10% NaOH and brine, dried over $MgSO_4$ and concentrated to give cyclopentene oxide **1h** (2.02g, 8.8 mmol) . **Epoxide 1h**:^{1}H NMR ($CDCl_3$, 600 MHz) δ 3.90 (d, *J* = 12.0 Hz, 1H), 3.84 (d, *J* = 12.0 Hz, 1H), 3.36 (br s, 1H), 1.91-2.00 (m, 2H), 1.59-1.70 (m, 3H), 1.41-1.48 (m, 1H), 0.90 (s, 9H),

9) Mordini, A.; Pecchi, S.; Capozzi, G.; Capperucci, A.; Degl'Innocenti, A.; Reginato, G.; Ricci, A. *J. Org. Chem.* **1994**, *59*, 4784.

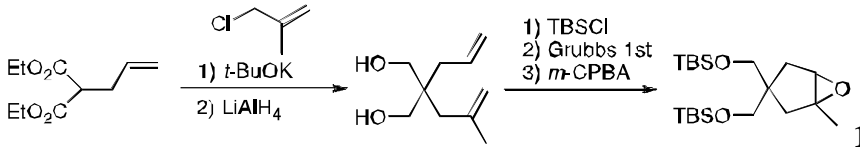
0.07 (s, 3H), 0.06 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 68.2, 63.5, 61.5, 27.3, 27.2, 25.9, 19.5, 18.4, -5.31, -5.33; IR (Neat) 2955, 2857, 1471, 1255, 1091, 838, 777 cm^{-1}.
HR-MS: *m/z*= calcd For $C_{13}H_{26}NaO_2Si$ $[M+Na]^+$: 265.1600, found 265.1610.

According to the scheme below with a similar procedure to that for preparation of **1h**, cyclohexene oxide derivative **1i** was synthesized from ethyl 2-cyclohexanonecarboxylate.



1i[10]

Tosylate Intermediate: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.77 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 5.17 (br s, 1H), 3.83-4.00 (m, 2H), 2.47-2.53 (m, 1H), 2.44 (s, 3H), 1.21-1.95 (m, 8H), 1.17 (t, *J* = 7.3 Hz, 3H).
Allyl Silyl Ether Intermediate: ^{1}H NMR ($CDCl_3$, 600 MHz) δ 5.65 (br s, 1H), 3.99 (s, 2H), 1.99-2.03 (m, 2H), 1.94 (br s, 2H), 1.56-1.66 (m, 4H), 0.91 (s, 9H), 0.06 (s, 6H).
Epoxide 1i[10]: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.61 (d, *J* = 11.5 Hz, 1H), 3.58 (d, *J* = 11.5 Hz, 1H), 3.09 (d, *J* = 2.0 Hz, 1H), 1.91-1.96 (m, 1H), 1.78-1.84 (m, 3H), 1.20-1.50 (m, 4H), 0.89 (s, 9H), 0.06 (s, 3H), 0.05 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 67.3, 60.1, 56.6, 25.9, 25.1, 24.6, 20.0, 19.8, 18.3, -5.30, -5.34; IR (Neat) 2935, 2857, 1471, 1255, 1095, 838, 777 cm^{-1}.



1j [new compound]

To a mixture of *t*-BuOK (1.68 g, 15 mmol) in dry acetonitrile (20 mL) was added diethyl allylmalonate (2.0 ml, 10 mmol) at 0 ºC. After being stirred for 1 h at 50 ºC, to the mixture was added 3-chloro-2-methyl-1-propene (1.65 ml, 17 mmol) and the mixture was stirred for 3 h at 50 ºC. The resulting mixture was quenched by addition of saturated aqueous NH_4Cl, extracted with AcOEt, washed with brine, dried over $MgSO_4$ and concentrated to give the diene diester intermediate (2.14 g, 8.0 mmol). To a mixture of $LiAlH_4$ (910 mg, 24 mmol) in ether (60 mL) was added dropwise the diene (2.14 g, 8.0 mmol) at 0 ºC and the mixture was stirred at room temperature for 2 h. After quenching by addition of 1 M HCl, the mixture was extracted with AcOEt, washed with brine, dried over Na_2SO_4 and concentrated to give the diol intermediate (1.47 g, 8.0 mmol). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.86-5.95 (m, 1H, $CH_2C\underline{H}=CH_2$), 5.13 (d, *J* = 10 Hz, 1H), 5.11 (br s, 1H), 4.92 (br s, 1H), 4.79 (s, 1H), 3.64 (d, *J* = 7.5 Hz, 2H), 3.60 (d, *J* = 7.5 Hz, 2H), 2.17 (d, *J* = 7.5 Hz, 2H), 1.83 (s, 3H).

To a stirred solution of the diol (8.0 mmol) in DMF (16 mL) were added imidazole (1.6 g, 24 mmol) and *tert*-buthyldimethylsilyl chloride (3.6 g, 24 mmol). After 12 h, the mixture was quenched by addition of saturated aqueous NH_4Cl, extracted with ether, washed with water, dried over $MgSO_4$ and concentrated to give the disilyl ether intermediate (3.0 g, 7.4 mmol). A solution of the disilyl ether (3.0 g, 7.4 mmol) and the Grubbs 1st Ru-carbene catalyst (120 mg, 0.15 mmol) in dry CH_2Cl_2 (75 mL) was stirred for 20 h at room temperature. The mixture was filtered through a pad of SiO_2, concentrated and chromatographed to give the cyclopentene intermediate (2.64g, 7.2 mmol). *m*-Chloroperbenzoic acid (65%, 2.1 g 7.8 mmol) was added to a stirred solution of the resulting cyclopentene derivative (2.64 g, 6.5 mmol) and $NaHCO_3$

10) Jung, M. E.; van den Heuvel, A. *Tetrahedron Lett*. **2002**, *43*, 8169.

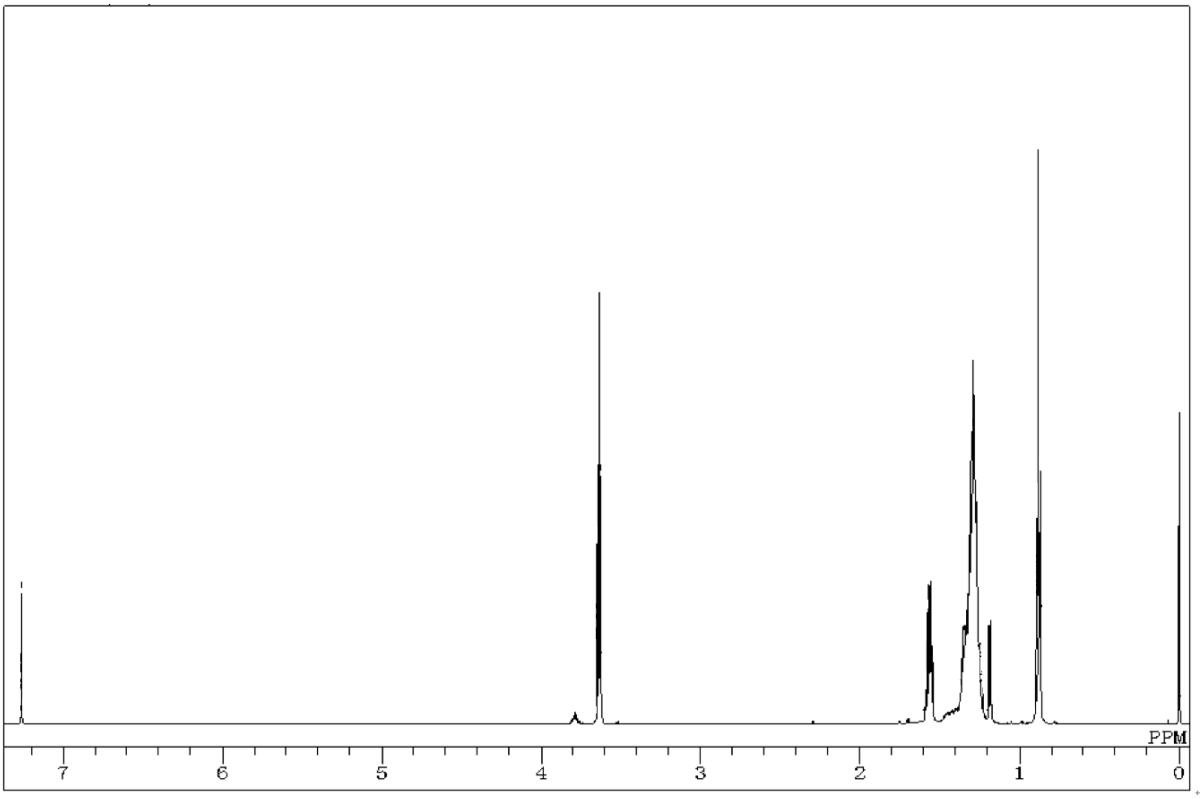
(13 mg) in CH_2Cl_2 (16 ml). After 1 h, the mixture was quenched by addition of water, washed with aqueous NaOH (10 wt%) and brine, dried over $MgSO_4$ and concentrated to give the cyclopentene oxide **1j** (2.02g, 8.8 mmol).

Epoxide 1j: ^{1}H NMR ($CDCl_3$, 600 MHz) δ 3.41 and 3.39 (2d, each J = 9.6 Hz, each 1H), 3.38 (s, 2H), 3.24 (br s, 1H), 1.75 (d, J = 15 Hz, 1H), 1.71 (d, J = 15 Hz, 1H), 1.61 (d, J = 14.1 Hz, 1H), 1.55 (d, J = 14.1 Hz, 1H), 1.41 (s, 3H), 0.88 (s, 9H), 0.87 (s, 9H), 0.02 (s, 6H), 0.01 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 66.8, 66.5, 66.1, 65.1, 49.1, 36.9, 33.1, 25.91, 25.88, 18.32, 18.25, 18.23, -5.4, -5.5; IR (Neat) 2952, 2857, 1472, 1255, 1086, 838, 775 cm^{-1}.

HR-MS: m/z= calcd For $C_{20}H_{42}NaO_3Si_2$ $[M+Na]^+$: 409.2570, found 409.2564.

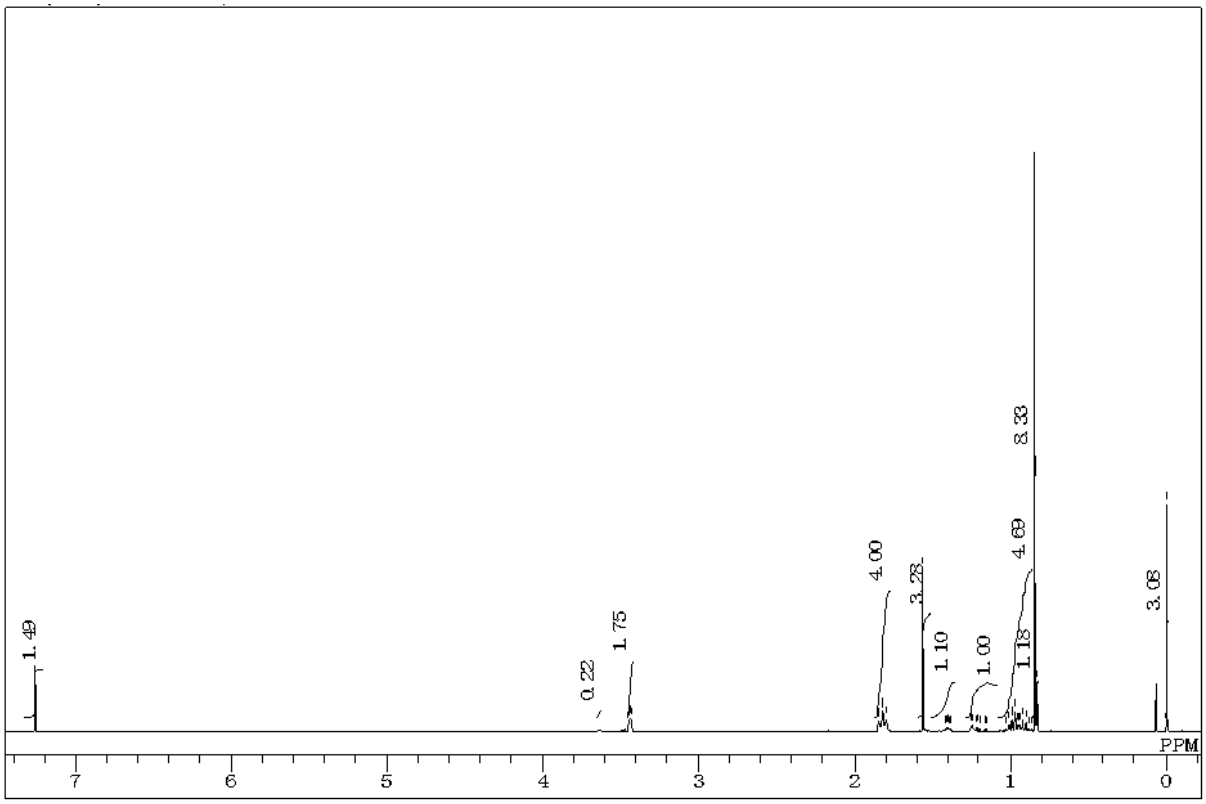
Compound **2a** + **2a'**

^{1}H NMR



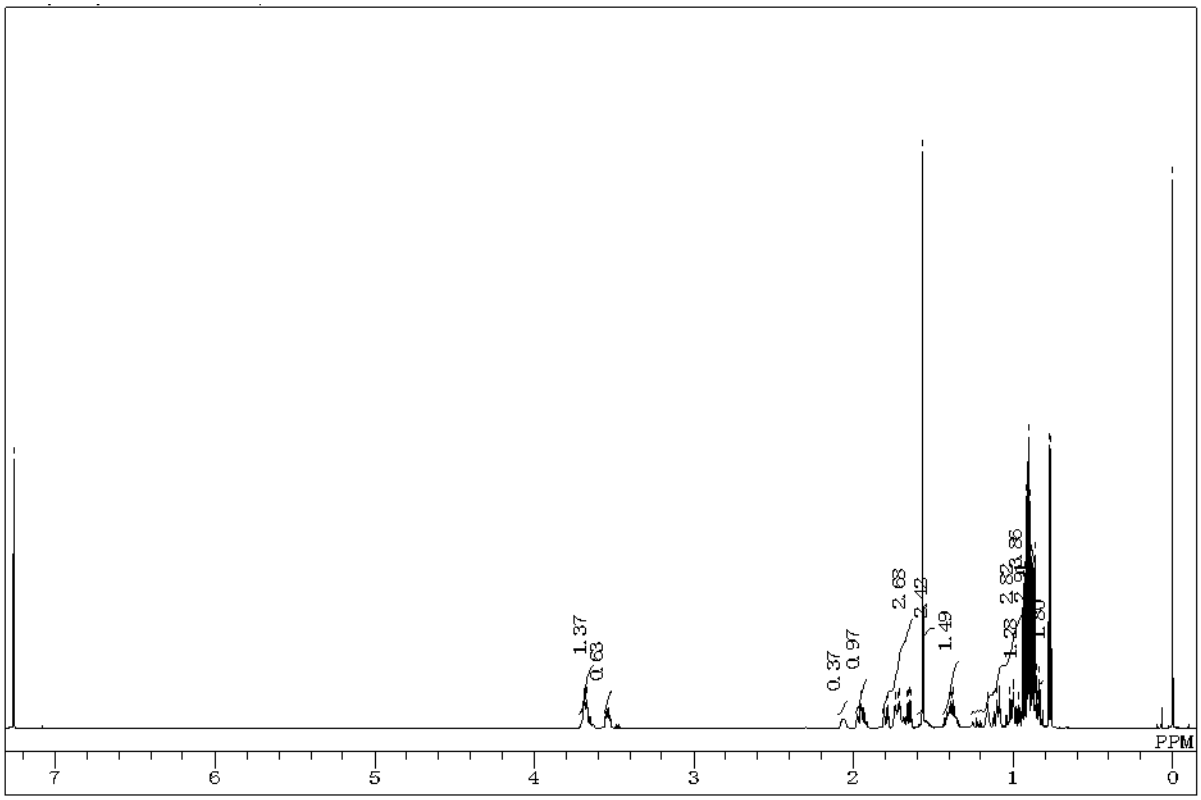
Compound **2b** (a diastereomeric mixture)

^{1}H NMR



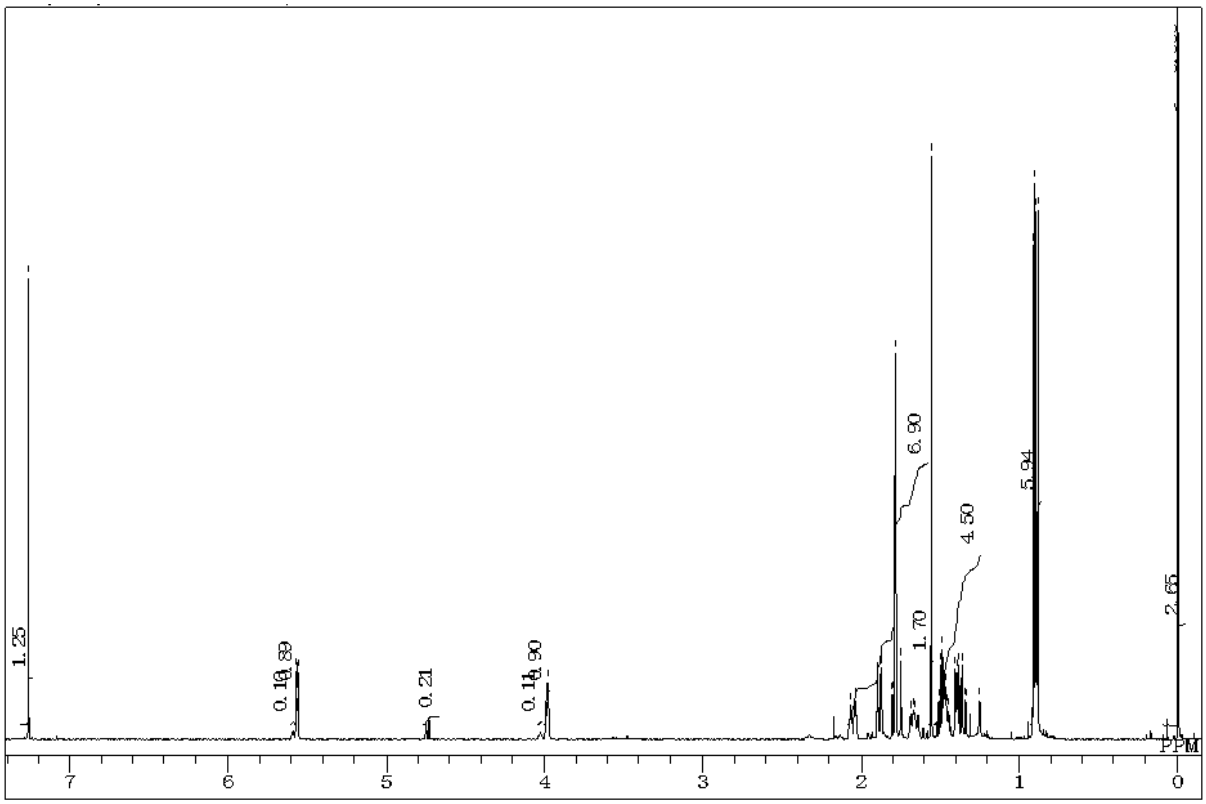
Compound **2c** (a diastereomeric mixture)

^{1}H NMR



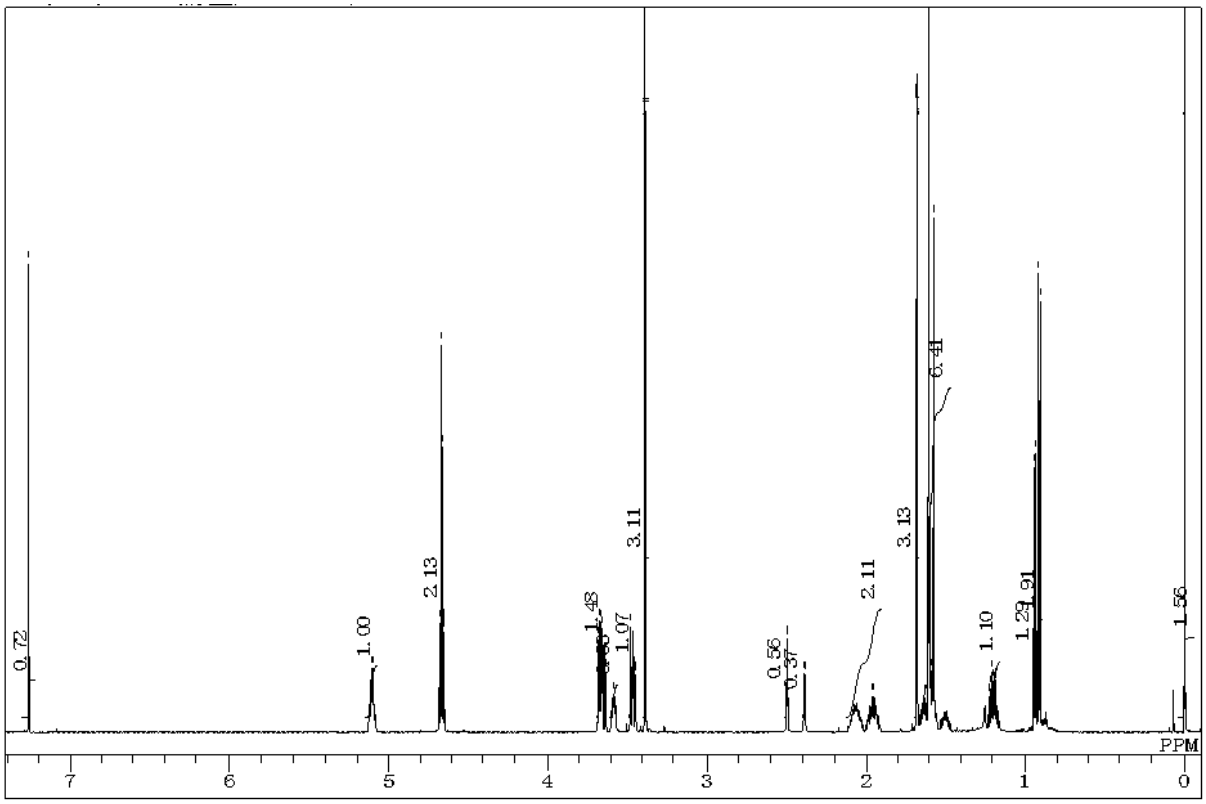
Compound **2d** + **2d''**

^{1}H NMR

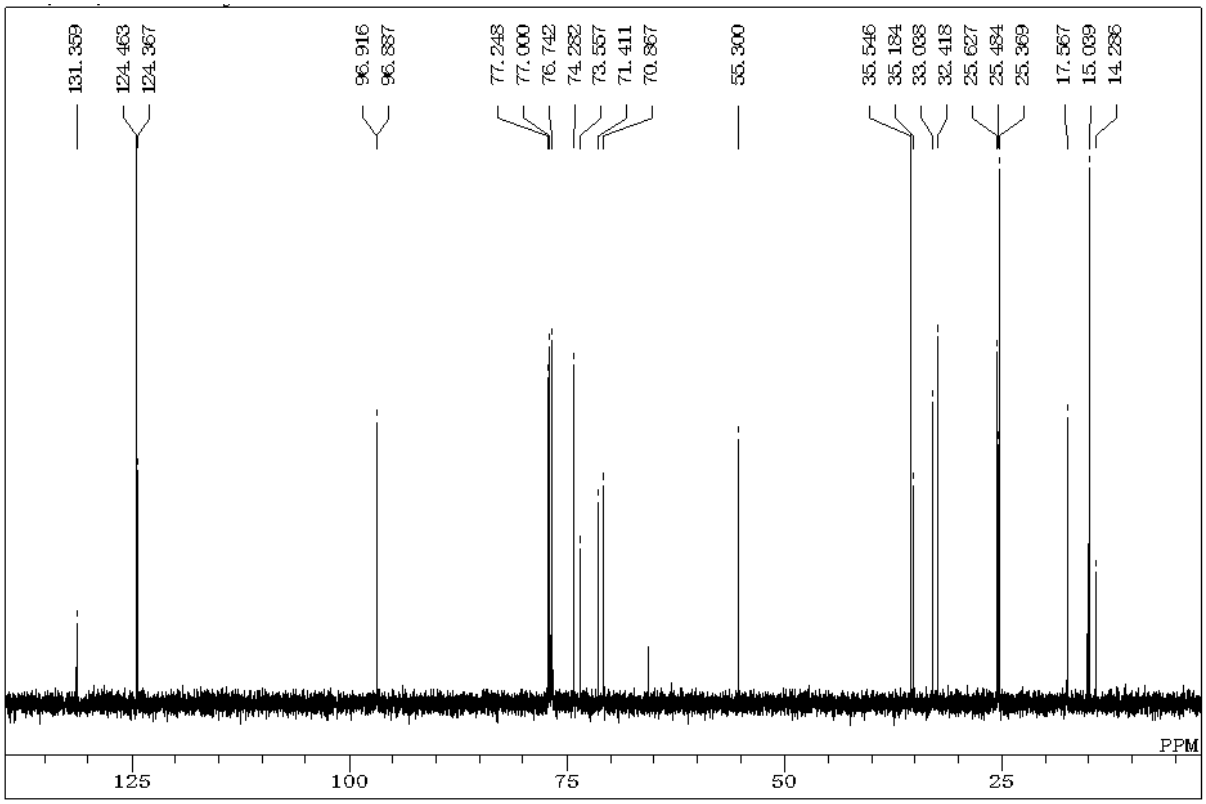


Compound **2e** (a diastereomeric mixture) [new compound]

^{1}H NMR

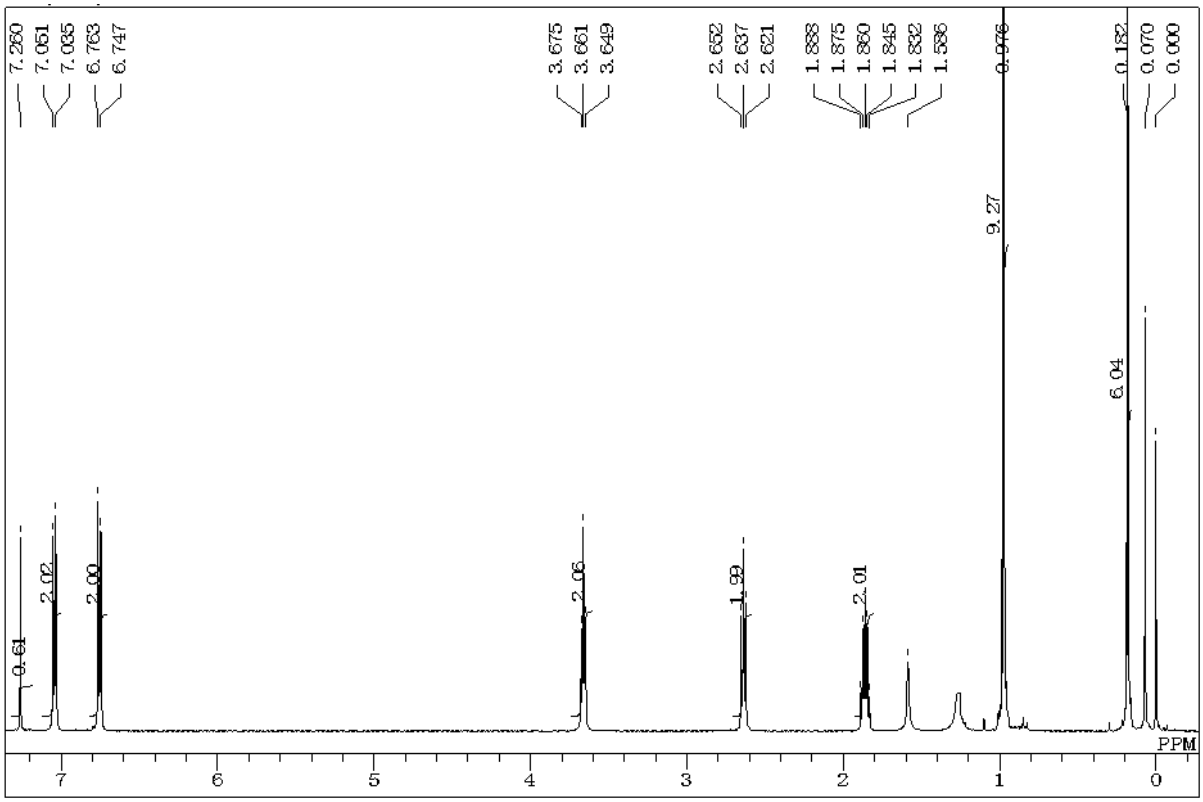


^{13}C NMR



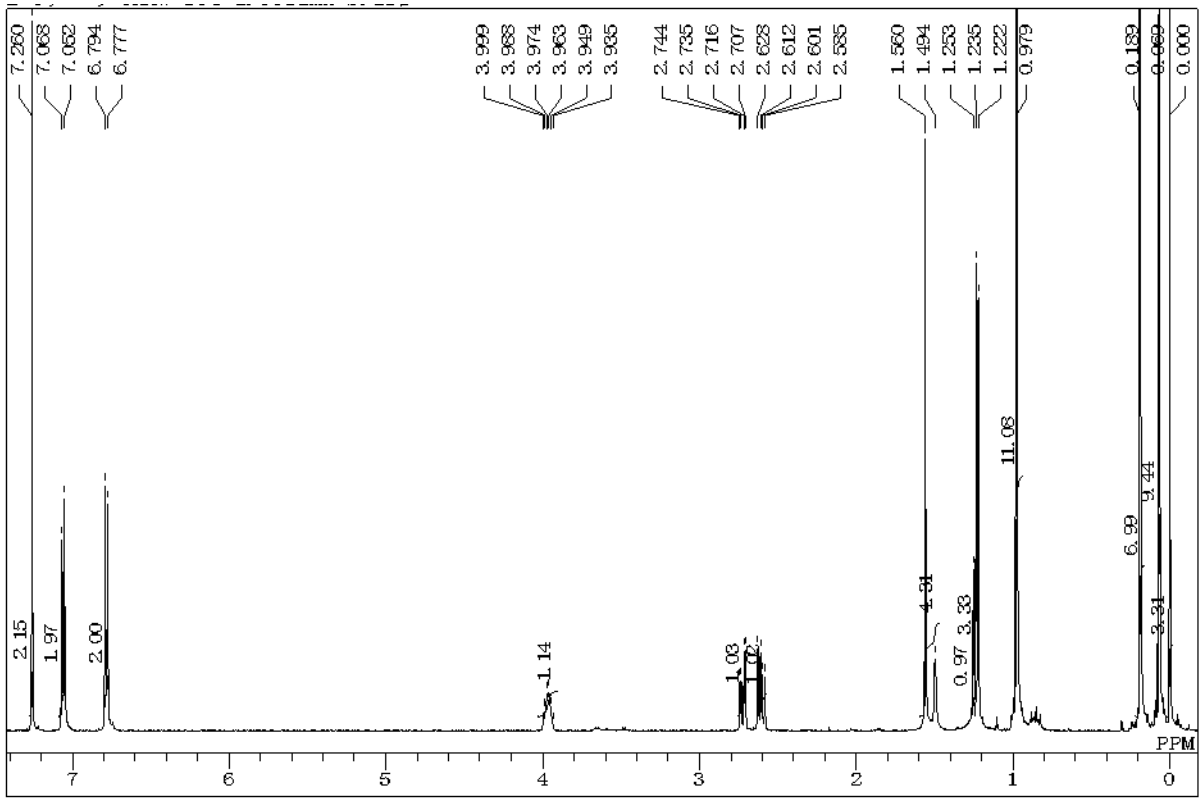
Compound **2g**

^{1}H NMR



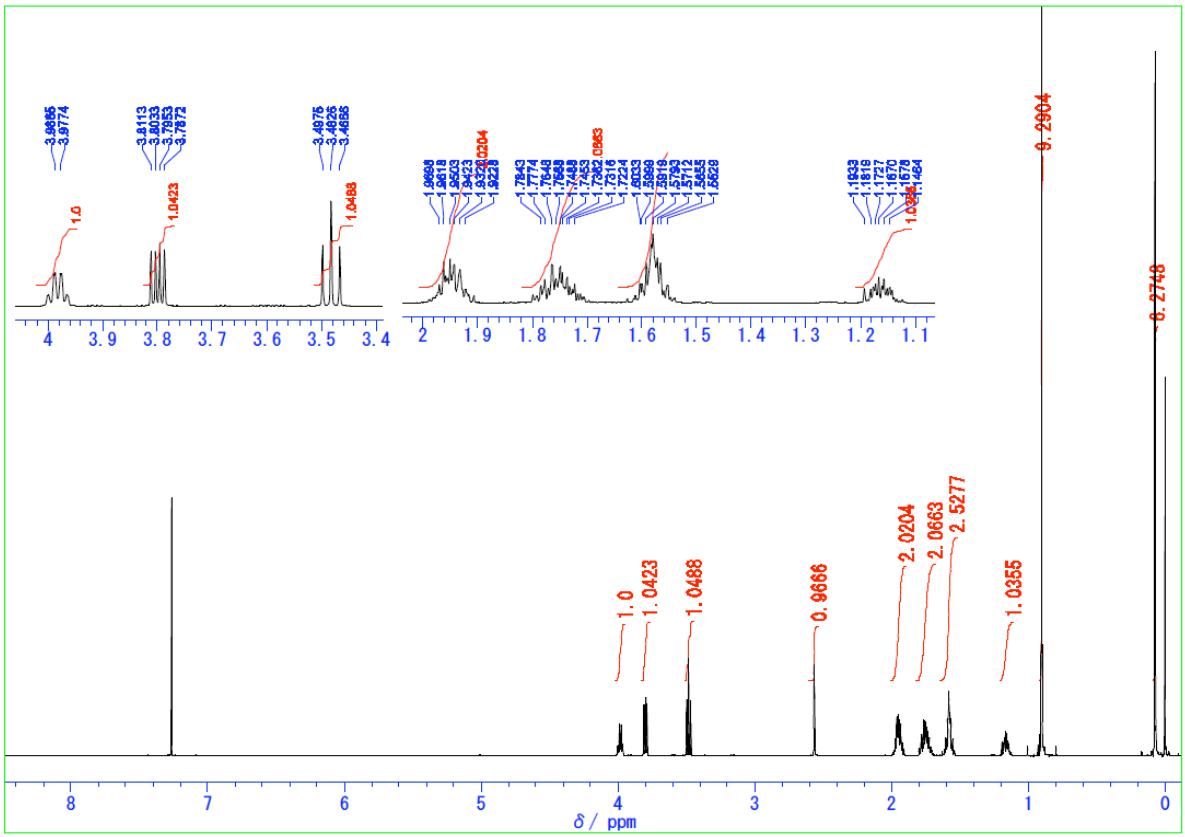
Compound **2g'**

^{1}H NMR



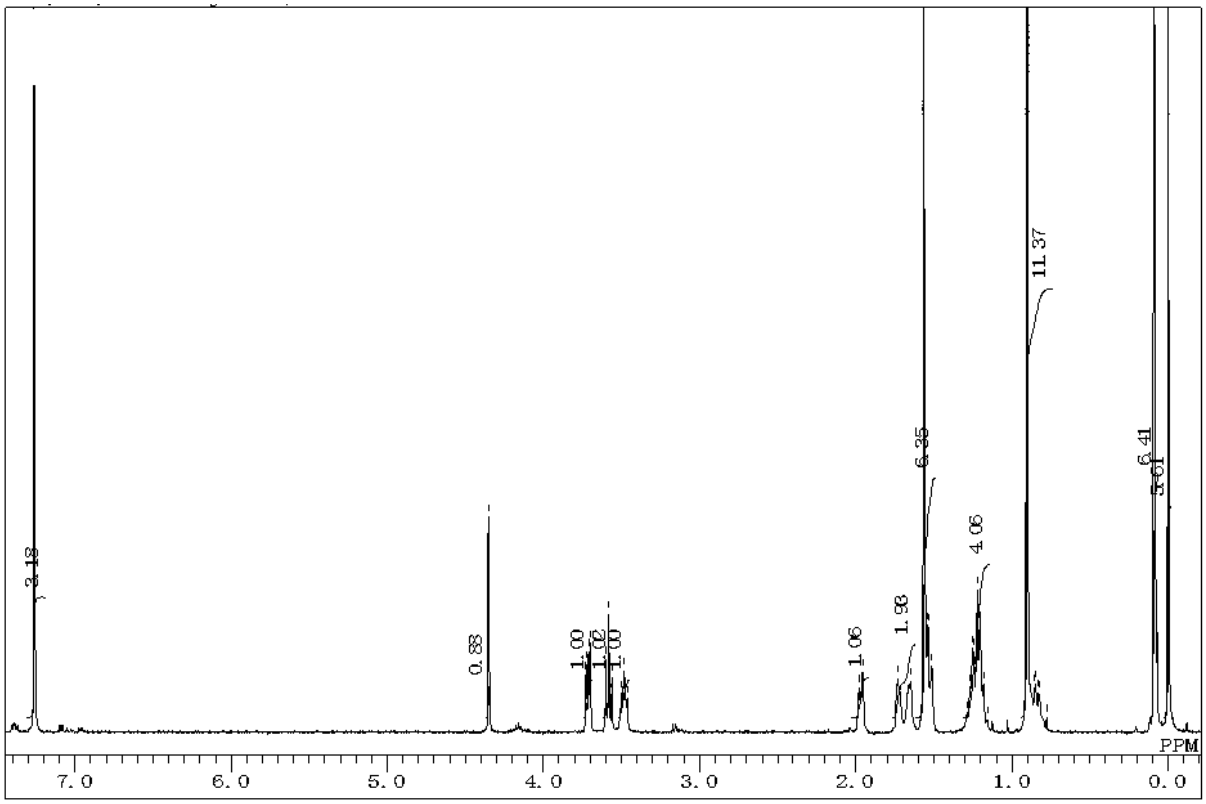
Compound **2h** (***anti***)

^{1}H NMR



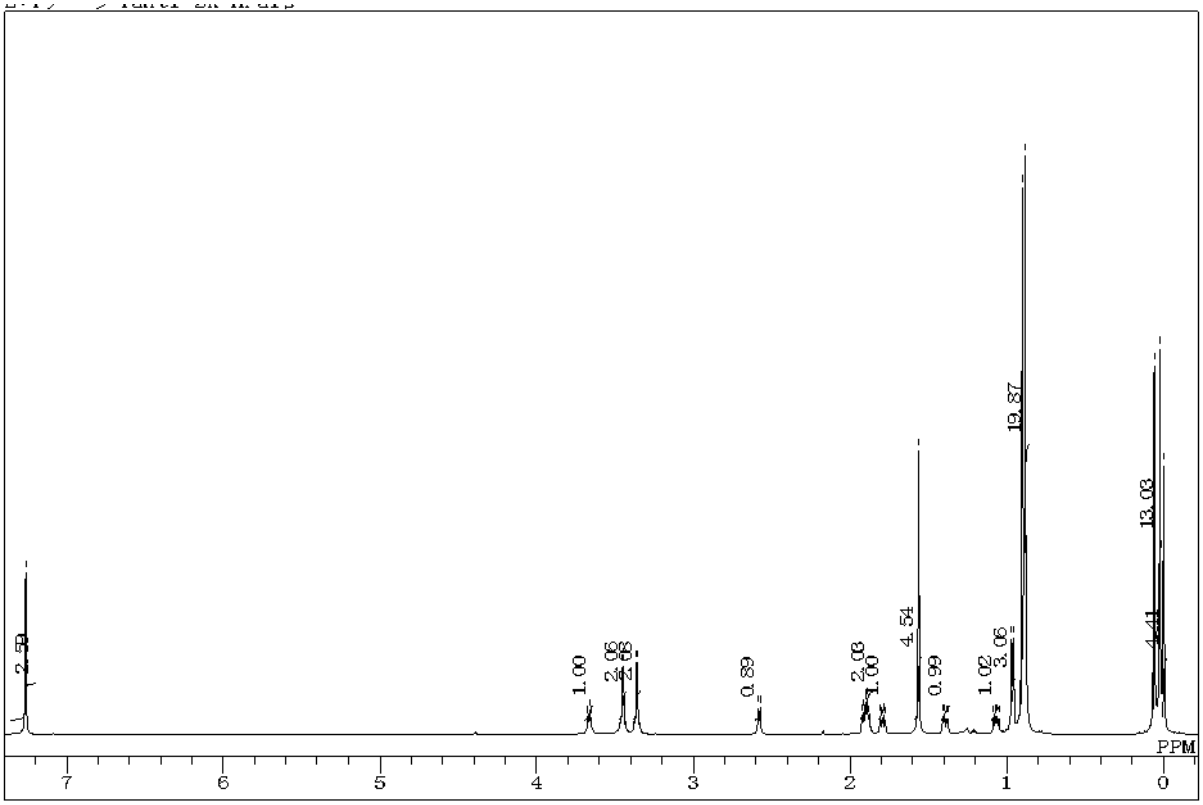
Compound **2i** (***anti*** **major**)

^{1}H NMR

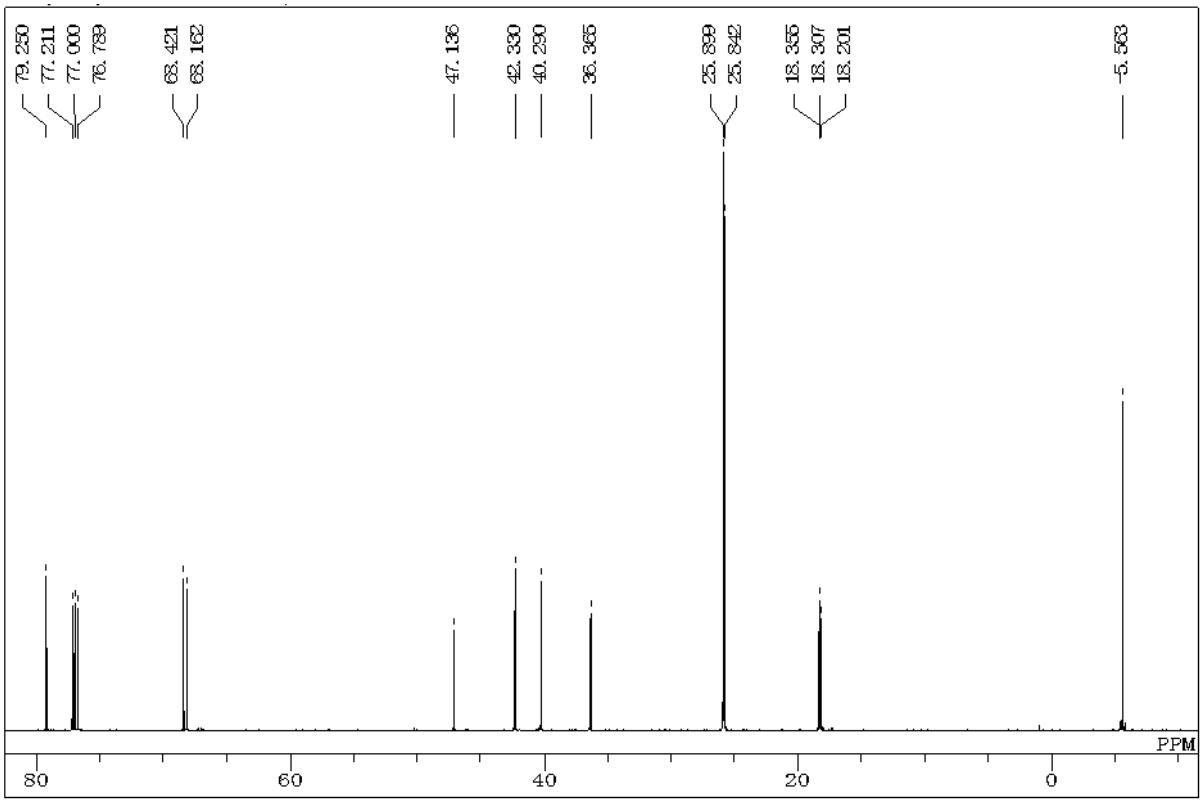


Compound **2j (*anti* major)** [new compound]

^{1}H NMR

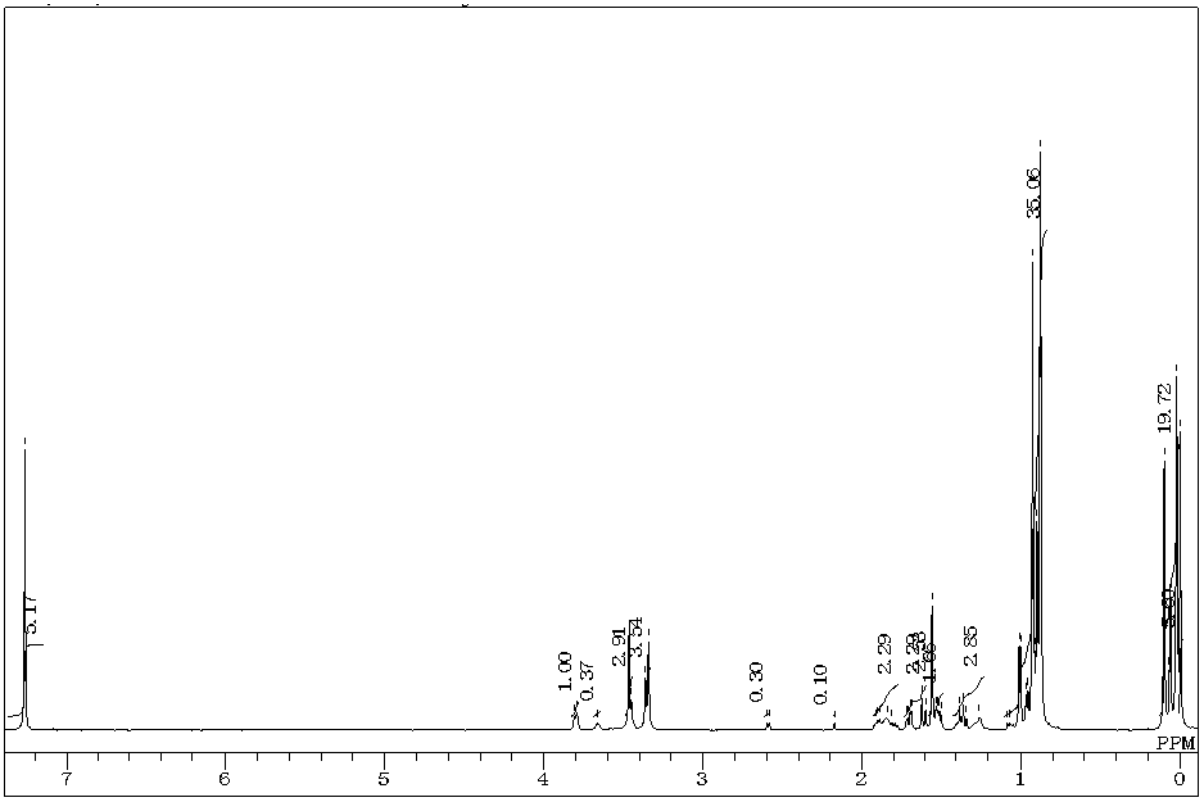


^{13}C NMR

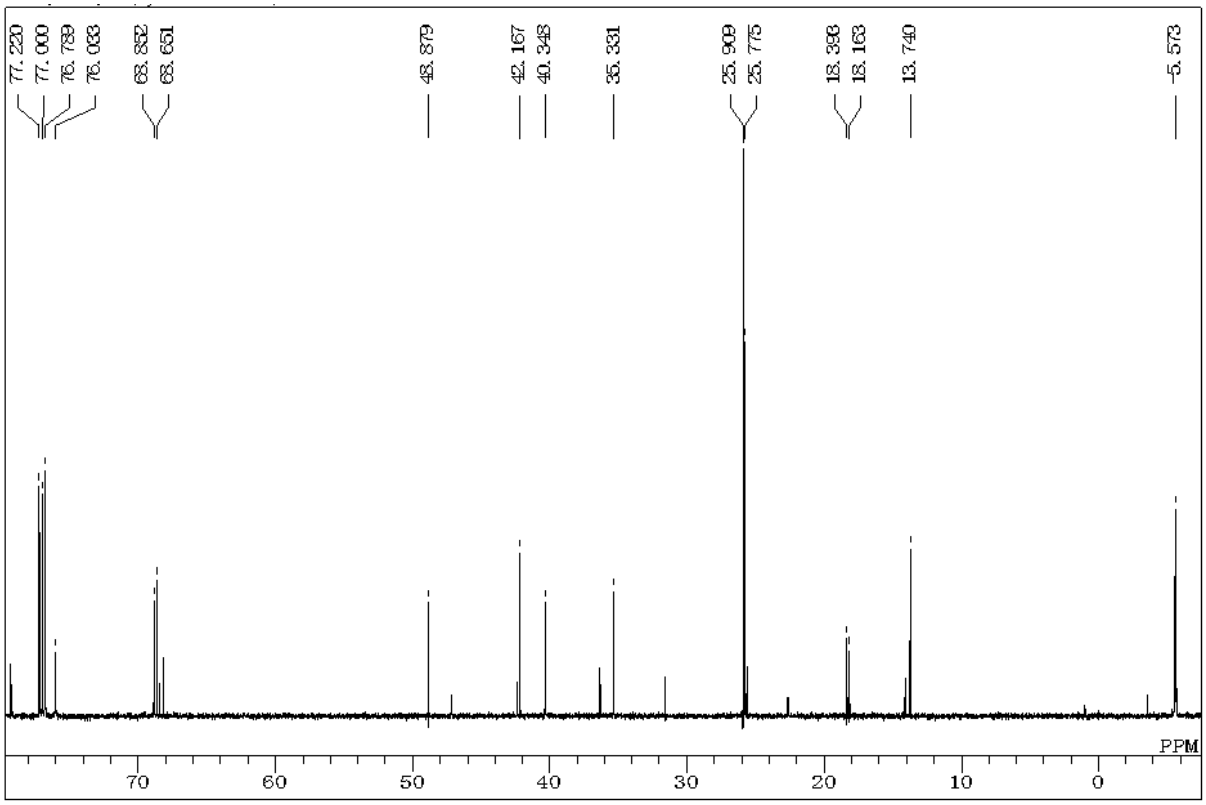


Compound **2j (*syn* major)** [new compound]

^{1}H NMR

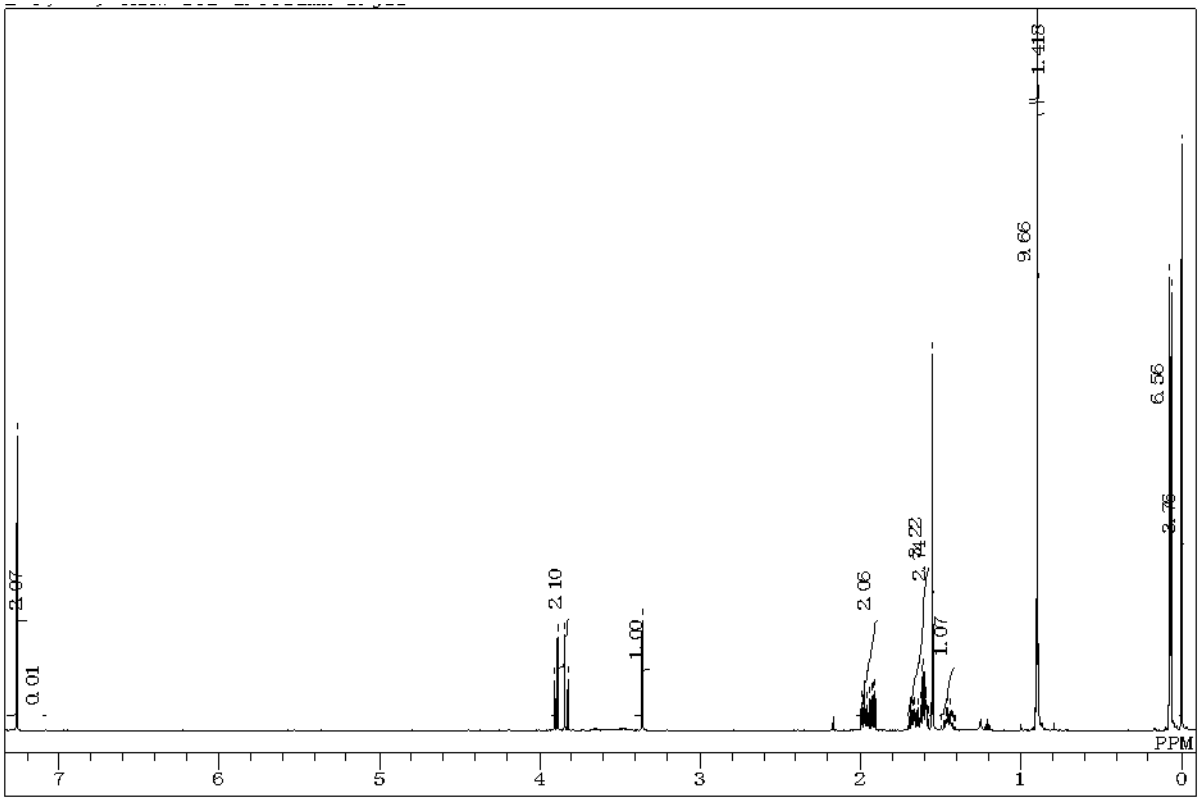


^{13}C NMR

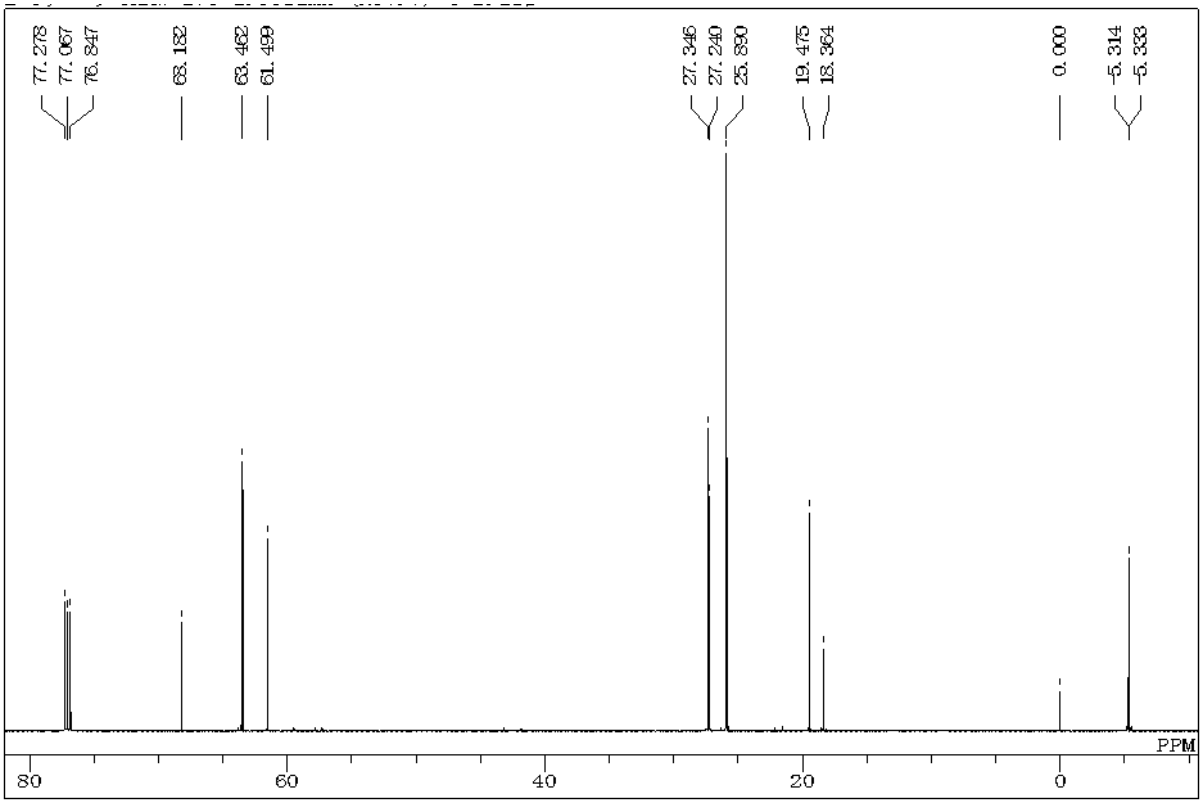


Compound **1h** [new compound]

^{1}H NMR

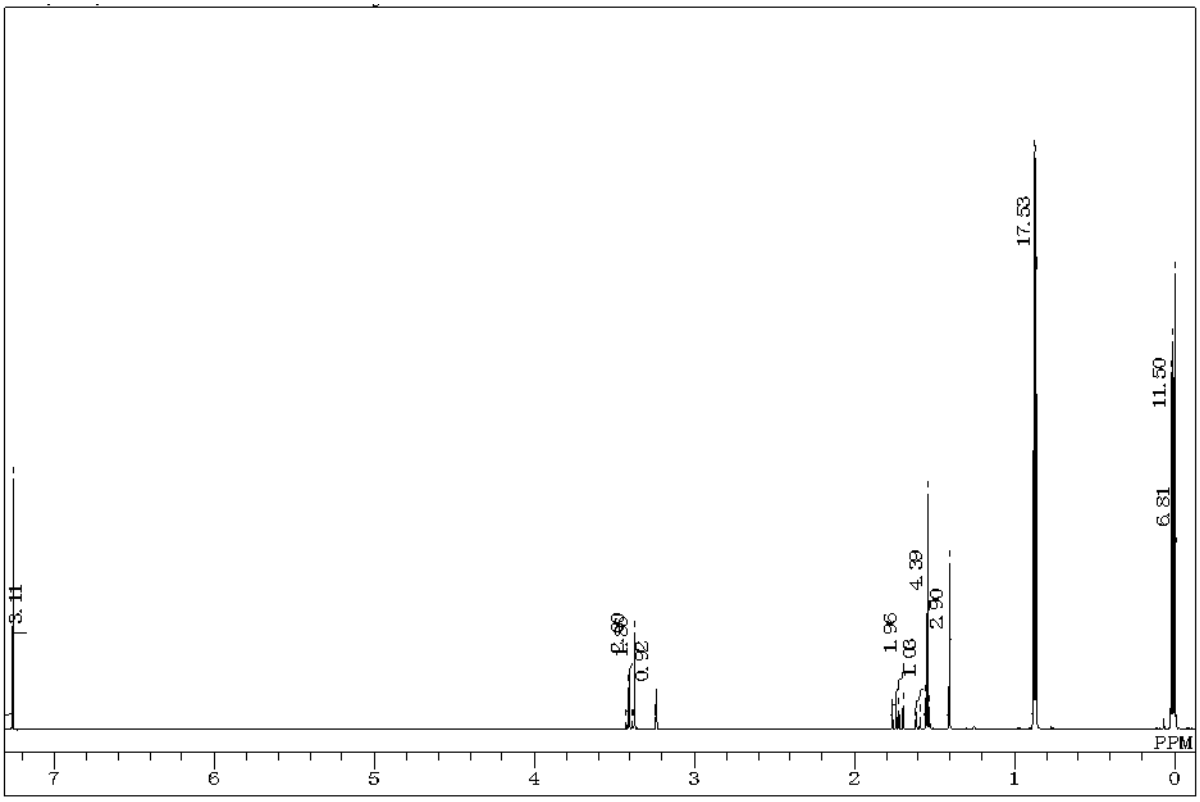


^{13}C NMR



Compound **1j** [new compound]

^{1}H NMR



^{13}C NMR