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Supporting Information

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Novel Photooxygenation of Masked *o*-Benzoquinones: A Short and Efficient Entry to Highly Functionalized Cyclopentenones from 2-Methoxyphenols**

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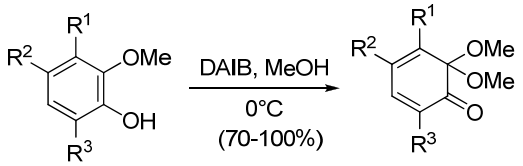
1. General Procedures

^{1}H NMR spectra were recorded in $CDCl_3$ at 400 and 600 MHz. ^{13}C NMR spectra were recorded in $CDCl_3$ at 100 and 150 MHz. All reactions were monitored by ^{1}H NMR and thin-layer chromatography (TLC) that was performed on pre-coated sheets of silica gel 60 impregnated with a fluorescent indicator (254 nm). Flash column chromatography was done with silica gel 60 (the particle size: 43-60 μm).

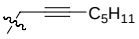
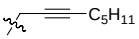
All commercial reagents and solvents were used as received without further purification.

Preparation of masked *o*-benzoquinones 1a-j

To a solution of the corresponding 2-methoxyphenol (1.2 mmol, 0.5M) and methanol at 273.15K, 1.2 eq. of diacetoxyiodobenzene (DAIB) was added. After 10~15 min, the solution was evaporated, extracted with EtOAc, washed with pH = 7 KH_2PO_4/NaOH buffer solution for 3 times (the removal of acetic acid), dry over $MgSO_4$ and finally evaporated in vacuo to obtain the pure MOBs **1a-j**. [1]



0a-j **1a-j**

Entry	MOB	R^1	R^2	R^3	Yield [%]
1	**1a**	H	*i*Pr	H	100
2	**1b**	H	*t*Bu	*t*Bu	95
3	**1c**	H	*i*Pr	Me	95
4	**1d**	Me		H	95
5	**1e**	Me	H	H	100
6	**1f**	OMe	H	H	90
7	**1g**	H		H	97
8	**1h**	H	$nC_{16}H_{33}$	H	95
9	**1i**	H		H	85
10	**1j**	H		Cl	70

General procedures for photooxygenation of masked *o*-benzoquinones 1a-j

To a solution of the corresponding masked *o*-benzoquinones (1.2 mmol), the sensitizer (tetraphenylporphyrin, TPP or rose bengal, 2~3mg, ~2.5x10^{-3} mmol) was put and the reaction tube was placed in the cooling tank (at 273.15 K for compound **2d-f** and at 258.15 K for the other compounds). Oxygen was bubbling into the solution constantly under the irradiation with five 500 watt of halogen lamps until the reaction was completed. The reaction mixture was tracked by ^{1}H NMR and thin-layer chromatography.

1) Procedure A after completion of photooxygenation

To the solution at 273.15K, charcoal was added, and then the residues was filtered, concentrated in vacuo to yield the pure product without further purification.

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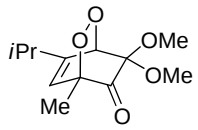
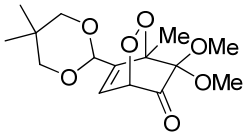
[1] C.-C. Liao, R. K. Peddinti, *Acc. Chem. Res.* **2002**, *35*, 856-866.



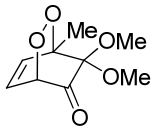
2c

7-isopropyl-6,6-dimethoxy-4-methyl-2,3-dioxabicyclo[2.2.2]oct-7-en-5-one (2c) was obtained from photooxygenation of 0.05M of **1c** in chloroform (TPP as the sensitizer) and the and the and the following procedure A, in 87% yield, as a colorless liquid; IR (film) 2965(m), 1758(s), 1465(s), 1071(s) cm^{-1}; ^1H NMR (400Mz, $CDCl_3$) δ5.89 (s, 1H), 4.81(s, 1H), 3.45 (s, 3H), 3.42 (s, 3H), 2.50 (septd, J = 6.8, 1.6 Hz, 1H), 1.38 (s, 3H), 1.13 (dd, J = 6.8, 1.6 Hz, 3H), 1.11 (dd, J = 6.8, 1.6 Hz, 3H); ^{13}C NMR (100Mz, CDCl3) δ 195.0 (C), 157.2 (C), 121.5 (CH), 91.2 (C), 81.9 (C), 77.7 (CH), 51.5 (CH_3), 50.3 (CH_3), 32.0 (CH), 20.4 (CH_3), 20.0 (CH_3), 13.6 (CH_3); HRMS (EI) calcd for $C_{12}H_{18}O_5$ $(M)^+$ 242.1154, found 242.1152.



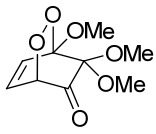
2d

7-(5,5-dimethyl-1,3-dioxan-2-yl)-6,6-dimethoxy-1-methyl-2,3-dioxabicyclo[2.2.2]oct-7-en-5-one (2d) was obtained from photooxygenation of 0.05M of MOB **1d** in chloroform (TPP as the sensitizer) and the following procedure A, in 90% yield, as a colorless liquid; IR (film) 2954(s), 2846(m), 1750(s), 1669(s), 1069(m) cm^{-1}; ^1H NMR (400Mz, $CDCl_3$) δ6.76 (d, J = 6.4 Hz, 1H)), 4.93 (s, 1H), 4.65 (d, J = 6.4 Hz, 1H), 3.57 (s, 3H), 3.66 (d, J = 11.0 Hz, 2H), 3.48 (d, J = 11.0 Hz, 2H), 3.38 (s, 3H), 1.50 (s, 3H), 1.17 (s, 3H), 0.72 (s, 3H); ^{13}C NMR (100Mz, $CDCl_3$) δ 194.7 (C), 149.2 (C), 123.0 (CH), 97.6 (CH), 92.7 (C), 86.2 (C), 79.0 (CH), 76.6 (CH_2 x 2), 54.4 (CH_3), 52.9 (CH_3), 30.2 (C), 23.0 (CH_3), 21.7 (CH_3), 10.7 (CH_3); HRMS (EI) calcd for $C_{15}H_{22}O_7$ $(M)^+$ 314.1366, found 314.1361.



2e

6,6-dimethoxy-1-methyl-2,3-dioxabicyclo[2.2.2]oct-7-en-5-one (2e) was obtained from photooxygenation of 0.05M of MOB **1e** in chloroform (TPP as the sensitizer) and the following procedure A, in 82% yield, as a colorless liquid; IR (film) 2957(m), 2618(m), 1714(s), 1457(m), 1252(m), 1114(w) cm^{-1}; ^1H NMR (400Mz, $CDCl_3$) δ6.62~6.56 (m, 2H), 4.61 (d, J = 5.6 Hz, 1H), 3.60 (s, 3H), 3.41 (s, 3H), 1.44 (s, 3H); ^{13}C NMR (100Mz, $CDCl_3$) δ 195.1 (C), 142.6 (CH), 126.4 (CH), 93.0 (C), 84.9 (C), 79.1 (CH), 54.7 (CH_3), 52.8 (CH_3), 14.2 (CH_3); HRMS (EI) calcd for $C_9H_{12}O_5$ $(M)^+$ 200.0685, found 200.0686.



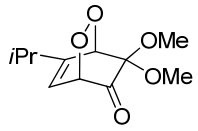
2f

1,6,6-trimethoxy-2,3-dioxabicyclo[2.2.2]oct-7-en-5-one (2f) was obtained from photooxygenation of 0.05M of MOB **1f** in chloroform (TPP as the sensitizer) and the following procedure A, in 90% yield, as a colorless liquid; IR (film) 2956(m), 2835(m), 1748(d), 1473(m), 1208(m), 1076(m), 990(w) cm^{-1}; ^1H NMR

(400Mz, CDCl3) δ6.89 (d, J = 9.2 Hz, 1H), 6.74 (dd, J = 9.2, 6.0Hz, 1H), 4.64 (d, J = 6.0 Hz, 1H), 3.62 (s, 3H), 3.57 (s, 3H), 3.44 (s, 3H); ^{13}C NMR (100Mz, $CDCl_3$) δ 193.6 (C), 136.7(CH), 128.9 (CH), 105.2 (C), 92.7 (C), 78.7 (CH), 53.4 (CH_3), 53.1 (CH_3), 52.2 (CH_3); LRMS (ESI) calcd for $C_9H_{12}O_6K$ $(M+K)^+$ 255.0, found 255.1.

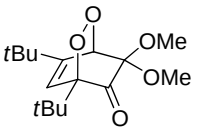
2) Procedure B after photooxygenation

Thiourea (0.5~2.4 mmol) was added into the photooxygenated solution at 273.15K, and the mixture was stirred until completion of the reaction. The mixture was evaporated and then extracted three times with EtOAc/H_2O. Combined organic extracts were dried over $MgSO_4$ and concentrated in vacuo to yield the crude product. After chromatography using EtOAc/ *n*-hexane, the pure product was obtained.



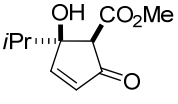
2a

7-Isopropyl-6,6-dimethoxy-2,3-dioxabicyclo[2.2.2]oct-7-en-5-one (2a) was obtained from photooxygenation of 0.25M of MOB **1a** in chloroform (TPP as the sensitizer) and the following procedure B (55 mg, 0.6mmol of thiourea), in 74% yield, as a colorless liquid (and compound **3a**, in 10% yield); IR (film): 2968(m), 2840(w), 1758(s), 1465(s), 1072(s), 745(w) cm^{-1}; ^{1}H NMR (400Mz, $CDCl_3$) δ 6.21 (d, J = 6.8 Hz, 1H), 4.84 (s,1H), 4.62 (d, J = 6.8 Hz, 1H); 3.44 (s, 3H), 3.42 (s, 3H), 2.51 (sept, J = 6.8, 1H), 1.27 (d, J = 6.8 Hz, 3H), 1.11 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100Mz, $CDCl_3$) δ 194.0 (C), 157.6 (C), 117.2 (CH), 91.3 (C), 79.2 (CH); 77.9 (CH), 51.5 (CH_3), 50.5 (CH_3), 32.1 (CH), 20.4 (CH_3), 19.2 (CH_3); HRMS (ESI) calcd for $C_{11}H_{16}O_5Na$ $(M+Na)^+$ 251.0895, found 251.0924.



2b

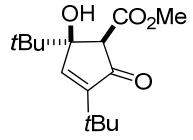
4,7-di-*tert*-Butyl-6,6-dimethoxy-2,3-dioxabicyclo[2.2.2]oct-7-en-5-one (2b) was obtained from photooxygenation of 0.05M of MOB **1b** in chloroform (TPP as the sensitizer) and the following procedure B (46 mg, 0.5 mmol of thiourea), in 68% yield, as a colorless liquid (and compound **3b**, in 17% yield); IR (film): 2965(m), 1753(s), 1464(m), 1367(m), 1159(w), 861(w) cm^{-1}; ^{1}H NMR (400Mz, $CDCl_3$) δ6.10 (s, 1H), 4.86 (s, 1H), 3.42 (s, 3H), 3.39 (s, 3H), 1.11 (s, 9H), 1.08 (s, 9H); ^{13}C NMR (100Mz, $CDCl_3$) δ 195.0 (C), 159.9 (C), 118.0 (CH), 91.0 (C), 87.1 (C), 75.4 (CH), 51.4 (CH_3), 50.5 (CH_3), 34.8 (C), 34.2 (C), 28.2 (CH_3 x 3), 25.1 (CH_3 x 3); HRMS (ESI) calcd for $C_{16}H_{26}O_5Na$ $(M+Na)^+$ 321.1678, found 321.1687.



3a

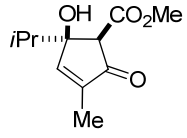
Methyl (1*R,2*R**)-2-hydroxy-2-isopropyl-5-oxocyclopent-3-ene-1-carboxylate (3a)** was obtained from photooxygenation of 0.05M of MOB **1a** in methanol (rose bengal as the sensitizer) and the following procedure B (200 mg, 2.4 mmol of thiourea), in 70% yield, as a colorless liquid; IR (film): 3479(br), 2964(m), 2880(m), 1773(s), 1317(m), 815(m), 765(m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ7.49 (d, J = 5.8 Hz, 1H), 6.18 (d, J = 5.8 Hz, 1H), 3.74 (s, 3H), 3.68 (OH, 1H), 3.44 (s, 1H), 1.96 (sept, J = 6.8 Hz, 1H), 0.98 (d, J = 6.8 Hz, 3H), 0.90 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100Mz, $CDCl_3$) δ 200.4 (C), 169.4 (C), 166.5

(CH), 132.7 (CH), 82.7 (C), 58.2 (CH), 52.8 (CH_3), 36.4 (CH), 17.2 (CH_3), 16.8 (CH_3); HRMS (FAB) calcd for $C_{10}H_{15}O_4$ $(M+H)^+$ 198.0965, found 199.0971.



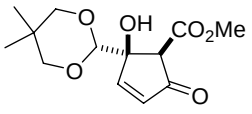
3b

Methyl (1*R,2*R**)-2,4-di-*tert*-butyl-2-hydroxy-5-oxocyclopent-3-ene-1-carboxylate (3b)** was obtained from photooxygenation of 0.05M of MOB **1b** in chloroform (rose bengal as the sensitizer) and the following procedure B (203 mg, 2.4 mmol of thiourea), in 78% yield, as a colorless liquid; IR (film) 3500(br), 2959(s), 1740(s), 1706(s), 1463(m), 1322(m), 1087(m), 970(m) cm^{-1}; ^1H NMR (400Mz, $CDCl_3$) δ7.100 (s, 1H), 3.73 (s, 1H), 3.62 (s, 3H), 1.81 (s, 1H), 1.17 (s, 9H), 0.94 (s, 9H); ^{13}C NMR (100Mz, $CDCl_3$) δ 199.7 (C), 170.1 (C), 156.3 (CH), 154.2 (C), 81.4 (C), 59.7 (CH), 52.7 (CH_3), (CH), 52.7 (CH_3), 37.9 (C), 32.0 (C), 28.2 (CH_3), 25.0 (CH_3); HRMS (ESI) calcd for $C_{15}H_{24}O_4Na$ $(M+Na)^+$ 291.1572, found 291.1592.



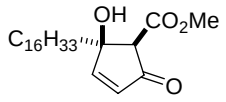
3c

Methyl (1*R,2*R**)-2-hydroxy-2-isopropyl-4-methyl-5-oxocyclopent-3-ene-1-carboxylate (3c)** was obtained from photooxygenation of 0.05M of MOB **1c** in methanol (rose bengal as the sensitizer) and the following procedure B (200 mg, 2.4 mmol of thiourea), in 75% yield, as colorless liquid; IR (film) 3494(br), 2963(s), 2879(m), 1709(s), 1644(m), 1436(m), 1326(m), 989(w) cm^{-1}; ^1H NMR (400Mz, $CDCl_3$) δ7.14 (s, 1H), 3.76 (s, 3H), 3.48 (s, 1H), 1.94 (sept, J = 6.8 Hz, 1H), 1.81 (s, 3H), 0.98 (d, J =6.8, 3H), 0.90 (d, J =6.8, 3H); ^{13}C NMR (100Mz, CDCl3) δ 200.7 (C), 169.7 (C), 160.2 (CH), 141.6 (C), 80.7 (C), 58.6 (CH), 52.8 (CH_3), 36.6 (CH), 17.3 (CH_3), 16.9 (CH_3), 10.0 (CH_3); HRMS (ESI) calcd for $C_{11}H_{16}O_5Na$ $(M+Na)^+$ 235.0946, found 235.0948.



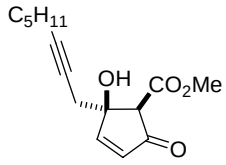
3g

Methyl (1*R,2*R**)-2-(5,5-dimethyl-1,3-dioxan-2-yl)-2-hydroxy-5-oxocyclopent-3-ene-1-carboxylate (3g)** was obtained from photooxygenation of 0.01M of MOB **1g** in methanol (rose bengal as the sensitizer) and the following procedure B (200 mg, 2.4 mmol of thiourea), in 75% yield, as colorless solid; IR (film) 3469 (br), 2958(s), 2856(m), 1744(s), 1597(m), 1308(m), 1104(m), 774(m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, J = 5.8 Hz, 1H), 6.26 (d, J = 5.8 Hz, 1H), 4.58 (s, 1H), 3.75 (s, 3H), 3.74 (s, 1H), 3.67-3.41 (m, 4H), 1.09 (s, 3H), 0.69 (s, 3H); ^{13}C NMR (100Mz, CDCl3) δ 199.8 (C), 168.6 (C), 161.3 (CH), 134.8 (CH), 101.4 (CH), 80.8 (C), 77.3 (CH_2 x 2), 56.3 (CH), 52.7 (CH_3), 30.3 (C), 22.9 (CH_3), 21.5 (CH_3); HRMS (FAB^+) calcd for $C_{13}H_{19}O_6^+$ $(M+H)^+$ 271.1176, found 271.1179.



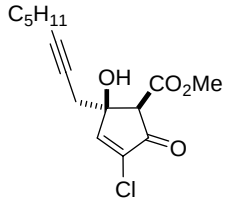
3h: Untenone A

Methyl (1*R,2*R**)-2-hexadecyl-2-hydroxy-5-oxocyclopent-3-ene-1-carboxylate (3h)** was obtained from photooxygenation of 0.01M of MOB **1h** in methanol (rose bengal as the sensitizer) and the following procedure B (200 mg, 2.4 mmol of thiourea), in 65% yield, as a colorless solid; ^{1}H NMR (400Mz, $CDCl_3$) δ7.50 (d, J = 5.6 Hz, 1H), 6.17 (d, J = 5.6 Hz, 1H), 3.77 (s, 3H), 3.44 (s, 1H), 1.823-1.228 (m, 30H), 0.856 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100Mz, CDCl3) δ 199.9 (C), 169.0 (C), 167.0 (CH), 132.7 (CH), 79.9 (C), 60.8 (CH), 52.9 (CH_3), 40.4 (CH_2), 31.9 (CH_2), 29.7-22.7 (CH_2 x 13), 14.1 (CH_3); HRMS (FAB^+) calcd for $C_{23}H_{41}O_4$ ($M+H^+$) 381.2999, found 381.3002. The spectrums of ^{1}H-NMR and ^{13}C-NMR were matched with the literature. [2]



3i

Methyl (1*R,2*R**)-2-hydroxy-2-oct-2-yn-1-yl-5-oxocyclopent-3-ene-1-carboxylate (3i)** was obtained from photooxygenation of 0.01M of MOB **1i** in methanol (rose bengal as the sensitizer) and the following procedure B (200 mg, 2.4 mmol of thiourea), in 79% yield, as colorless liquid; IR (film) 3448(br), 2956(m), 2860(m), 1742(s), 1717(s), 1436(m), 1324(m), 1158(m), 1011(m), 817(w) cm^{-1}; ^{1}H NMR (600Mz, $CDCl_3$) δ7.43 (d, J = 5.7 Hz, 1H), 6.22 (d, J = 5.7 Hz, 1H), 3.76 (s, 3H), 3.66 (s, OH, 1H), 2.72 (ABq, J = 16.5 Hz, 1H), 2.64 (ABqt, J = 16.5 Hz, 1H), 2.06 (tt, J = 7.2, 2.4 Hz, 2H), 1.39 (sextet, J = 7.2 Hz, 2H), 1.27-1.24 (m, 4H), 0.85 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100Mz, $CDCl_3$) δ 199.3 (C), 168.8 (C), 164.9 (CH), 133.4 (CH), 84.9 (C), 79.3 (C), 73.4 (C), 59.7 (CH), 52.9 (CH_3), 30.9 (CH_2), 30.8 (CH_2), 28.3 (CH_2), 22.8 (CH_2), 18.5 (CH_2), 13.9 (CH_3); HRMS (ESI) calcd for $C_{15}H_{20}O_4Na$ $(M+Na)^+$ 287.1259, found 287.1251.



3j

Methyl (1*R,2*S**)-4-chloro-2-hydroxy-2-oct-2-yn-1-yl-5-oxocyclopent-3-ene-1-carboxylate (3j)** was obtained from photooxygenation of 0.01M of MOB **1j** in methanol (rose bengal as the sensitizer) and the following procedure B (200 mg, 2.4 mmol of thiourea), in 50% yield, as colorless liquid; IR (film): 3471(br), 2932(s), 1747(s), 1604(m), 1435(m), 757(w) cm^{-1}; ^{1}H NMR (400Mz, $CDCl_3$) δ 7.35 (s, 1H), 3.80 (s, 1H), 3.78 (s, 3H), 3.75 (s, OH), 2.73 (ABqt, J = 16.6, 2.4 Hz, 1H), 2.69 (ABqt, J = 16.6, 2.4 Hz, 1H), 2.06 (tt, J = 7.0, 2.4 Hz, 2H), 1.39 (sextet, J = 6.9 Hz, 2H), 1.31-1.22 (m, 4H), 0.86 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100Mz, $CDCl_3$) δ 191.5 (C), 167.9 (C), 157.6 (CH), 136.4 (C), 85.8 (C), 76.7 (C), 73.0 (C), 59.3 (CH), 53.2 (CH_3), 31.2 (CH_2), 31.0 (CH_2), 28.2 (CH_2), 22.1 (CH_2), 18.5 (CH_2), 13.9 (CH_3); HRMS (ESI) calcd for $C_{15}H_{19}ClO_4Na$ $(M+Na)^+$ 321.0870, found 321.0896.

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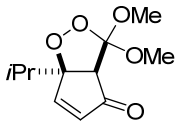
[2] S. Al-Busafi, J. R. Doncaster, M. G. B. Drew, A. C. Regana, R. C. Whitehead, *J. Chem. Soc., Perkin Trans. 1* **2002**, 476-484.

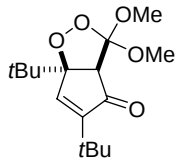
3) Procedure C after photooxygenation

Put the solution at 268.15K overnight and warmed it up to room temperature and then charcoal was added into the solution. The residue was filtered and concentrated to get the crude product without further purification.



5a

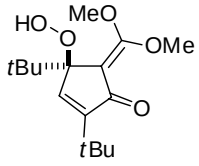
(3a*R*,6a*R*)-6a-Isopropyl-3,3-dimethoxy-3a,6a-dihydrocyclopenta[*c*][1,2]dioxol-4(3*H*)-one (5a) was obtained from photooxygenation of 0.01M of MOB **1a** in methanol (rose bengal as the sensitizer) and the following procedure C, in 90% yield, as colorless liquid; IR (film) 2966(s), 2880(m), 1717(s), 1594(w), 1468(m), 1349(m), 1254(m), 1183(m), 1045(m) cm^{-1}; ^{1}H NMR (400Mz, $CDCl_3$) δ7.42 (d, J = 5.8 Hz, 1H), 6.32 (d, J = 5.8 Hz, 1H), 3.45 (s, 3H), 3.33 (s, 3H), 3.14 (s, 1H), 2.17 (sept, J = 7.0 Hz, 1H), 0.94 (t, J = 7.0 Hz, 6H); ^{13}C NMR (100Mz, $CDCl_3$) δ200.9 (C), 159.4 (CH), 136.5 (CH), 122.2 (C), 98.9 (C), 60.6 (CH), 52.7 (CH_3), 49.3 (CH_3), 31.1 (CH), 17.7 (CH_3), 17.6 (CH_3); HRMS (ESI) calcd for $C_{11}H_{16}O_5Na$ $(M+Na)^+$ 251.0895, found 251.0929.



6b

(4*S)-2,4-di-*tert*-Butyl-5-(dimethoxymethylene)-4-hydroperoxycyclopent-2-en-1-one (5b)** was obtained from photooxygenation of 0.01M of MOB **1b** in methanol (rose bengal as the sensitizer), and the following procedure C, in 85% yield, as colorless liquid; IR (film) 2959(br), 2873(m), 1716(s), 1464(m), 1166(m), 946(m) cm^{-1}; ^{1}H NMR (400Mz, $CDCl_3$) δ7.07 (s, 1H), 3.41 (s, 3H), 3.30 (s, 3H), 3.25 (s, 1H), 1.20 (s, 9H), 0.97 (s, 9H); ^{13}C NMR (100Mz, $CDCl_3$) δ202.2 (C), 157.2 (C), 150.2 (CH), 122.3 (C), 97.8 (C), 62.1 (CH), 52.3 (CH_3), 49.2 (CH_3), 34.8 (C), 32.1 (C), 28.1 (CH_3 x 3), 25.7 (CH_3 x 3); HRMS (ESI) calcd for $C_{16}H_{26}O_5Na$ $(M+Na)^+$ 321.1678, found 321.1672.

4) Isolation of compound 4b

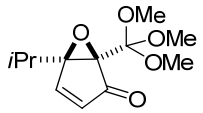


4b

After completion of photooxygenation of 0.01M of MOB **1b** in methanol, the solution was placed at 268.15K overnight and then evaporated in vacuo. **(3a*R*,6a*R*)-5,6a-di-*tert*-Butyl-3,3-dimethoxy-3a,6a dihydrocyclopenta[*c*][1,2]dioxol-4(3*H*)-one (4b)** was obtained without further purification, as white solid; ^{1}H NMR (400Mz, $CDCl_3$) δ7.63 (s, OOH, 1H), 6.75 (s, 1H), 4.18 (s, 3H), 3.75 (s, 3H), 1.21 (s, 9H), 0.95 (s, 9H); ^{13}C NMR (100Mz, $CDCl_3$) δ192.1(C), 163.7(C), 156.3(C), 145.9(CH), 96.8(C), 94.5(C), 64.0(CH_3), 53.9(CH_3), 38.6(C), 32.3(C), 28.5 (CH_3 x 3), 26.8 (CH_3 x 3); LRMS (ESI) calcd for $C_{16}H_{26}O_5Na$ $(M+Na)^+$ 321.2, found 321.2.

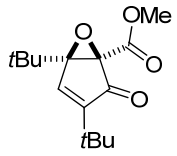
5) Procedure D after photooxygenation

$NaHCO_3$ (500mg, 5.0 eq) was added into the solution at 258.15K, and the mixture was stirred for 2-4 hr. Methanol was evaporated in vacuo at least below 273.15K to prevent formation of the side-product. Charcoal was added into the solution. Then the residue was filtered and extracted three times with EtOAc. Combined organic extracts were dried over $MgSO_4$ and concentrated in vacuo to yield the product without purification.



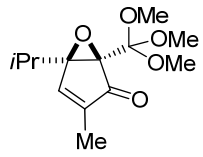
6a

(1*R,5*R**)-5-Isopropyl-1-(trimethoxymethyl)-6-oxabicyclo[3.1.0]hex-3-en-2-one (6a)** was obtained from photooxygenation of 0.01M of MOB **1a** in methanol (rose bengal as the sensitizer) and the following procedure D, in 92% yield, as colorless liquid; IR (film) 2951(br), 2841(m), 1731(s), 1686(m), 1468(m), 1278(m), 1042(m), 839(m), 575(m) cm^{-1}; ^1H NMR (400Mz, $CDCl_3$) δ 7.61 (d, J = 6.2 Hz, 1H), 5.98 (d, J = 6.2 Hz, 1H), 3.36 (s, 9H), 2.59 (sept, J = 7.2 Hz, 1H), 1.20 (d, J = 7.2 Hz, 3H), 1.05 (d, J = 7.2 Hz, 3H); ^{13}C NMR (100Mz, $CDCl_3$) δ 197.5 (C), 154.3 (CH), 133.4 (CH), 111.3 (C), 71.7 (C), 63.6 (C), 50.5 (CH_3 x 3), 25.2 (CH), 18.8 (CH_3), 18.7 (CH_3); HRMS (FAB^+) calcd for $C_{12}H_{19}O_5$ $(M+H)^+$ 243.1227, found 243.1230.



7b

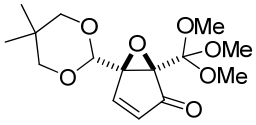
Methyl (1*R,5*S**)-3,5-di-*tert*-butyl-2-oxo-6-oxabicyclo[3.1.0]hex-3-ene-1-carboxylate (7b)** was obtained from photooxygenation of 0.01M of MOB **1b** in methanol (rose bengal as the sensitizer) and the following procedure D, in 90% yield, as colorless liquid; IR (film) 2963(s), 2911(m), 1751(s), 1718(s), 1440(w), 1318(m), 1248(m), 772(m) cm^{-1}; ^1H NMR (400Mz, $CDCl_3$) δ 7.30 (s, 1H), 3.90 (s, 3H), 1.19 (s, 9H), 1.13 (s, 9H); ^{13}C NMR (100Mz, $CDCl_3$) δ 195.6 (C), 165.3 (C), 153.6 (C), 146.3 (CH), 75.0 (C), 64.0 (C), 52.7 (CH_3), 32.4 (C), 31.4 (C), 28.1 (CH_3 x 3), 26.0 (CH_3 x 3); HRMS (ESI) calcd for $C_{15}H_{22}O_4Na$ $(M+Na)^+$ 289.1416, found 289.1428.



6c

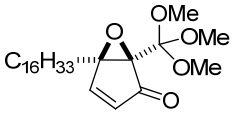
(1*R,5*R**)-5-Isopropyl-3-methyl-1-(trimethoxymethyl)-6-oxabicyclo[3.1.0]hex-3-en-2-one (6c)** was obtained from photooxygenation of 0.01M of MOB **1c** in methanol (rose bengal as the sensitizer) and the following procedure D, in 95% yield, as colorless liquid; IR (film) 2952(br), 2875(m), 2840(m), 1729(s), 1466(m), 1311(m), 1100(br), 827(s) cm^{-1}; ^1H NMR (400Mz, $CDCl_3$) δ 7.20 (d, J = 1.6 Hz, 1H), 3.34 (s, 9H), 2.56 (sept, J = 7.0 Hz, 1H), 1.71 (d, J = 1.6 Hz, 3H), 1.16 (d, J = 7.0 Hz, 3H), 1.02 (d, J = 7.0 Hz, 3H); ^{13}C NMR (100Mz, CDCl3) δ 198.0 (C), 147.1 (CH), 142.0 (C), 111.4 (C), 70.6 (C), 63.9 (C), 50.4 (CH_3 x

3), 25.3 (CH), 18.9 (CH_3), 18.7 (CH_3), 10.7 (CH_3); HRMS (ESI) calcd for $C_{13}H_{20}O_5Na$ $(M+Na)^+$ 279.1208, found 279.1199.



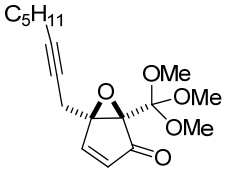
6g

(1*R,5*R**)-5-(5,5-Dimethyl-1,3-dioxan-2-yl)-1-(trimethoxymethyl)-6-oxabicyclo[3.1.0]hex-3-en-2-one (6g)** was obtained from photooxygenation of 0.01M of MOB **1g** in methanol (rose bengal as the sensitizer) and the following procedure D, in 92% yield, as colorless liquid; IR (film): 2956(s), 2870(m), 1749(s), 1437(m), 1094(m), 1031(m), 831(w) cm^{-1}; ^1H NMR (400Mz, $CDCl_3$) δ 7.81 (d, J = 6.4 Hz, 1H), 6.02 (d, J = 6.4 Hz, 1H), 5.09 (s, 1H), 3.72 (ABq, J = 11.1 Hz, 1H), 3.64 (ABq, J = 11.1 Hz, 1H) , 3.55 (ABq, J = 11.1 Hz, 1H) , 3.47 (ABq, J = 11.1 Hz, 1H), 3.31 (s, 9H), 1.24 (s, 3H), 0.75 (s, 3H); ^{13}C NMR (100Mz, $CDCl_3$) δ 195.1 (C), 153.8 (CH), 133.2 (CH), 111.3 (C), 97.6 (CH), 77.2 (CH_2), 76.9 (CH_2), 66.1 (C), 61.5 (C), 50.3 (CH_3 x 3), 30.3 (C), 23.0 (CH_3), 21.8 (CH_3); HRMS (ESI) calcd for $C_{15}H_{22}O_7Na$ $(M+Na)^+$ 337.1263, found 337.1251.



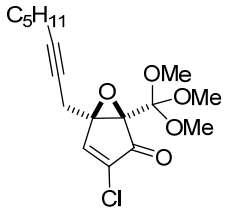
6h

(1*R,5*R**)-5-Hexadecyl-1-(trimethoxymethyl)-6-oxabicyclo[3.1.0]hex-3-en-2-one (6h)** was obtained from photooxygenation of 0.01M of MOB **1h** in methanol (rose bengal as the sensitizer), and the following procedure D, in 85% yield, as colorless liquid; IR (film): 2923(br), 2853(s), 1733(s), 1464(m), 1279(m), 1111(s), 1043(m), 1024(m), 835(w) cm^{-1}; ^1H NMR (400Mz, $CDCl_3$) δ 7.50 (d, J = 6.4, 1H), 5.94 (d, J = 6.4, 1H), 3.32 (s, 9H), 2.23-2.02 (m, 2H), 1.64-1.23 (m, 28 H), 0.85 (t, J = 6.8, 3H); ^{13}C NMR (100Mz, $CDCl_3$) δ 196.9 (C), 156.4 (CH), 132.8 (CH), 111.4 (C), 67.8 (C), 62.1 (C), 50.1 (CH_3 x 3), 31.9 (CH_2), 29.7-29.3 (CH_2 x 11), 26.7 (CH_2), 25.4 (CH_2), 22.6 (CH_2), 14.1 (CH_3); HRMS (ESI) calcd for $C_{25}H_{45}O_5$ $(M+H)^+$ 425.3267, found 425.3270.



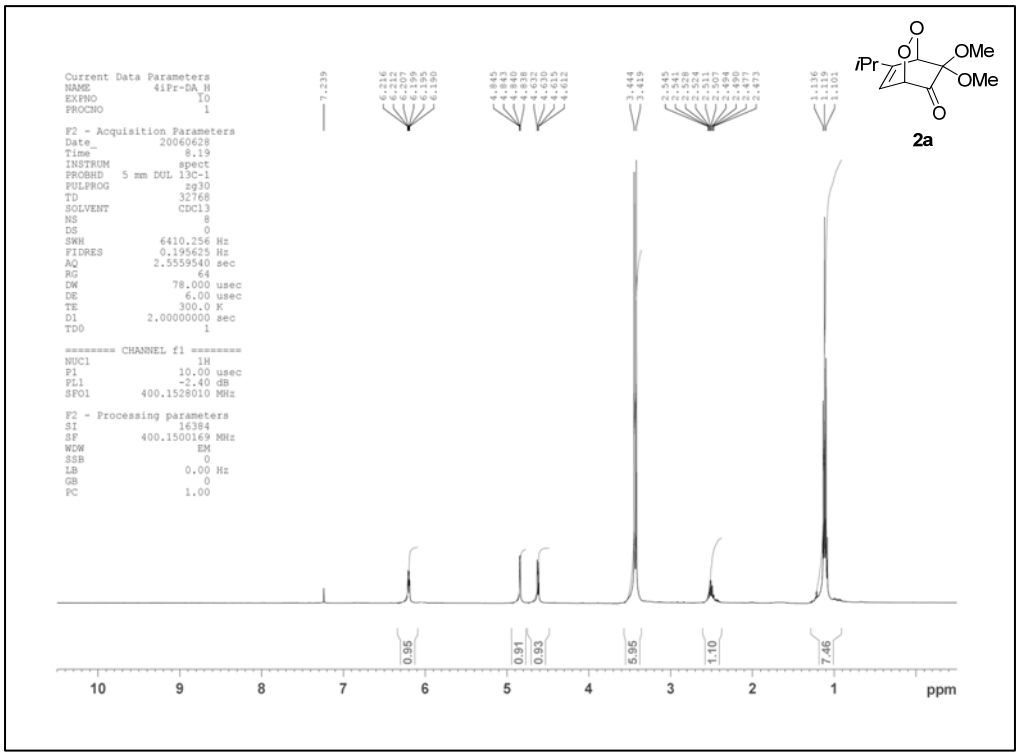
6i

(1*R,5*R**)-5-Oct-2-yn-1-yl-1-(trimethoxymethyl)-6-oxabicyclo[3.1.0]hex-3-en-2-one (6i)** was obtained from photooxygenation of 0.01M of MOB **1i** in methanol (rose bengal as the sensitizer) and the following procedure D, in 90% yield, as colorless liquid; IR (film) 2936(br), 2843(m), 1735(s), 1462(m), 1337(w), 1276(w), 1206(w), 1115(s), 1083(m), 988(w), 953(w), 824(w) cm^{-1}; ^1H NMR (600Mz, $CDCl_3$) δ7.69 (d, J = 6.2Hz, 1H), 5.98 (d, J = 6.2 Hz, 1H), 3.32 (s, 9H), 3.10 (ABqt, J = 17.7, 2.4 Hz, 1H), 3.07 (ABqt, J = 17.7, 2.4 Hz, 1H), 2.12 (tt, J = 7.2, 2.4 Hz, 2H), 1.44 (sextet, J = 7.2 Hz, 2H), 1.33-1.25 (m, 4H), 0.87 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100Mz, $CDCl_3$) δ195.9 (C), 156.2 (CH), 132.6 (CH), 111.5 (C), 83.1 (C), 73.7 (C), 65.9 (C), 61.7 (C), 50.2 (CH_3 x 3), 31.0 (CH_2), 28.4 (CH_2), 22.1 (CH_2), 18.6 (CH_2), 18.4 (CH_2) 13.9 (CH_3); HRMS (ESI) calcd for $C_{17}H_{24}O_5Na$ $(M+Na)^+$ 331.1521, found 331.1522.

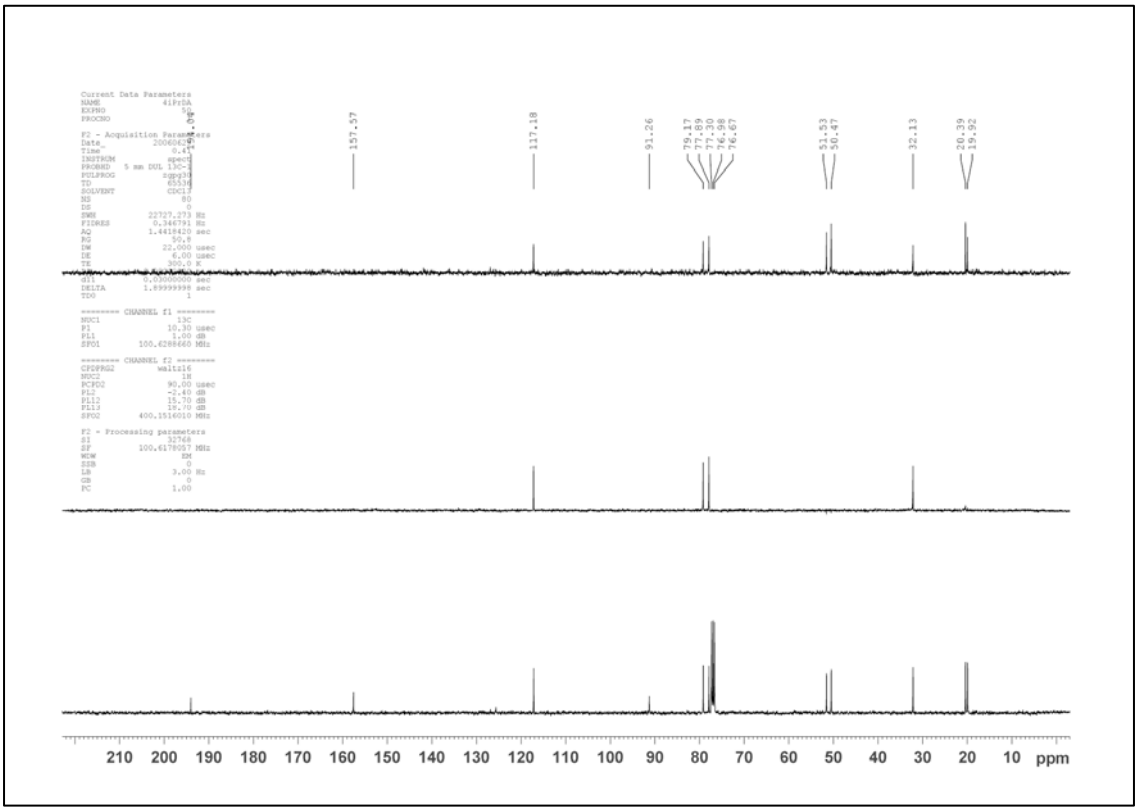


6j

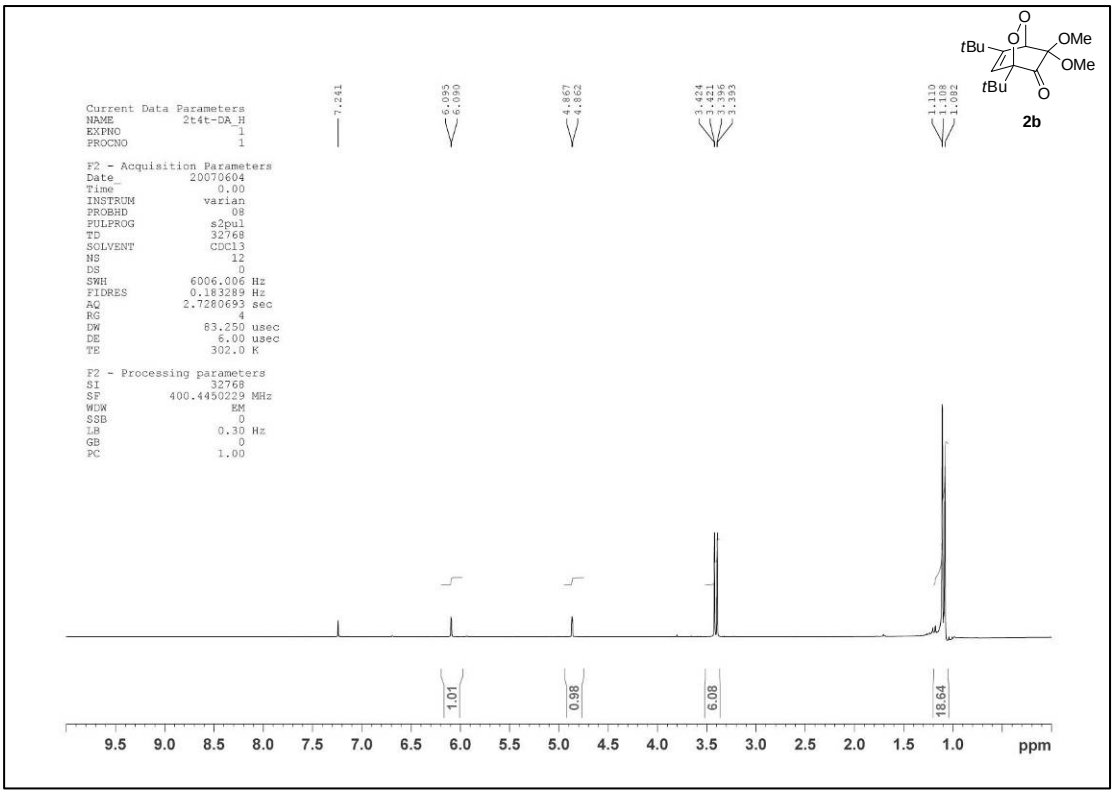
(1*R,5*R**)-3-Chloro-5-oct-2-yn-1-yl-1-(trimethoxymethyl)-6-oxabicyclo[3.1.0]hex-3-en-2-one (6j)** was obtained from photooxygenation of 0.01M of MOB **1j** in methanol (rose bengal as the sensitizer) and the following procedure D, in 70% yield, as colorless liquid; IR (film) 2954(br), 2872(m), 1749(s), 1593(m), 1465(m), 1458(m), 1120(br), 774(s) cm^{-1}; ^{1}H NMR (400Mz, $CDCl_3$) δ7.59 (s, 1H), 3.32 (s, 9H), 3.11 (ABqt, J = 17.5, 2.4 Hz, 1H), 3.07 (ABqt, J = 17.5, 2.4 Hz, 1H), 2.13 (tt, J = 7.1 Hz, 2.4 Hz, 2H), 1.449 (sextet, J = 7.1 Hz, 2H), 1.346-1.249 (m, 4H), 0.863 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100Mz, $CDCl_3$) δ188.5 (C), 149.0 (CH), 136.1 (C), 111.3 (C), 84.4 (C), 73.3 (C), 64.2 (C), 61.3 (C), 50.4 (CH_3 x 9), 31.0 (CH_2), 28.4 (CH_2), 22.2 (CH_2), 18.6 (CH_2), 18.5 (CH_2), 14.0 (CH_3); HRMS (ESI) calcd for $C_{17}H_{23}ClO_5Na$ $(M+Na)^+$ 365.1126, found 365.1138.



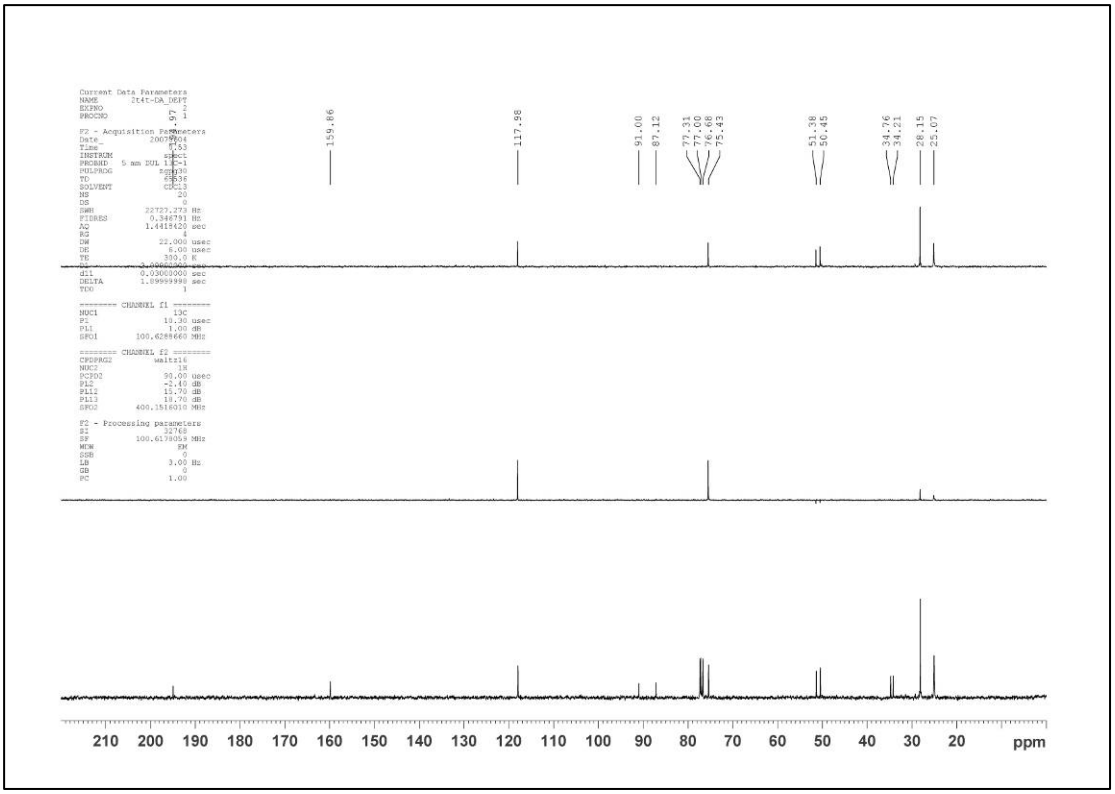
^{1}H NMR of Compound **2a**



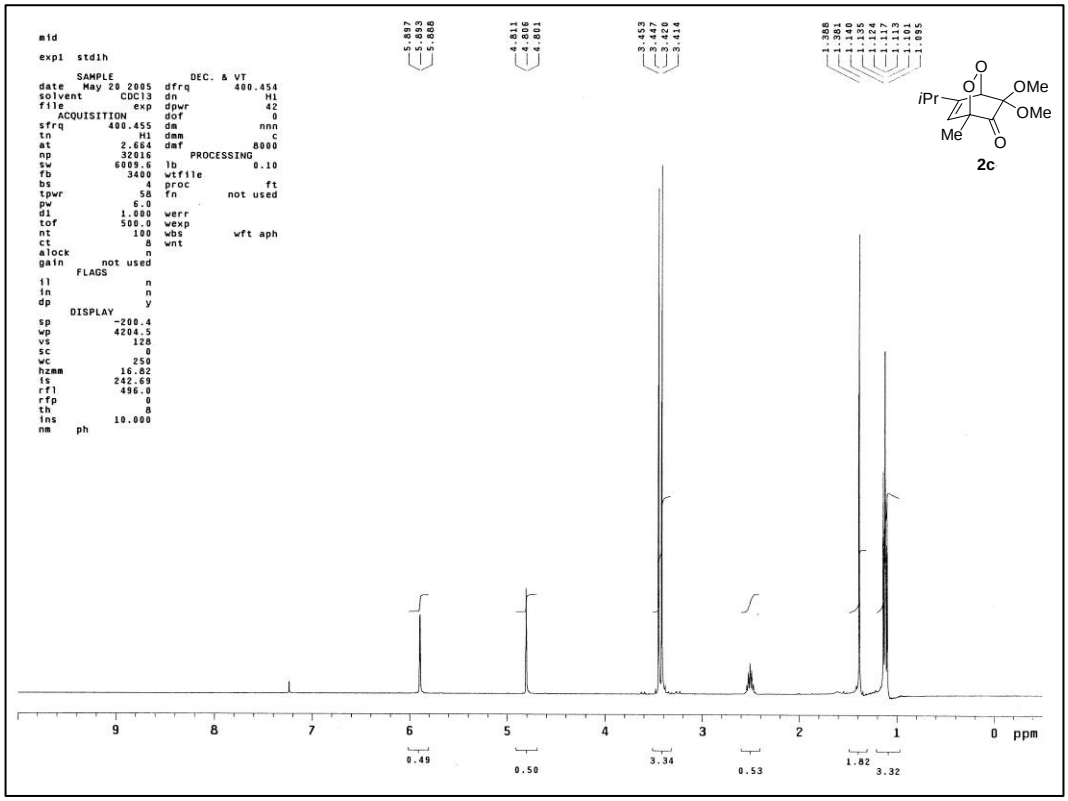
^{13}C NMR and DEPT of Compound **2a**



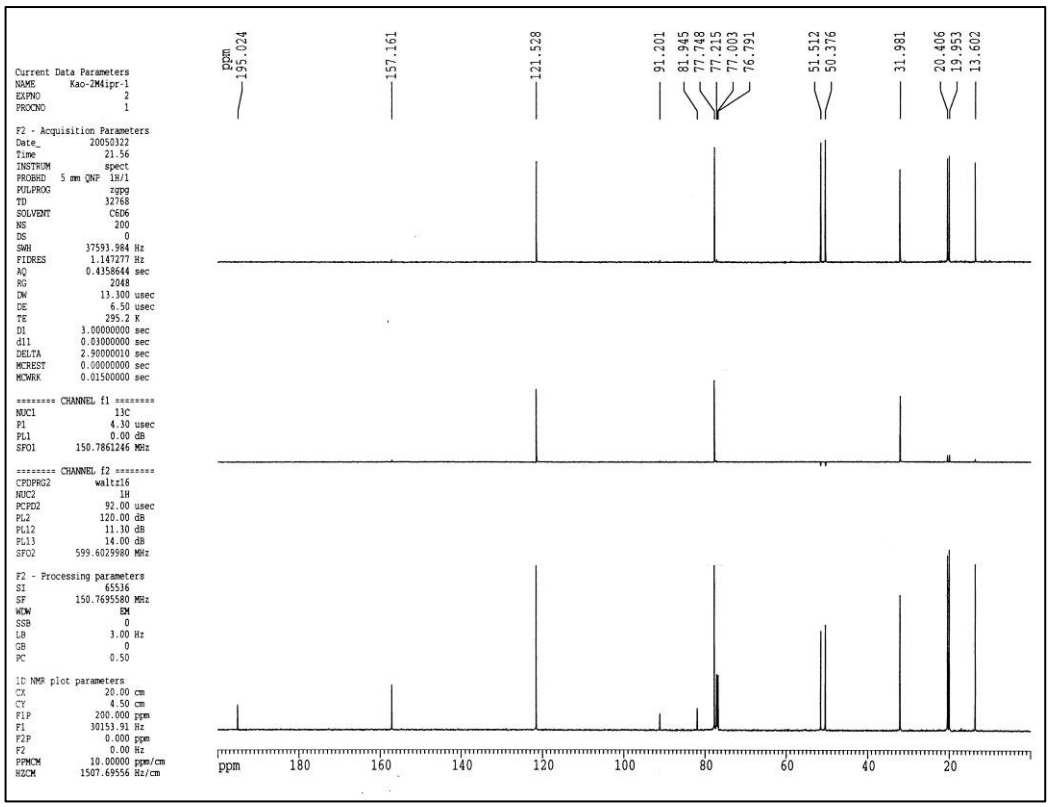
^{1}H NMR of Compound **2b**



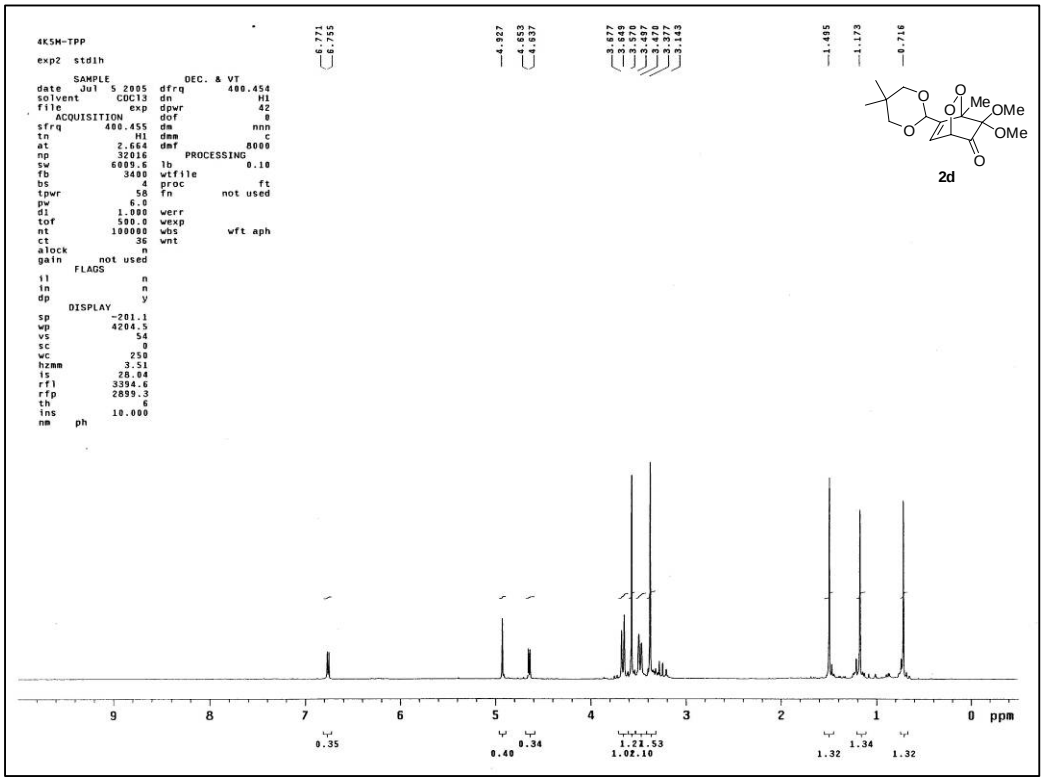
^{13}C NMR and DEPT of Compound **2b**



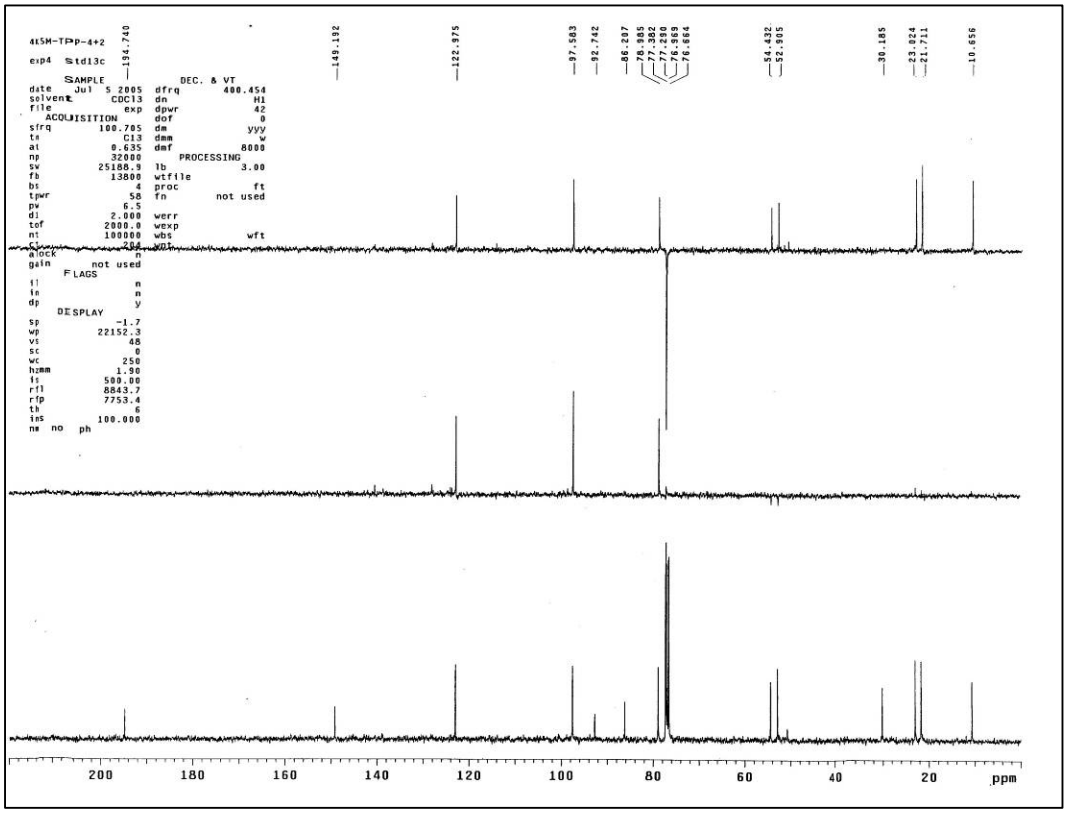
^{1}H NMR of Compound **2c**



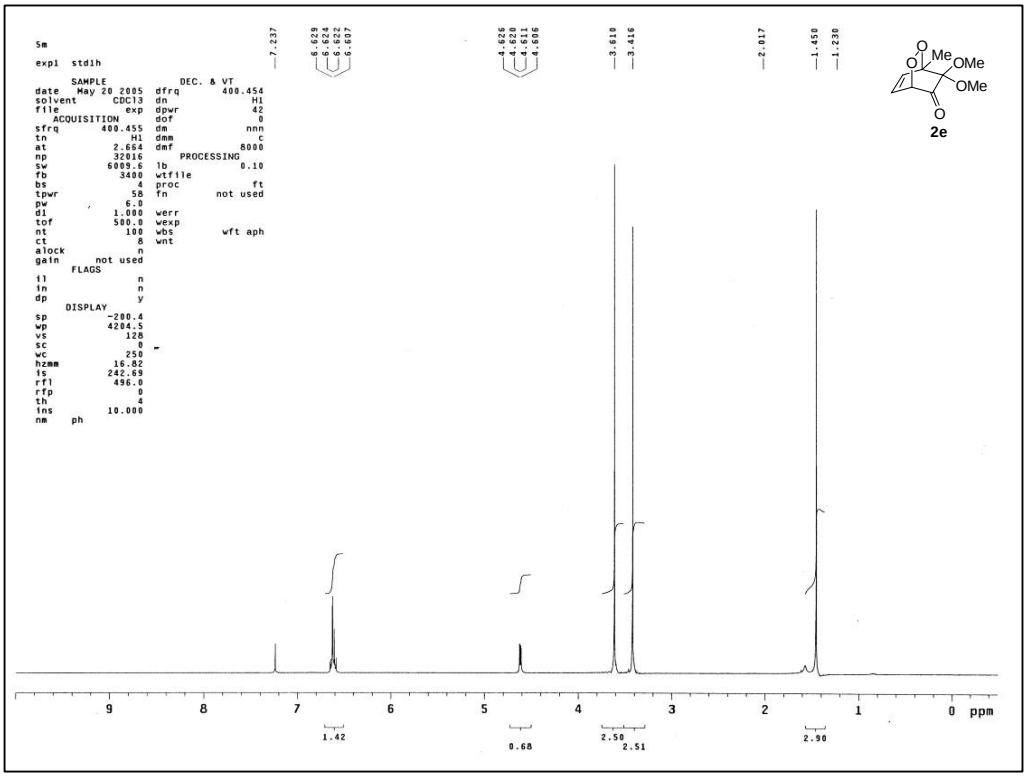
^{13}C NMR and DEPT of Compound **2c**



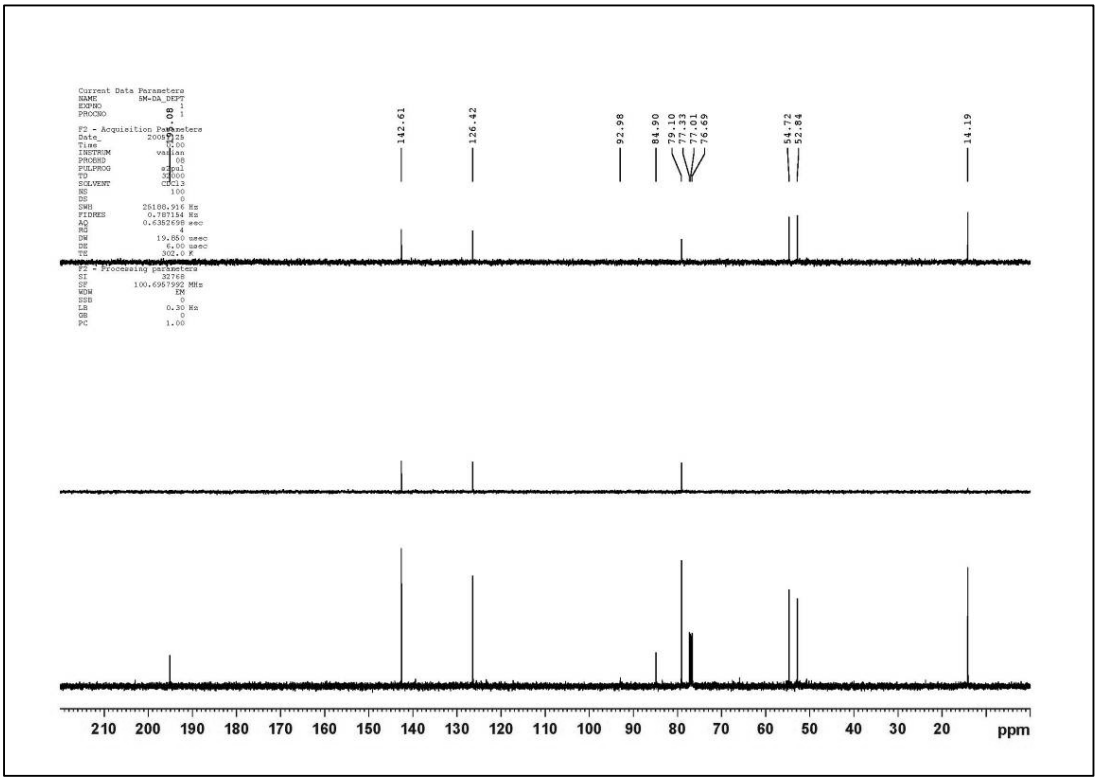
^{1}H NMR of Compound **2d**



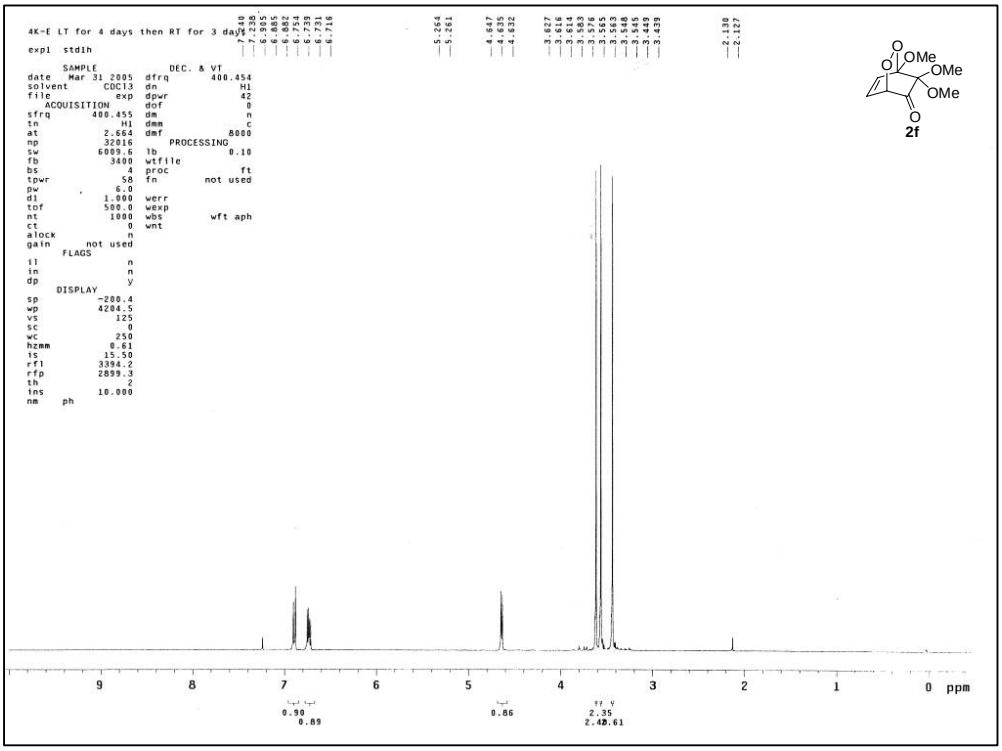
^{13}C NMR and DEPT of Compound **2d**



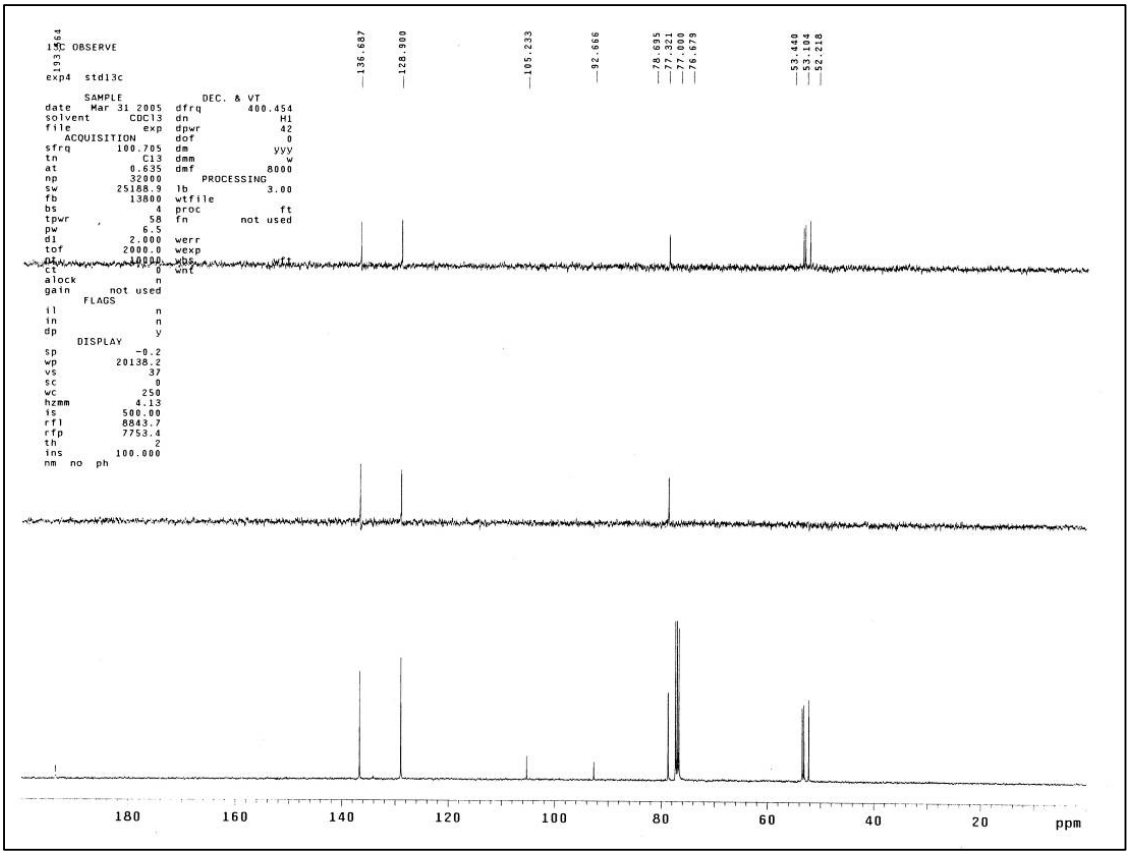
^{1}H NMR of Compound **2e**



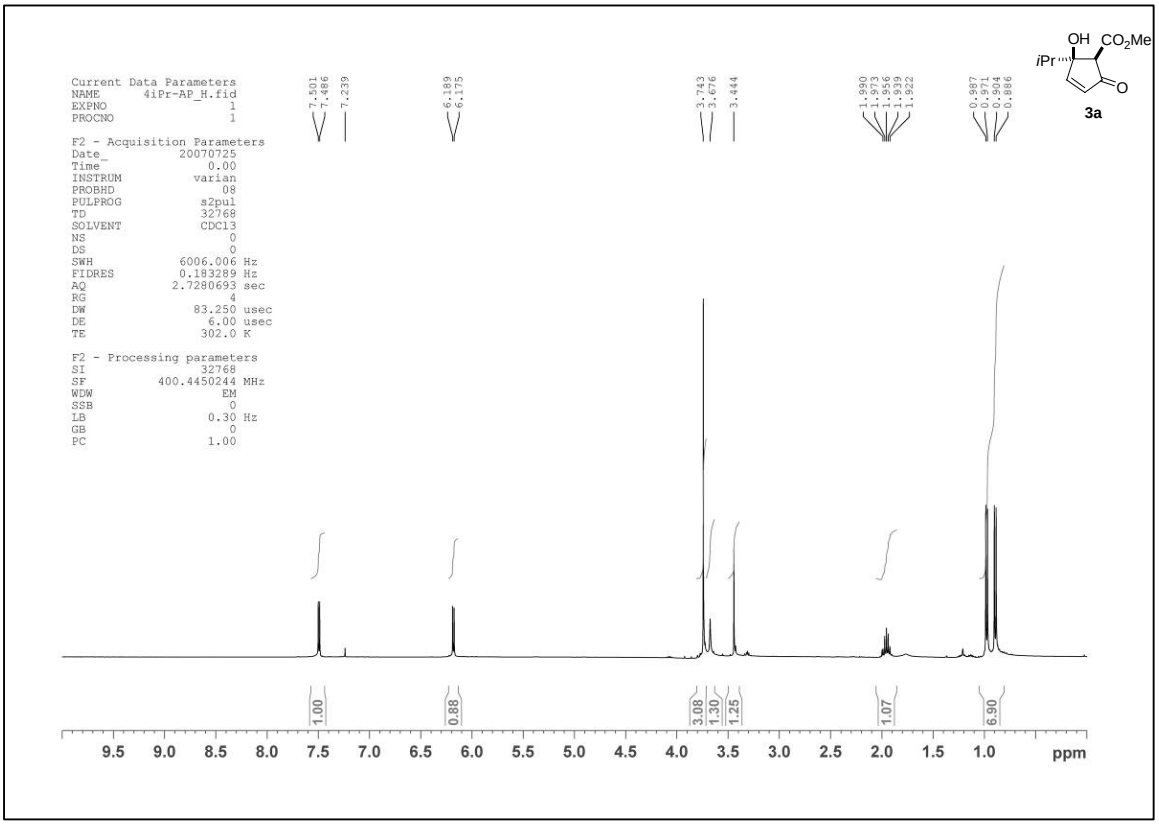
^{13}C NMR and DEPT of Compound **2e**



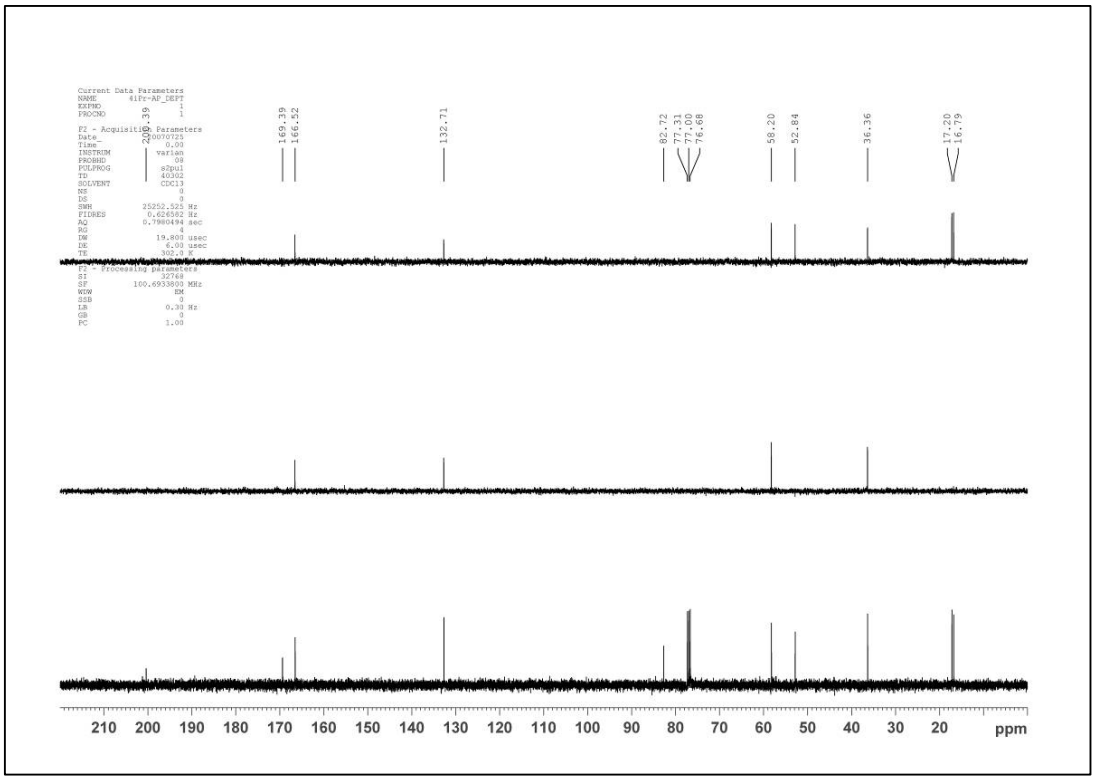
^{1}H NMR of Compound **2f**



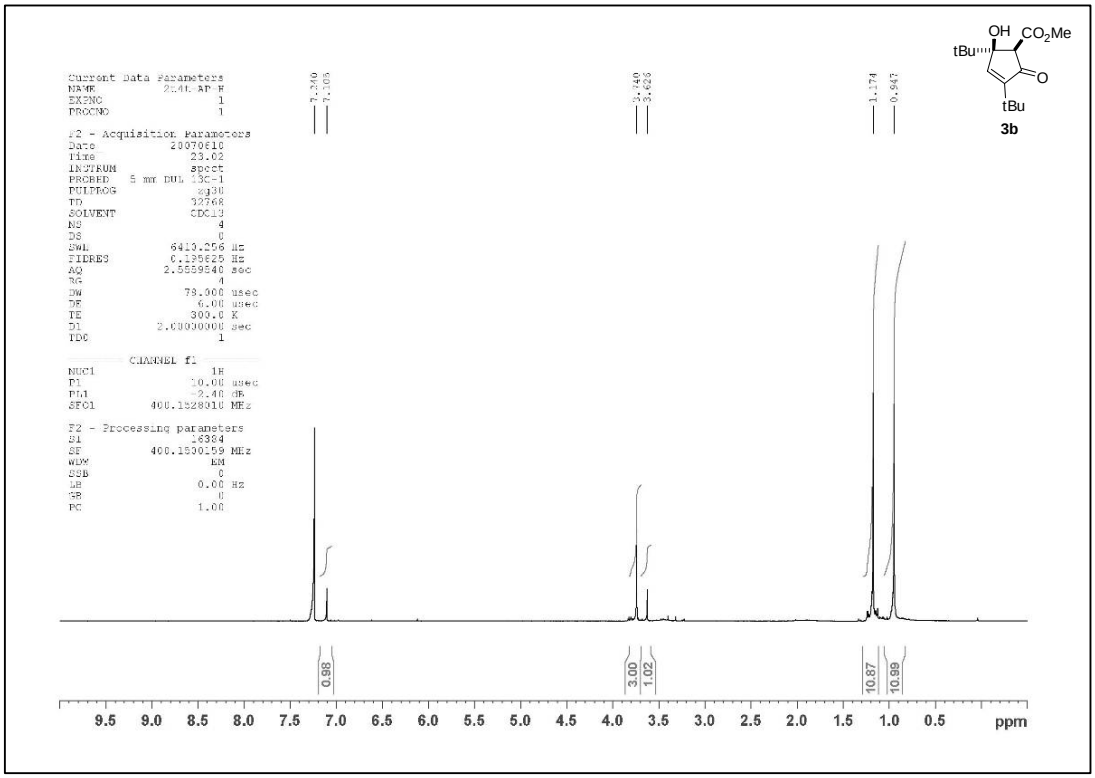
^{13}C NMR and DEPT of Compound **2f**



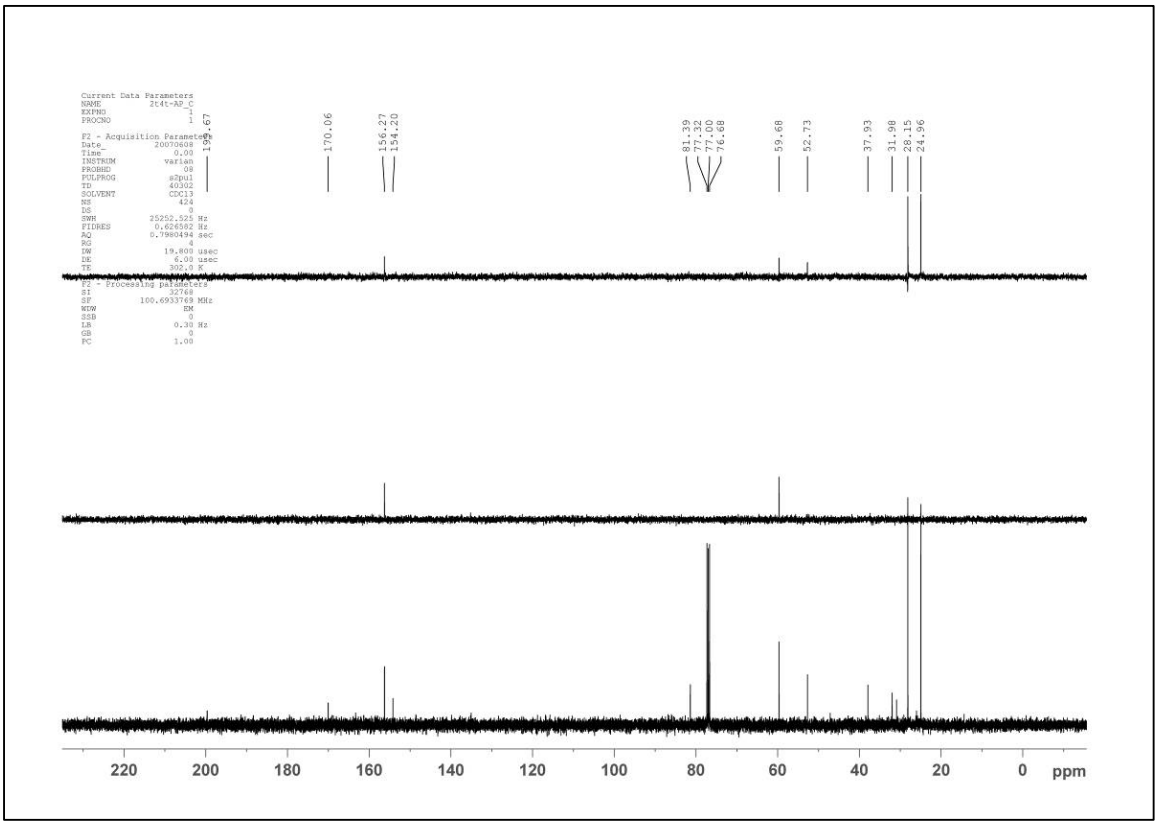
^{1}H NMR of Compound **3a**



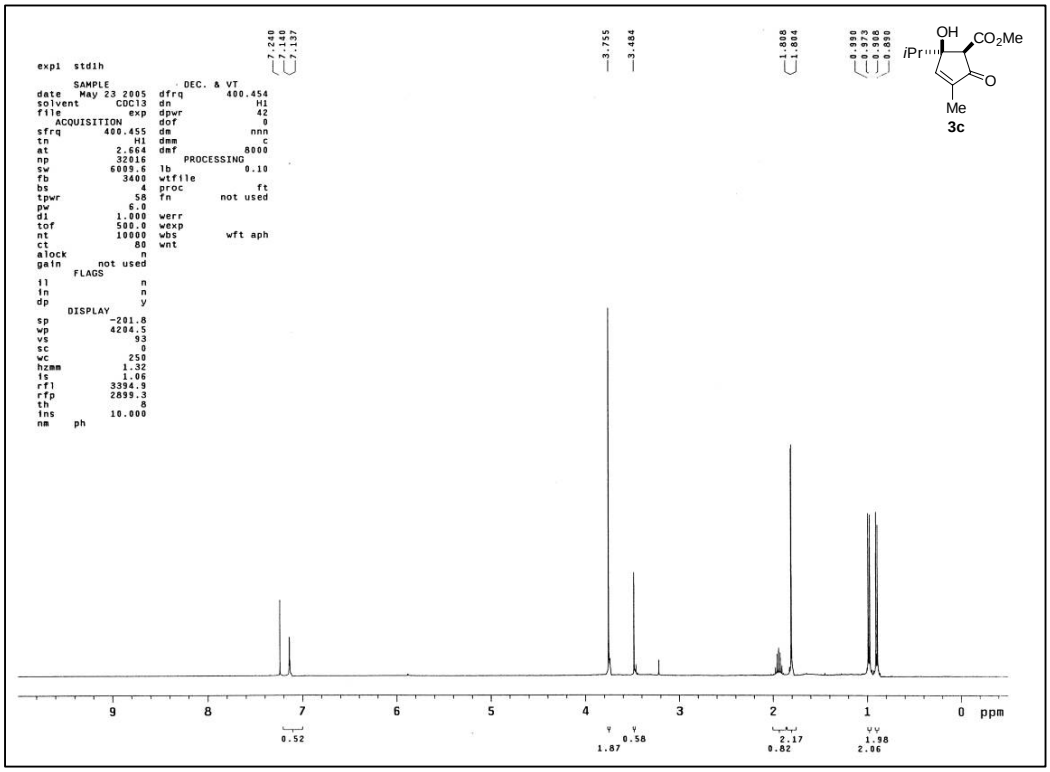
^{13}C NMR and DEPT of Compound **3a**



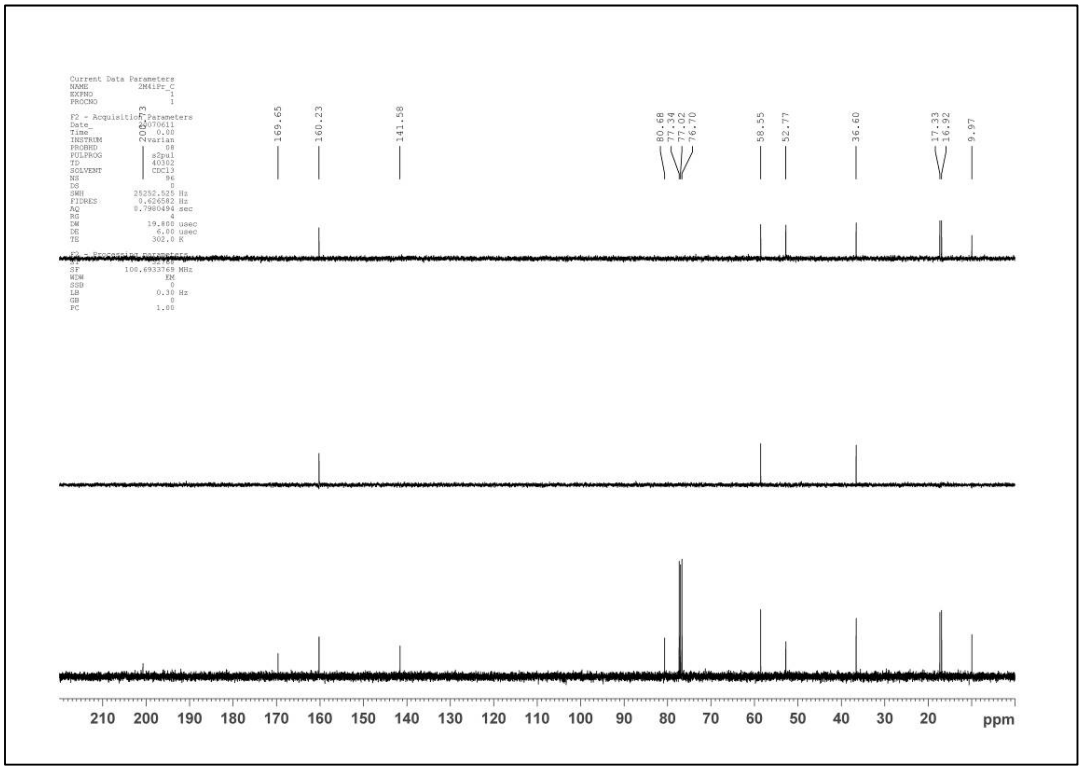
^{1}H NMR of Compound **3b**



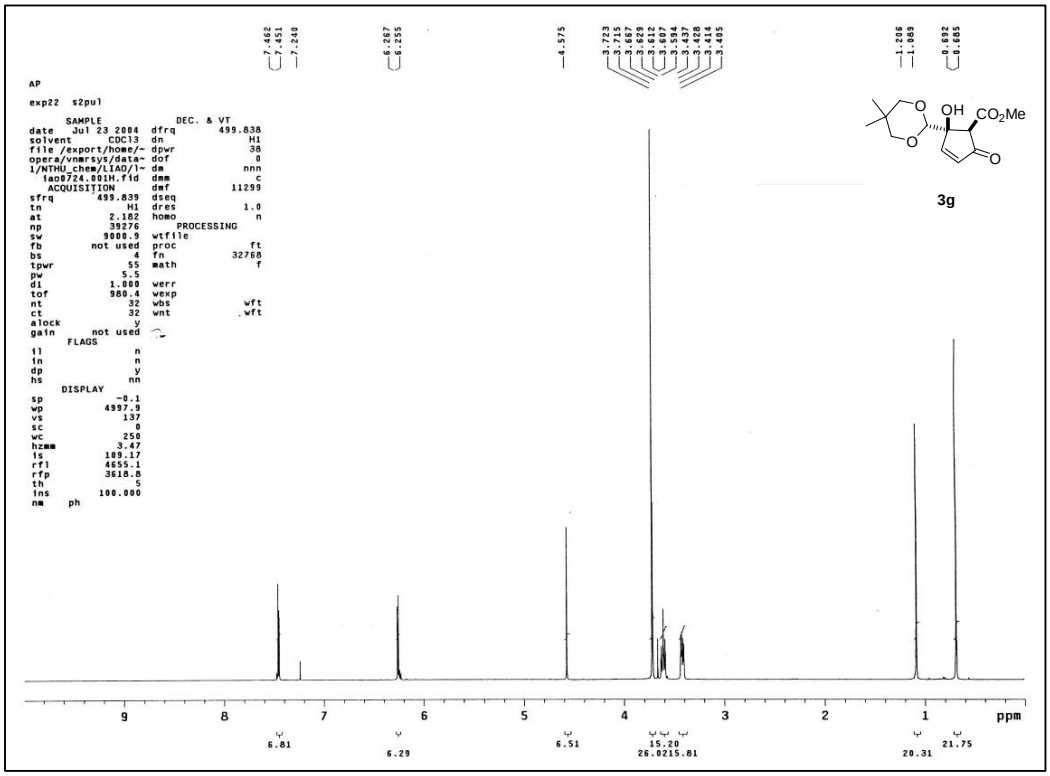
^{13}C NMR and DEPT of Compound **3b**



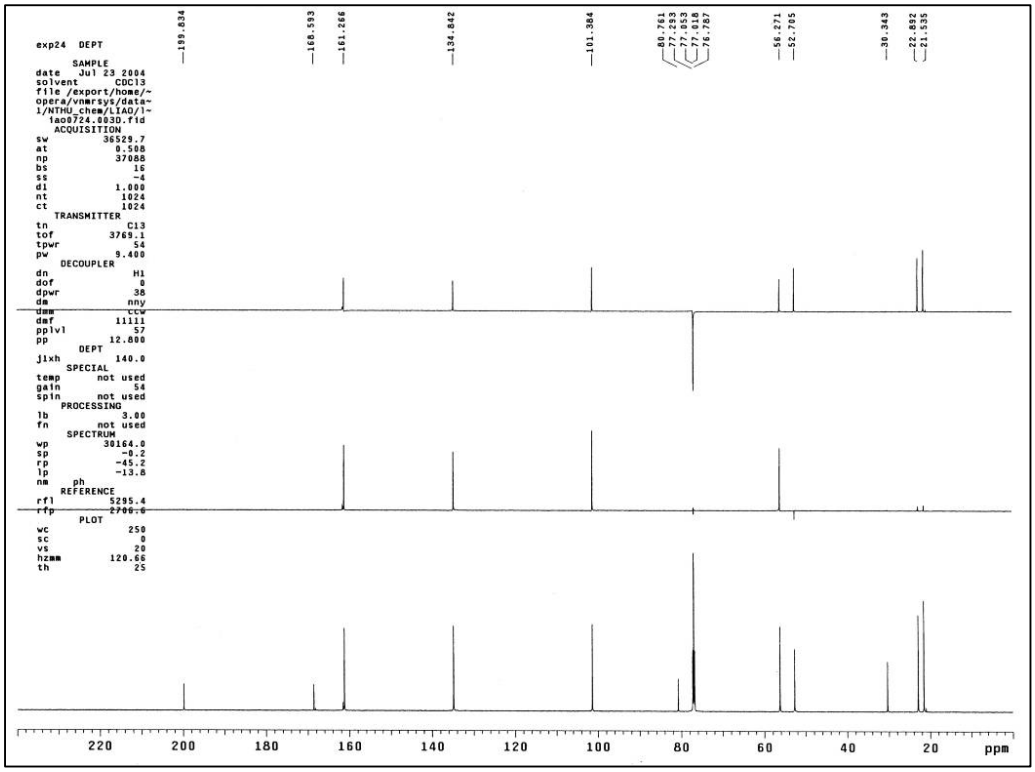
^{1}H NMR of Compound **3c**



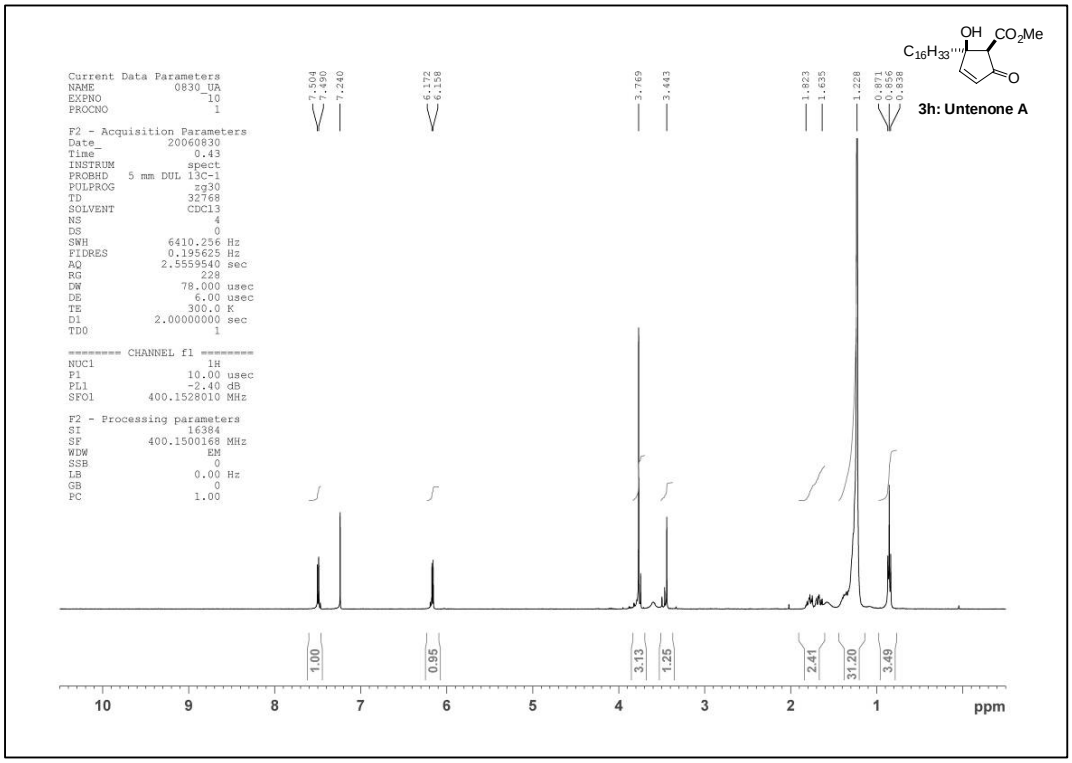
^{13}C NMR and DEPT of Compound **3c**



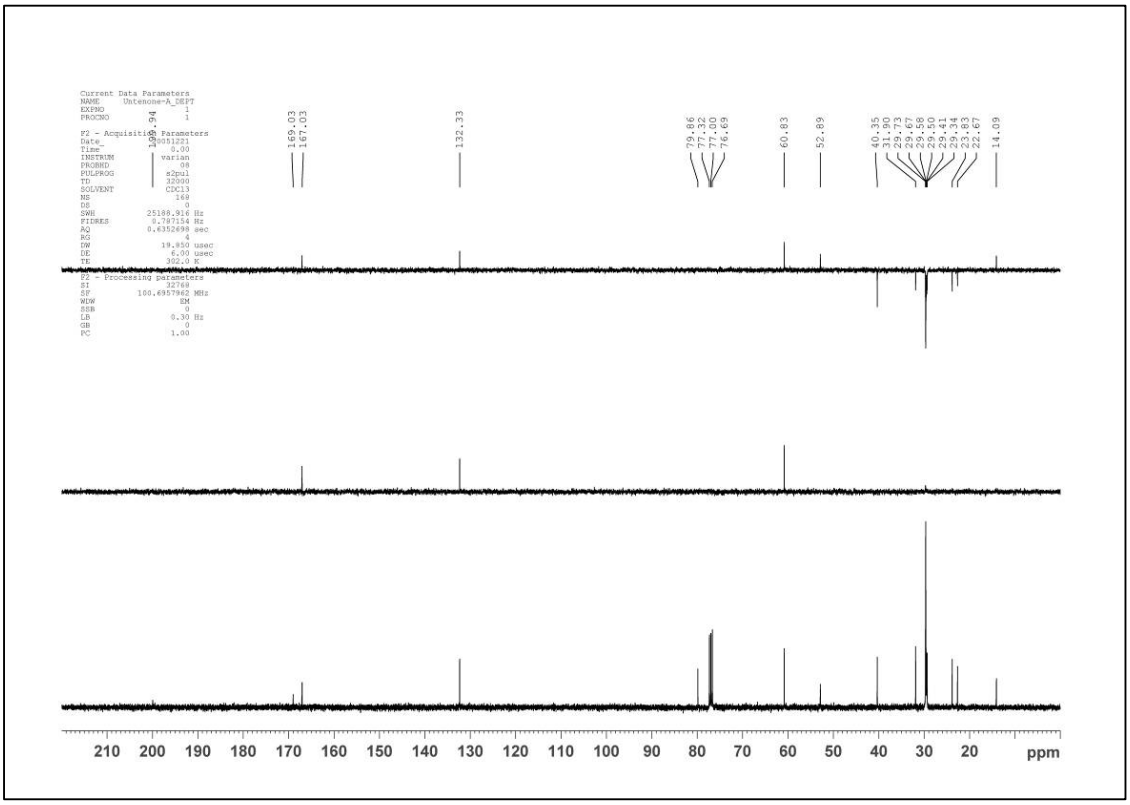
^{1}H NMR of Compound **3g**



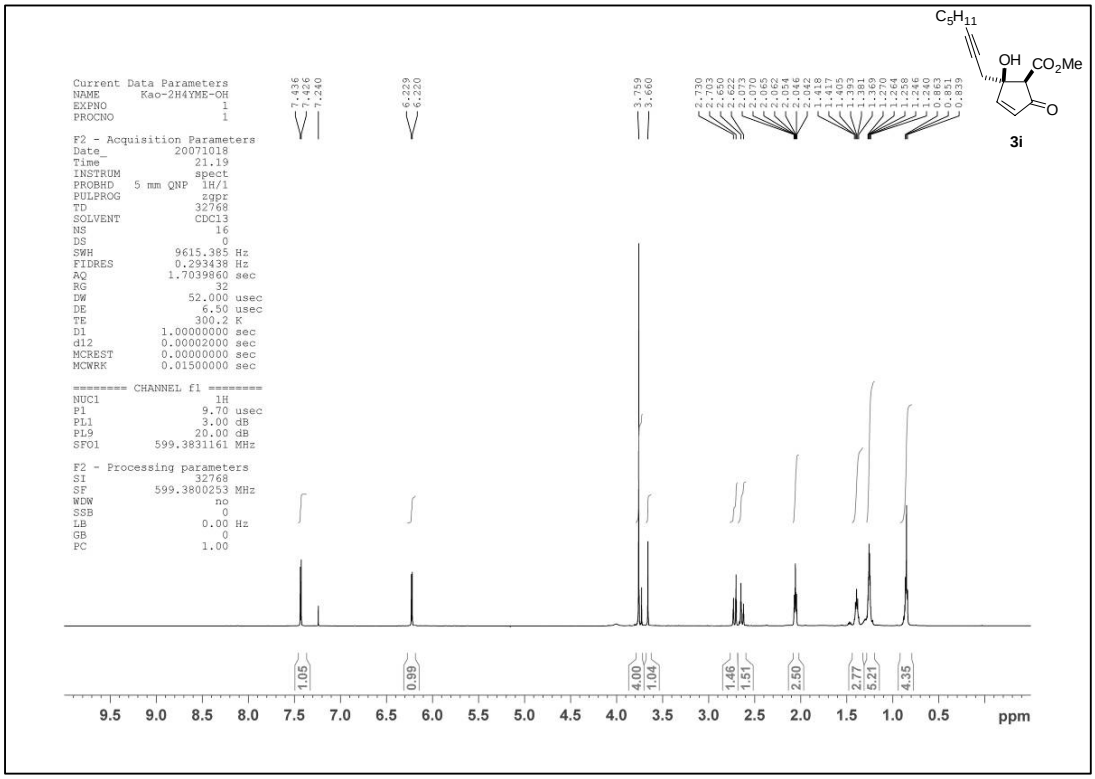
^{13}C NMR and DEPT of Compound **3g**



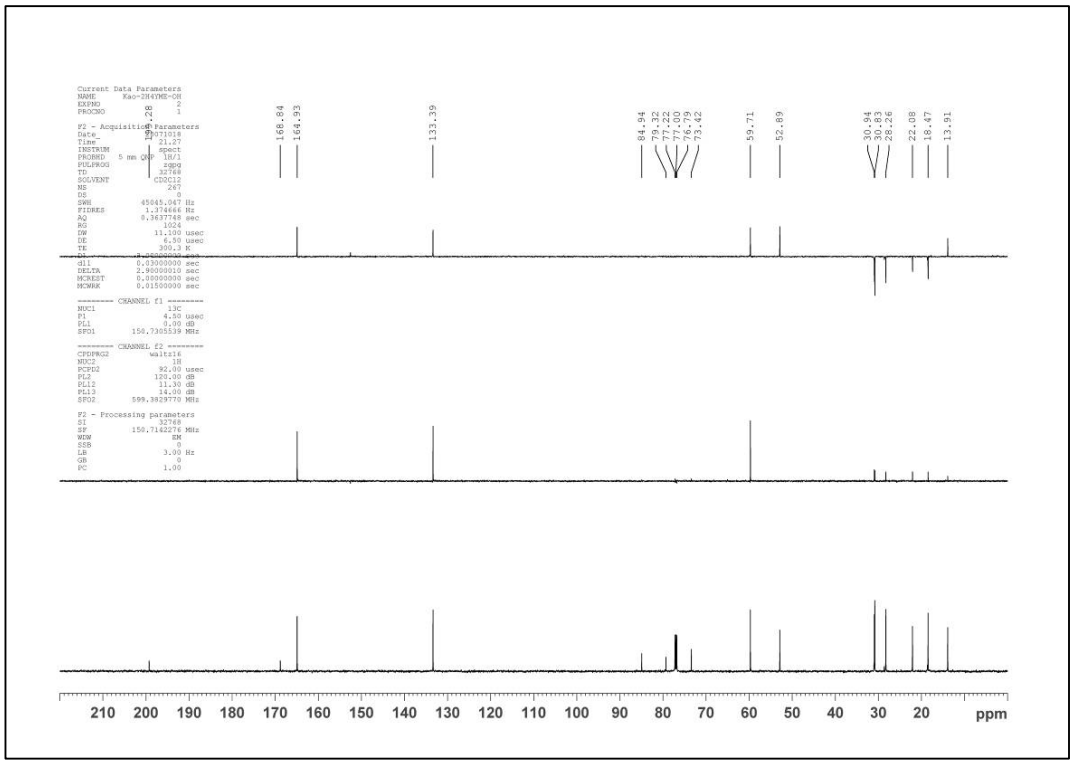
^{1}H NMR of Compound **3h**



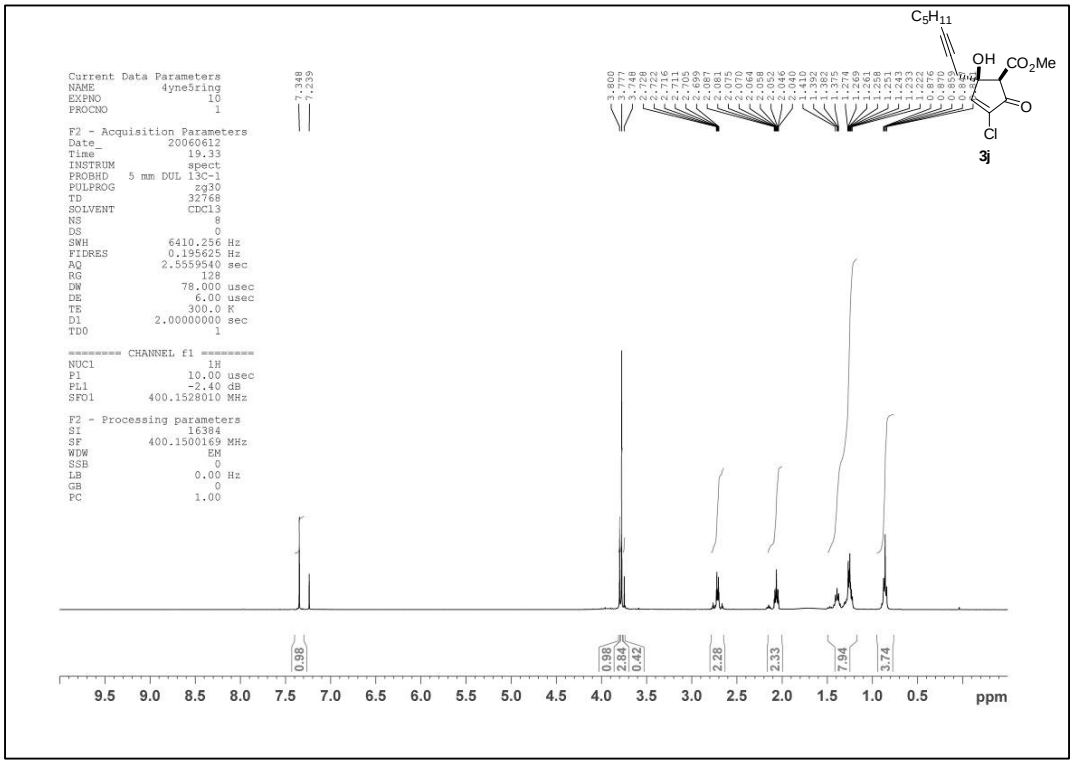
^{13}C NMR and DEPT of Compound **3h**



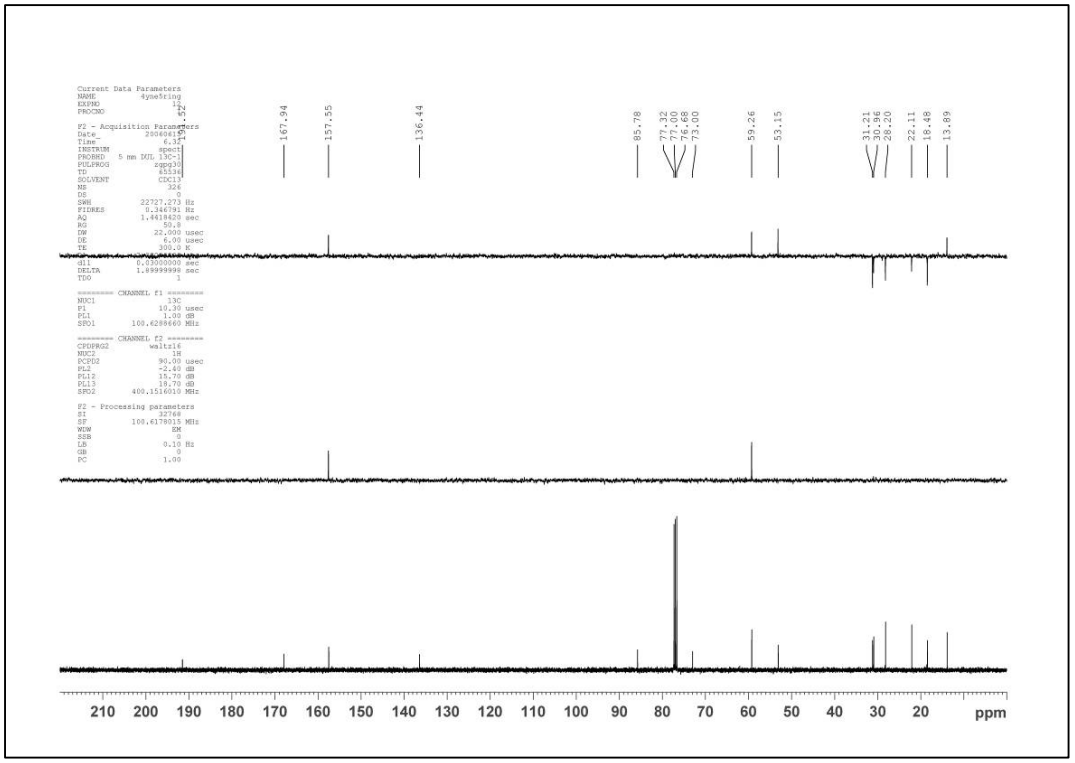
^{1}H NMR of Compound **3i**



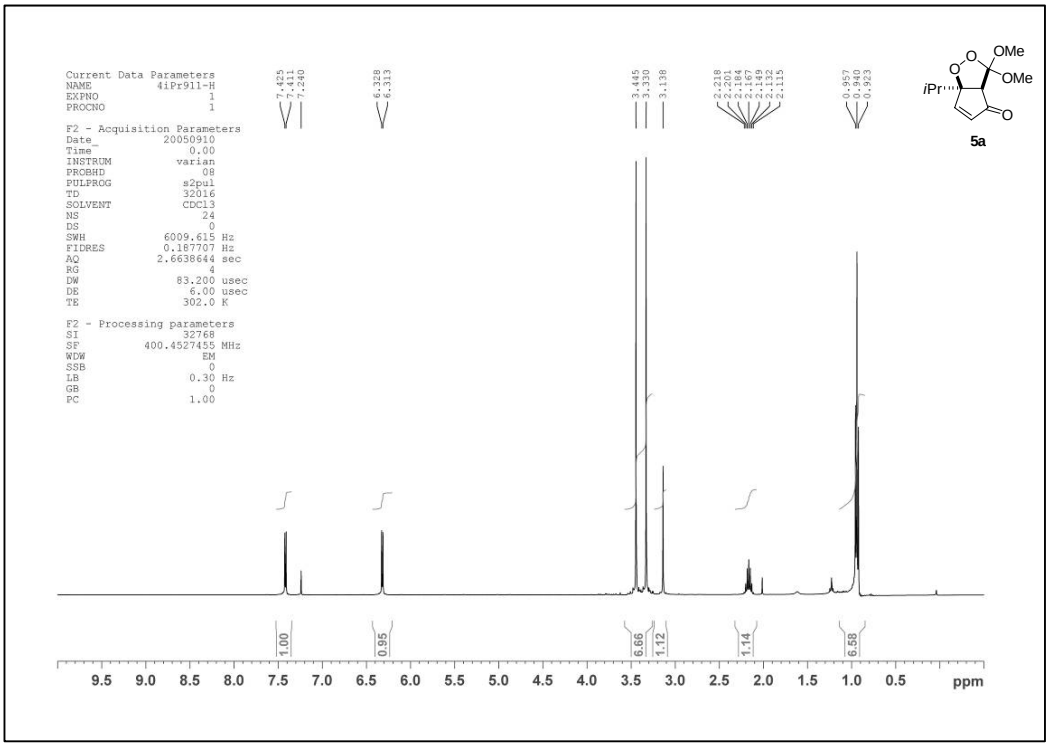
^{13}C NMR and DEPT of Compound **3i**



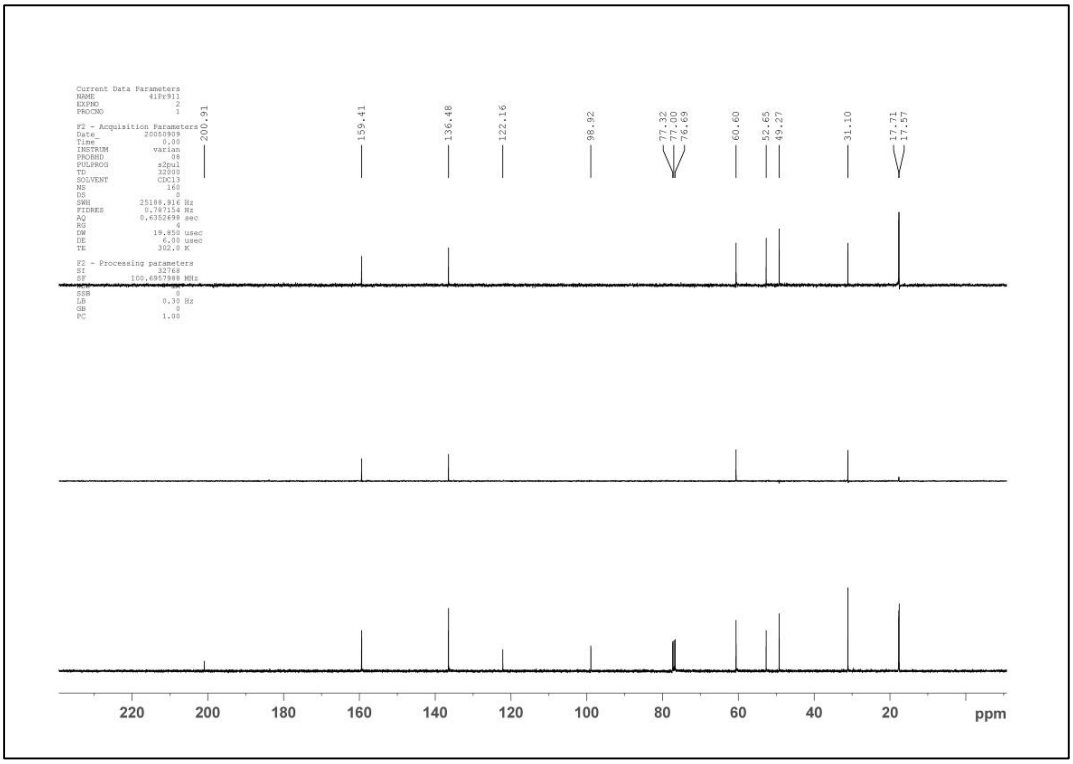
^{1}H NMR of Compound **3j**



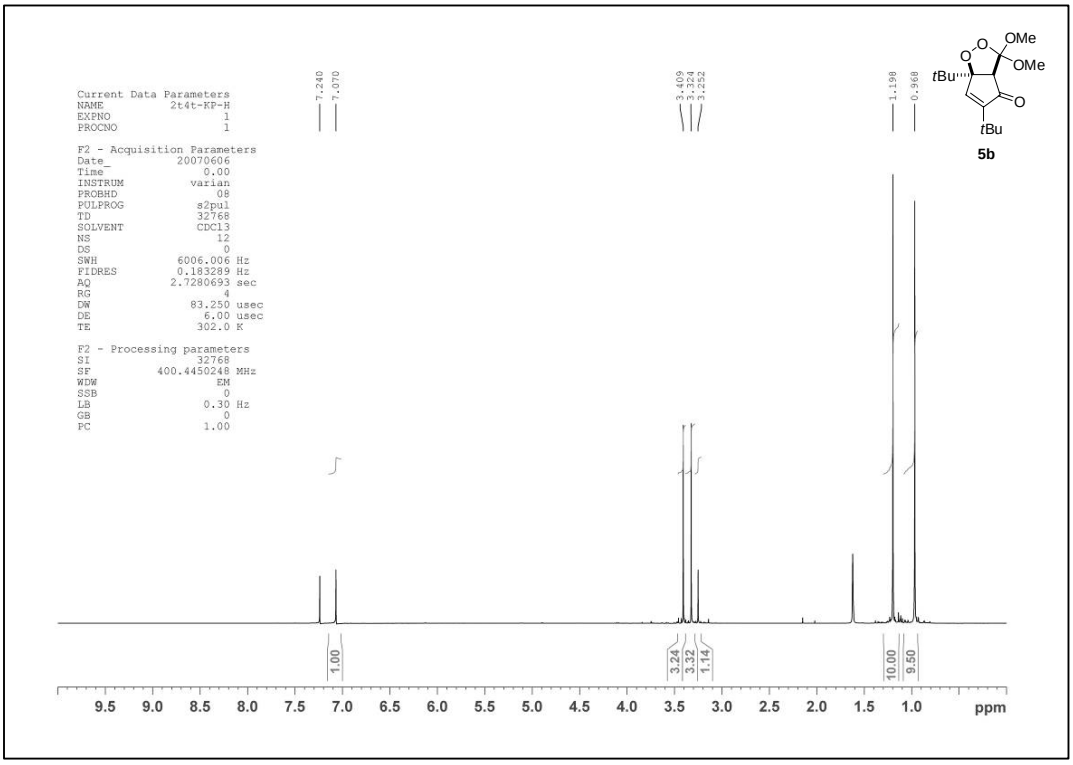
^{13}C NMR and DEPT of Compound **3j**



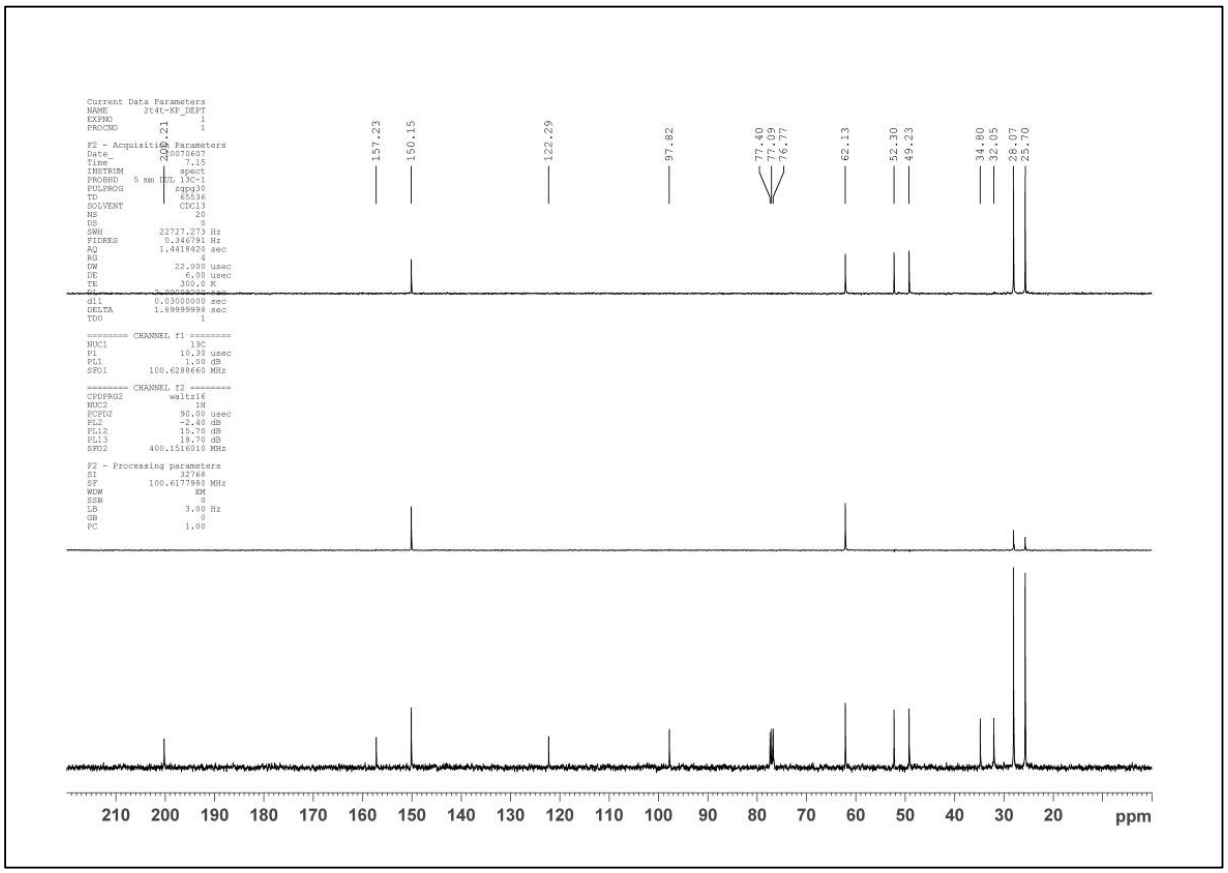
^{1}H NMR of Compound **5a**



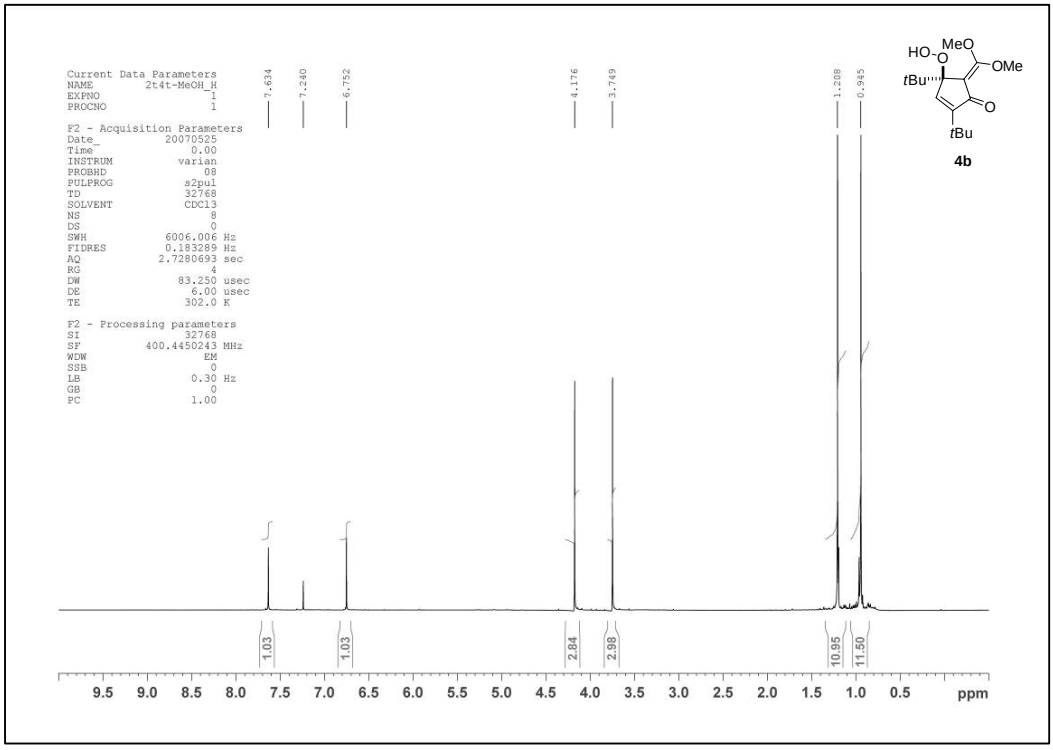
^{13}C NMR and DEPT of Compound **5a**



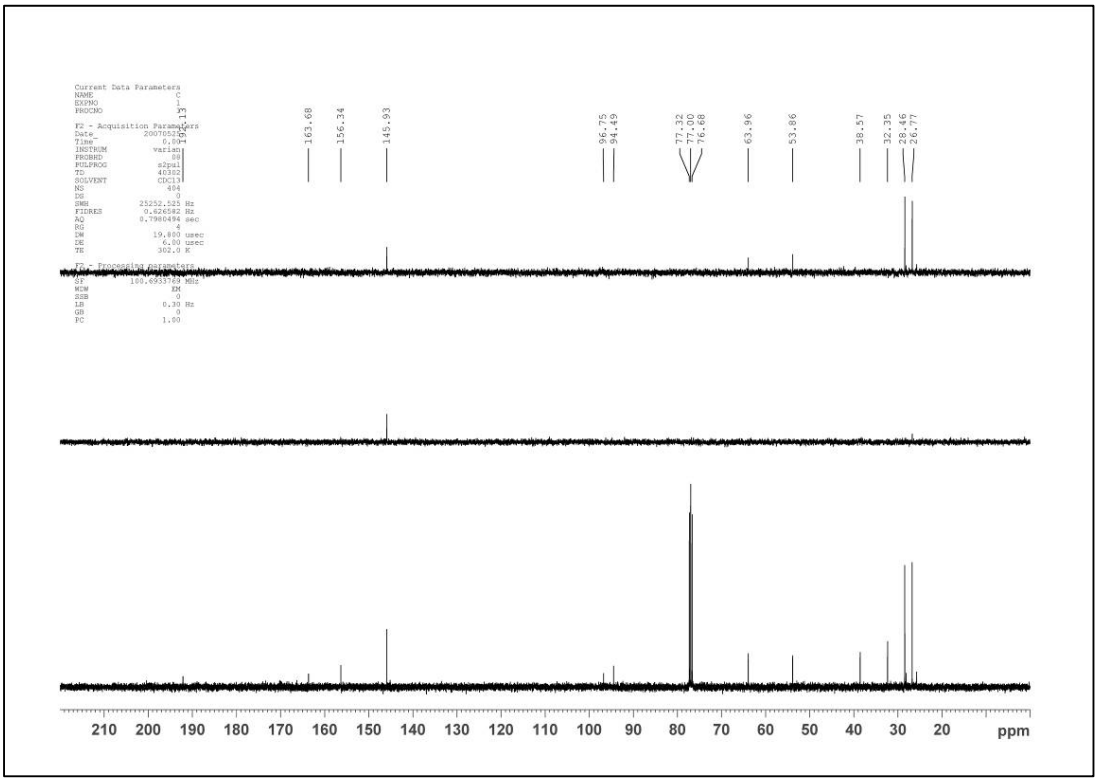
^{1}H NMR of Compound **5b**



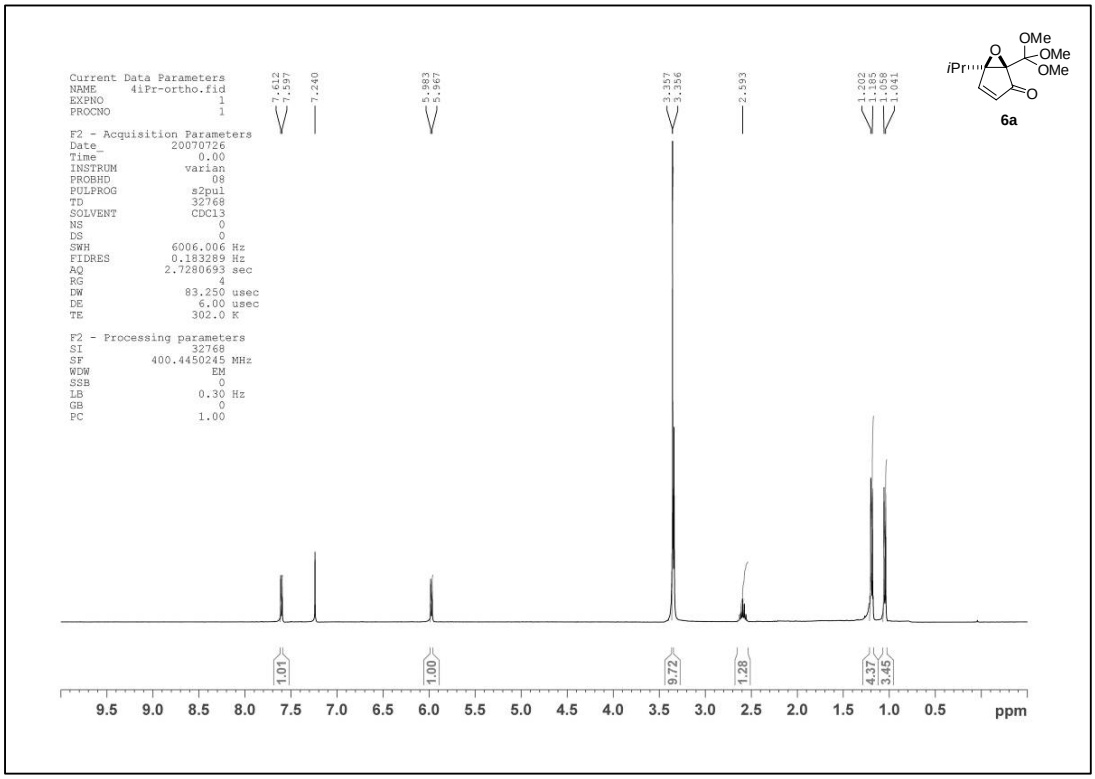
^{13}C NMR and DEPT of Compound **5b**



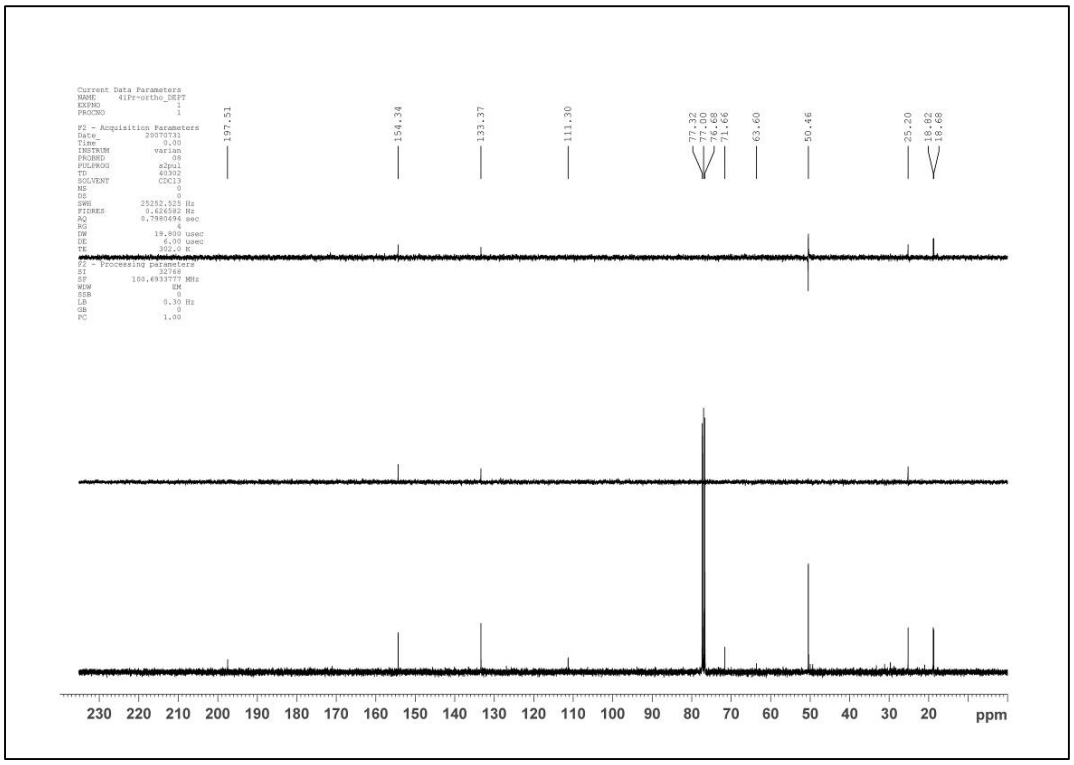
^{1}H NMR of Compound **4b**



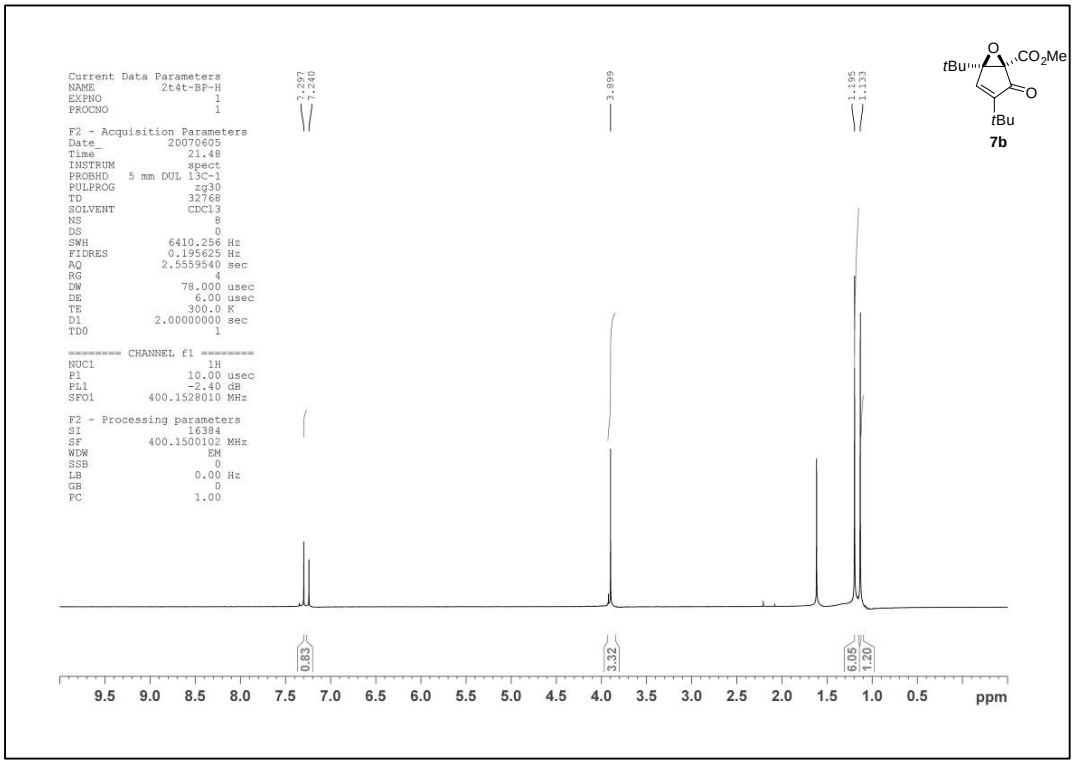
^{13}C NMR and DEPT of Compound **4b**



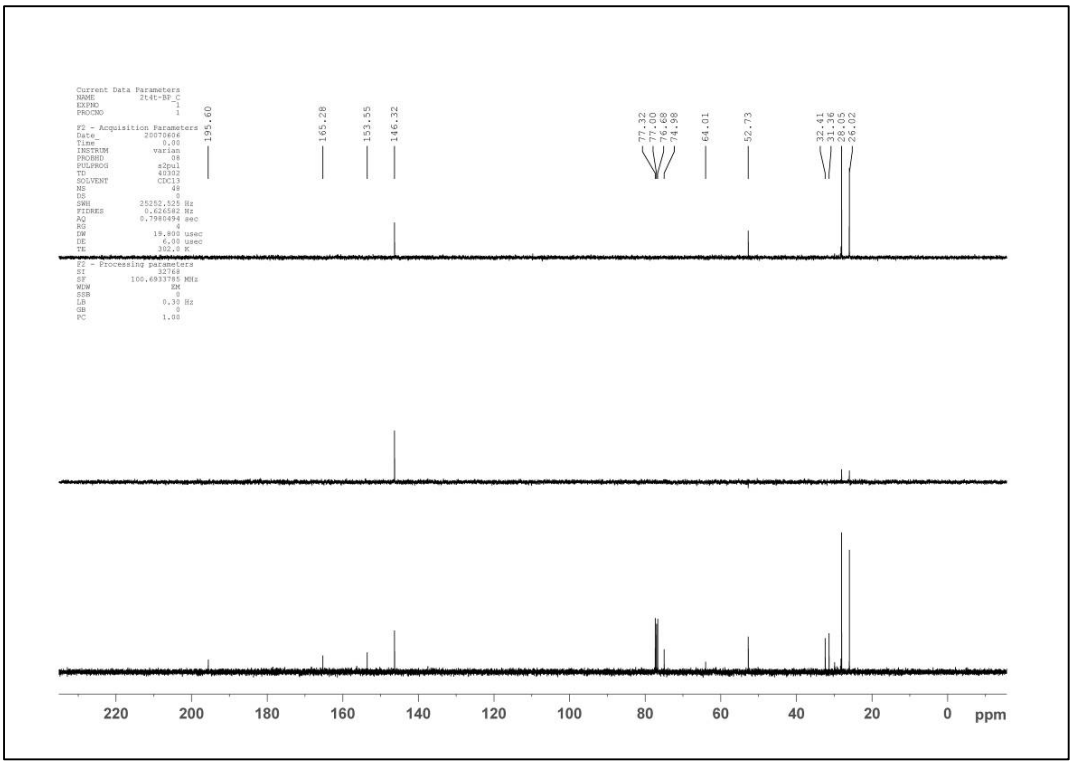
^{1}H NMR of Compound **6a**



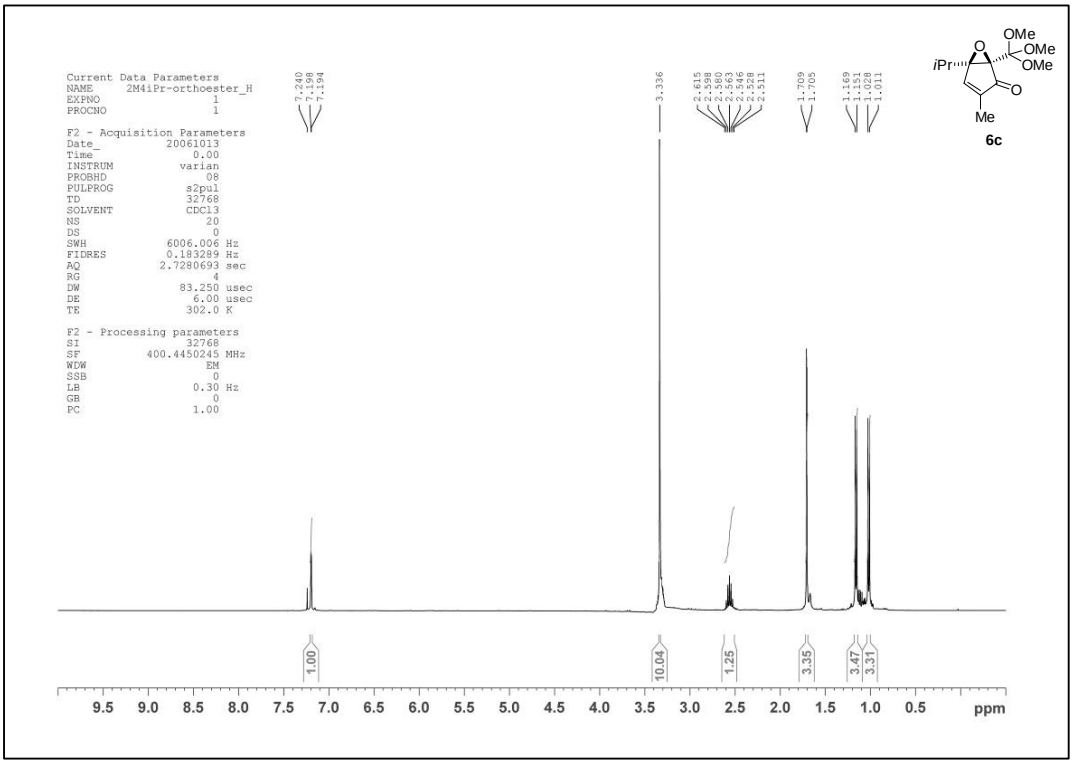
^{13}C NMR and DEPT of Compound **6a**



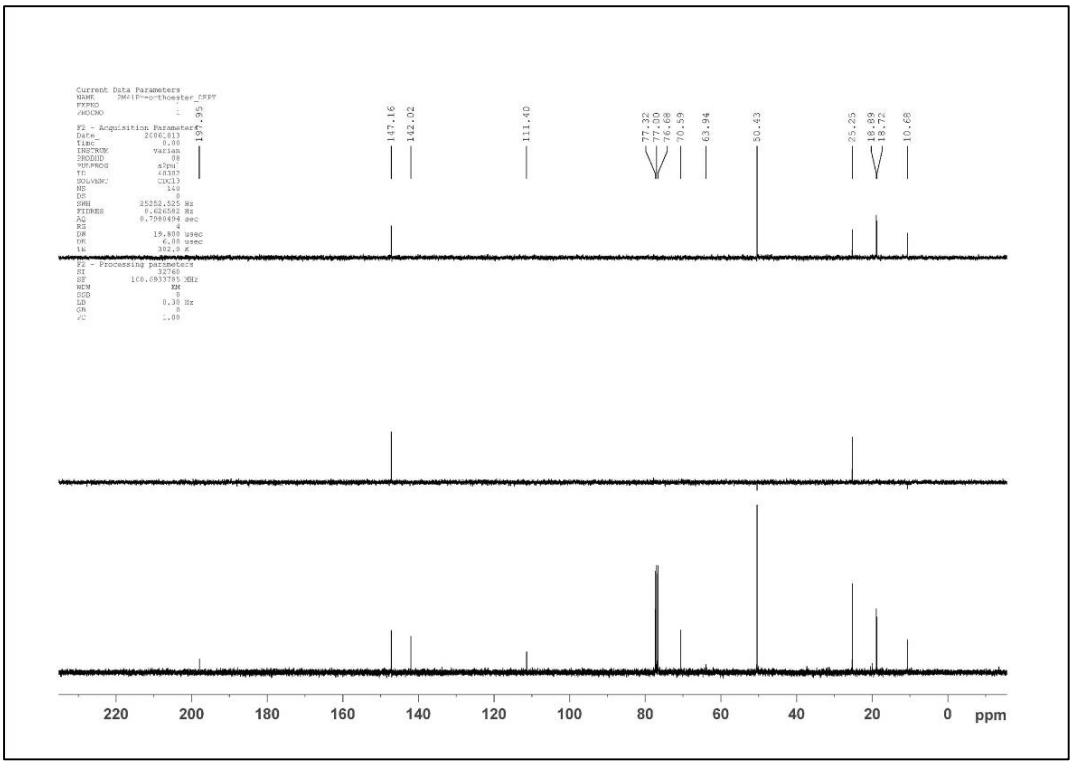
^{1}H NMR of Compound **7b**



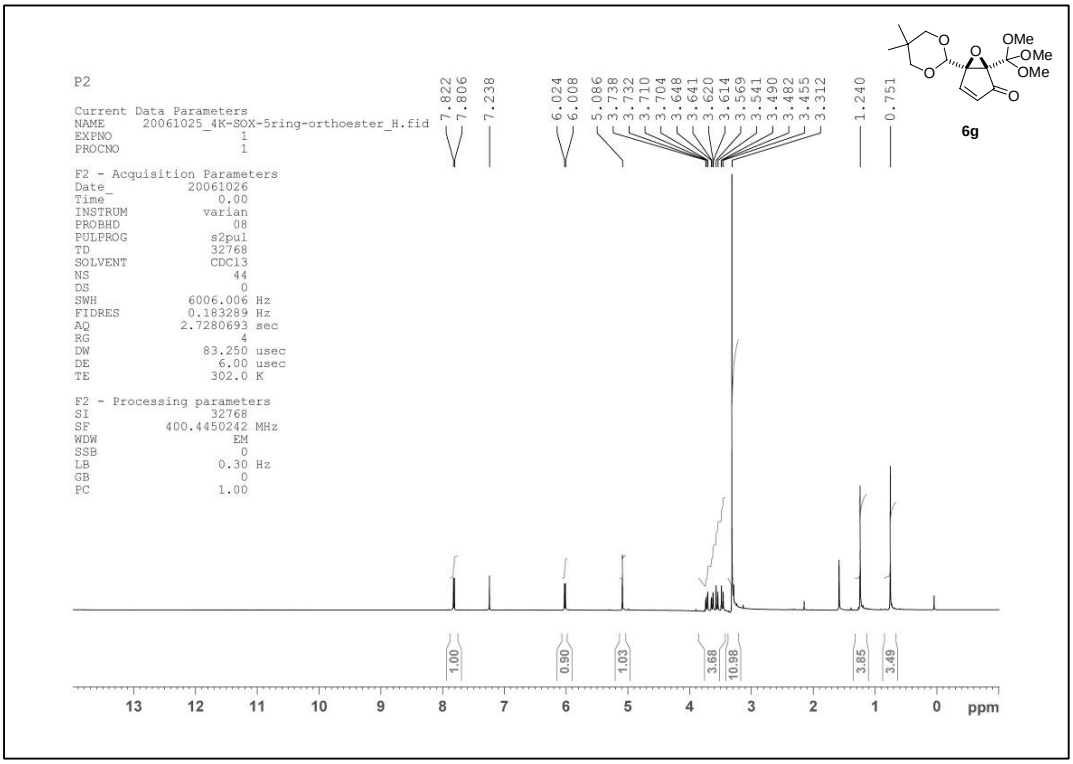
^{13}C NMR and DEPT of Compound **7b**



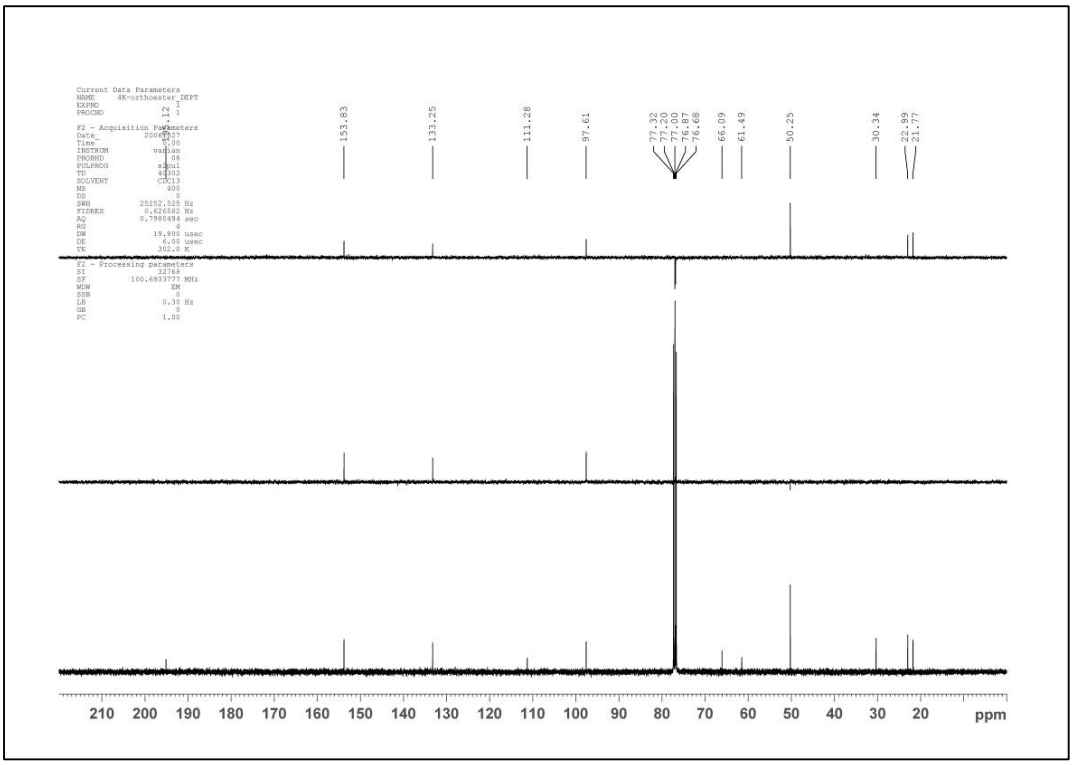
^{1}H NMR of Compound **6c**



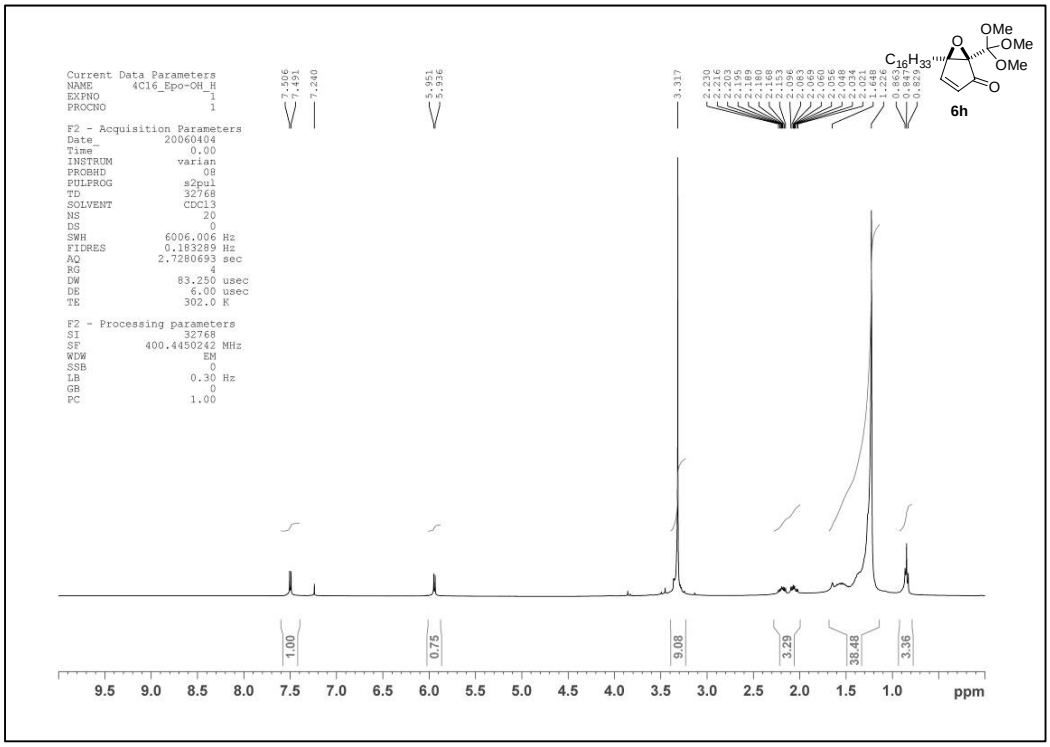
^{13}C NMR and DEPT of Compound **6c**



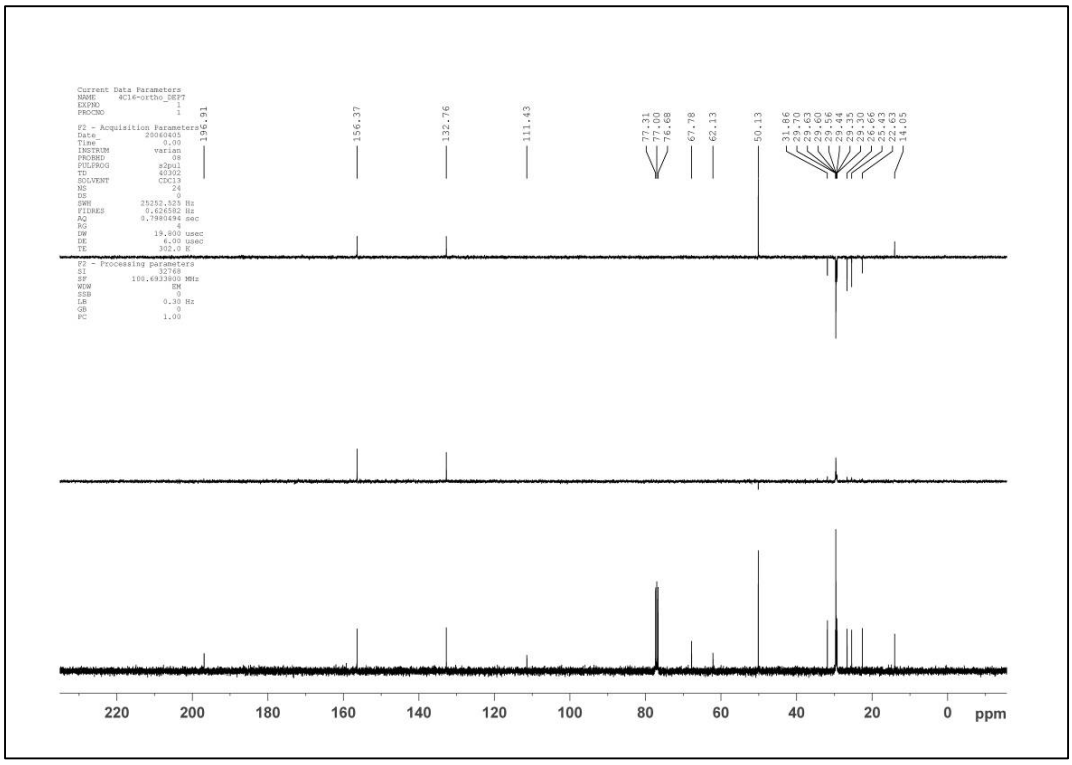
^{1}H NMR of Compound **6g**



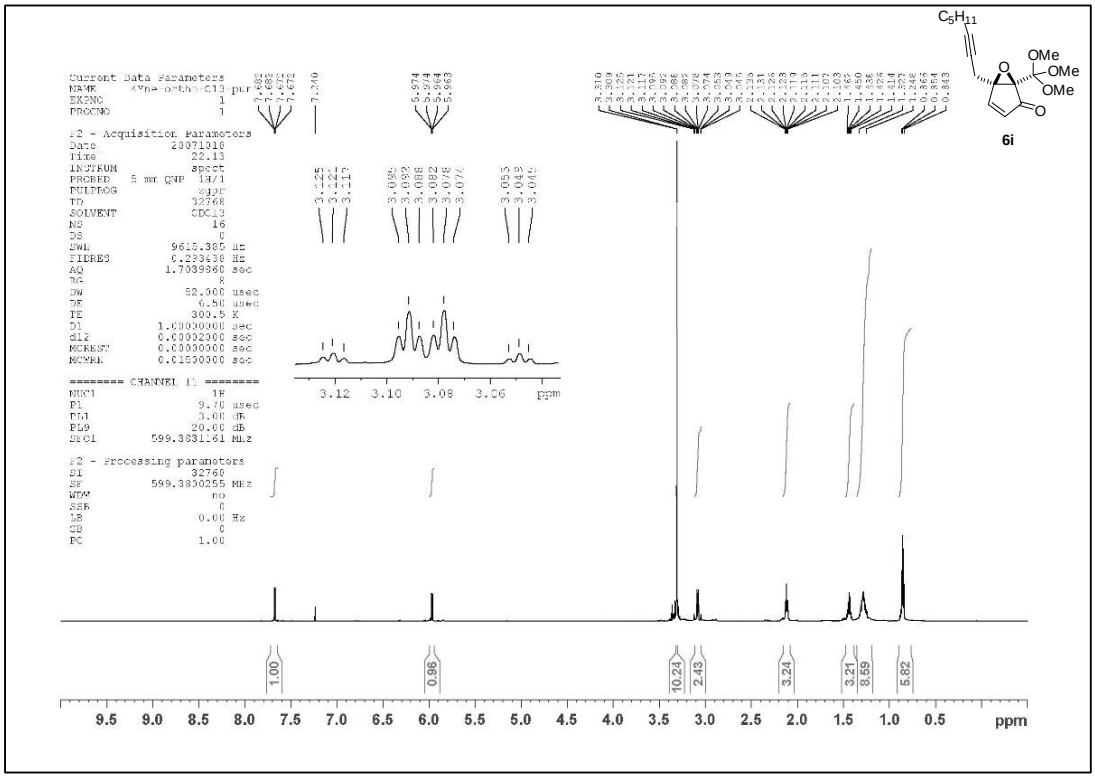
^{13}C NMR and DEPT of Compound **6g**



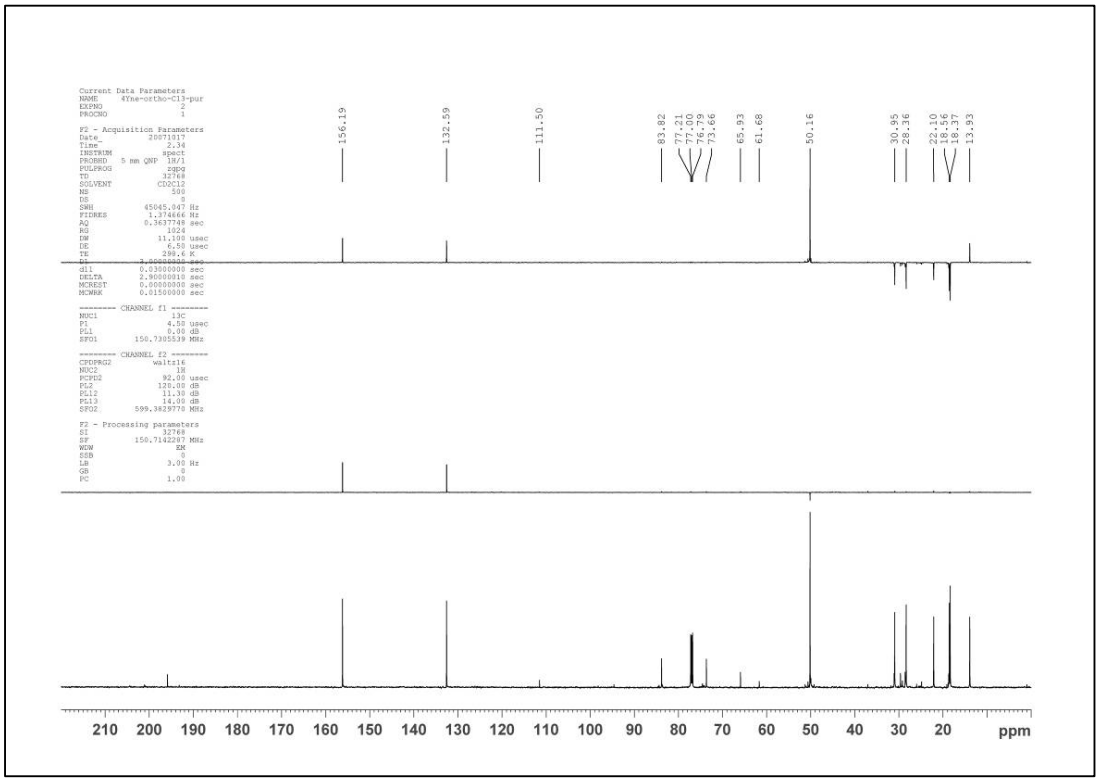
^{1}H NMR of Compound **6h**



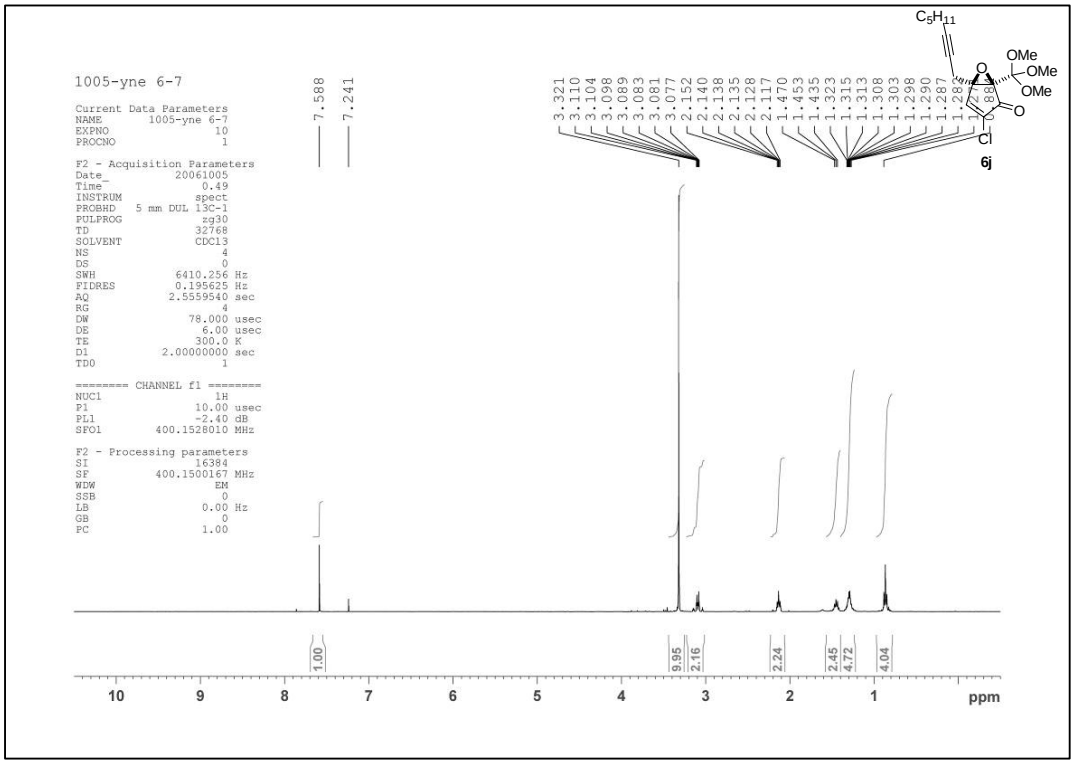
^{13}C NMR and DEPT of Compound **6h**



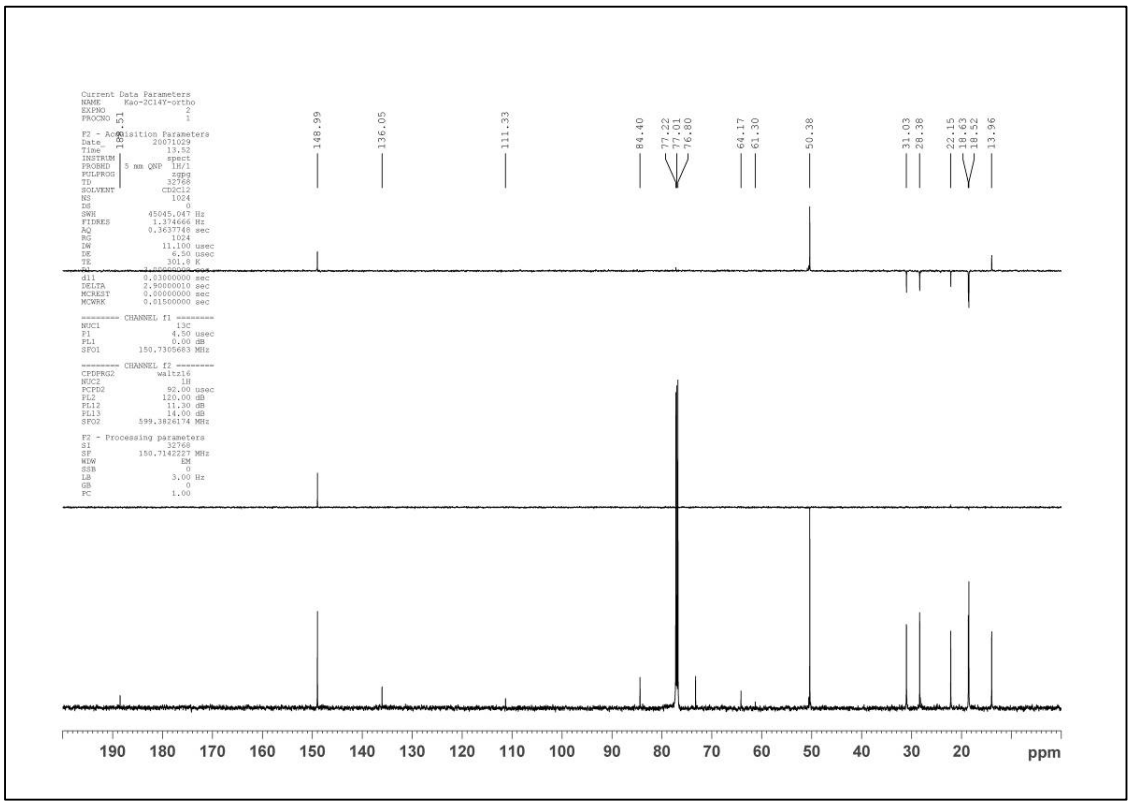
^{1}H NMR of Compound **6i**



^{13}C NMR and DEPT of Compound **6i**



^{1}H NMR of Compound **6j**



^{13}C NMR and DEPT of Compound **6j**