SUPPlEMENTARY INFORMATION

Oxidative Cleavage of Vicinal Diols: IBX can Do What Dess-Martin Periodinane (DMP) Can

Jarugu Narasimha Moorthy,* Nidhi Singhal and Kalyan Senapati

Department of Chemistry, Indian Institute of Technology, Kanpur 208 016, India

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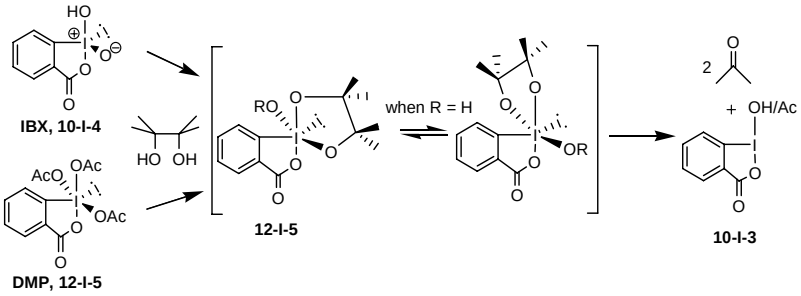
Graphic for TOC



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I. General

The melting points were determined with a Perfit Melting Point apparatus (Perfit, India) and are uncorrected. Column chromatography was conducted on Silica gel (particle size: 60–120 μ).

II. General Procedure for Oxidation of 1,2-Diols to the Corresponding Carbonyl Compounds with IBX in DMSO. In a typical experimental procedure, 1.2-2.5 equiv of IBX in 1.0 mL of DMSO was stirred for a while, and to this mixture 1-2 mmol of 1,2-diol was introduced. The reaction mixture was stirred at the appropriate temperature (see Table 1). The progress of the reaction was monitored by TLC analysis. After completion of the reaction, the reaction mixture was quenched with water and the organic matter was extracted with diethylether/CH_2Cl_2. The organic layer was washed with sodium bicarbonate and brine solution, dried over anhyd. Na_2SO_4 and solvent concentrated in vacuo. Silica-gel coulum chromatography of the crude reaction mixture yielded the products, which were characterized spectroscopically.

General Procedure for Oxidation of 1,2-Diols to the Corresponding Carbonyl Compounds with IBX in TFA. In a typical experiment, 1.2-2.0 equiv of IBX in 1.5-2.0 mL of TFA was stirred for 5 minutes, and to this mixture 1-2 mmol of 1,2-diol was introduced. The reaction mixture was stirred at appropriate temperature (see Table 1). The progress of the reaction was monitored by TLC analysis. After completion of the reaction, the reaction mixture was quenched with water and the organic matter was extracted with diethylether or CH_2Cl_2. The organic layer was washed with sodium bicarbonate and brine solution, dried over anhyd Na_2SO_4 and the solvent removed in vacuo. Silica-gel column chromatography of the crude reaction mixture yielded the products, which were characterized spectroscopically.

III. The Characterization Data of the Products Obtained from Oxidations with IBX

Benzophenone

White solid; mp 46-48 °C; IR (KBr) cm^{-1} 1651; ^1H NMR (400 MHz, $CDCl_3$) δ 7.49 (t, *J* = 8.0 Hz, 4H), 7.60 (t, *J* = 8.0 Hz, 2H), 7.81(d, *J* = 8.0 Hz, 4H).

Acetophenone

Colorless liquid; IR (neat) cm^{-1}1684; ^1H NMR (400 MHz, $CDCl_3$) δ 2.56 (s, 3H), 7.42 (t, *J* = 8.0 Hz, 2H), 7.52 (t, *J* = 8.0 Hz, 1H), 7.91-7.93 (m, 2H).

Benzaldehyde

Colorless liquid; IR (neat) cm^{-1} 1701; ^1H NMR (400 MHz, $CDCl_3$) δ 7.52 (t, *J* = 8.0 Hz, 1H), 7.62 (t, *J* = 8.0 Hz, 2H), 7.87 (d, *J* = 8.0 Hz, 2H), 10.00 (s, 1H).

Benzil

Yellow solid; mp 92-94 °C; IR (KBr) cm^{-1} 1674; ^1H NMR (400 MHz, $CDCl_3$) δ 7.45 (t, *J* = 8.0 Hz, 4H), 7.60 (t, *J* = 8.0 Hz, 2H), 7.91 (d, *J* = 8.0 Hz, 4H).

4-Methylbenzaldehyde

Colorless liquid; IR (neat) cm^{-1} 1745; ^1H NMR (400 MHz, $CDCl_3$) δ 2.41 (s, 3H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.75 (d, *J* = 8.0 Hz, 2H), 9.93 (s, 1H)

4,4'-Dimethylbenzil

Yellow solid; mp 100-102 °C; IR (KBr) cm^{-1} 1664; ^1H NMR (400 MHz, $CDCl_3$) δ 2.43 (s, 6H), 7.3 (d, *J* = 8.0 Hz, 4H), 7.86 (d, *J* = 8.0 Hz, 4H).

4-Bromobenzaldehyde

White solid; mp 56-58 °C; IR (KBr) cm^{-1}1687; ^1H NMR (400 MHz, $CDCl_3$) δ 7.67-7.77 (m, 4H), 9.98 (s, 1H).

4,4'-Dibromobenzil

Yellow solid; mp 220-222 °C; IR (KBr) cm^{-1} 1663; ^1H NMR (400 MHz, $CDCl_3$) δ 7.59-7.62 (m, 4H), 7.75-7.78 (m, 4H).

4-Fluorobenzaldehyde

Colorless liquid; IR (neat) cm^{-1} 1698; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13-7.19 (m, 2H), 7.84-7.87 (m, 2H), 9.90 (s, 1H).

4,4'-Difluorobenzil

Yellow solid; mp 112-114 °C; IR (KBr) cm^{-1} 1666; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18-7.23 (m, 4H), 8.0-8.04 (m, 4H).

1,2-Diphenyl-2-hydroxypropanone

White solid; mp 60-62 °C; IR (KBr) cm^{-1} 1669; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.9 (s, 3H), 7.27-7.47 (m, 8H), 7.68 (d, *J* = 8.0 Hz, 2H).

Acenaphthoquinone

Yellow solid; mp 255-257 °C; IR (KBr) cm^{-1}1719; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (t, *J* = 8.0 Hz, 2H), 8.12 (d, *J* = 8.0 Hz, 2H), 8.29 (d, *J* = 8.0 Hz, 2H).

2-Hydroxyacenaphthylen-1-one

White solid; mp 164-166 °C; IR (KBr) cm^{-1} 1685; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.94 (s, 1H), 7.64-7.73 (m, 3H), 7.99 (d, *J* = 8.0 Hz, 1H), 8.18 (d, *J* = 8.0 Hz, 1H), 8.48 (d, *J* = 8.0 Hz, 1H).

2-Methyl-2-phenylpropanal

Viscous oil; IR (neat) cm^{-1} 1719; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.47 (s, 6H), 7.22-7.78 (m, 3H), 7.34-7.38 (m, 2H), 9.50 (s, 1H).

2,5-Dimethyl-2,5-diphenylhexan-3,4-dione

Viscous yellow oil; IR (neat) cm^{-1} 1706; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.45 (s, 12H), 7.15-7.17 (m, 4H), 7.24-7.32 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.4, 49.8, 126.3, 126.9, 128.5, 142.3, 203.

Cylopentane-1,3-dicarbaldehyde

Colorless oil; IR (neat) cm^{-1} 1720; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.88-1.95 (m, 4H), 2.01-2.07 (m, 1H), 2.17-2.27 (m, 1H), 2.85-2.89 (m, 2H), 9.64 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.8, 26.1, 51.3, 202.6.

Camphorquinone

Yellow color solid; mp 196-198 °C; IR (KBr) cm^{-1} 1669; ^1H NMR (400 MHz, $CDCl_3$) δ 0.93 (s, 3H), 1.06 (s, 3H), 1.11 (s, 3H), 1.58-1.68 (m, 2H), 1.86-1.95 (m, 1H), 2.12-2.20 (m, 1H), 2.64 (d, *J* = 5.36 Hz, 1H).

6-Oxo-6-phenylhexanal

Viscous oil; IR (neat) cm^{-1}1638, 1722; ^1H NMR (400 MHz, $CDCl_3$) δ 1.72-1.78 (m, 4H), 2.50 (t, *J* = 7.0 Hz, 2H), 3.00 (t, *J* = 6.6 Hz, 2H), 7.45 (t, *J* = 7.8 Hz, 1H), 7.55 (t, *J* = 7.0 Hz, 2H), 7.94 (d, *J* = 7.8 Hz, 2H), 9.77 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 23.5, 38.1, 43.7, 128.0, 128.6, 133.1, 136.8, 199.7, 202.2.

2-Hydroxy-2-phenylcyclohexanone

Viscous oil; IR (neat) cm^{-1}1712, 2942; ^1H NMR (400 MHz, $CDCl_3$) δ 1.63-1.82 (m, 4H), 1.95-2.00. (m, 1H), 2.30-2.39 (m, 1H), 2.39-2.48 (m, 1H), 2.90-2.94 (m, 1H), 7.22-7.33 (m, 5H).

(3-Acetyl-2,2-dimethylcyclobutyl)acetaldehyde

Colorless oil; IR (neat) cm^{-1} 1704, 1722; ^1H NMR (400 MHz, $CDCl_3$) δ 0.85 (s, 3H), 1.34 (s, 3H), 1.9-2.10 (m, 1H), 2.05 (s, 3H), 2.40-2.51 (m, 3H), 2.9-3.0 (m, 1H), 9.74 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.8, 22.9, 30.3, 30.5, 35.9, 43.4, 45.2, 54.5, 201.7, 207.7.

3-(Acetyloxy)-1-oxo-secocholestan-6-al

Colorless oil; IR (neat) cm^{-1} 1705, 1738; ^1H NMR (400 MHz, $CDCl_3$) δ 0.68 (s, 3H), 0.86 (d, *J* = 4.0 Hz, 6H), 0.90 (d, *J* = 6.0 Hz, 3H), 1.03 (s, 3H), 2.01 (s, 3H), 3.00-3.07 (m, 1H), 5.30 (br s, 1H), 9.62 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.5, 17.6, 18.5, 21.2, 22.5, 22.8, 23.0, 23.7, 25.1, 25.3, 27.8, 28.0, 34.3, 34.8, 35.7, 35.9, 39.4, 39.8, 42.1, 42.5, 43.2, 44.0, 52.3, 54.1, 56.1, 73.4, 170.2, 202.7, 216.1.

3-(Acetyloxy)-5,20-dioxo-secopregnan-6-al.

Colorless oil; IR (neat) cm^{-1} 1702, 1735; ^1H NMR (400 MHz, $CDCl_3$) δ 0.64 (s, 3H), 1.02 (s, 3H), 2.02 (s, 3H), 2.12 (s, 3H), 3.00-3.01 (m, 1H), 5.39 (br s, 1H), 9.61 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.9, 17.7, 21.3, 22.6, 23.1, 25.1, 25.3, 31.5, 34.3, 34.8, 38.8, 41.7, 43.2, 43.7, 43.9, 52.3, 53.8, 63.5, 73.3, 170.3, 202.1, 209.1, 215.9.

IV. NMR spectra of the products

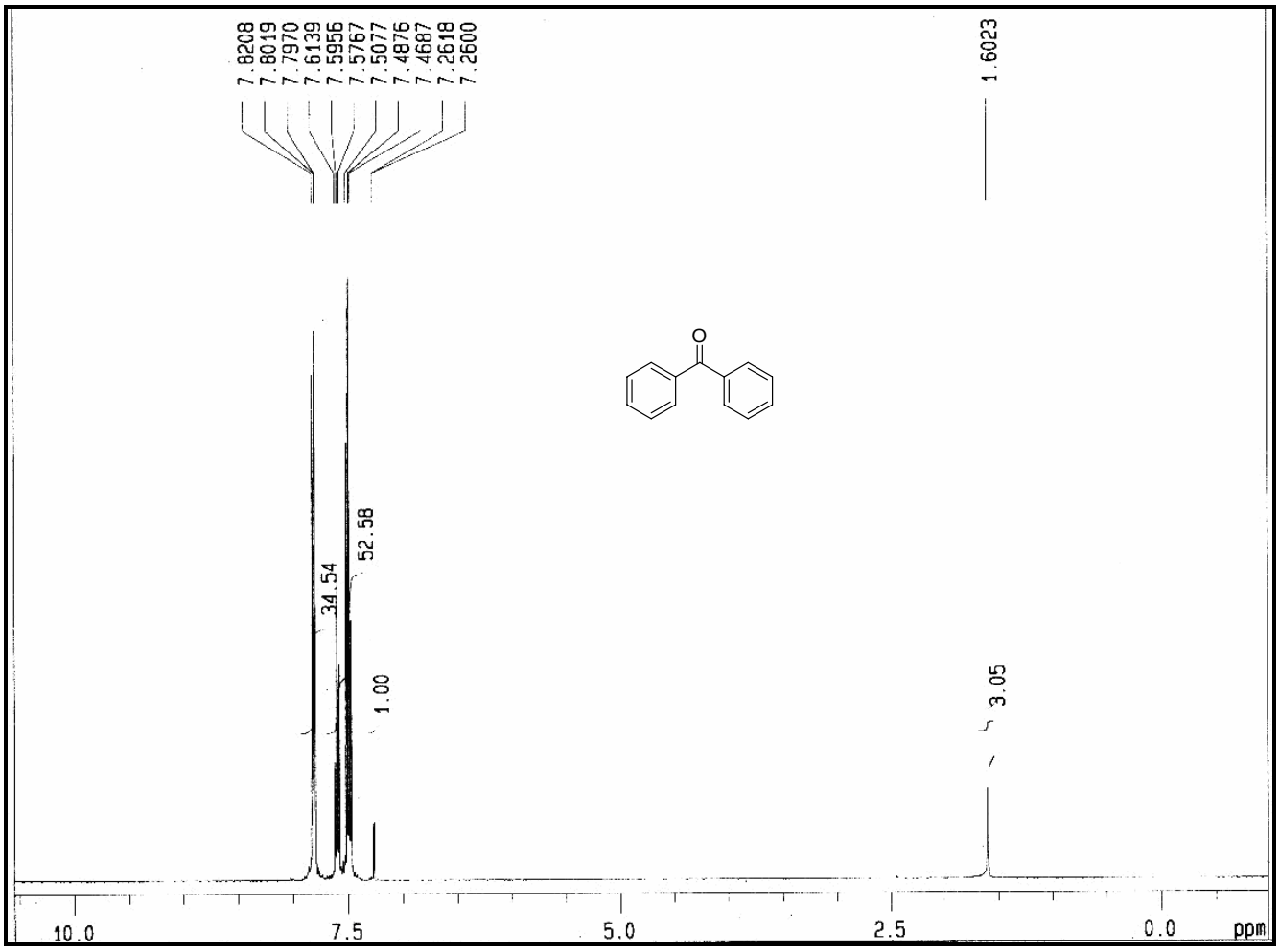


Figure S1. ^{1}H NMR spectrum of benzophenone.

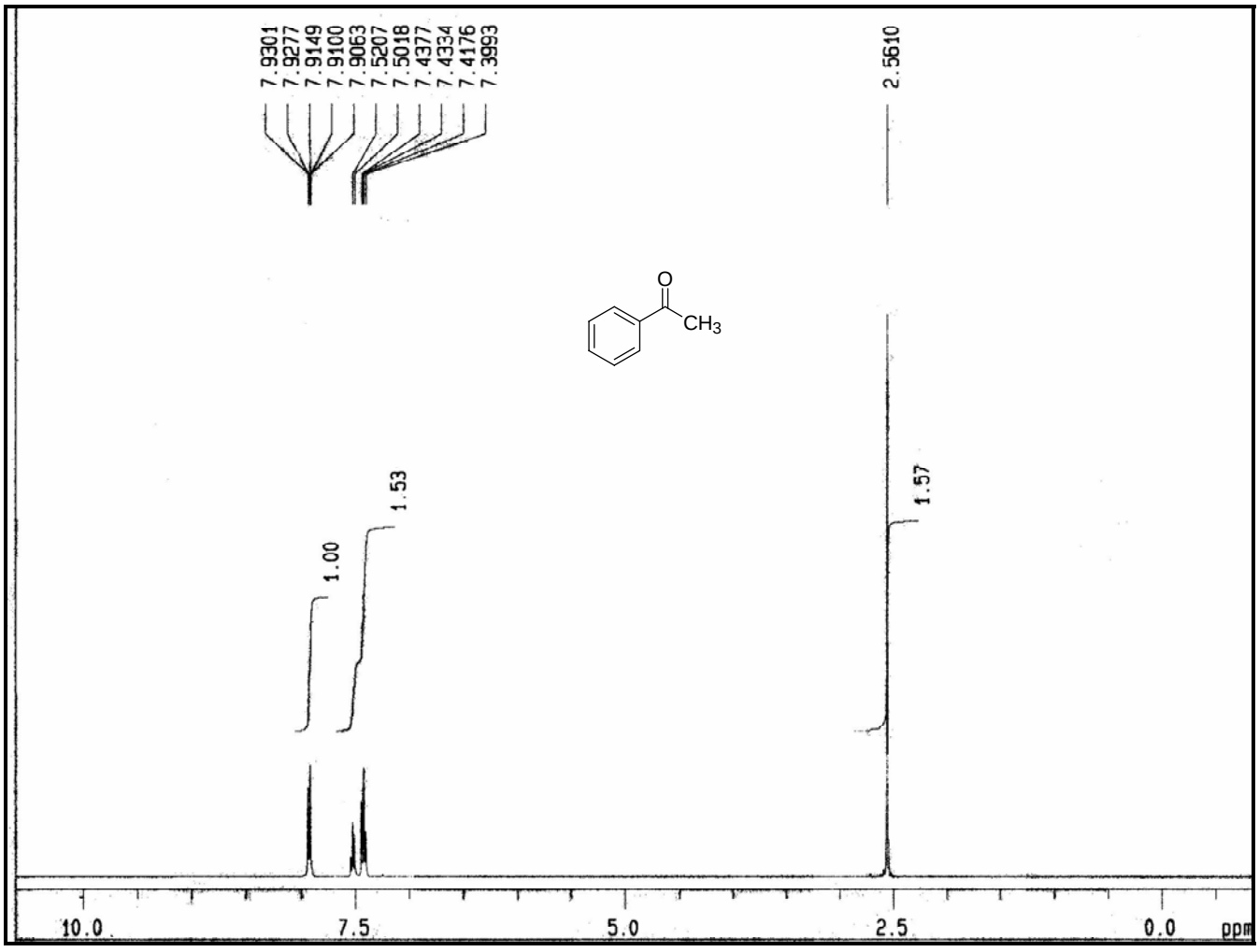


Figure S2. ^{1}H NMR spectrum of acetophenone.

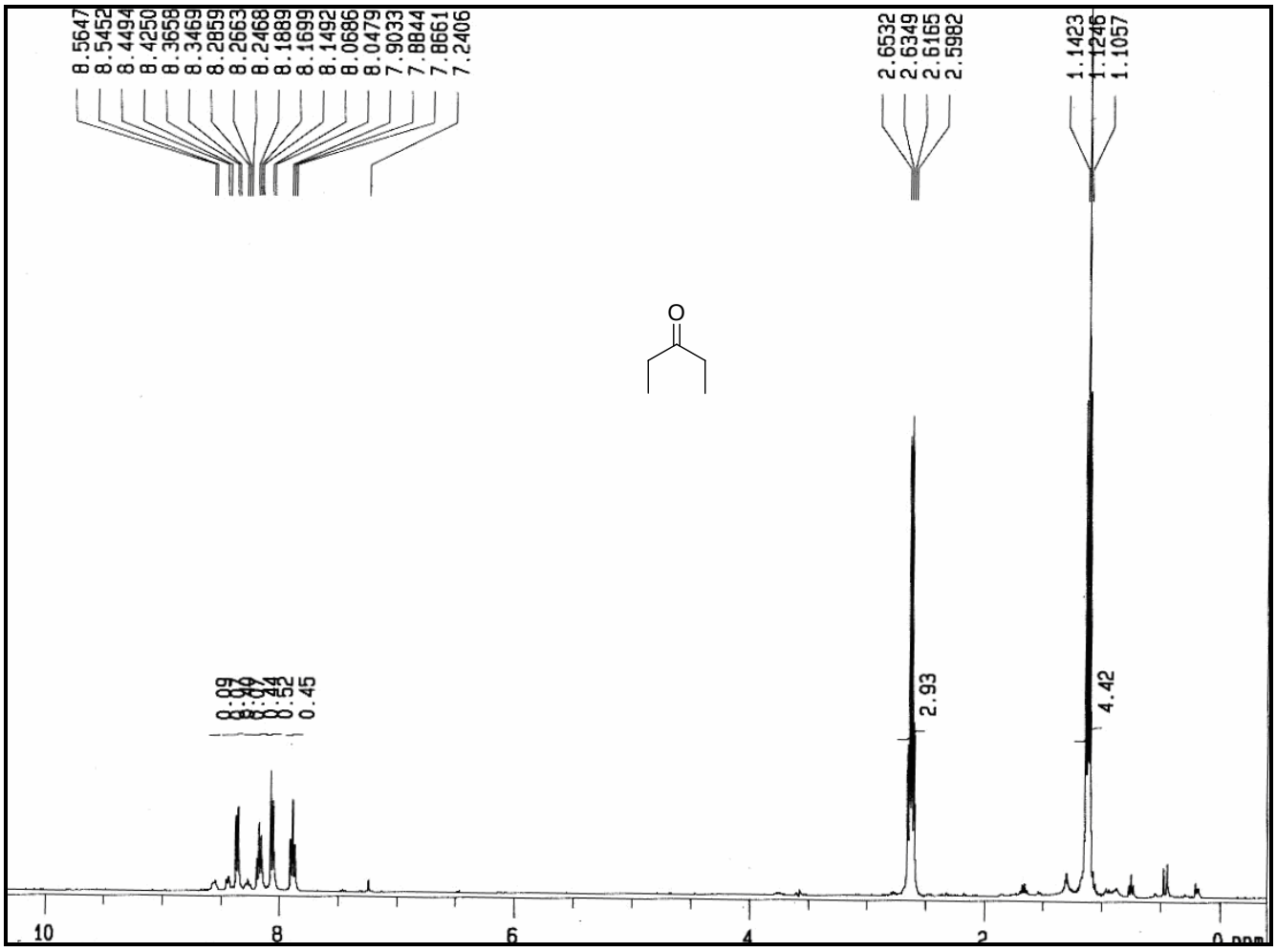


Figure S3. ^{1}H NMR spectrum for the reaction of 3,4-diethylhexane-3,4-diol with IBX in TFA. Note that the major signals in the aromatic region correspond to IBA.

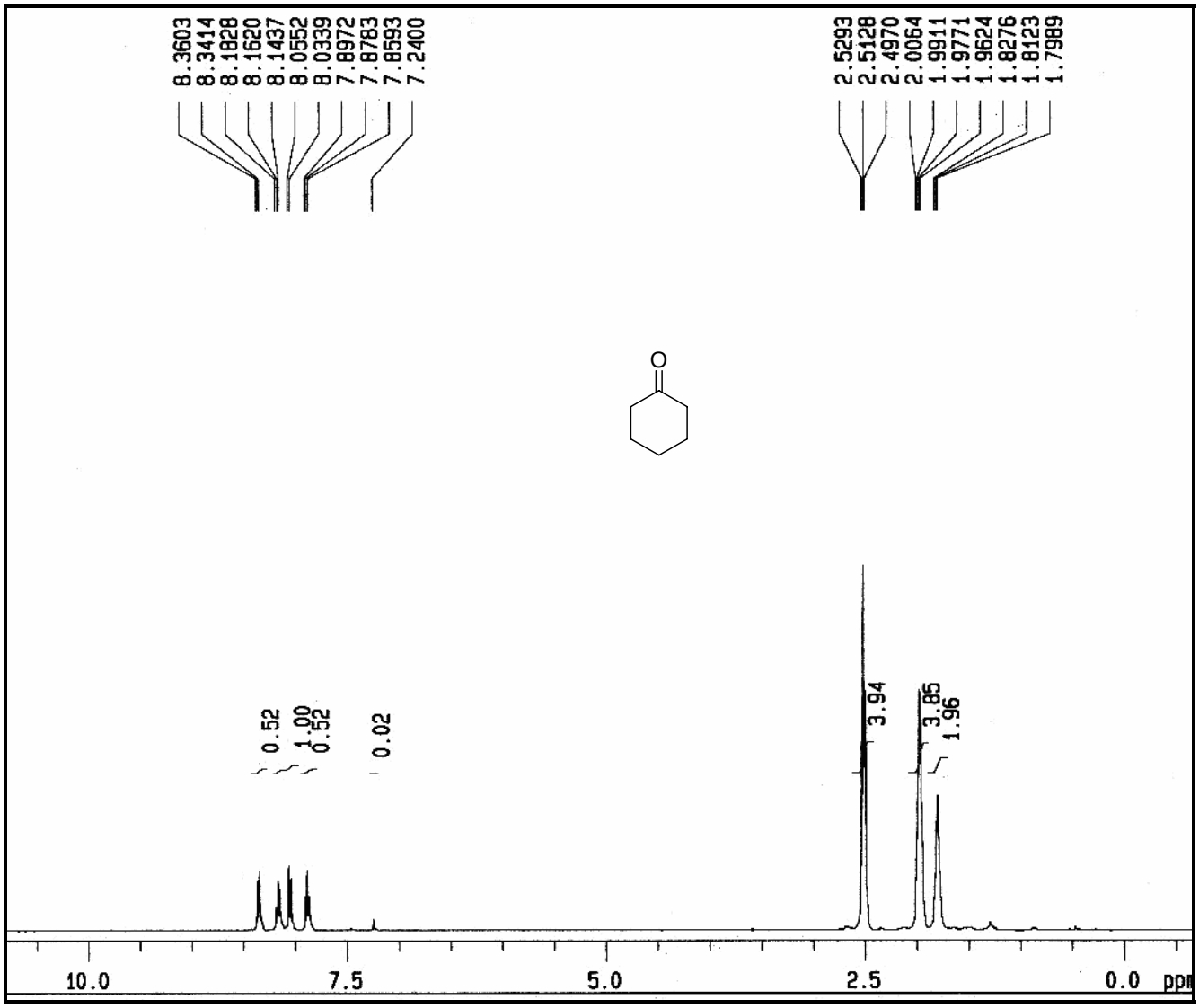


Figure S4. ^{1}H NMR spectrum for the reaction of [1,1'-bicyclohexyl]-1,1'-diol with IBX in TFA. Note that the signals in the aromatic region correspond to IBA.

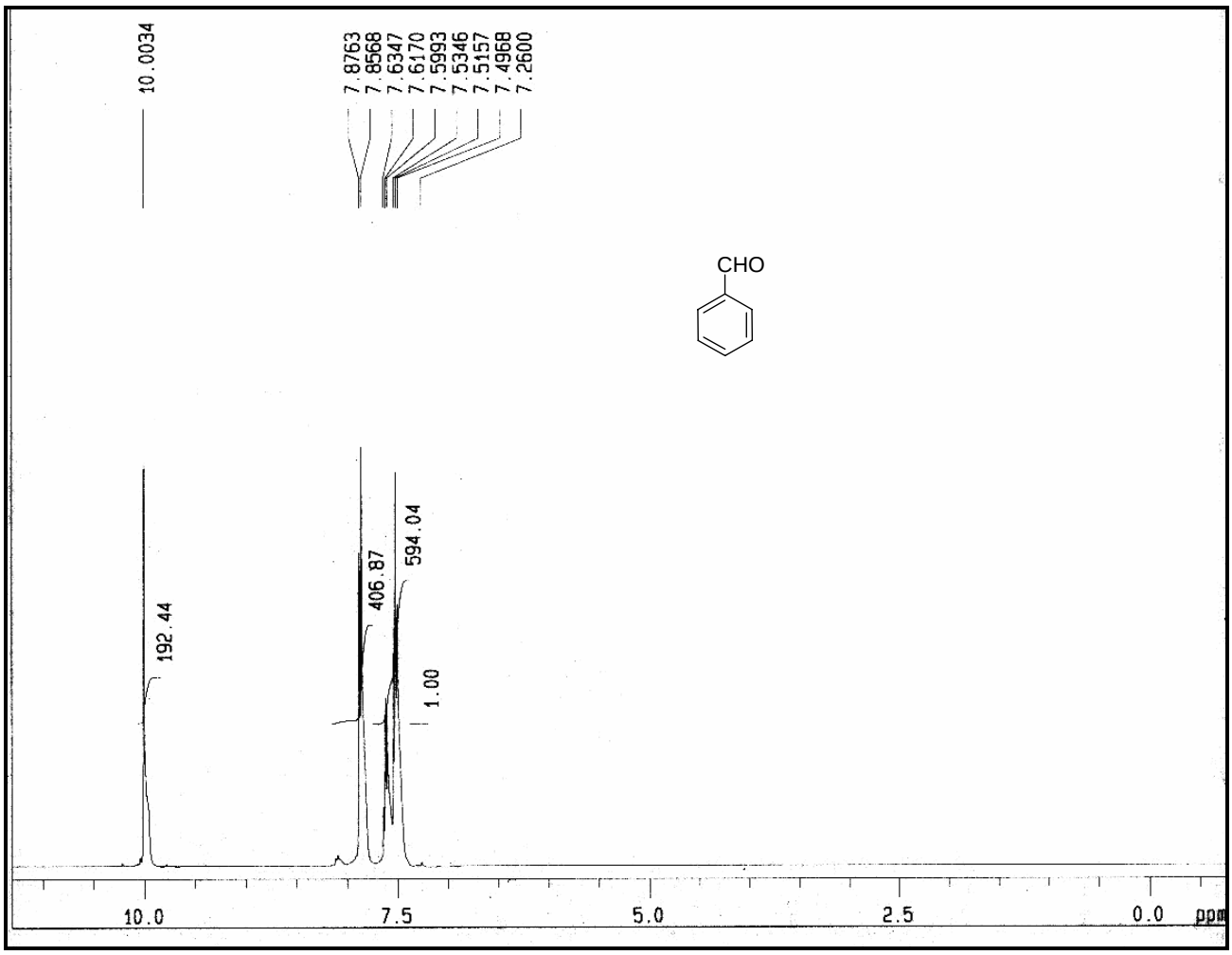


Figure S5. ^{1}H NMR spectrum of benzaldehyde.

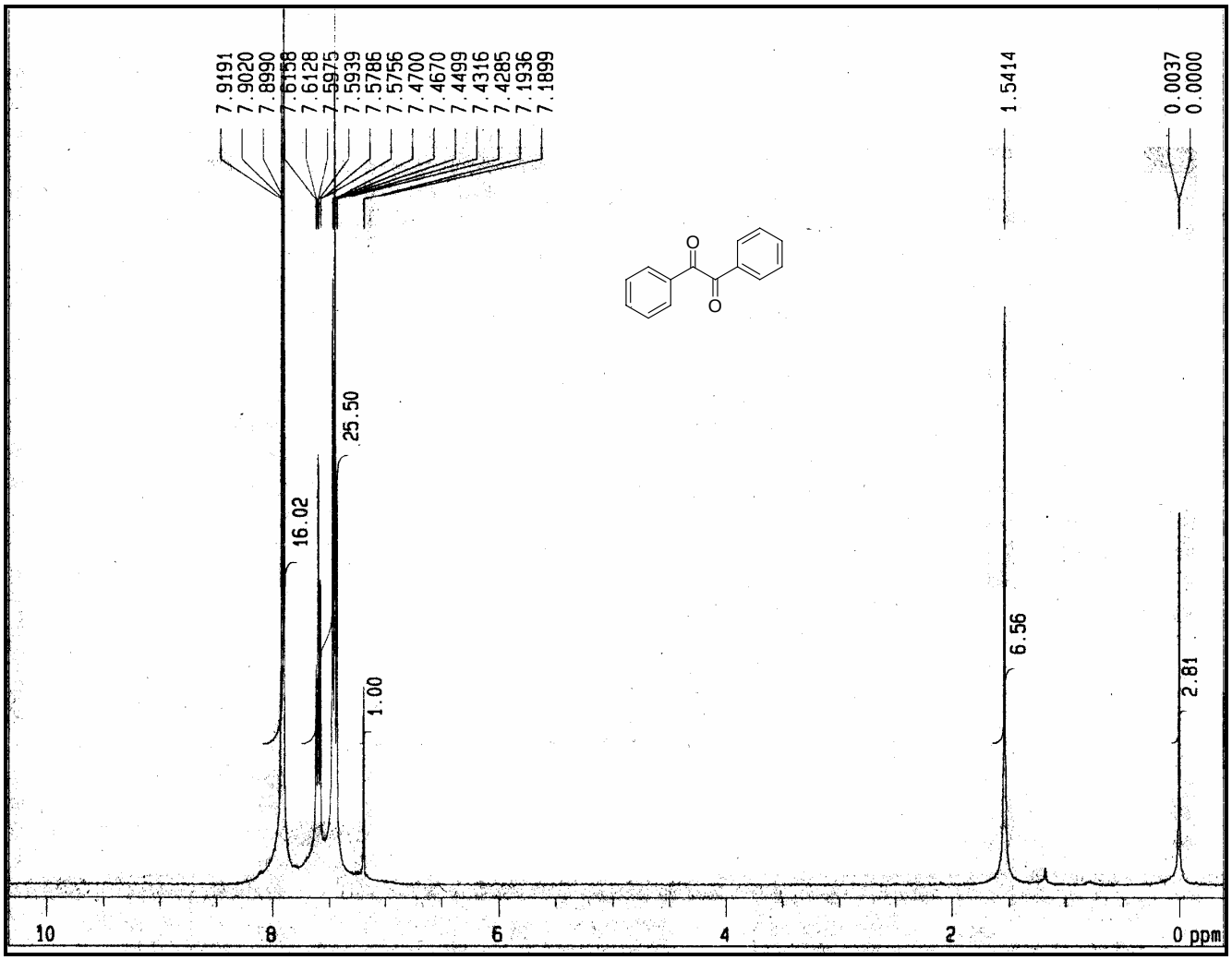


Figure S6. ^{1}H NMR spectrum of benzil.

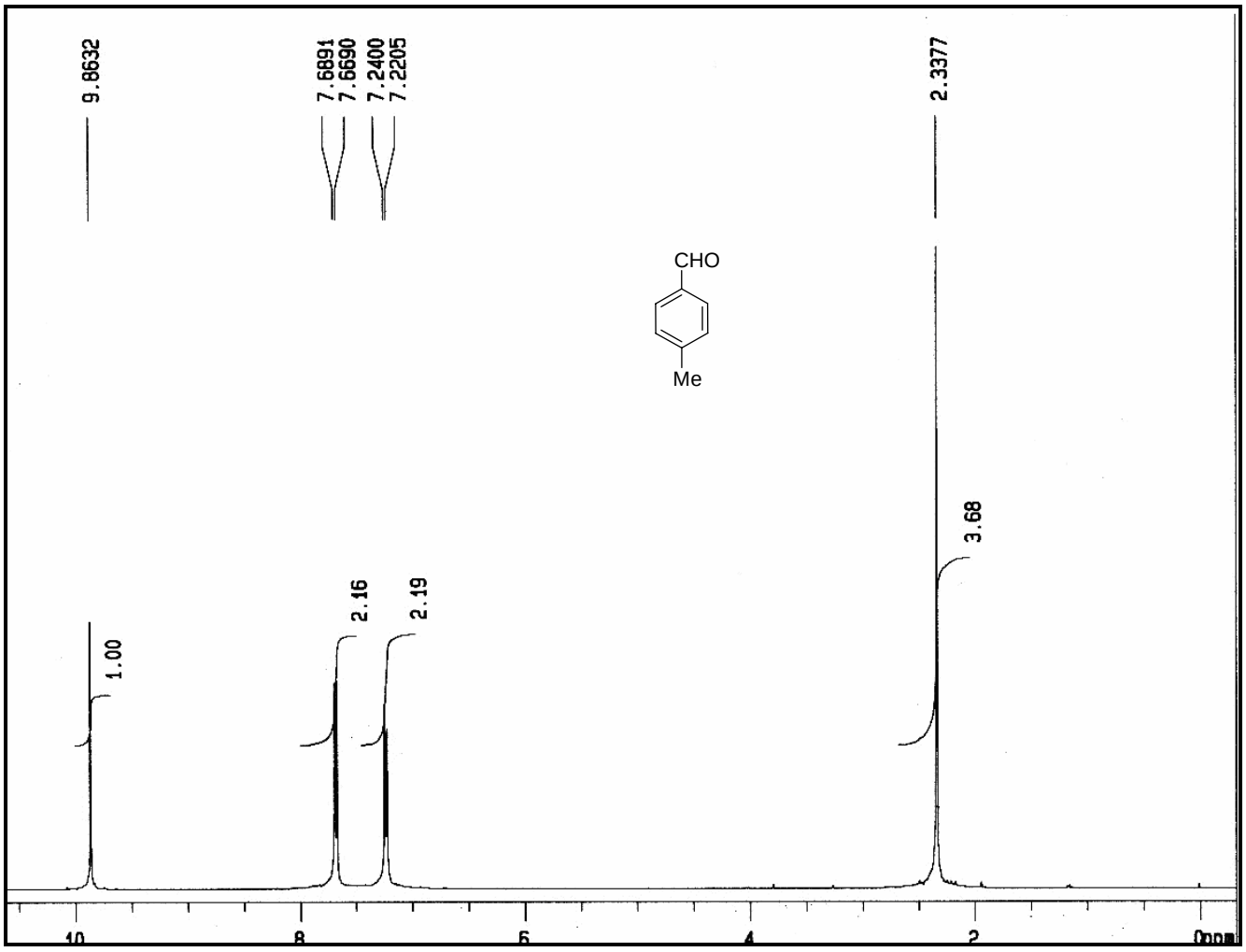


Figure S7. ^{1}H NMR spectrum of 4-methylbenzaldehyde.

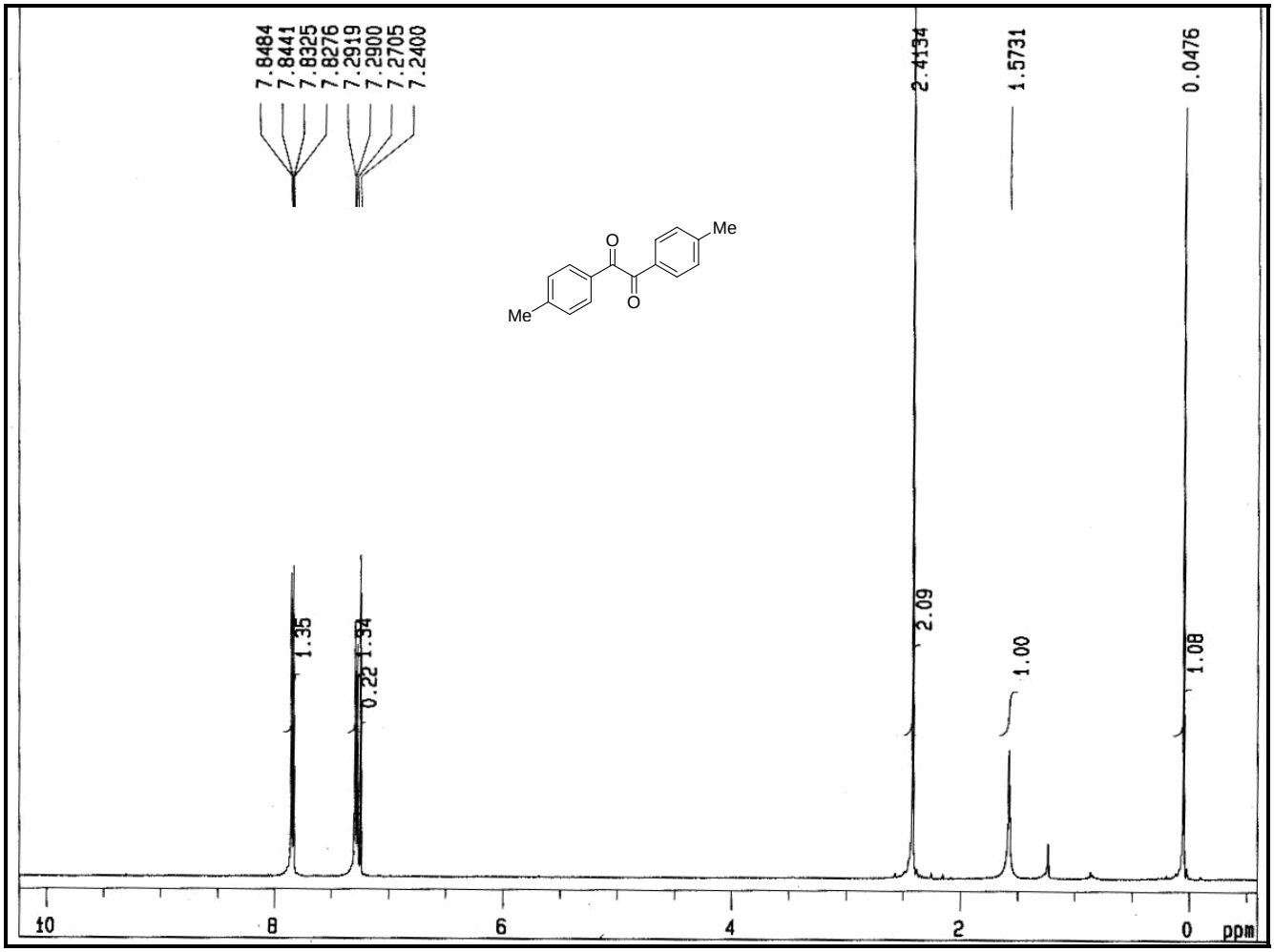


Figure S8. ^{1}H NMR spectrum of 4,4'-dimethylbenzil.

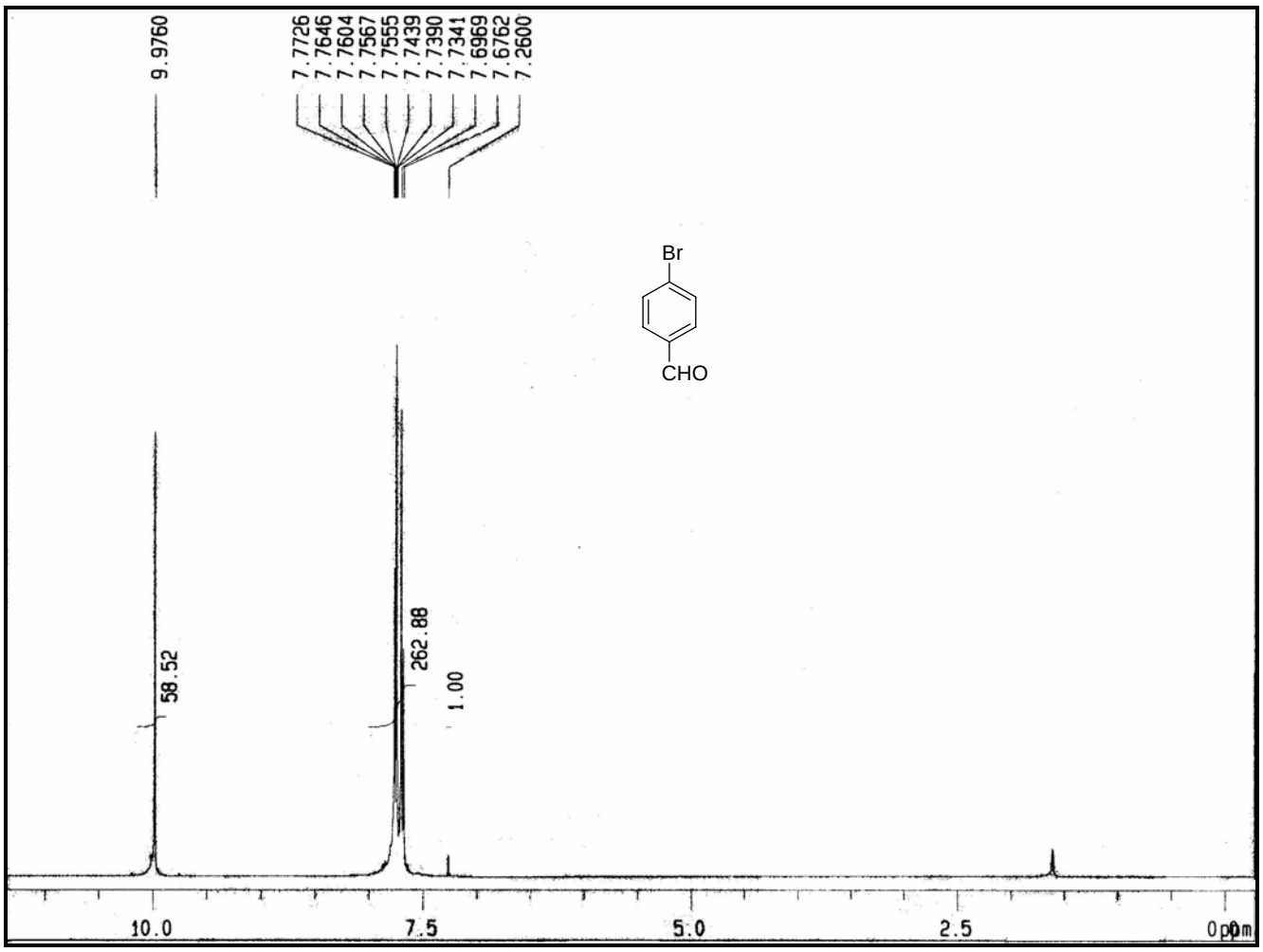


Figure S9. ^{1}H NMR spectrum of 4-bromobenzaldehyde.

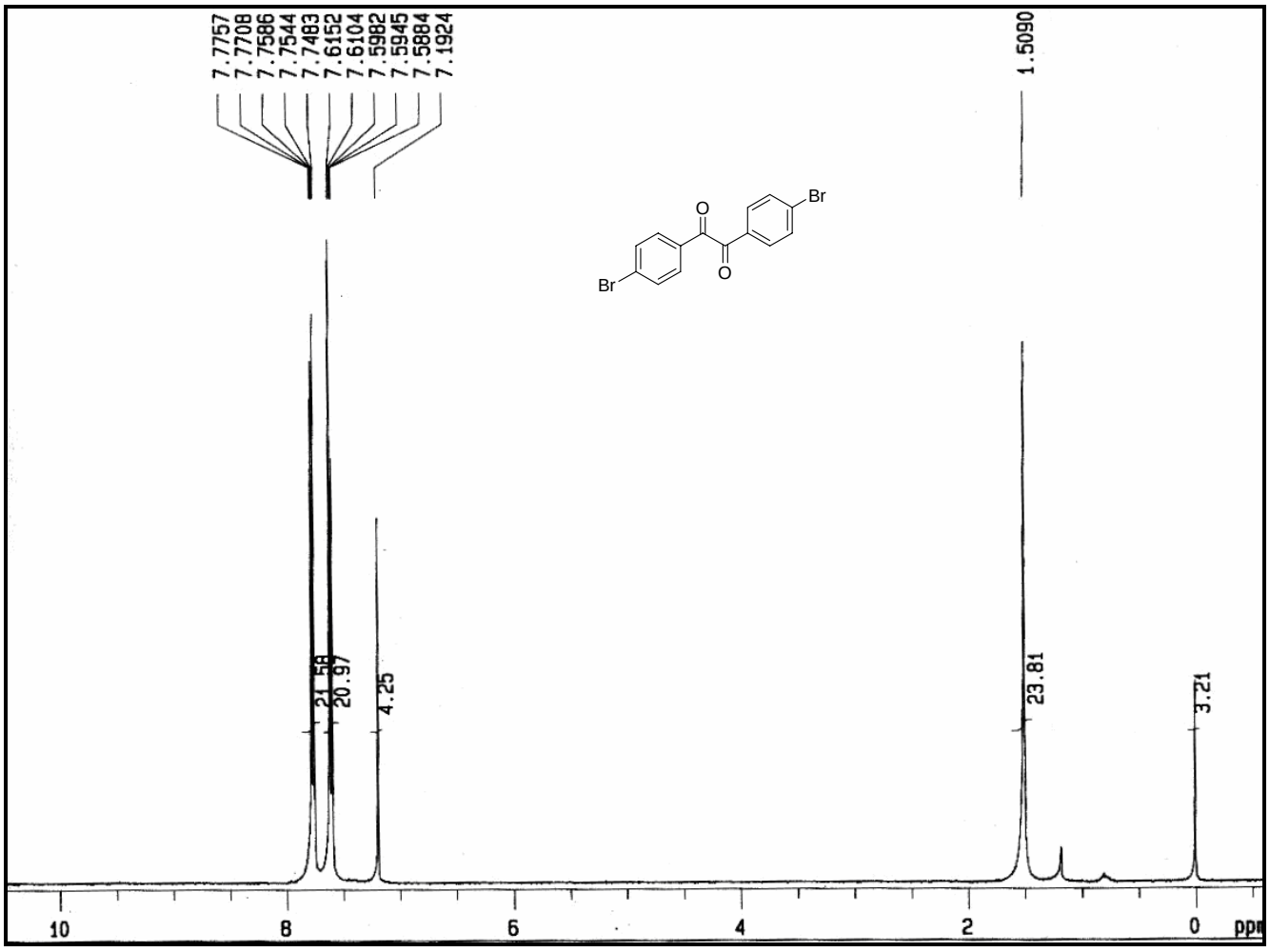


Figure S10. ^{1}H NMR spectrum of 4,4’-dibromobenzil.

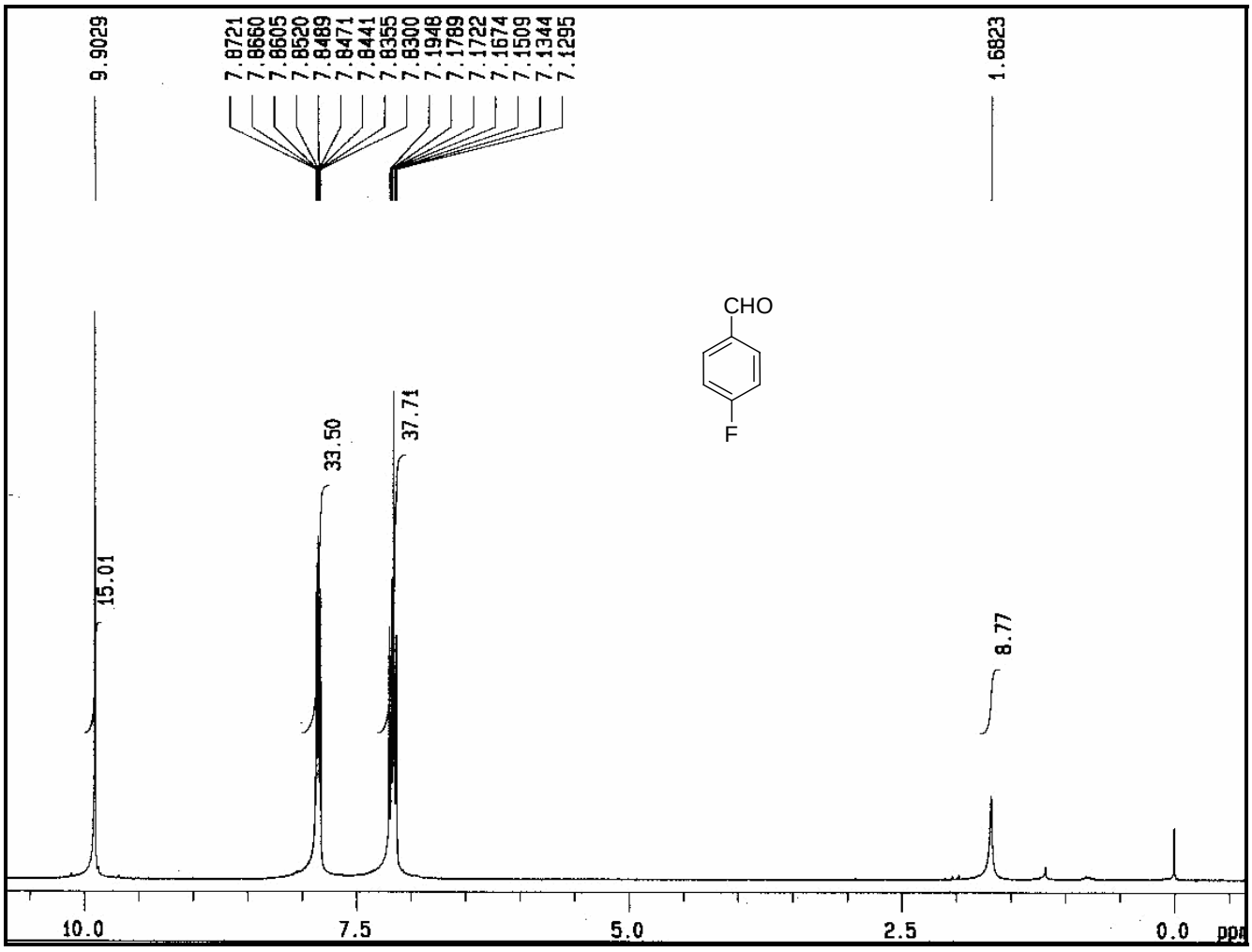


Figure S11. ^{1}H NMR spectrum of 4-fluorobenzaldehyde.

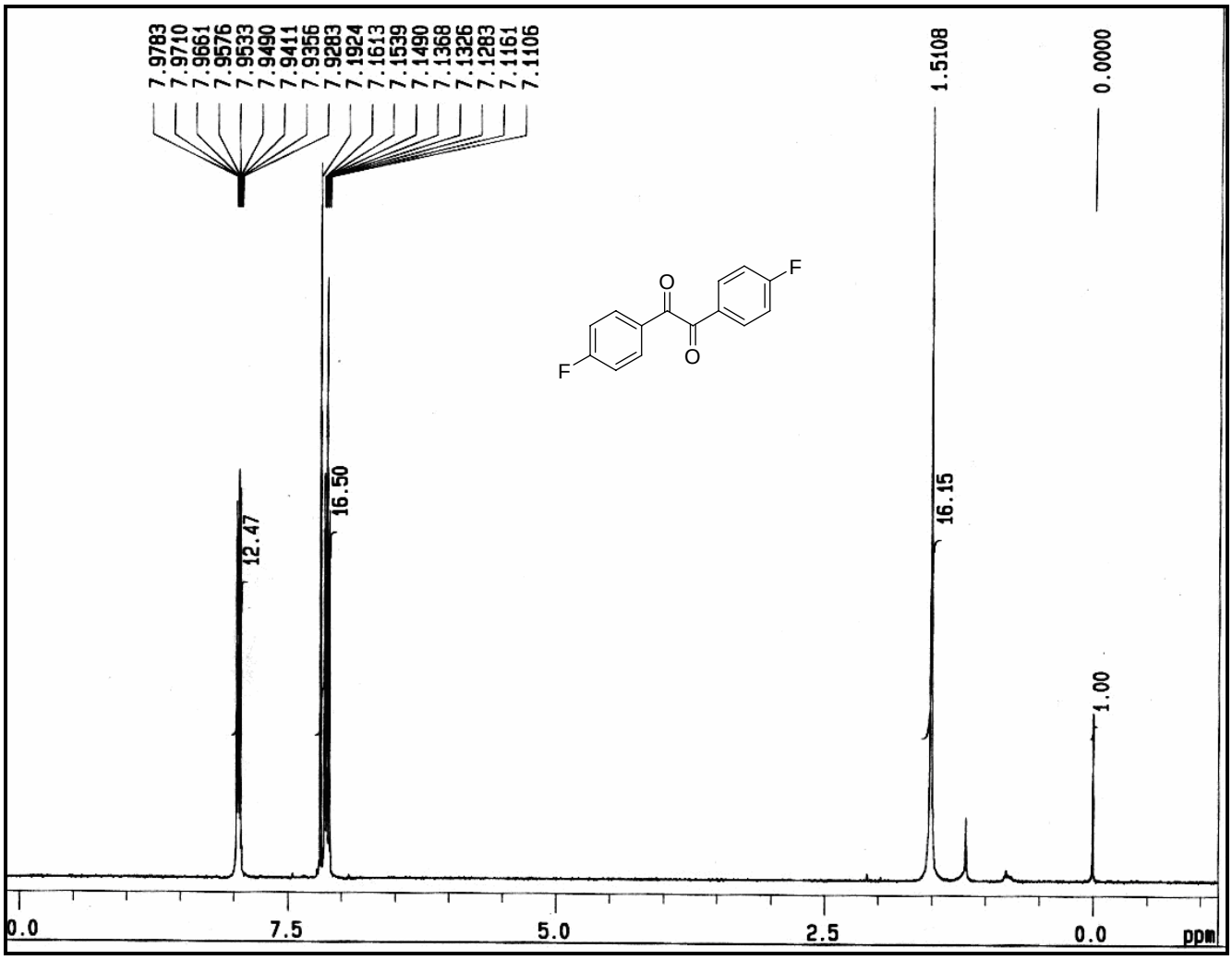


Figure S12. ^{1}H NMR spectrum of 4,4'-difluorobenzil.

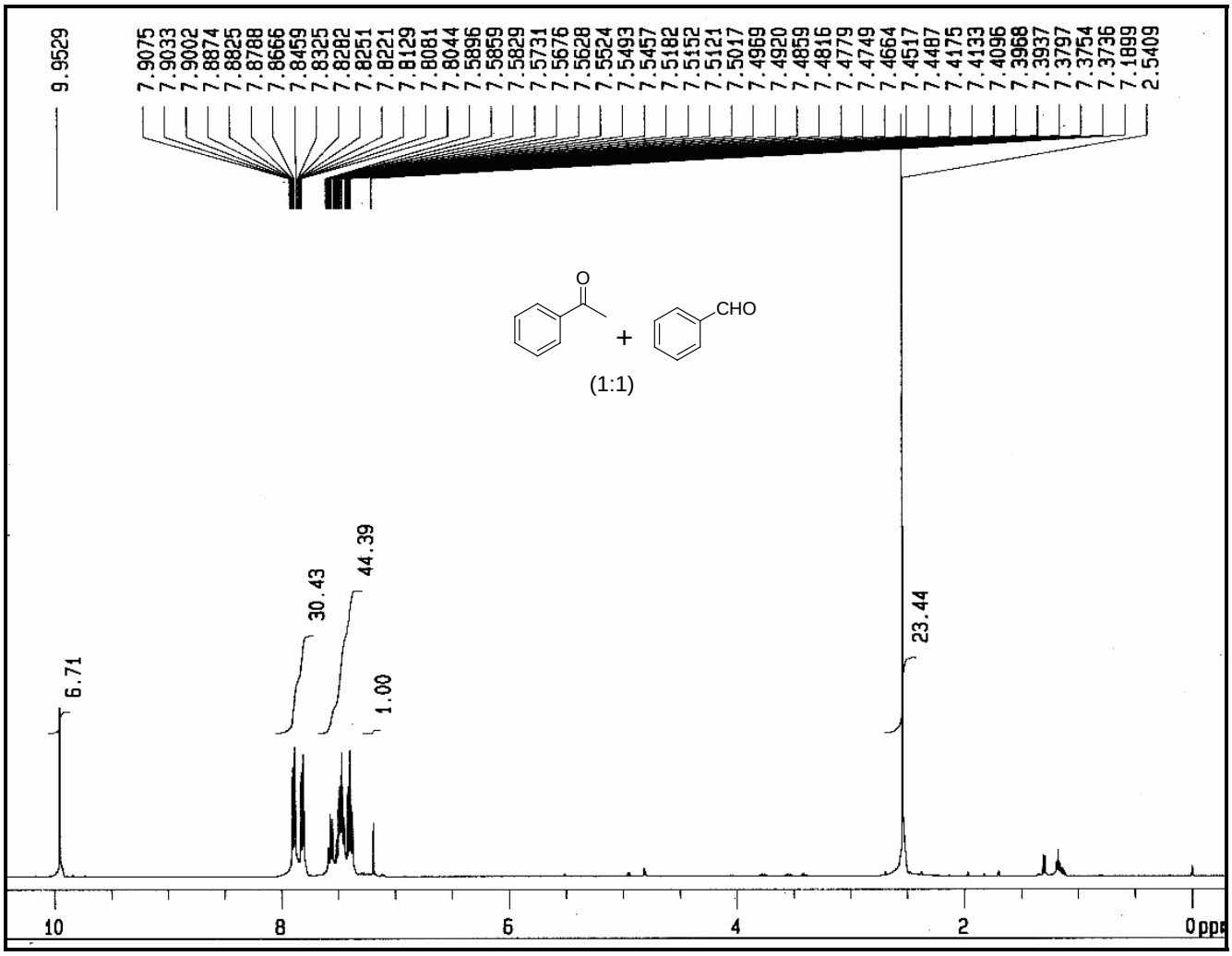


Figure S13. ^{1}H NMR spectrum of acetophenone+benzaldehyde (1:1) from the reaction of *sec,tert*-1,2-diol, viz., 1,2-diphenylpropan-1,2-diol.

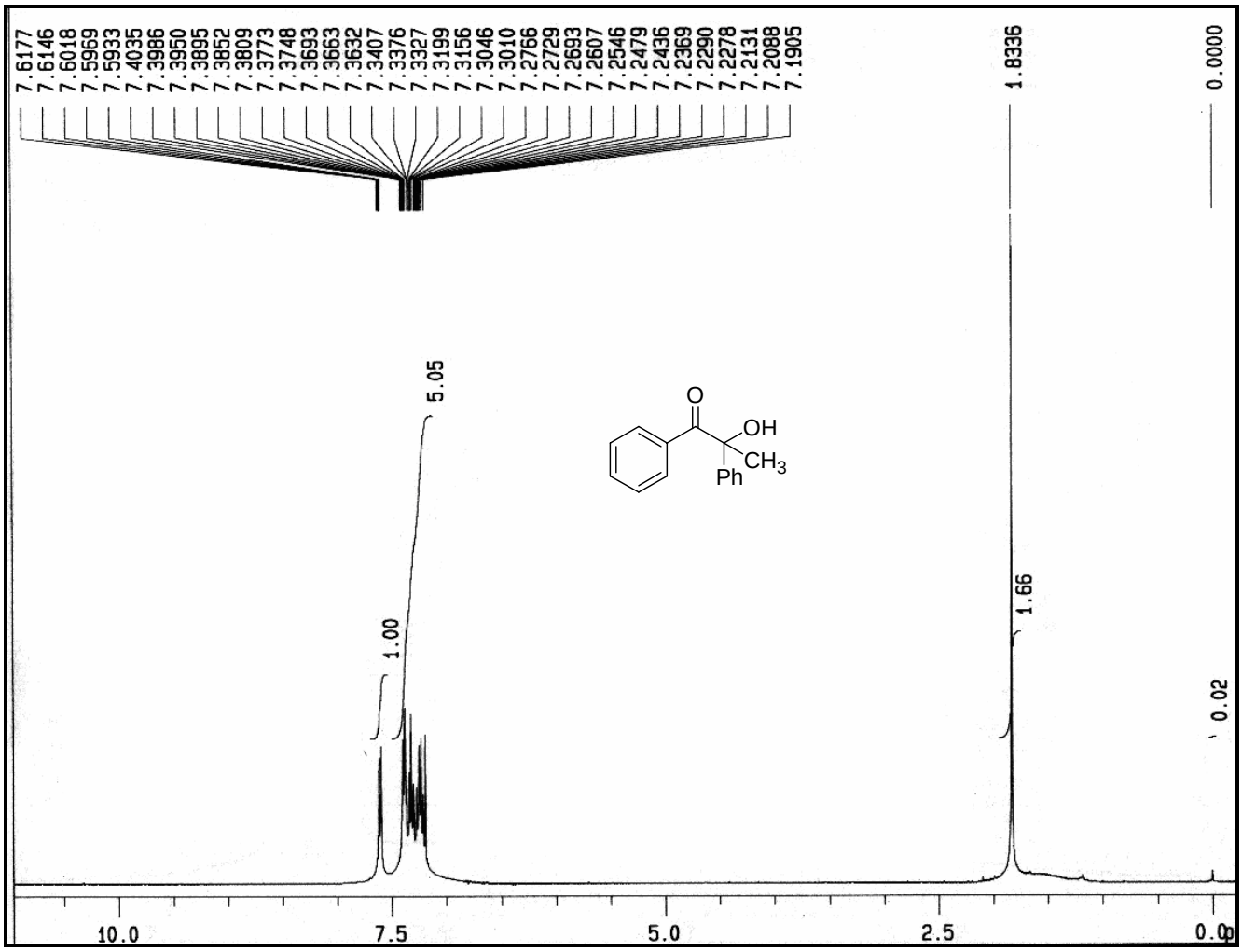


Figure S14. ^{1}H NMR spectrum of 1,2-diphenyl-2-hydroxypropanone.

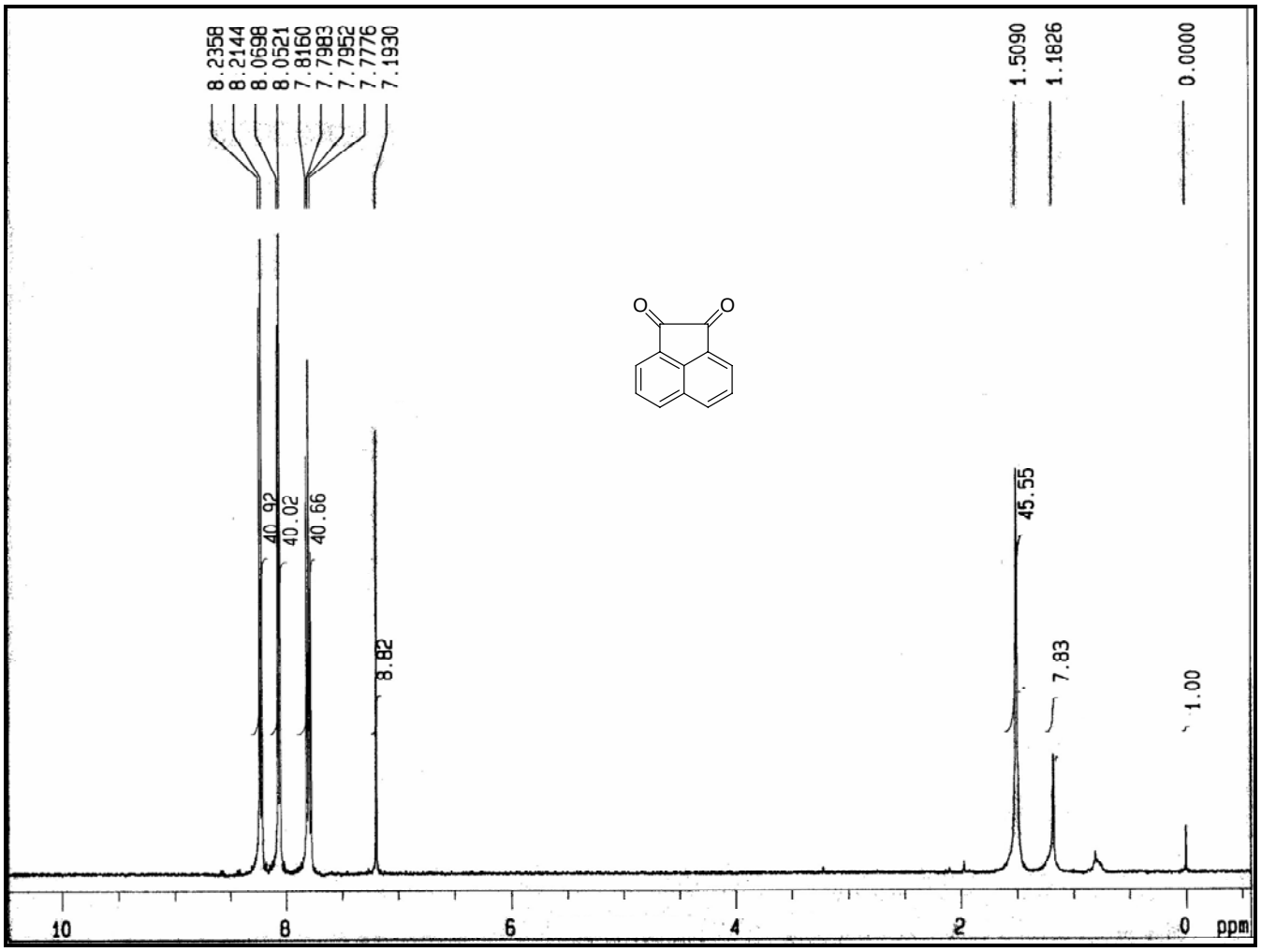


Figure S15. ^{1}H NMR spectrum of acenaphthoquinone.

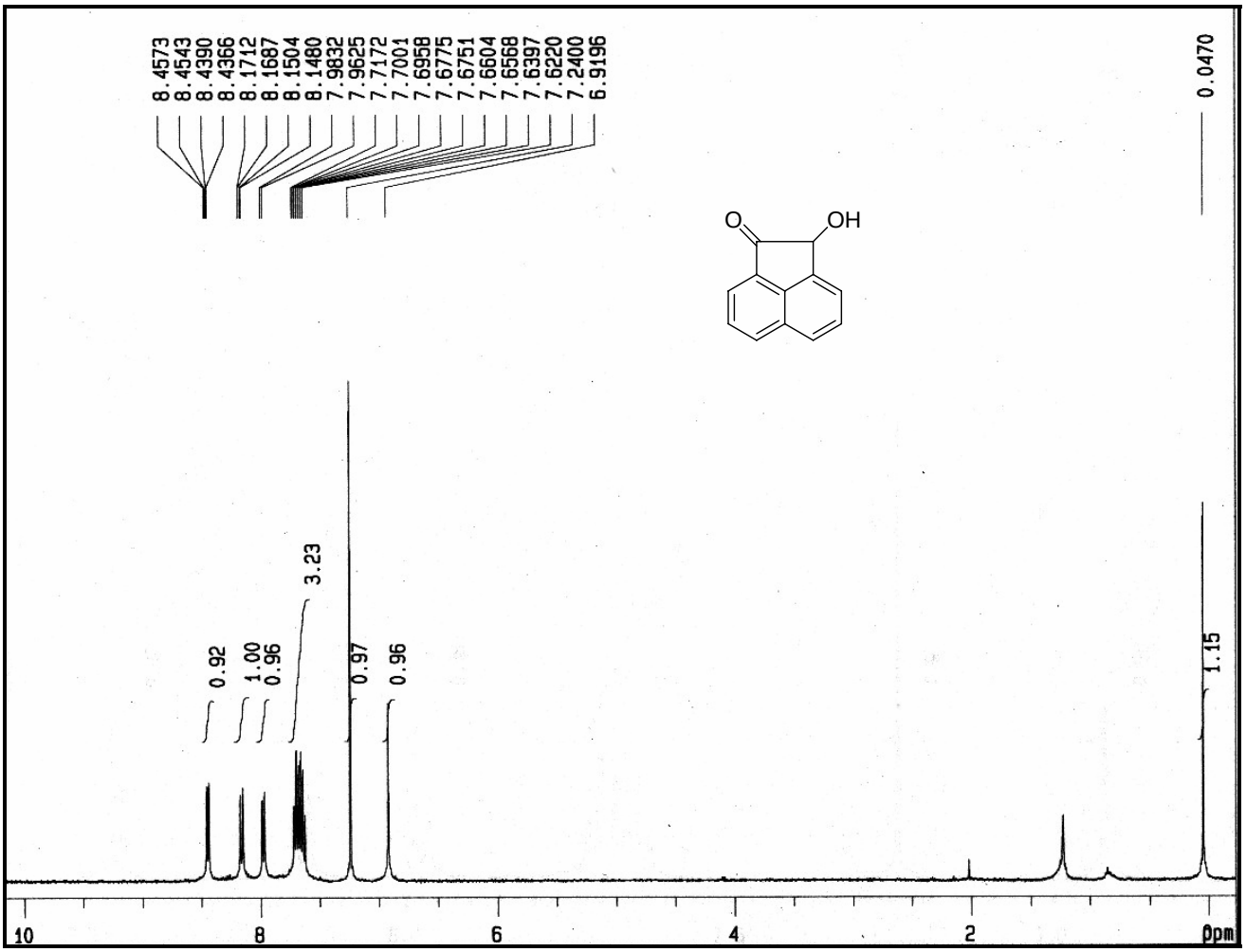


Figure S16. [1]H NMR spectrum of 2-hydroxyacenaphthylen-1-one.

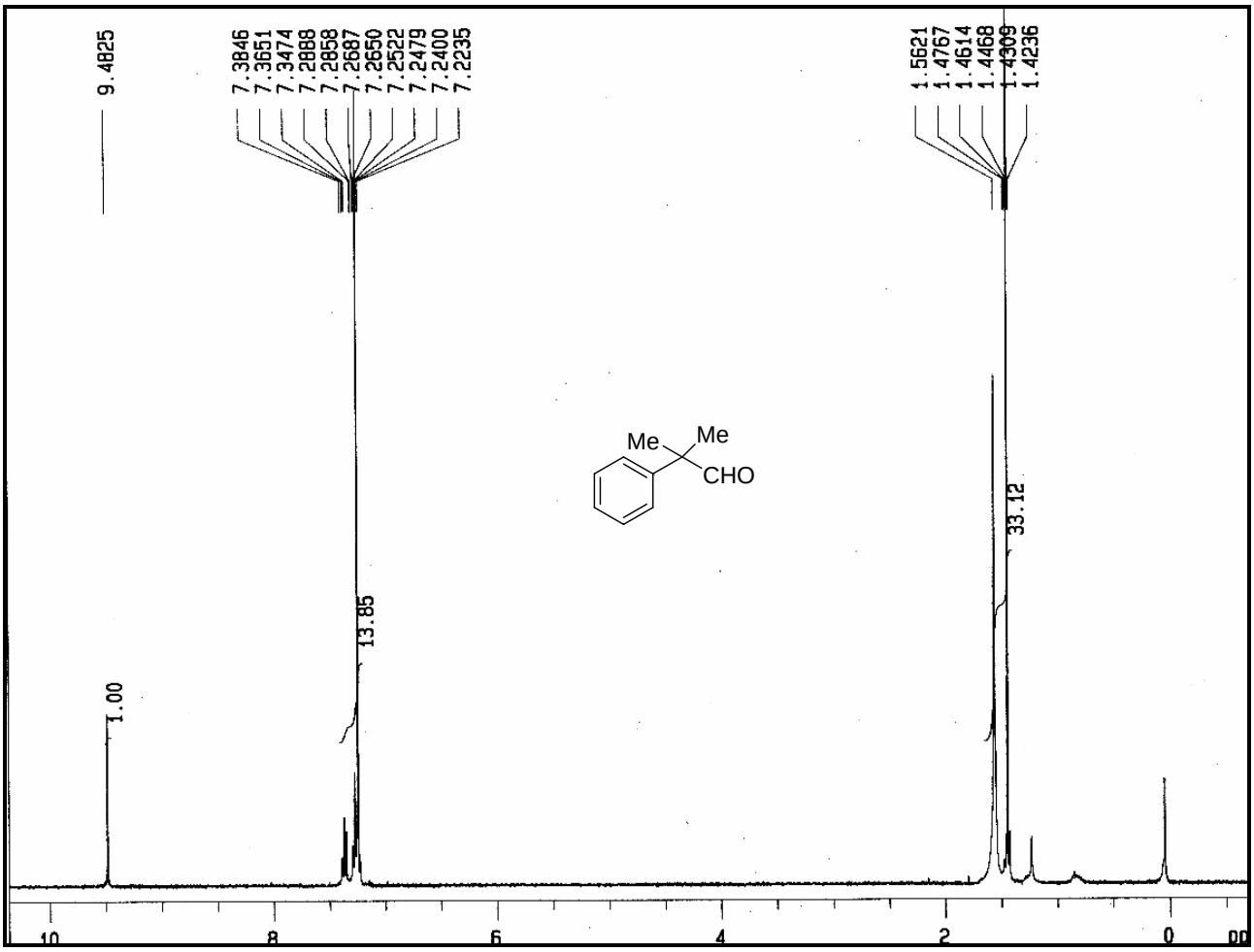


Figure S17. ^{1}H NMR spectrum of 2-methyl-2-phenylpropanal

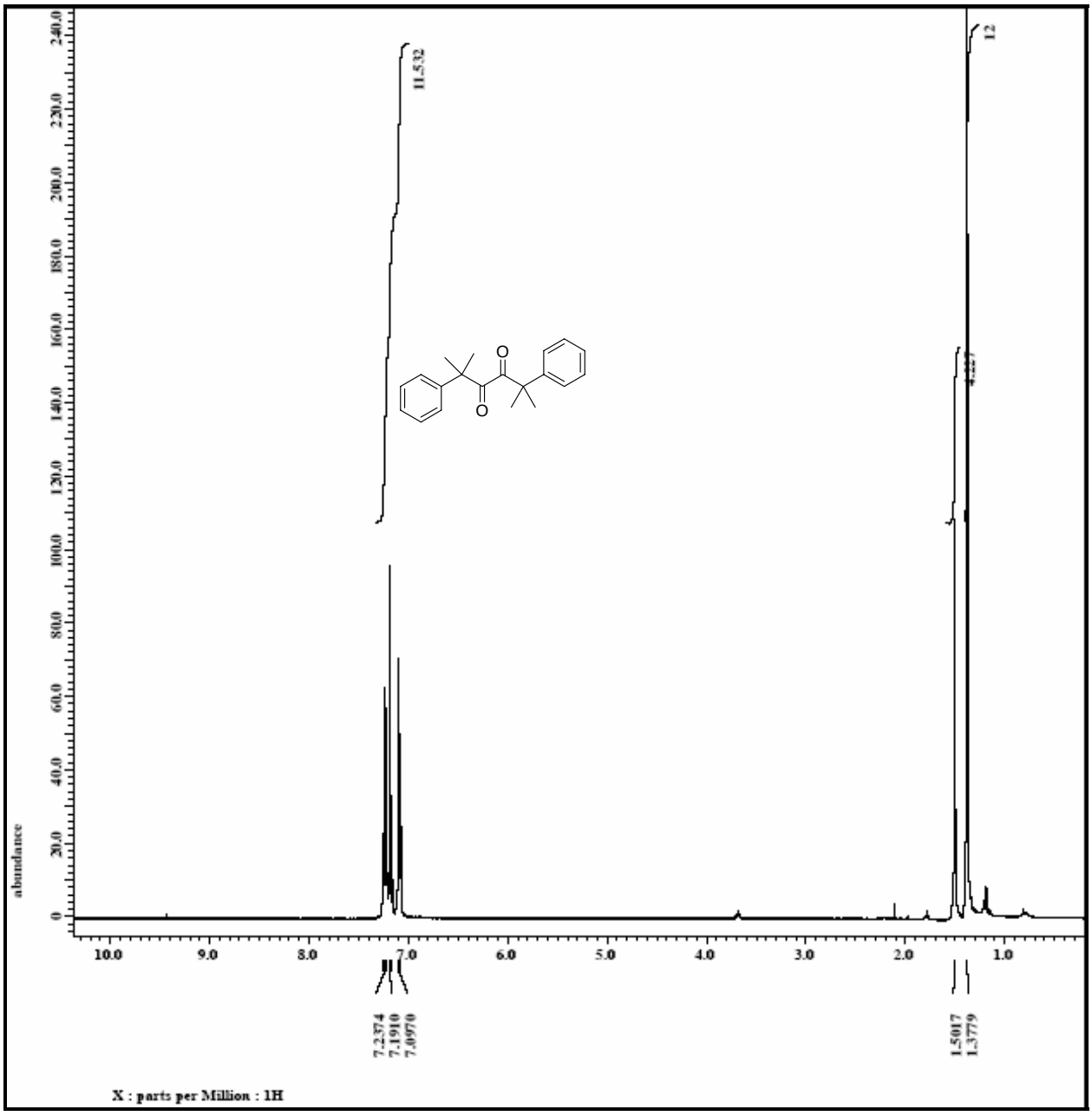


Figure S18.1 ^{1}H NMR spectrum of 2,5-dimethyl-2,5-diphenyl-hexane-3,4-dione

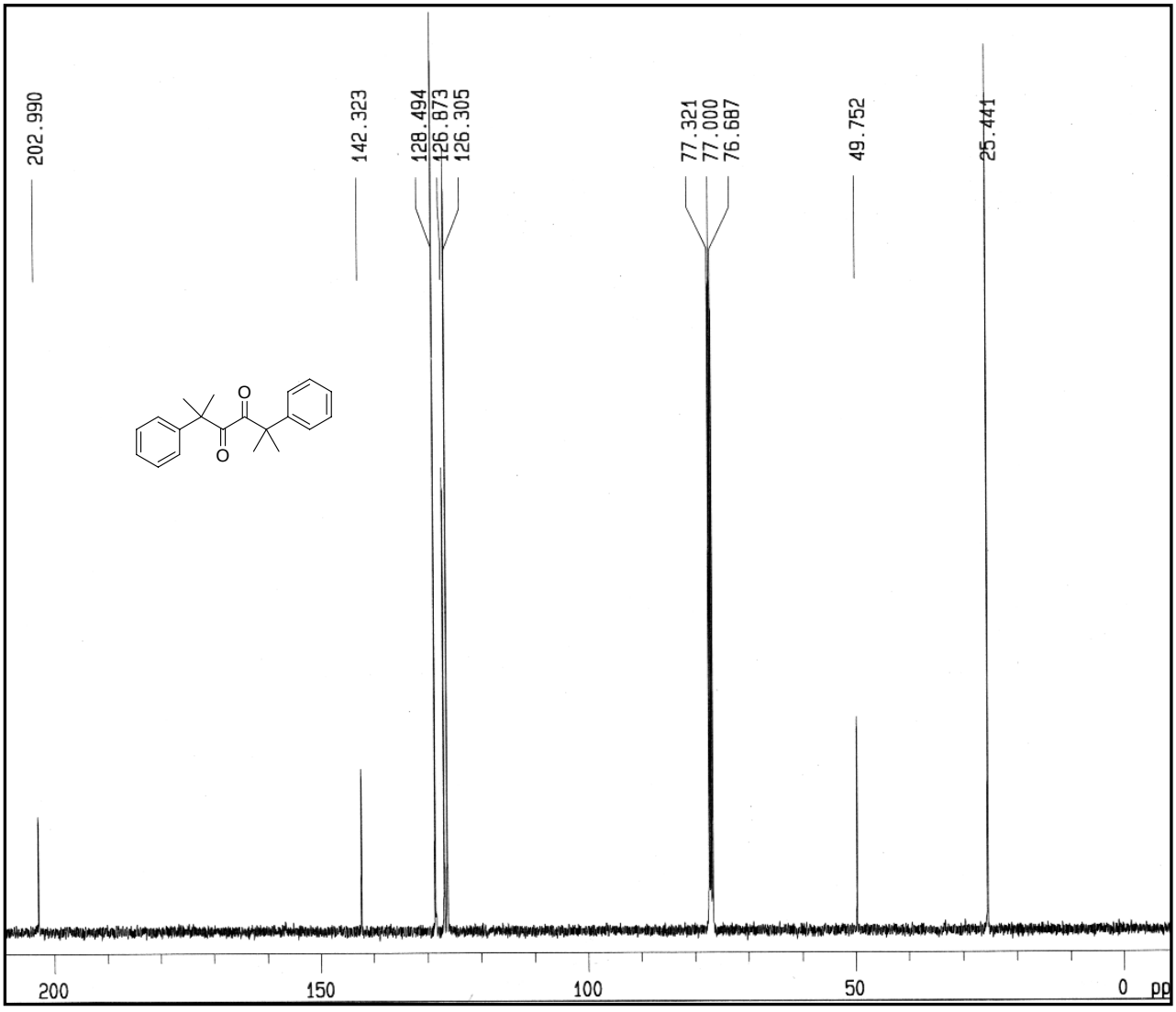


Figure S18.2 ^{13}C NMR spectrum of 2,5-dimethyl-2,5-diphenyl-hexane-3,4-dione

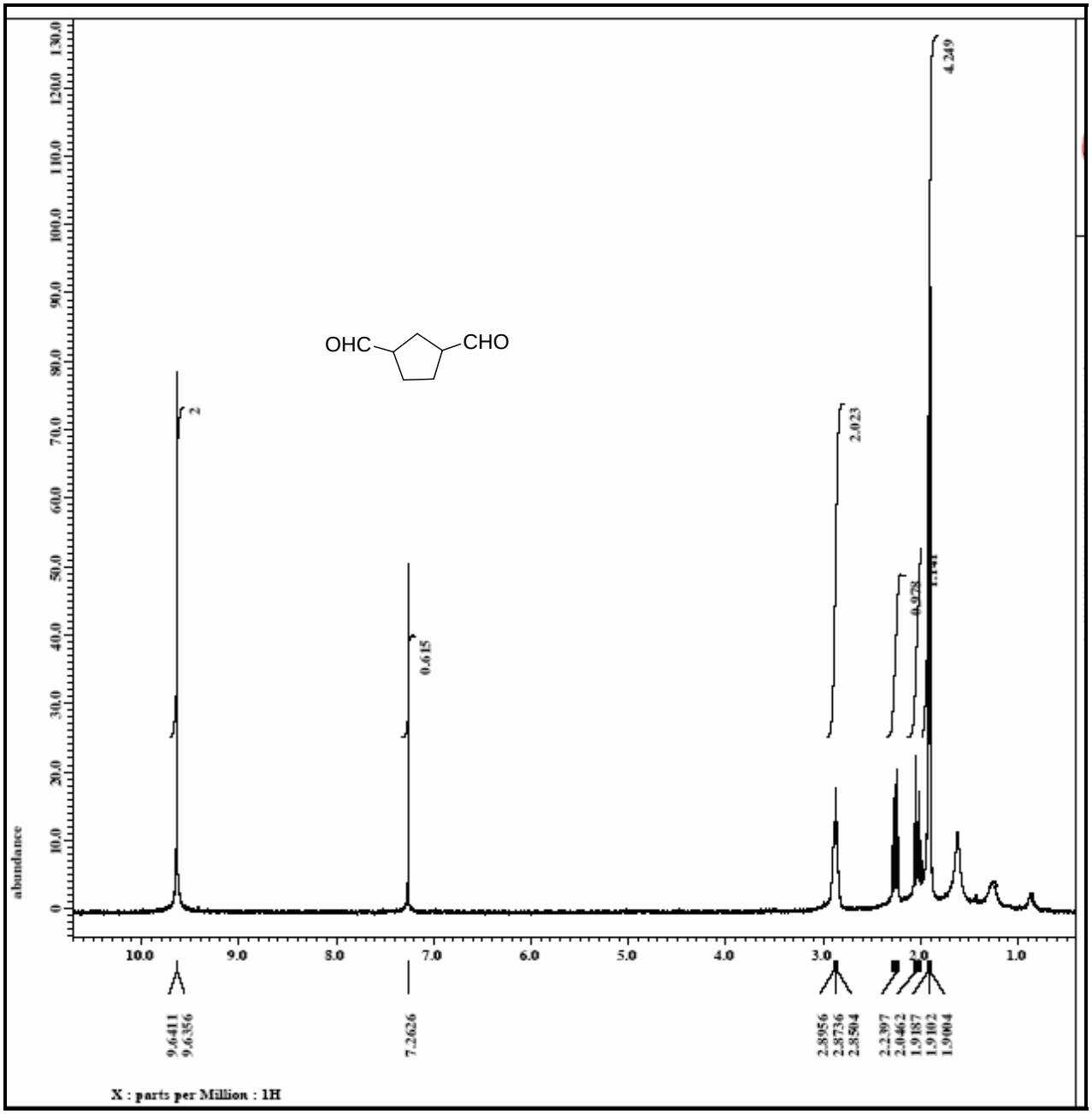


Figure S19.1. ^{1}H NMR spectrum of cylopentane-1,3-dicarbaldehyde.

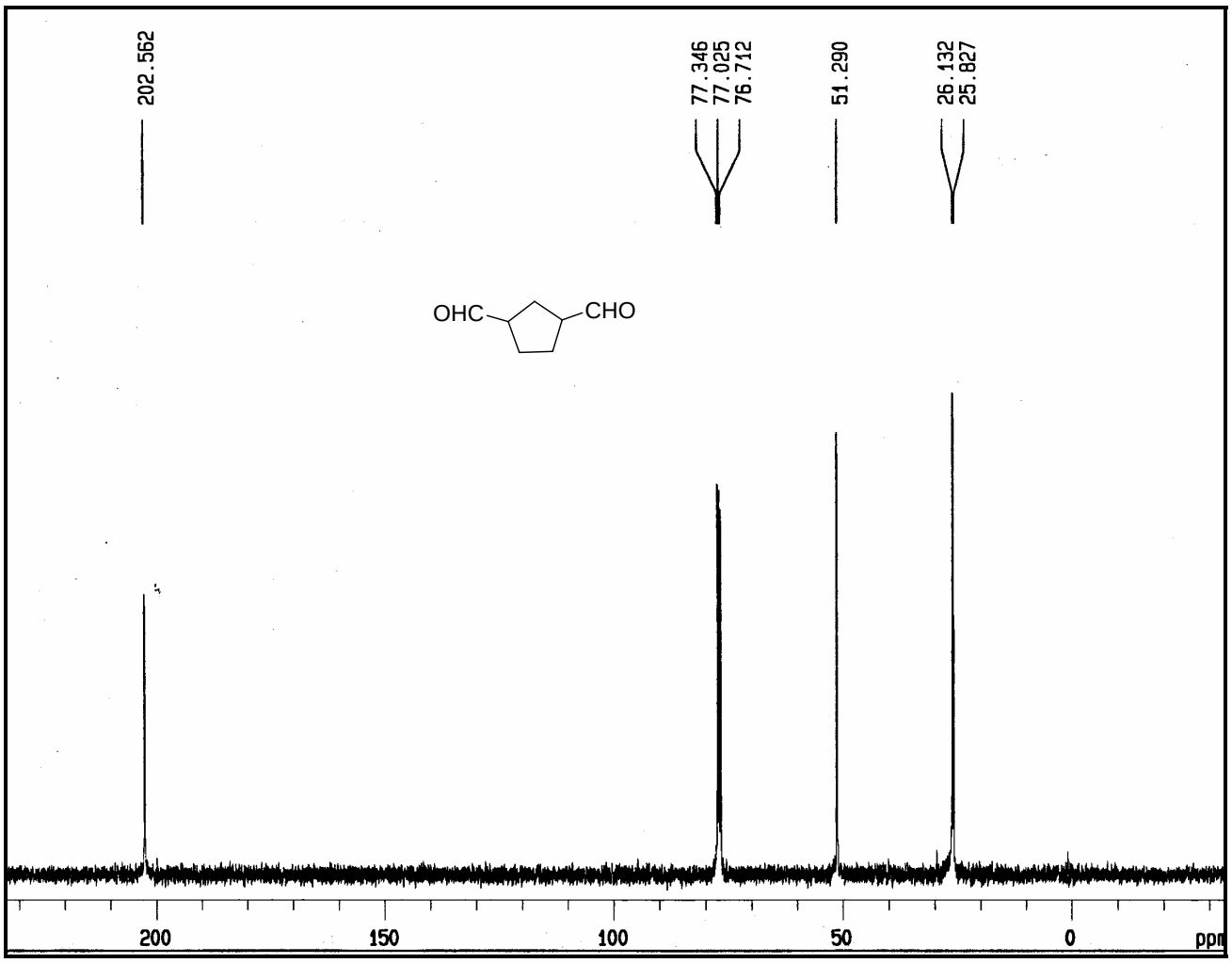


Figure S19.2. ^{13}C NMR spectrum of cylopentane-1,3-dicarbaldehyde.

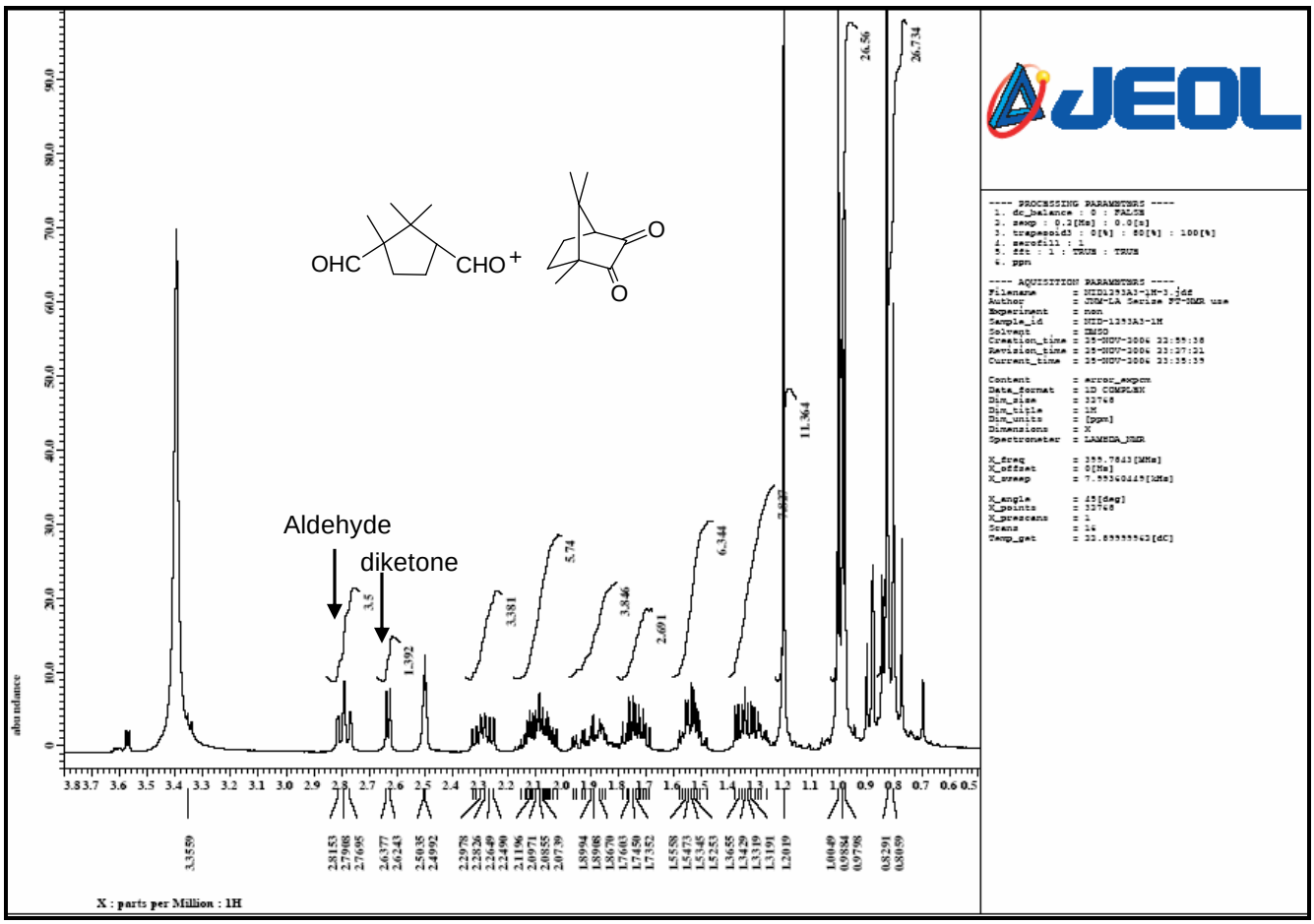


Figure S20.1. ^{1}H NMR monitoring of the reaction of camphane-2,3-diol in DMSO-d_6 with IBX (2.0 equiv), 2.5 h, 30 °C.

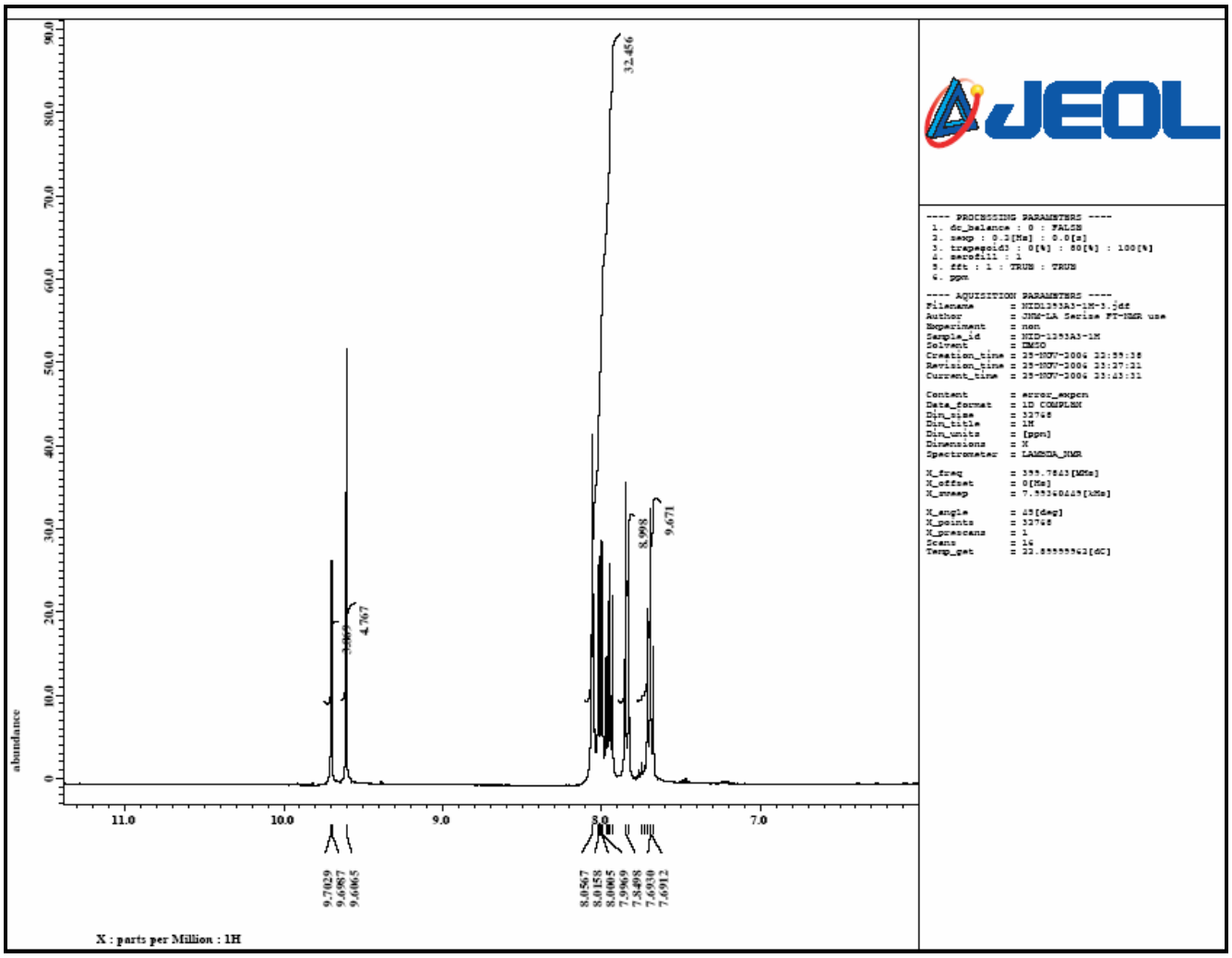


Figure S20.2. ^{1}H NMR monitoring of the reaction of camphane-2,3-diol in DMSO-d_6 with IBX (2.0 equiv), 2.5 h, 30 °C.

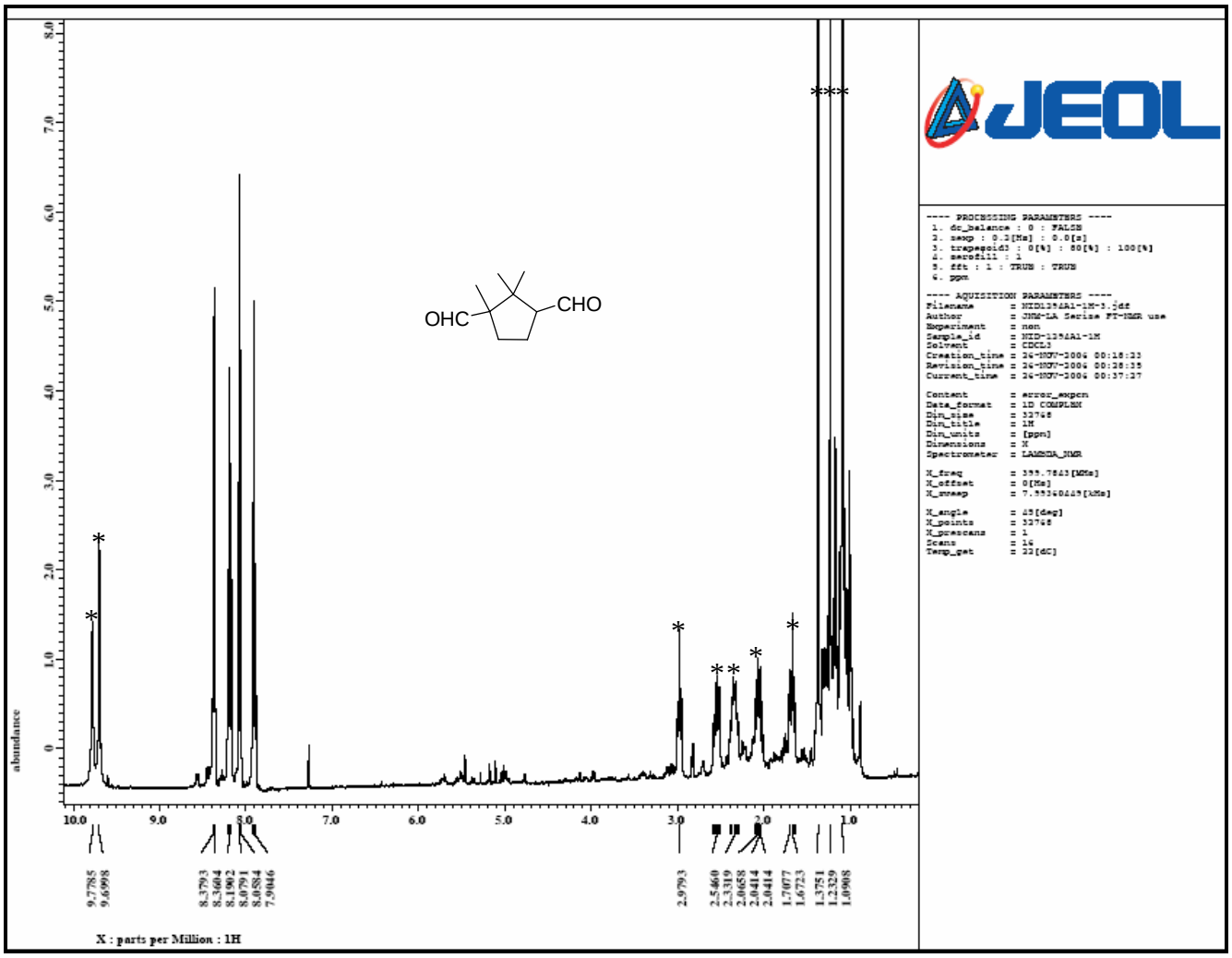


Figure S21. ^{1}H NMR monitoring of the reaction of camphane-2,3-diol in TFA with IBX (1.2 equiv), 0.2 h, 30 °C. (* = dialdehyde)

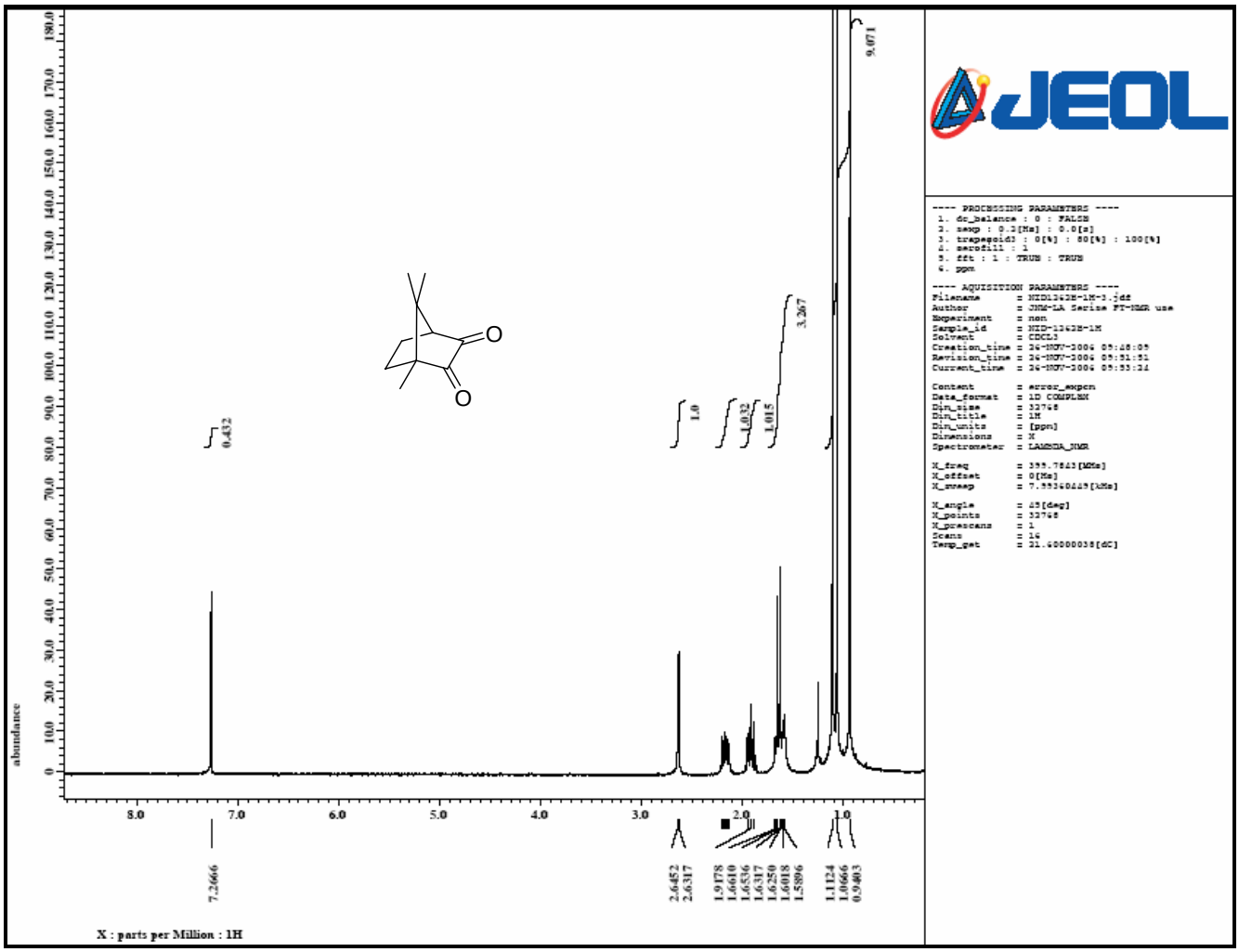


Figure S22. ^{1}H NMR spectrum of camphorquinone.

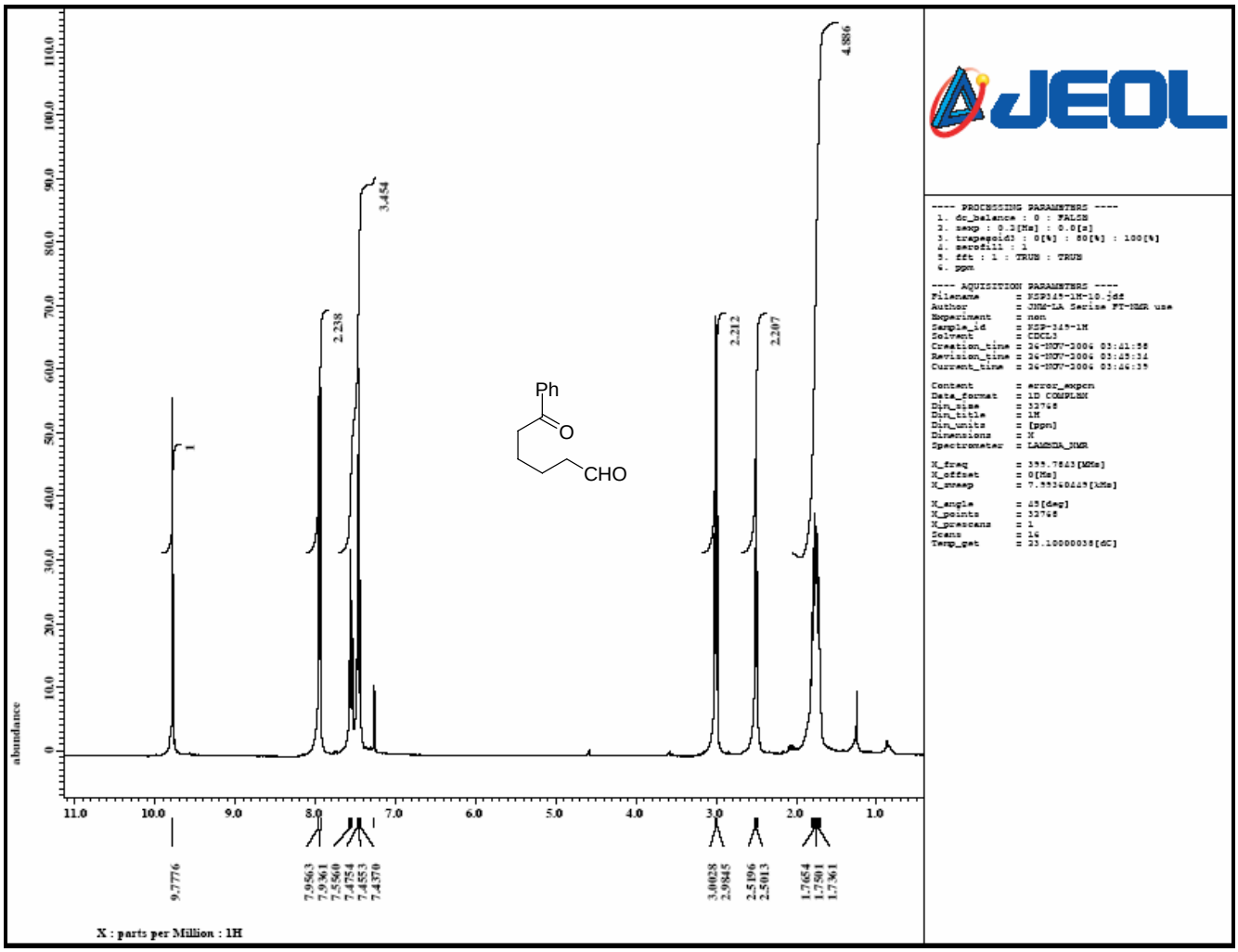


Figure S23.1. ^{1}H NMR spectrum of 6-oxo-6-phenylhexanal.

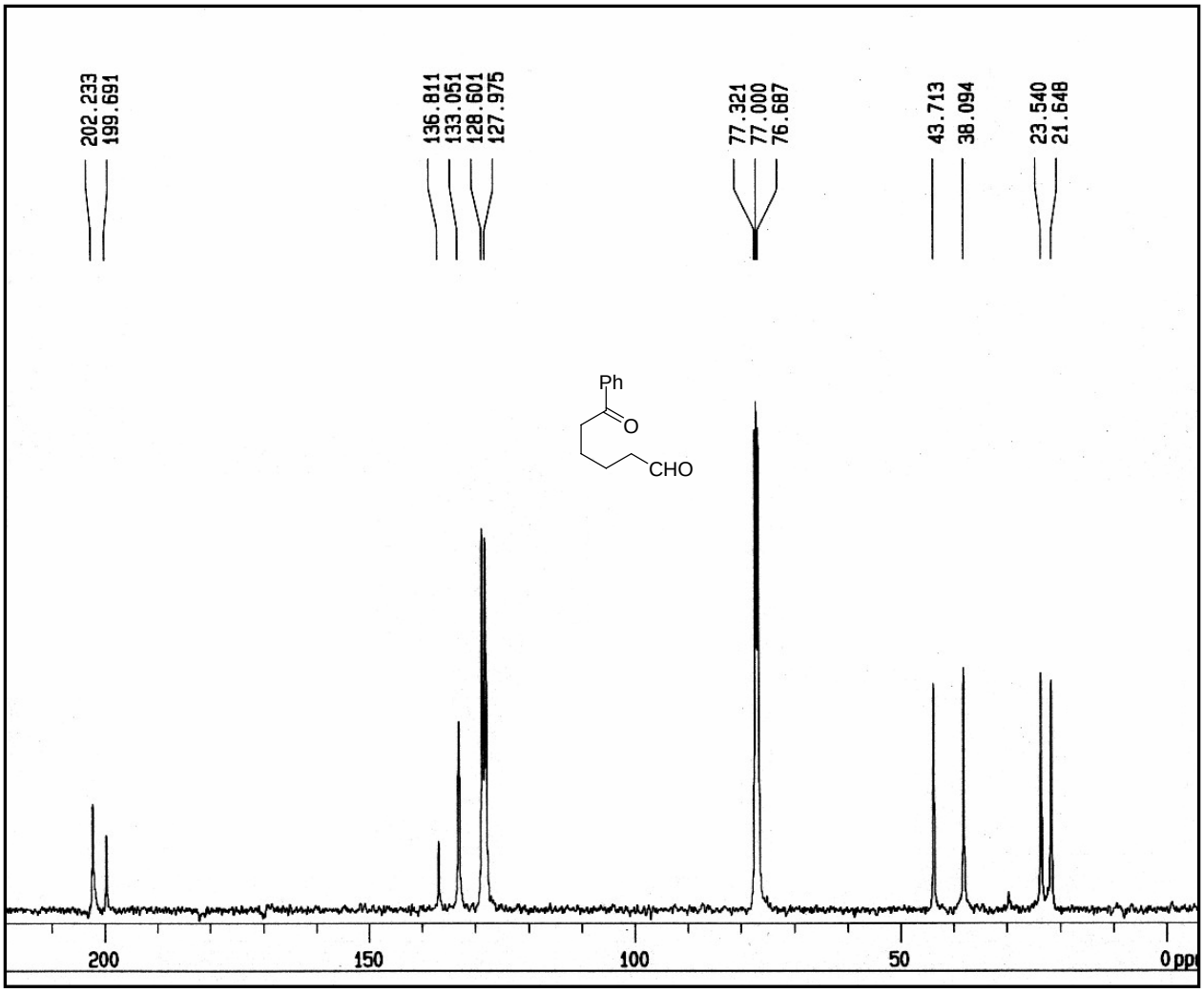


Figure S23.2. ^{13}C NMR spectrum of 6-phenylhexanal.

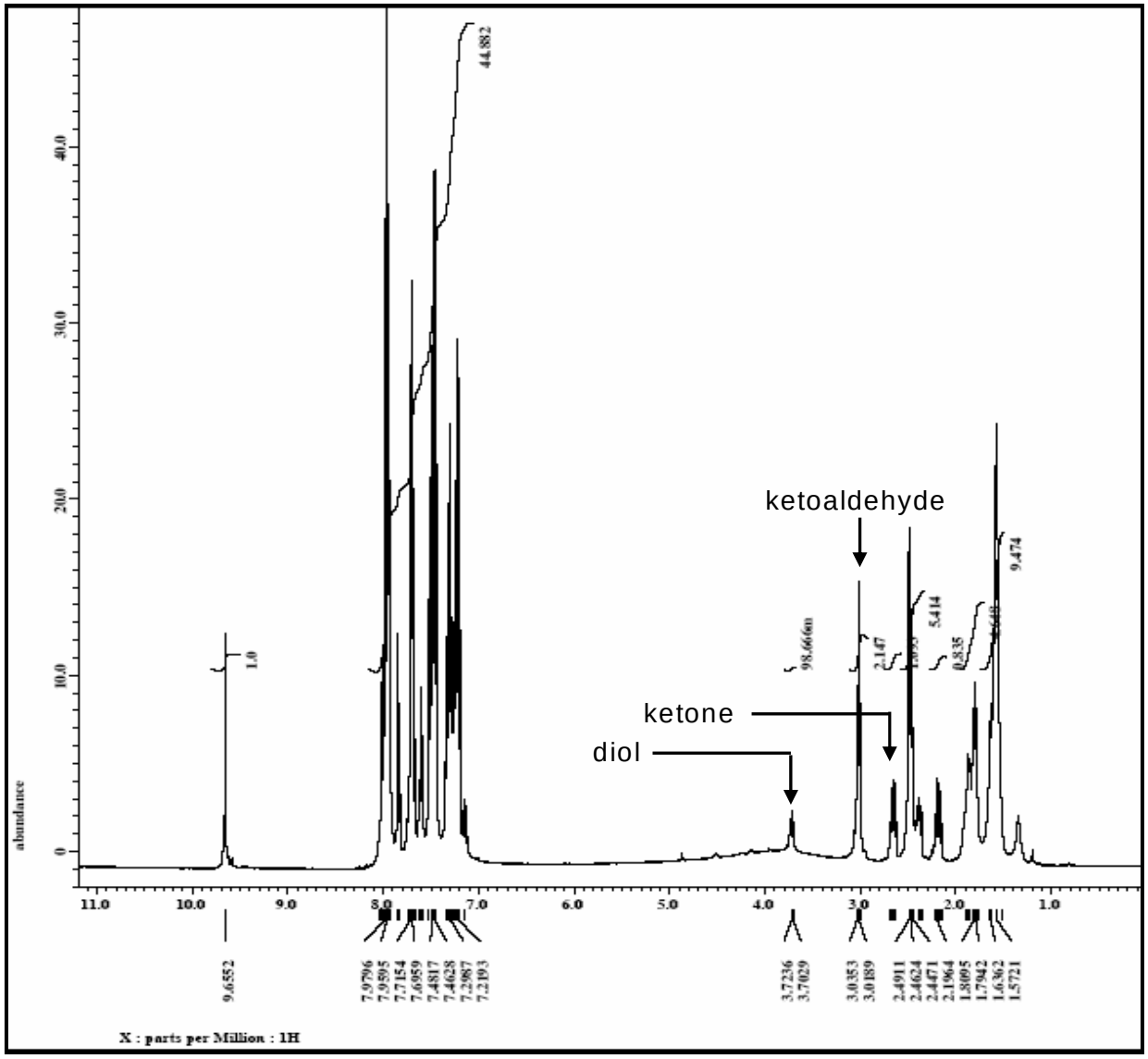


Figure S24. ^{1}H NMR monitoring of the reaction of 1-phenylcyclohexan-1,2-diol in DMSO-d_6 with IBX (2.0 equiv), 7.0 h, 80 °C.

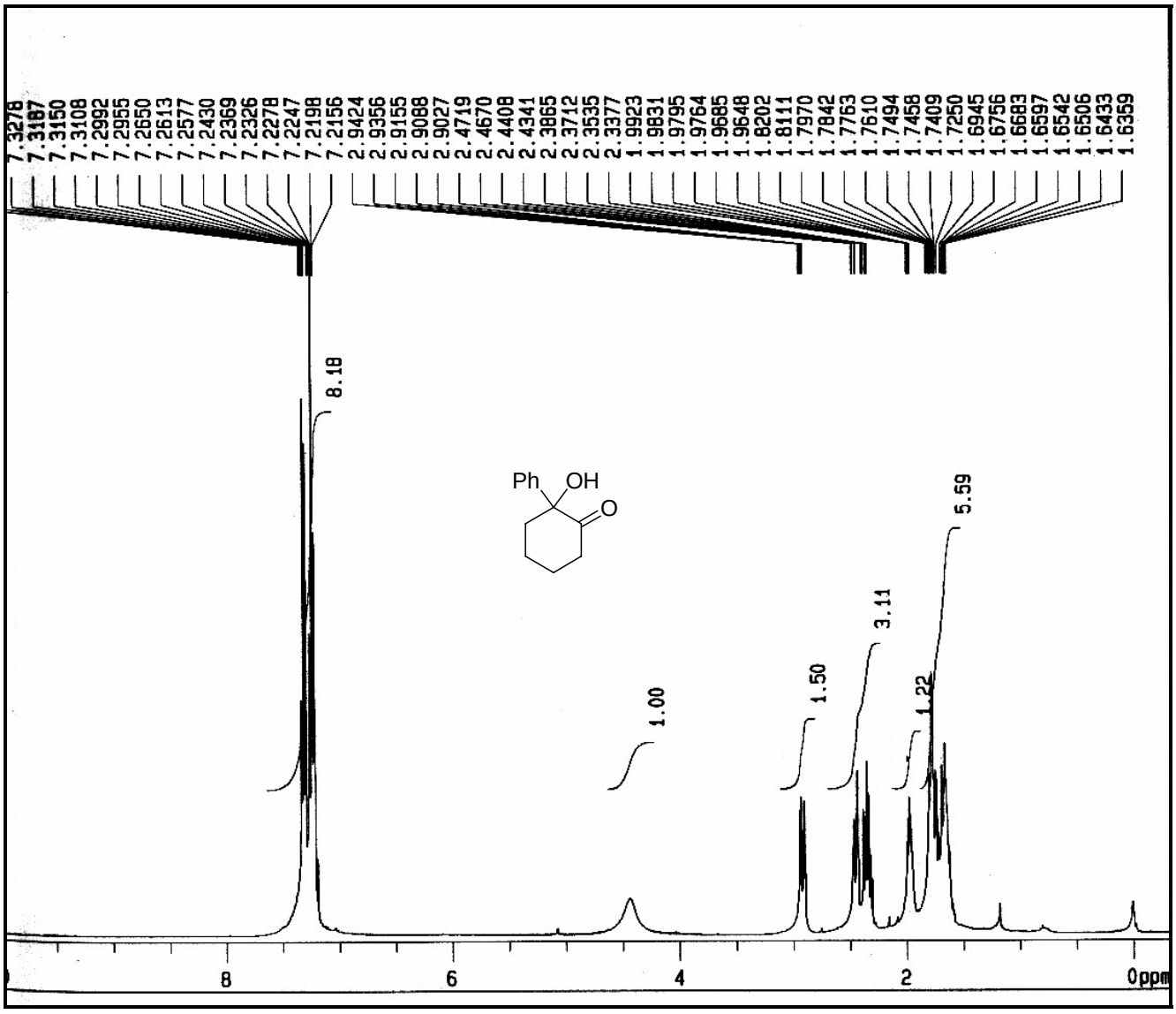


Figure S25. ^{1}H NMR spectrum of 2-hydroxy-2-phenylcyclohexanone.

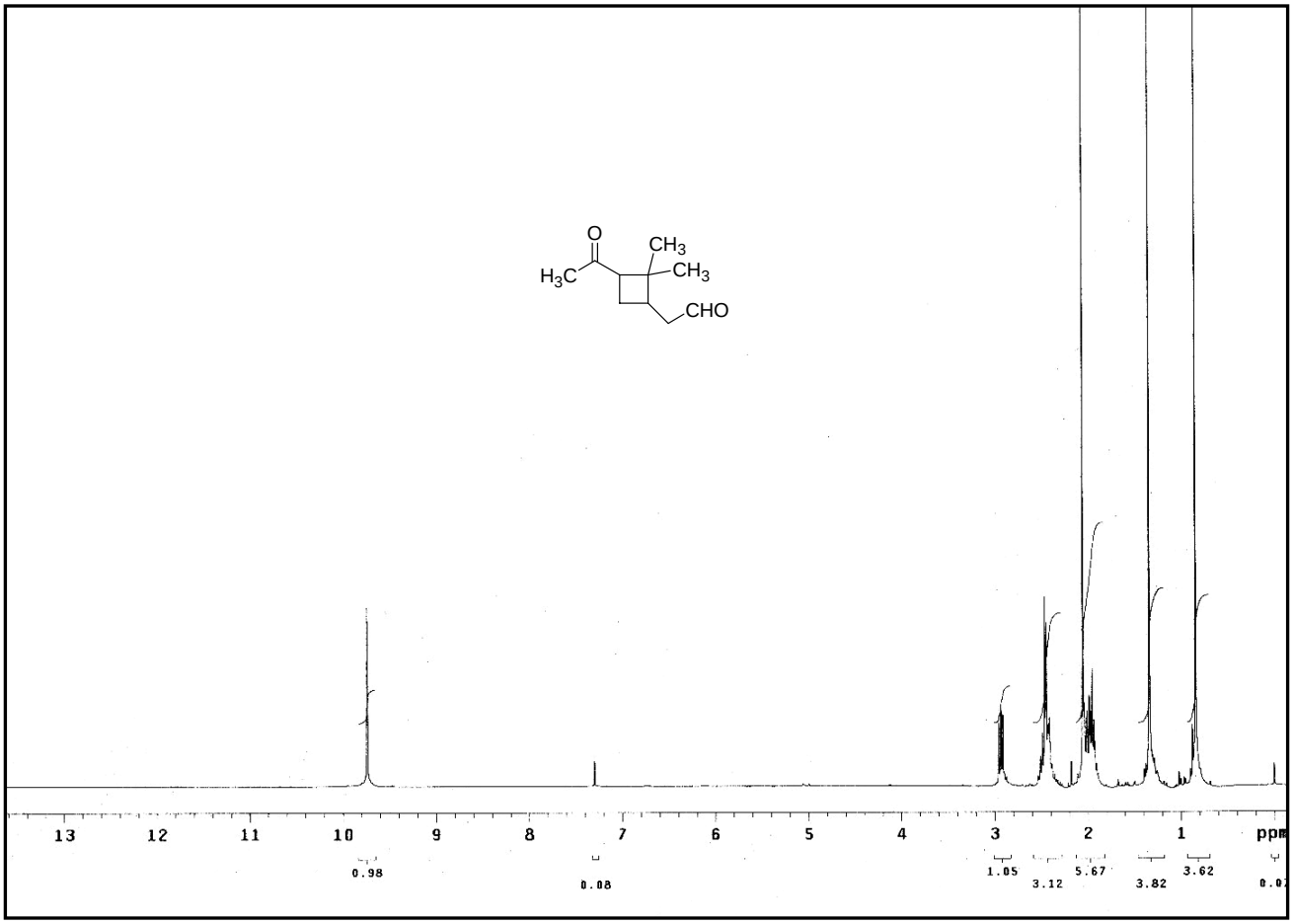


Figure S26.1. ^{1}H NMR spectrum of (3-acetyl-2,2-dimethylcyclobutyl)acetaldehyde.

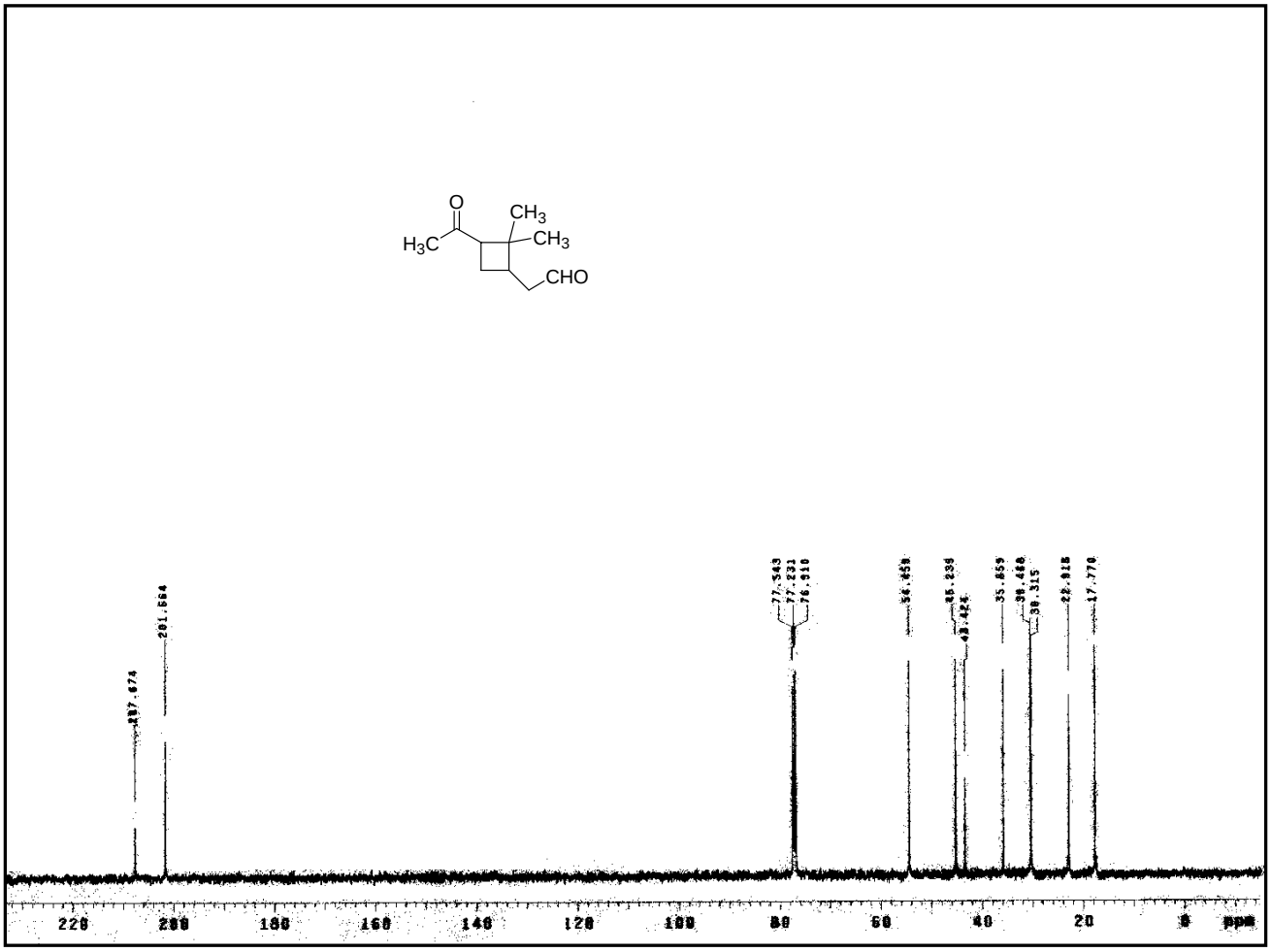


Figure S26.2. ^{13}C NMR spectrum of (3-acetyl-2,2-dimethylcyclobutyl)acetaldehyde.

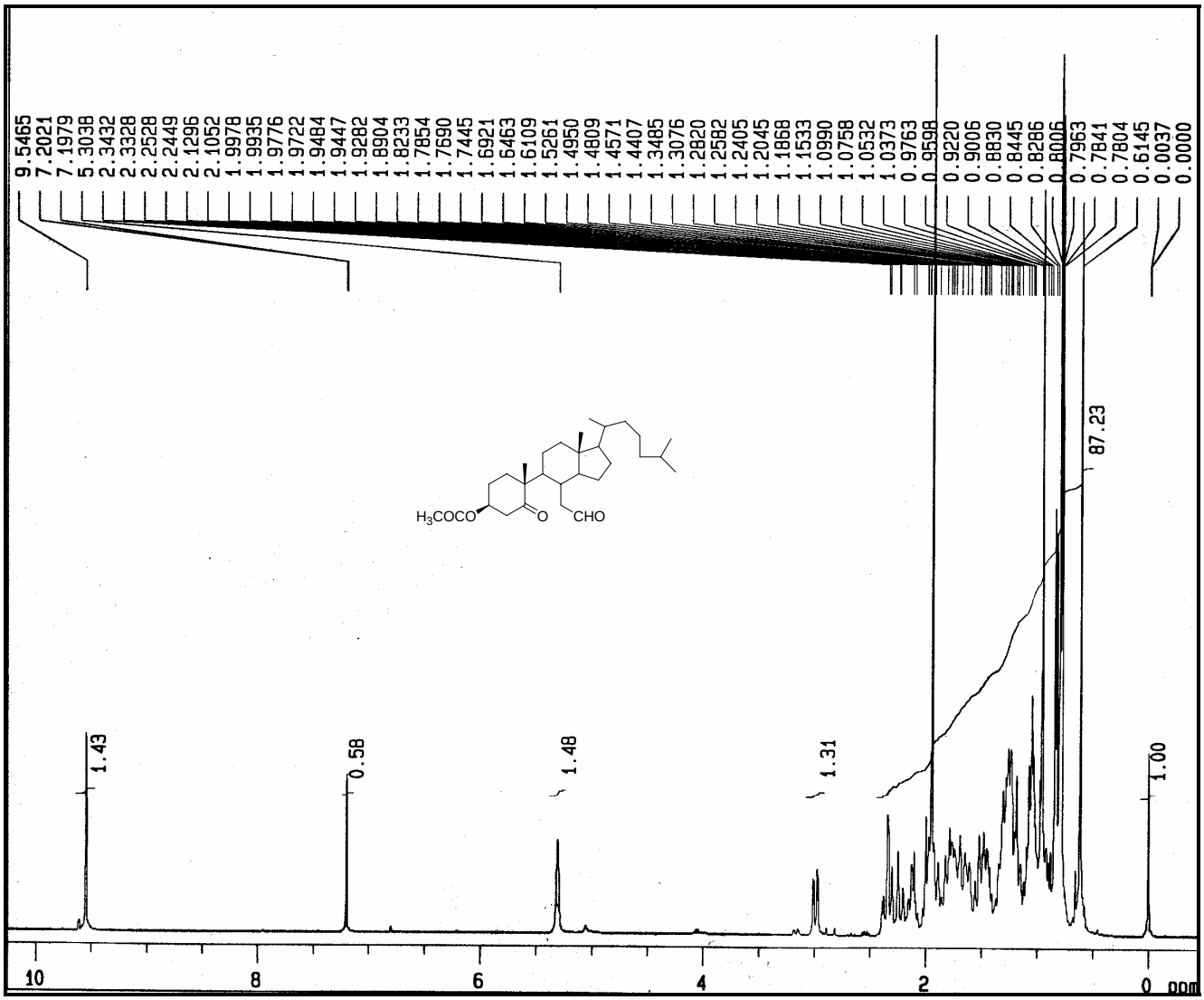


Figure S27.1. ^{1}H NMR spectrum of 3-(acetyloxy)-1-oxo-secocholestan-6-al.

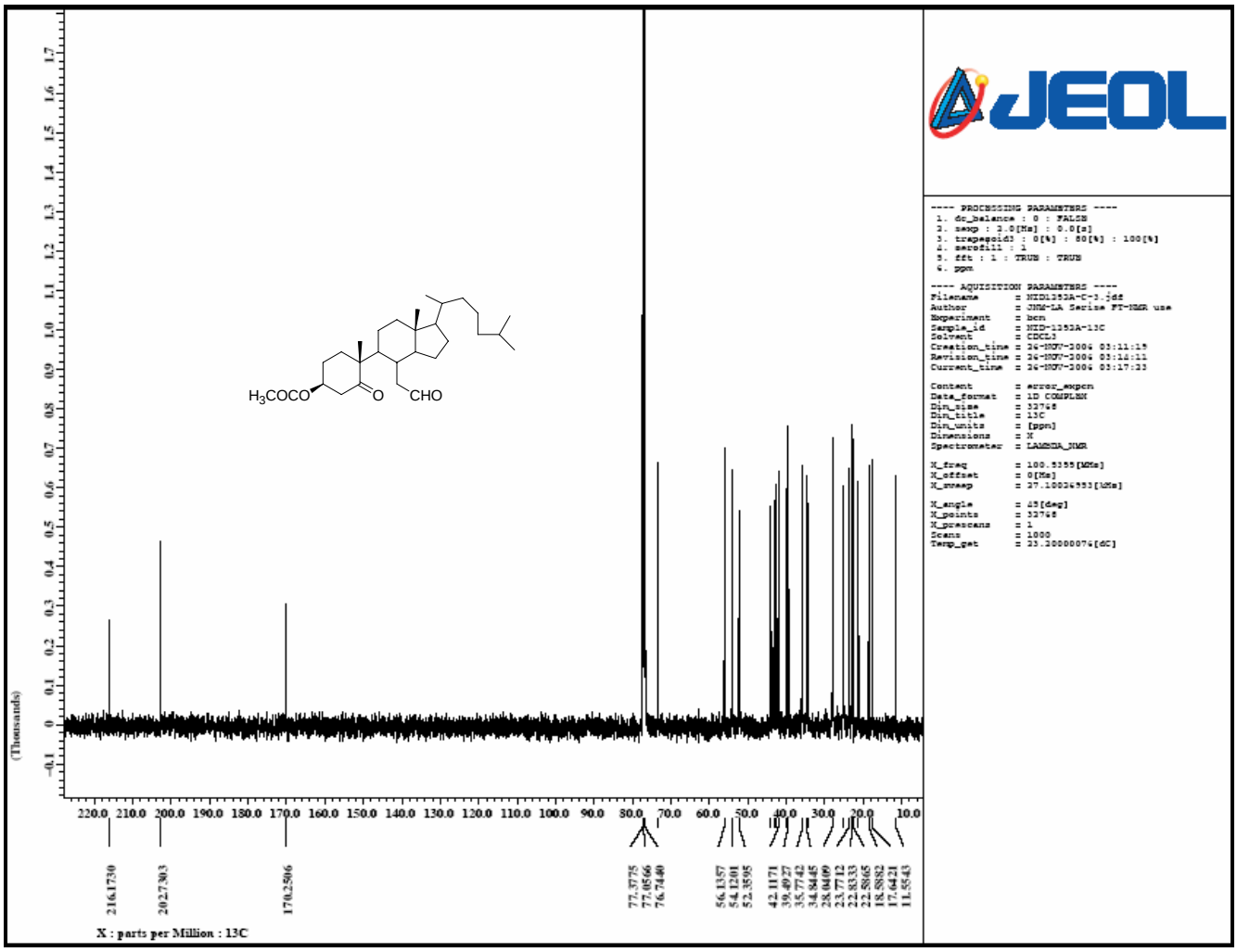


Figure S27.2. ^{13}C NMR spectrum of 3-(acetyloxy)-1-oxo-secocholestan-6-al.

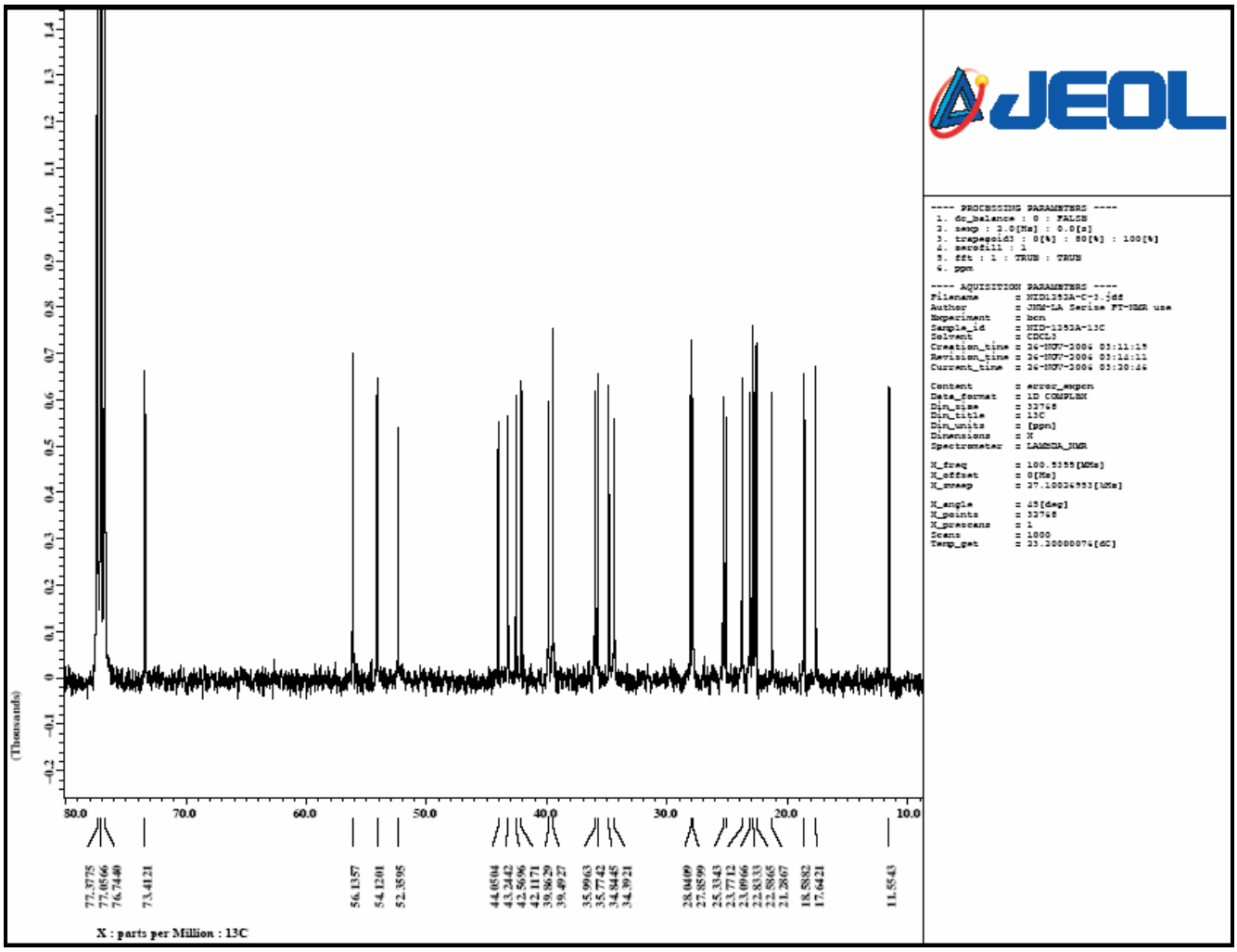


Figure S27.3. ^{13}C NMR spectrum of 3-(acetyloxy)-1-oxo-secocholestan-6-al.

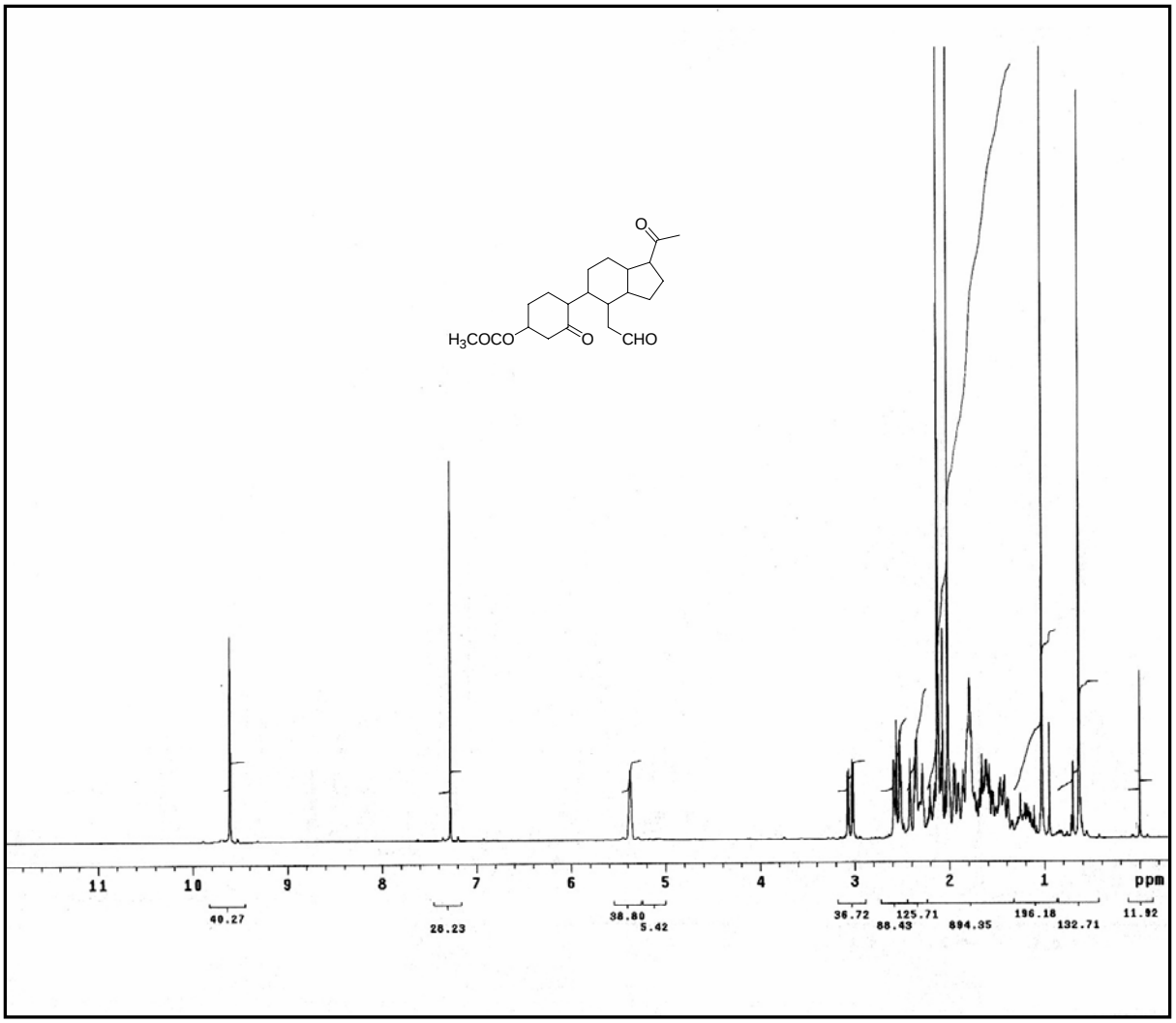


Figure S28.1. ^{1}H NMR spectrum of 3-(acetyloxy)-5,20-dioxo-secopregnan-6-al.

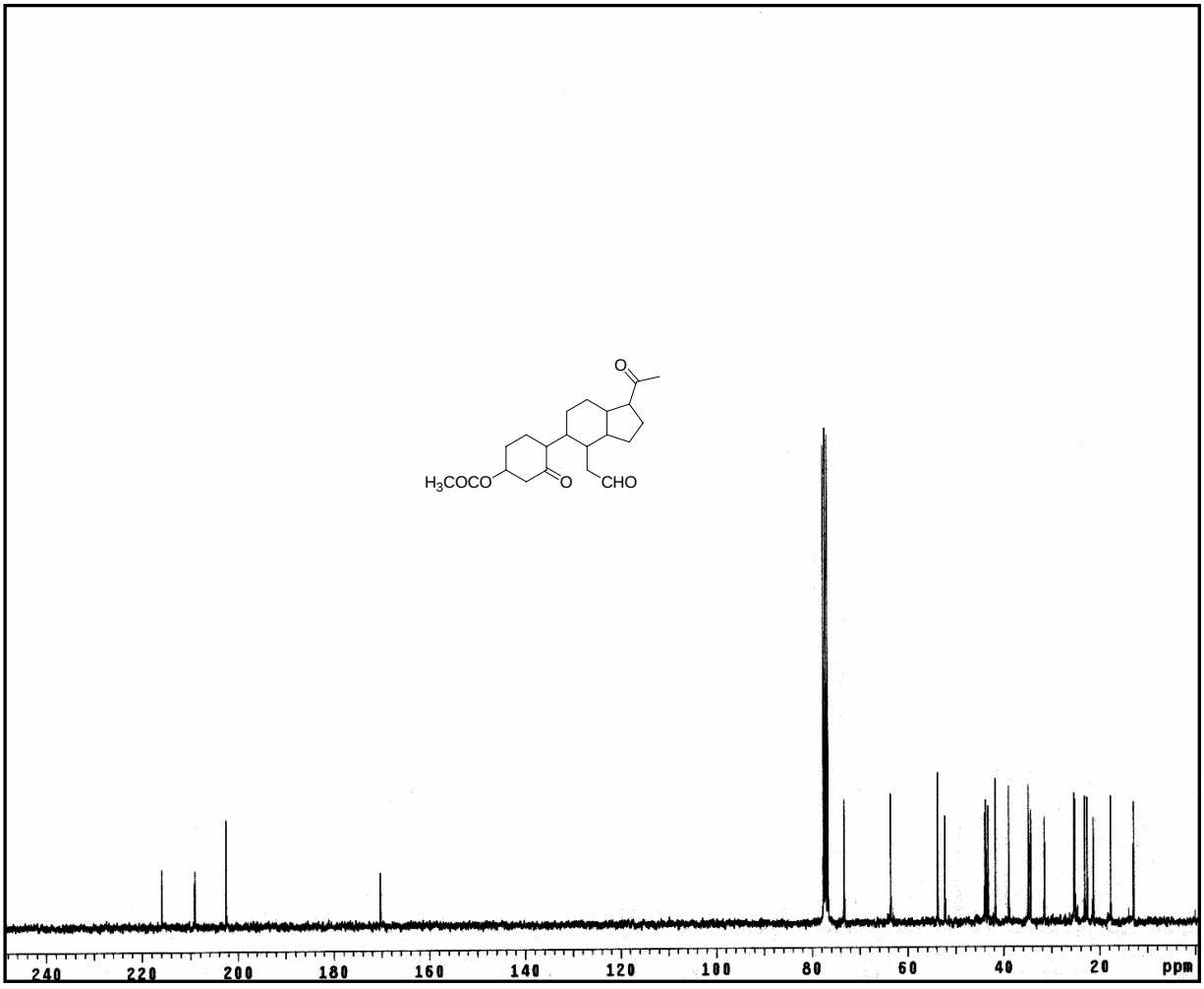


Figure S28.2. ^{13}C NMR spectrum of 3-(acetyloxy)-5,20-dioxo-secopregnan-6-al.

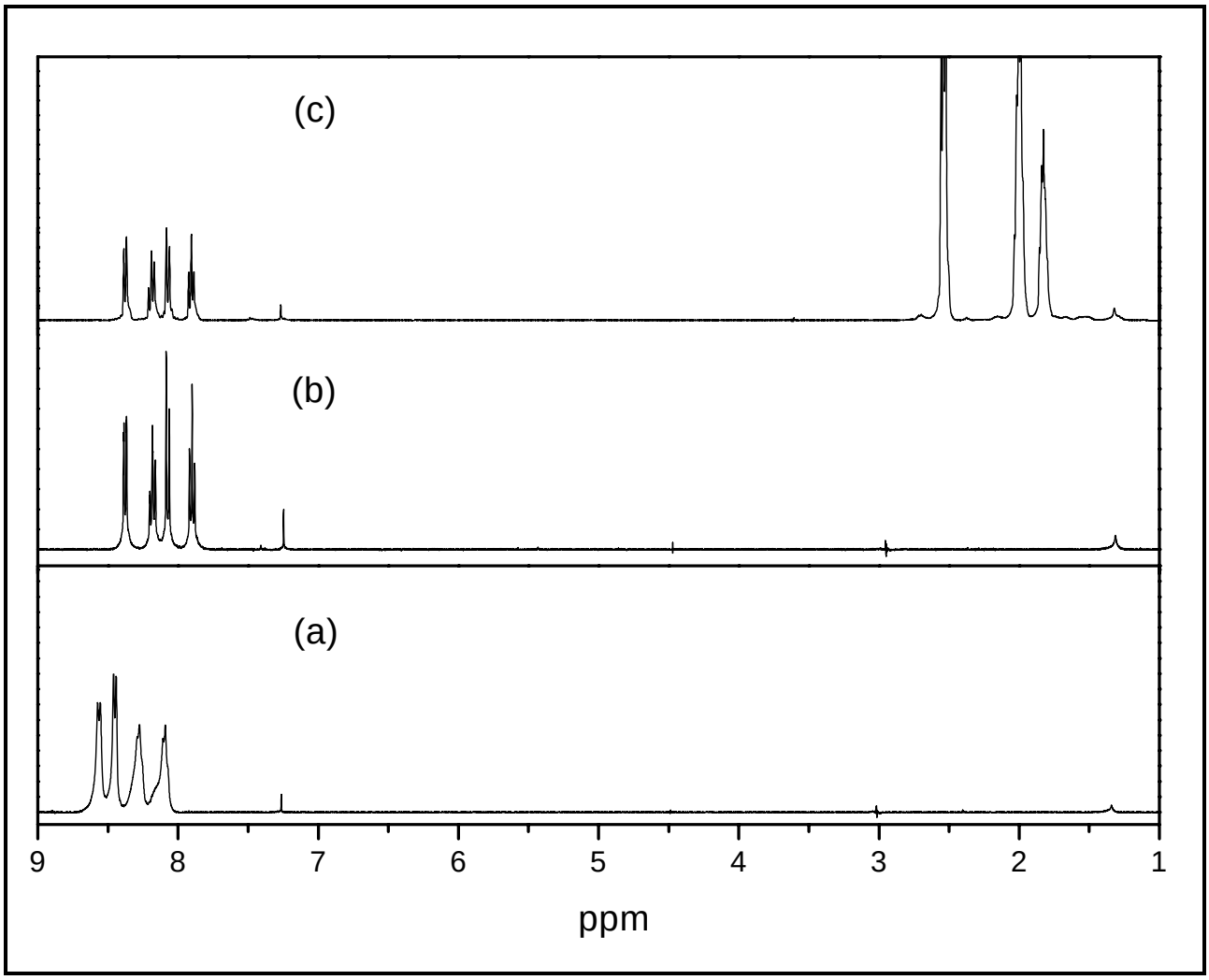
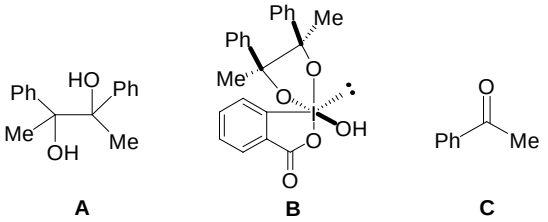


Figure S29. ^{1}H NMR monitoring of the reaction of [1,1'-bicyclohexyl]-1,1'-diol with IBX in TFA. (a) IBX in TFA; (b) IBA in TFA; (c) IBX (1.2 equiv) in TFA + [1,1'-bicyclohexyl]-1,1'-diol, 0.1 h, 30 ºC. Notice that the reduction product of IBX is IBA.



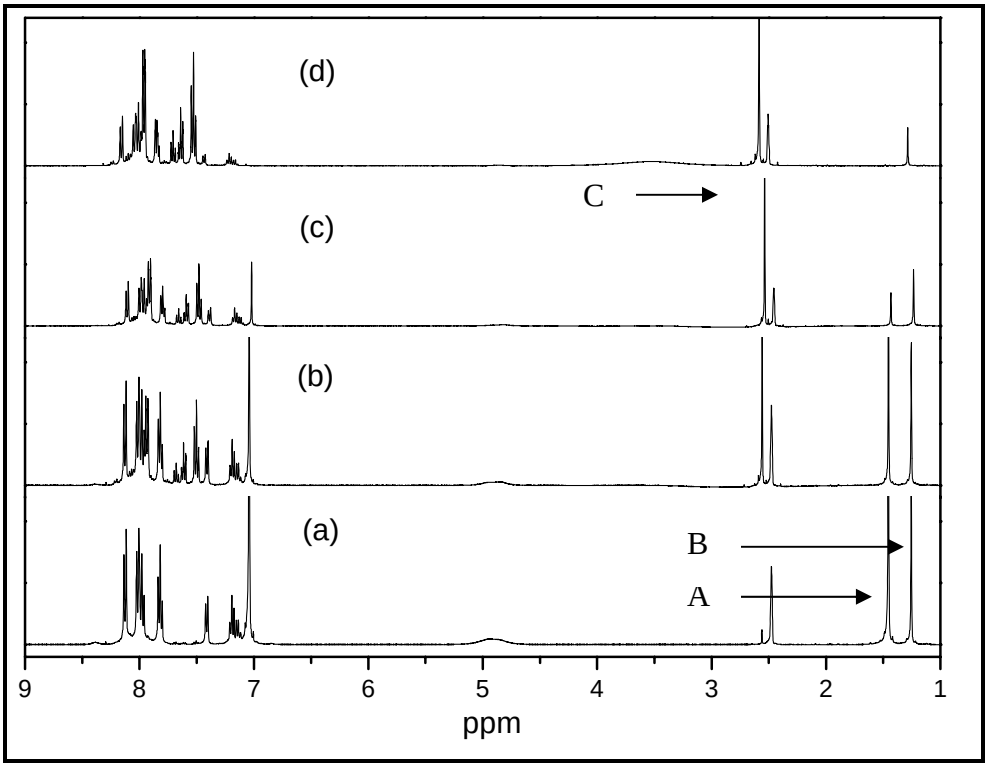


Figure S30. ^{1}H NMR monitoring of the reaction of 2,3-diphenylbutane-2,3-diol in DMSO-d_6. (a) IBX (2 equiv), 0.1 h, 30 °C; (b) IBX (2 equiv), 0.3 h, 80 °C; (c) IBX (2 equiv), 0.6 h, 80 °C; (d) IBX (2 equiv), 1.25 h, 80 °C.

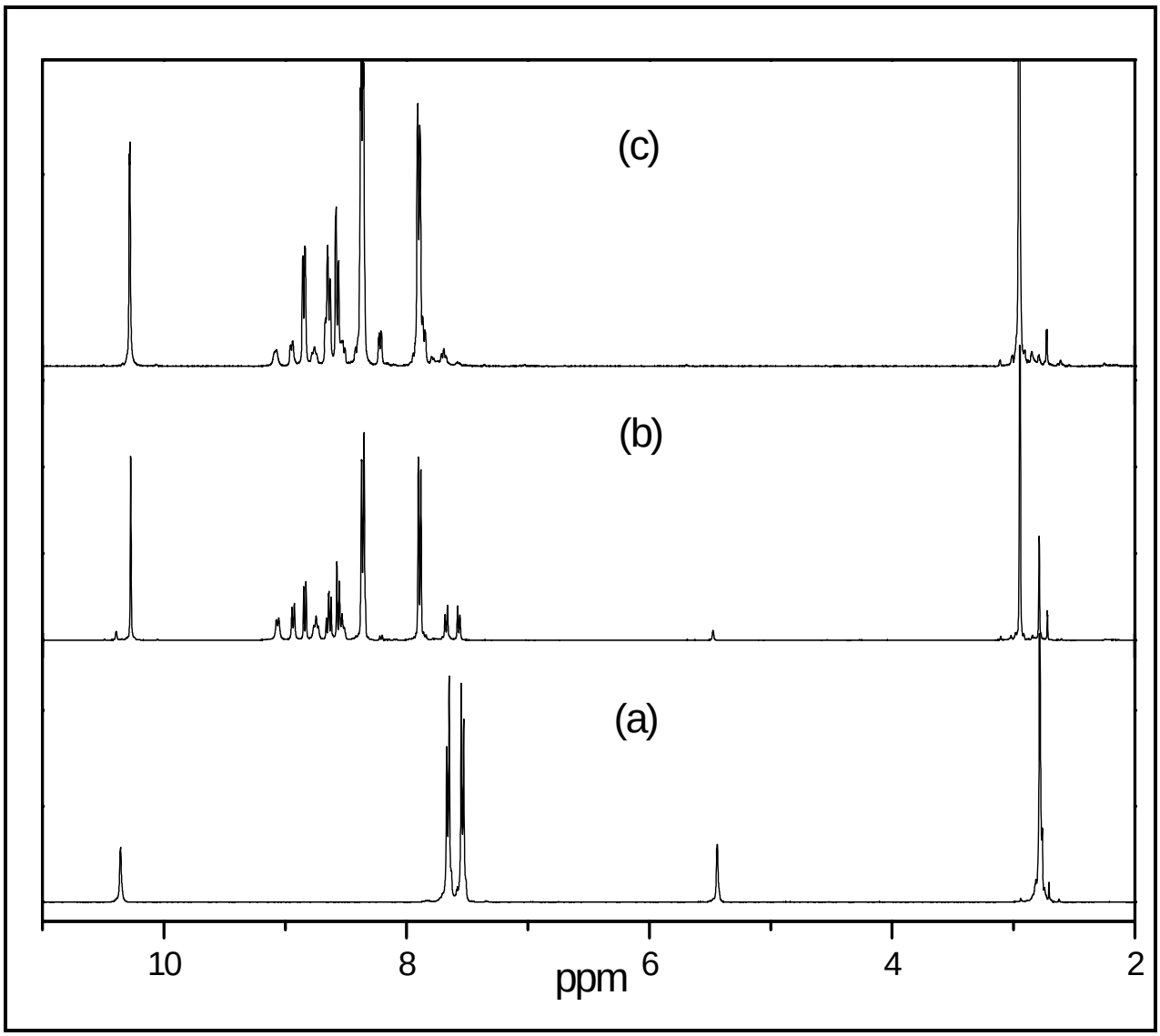


Figure S31. ^{1}H NMR monitoring of the reaction of 1,2-Di-*p*-tolylethane-1,2-diol in TFA-*d*. (a) Diol (without IBX), 0.1 h, 30 ºC; (b) Diol + IBX (2 equiv), TFA , 0.1 h, 30 ºC; (c) Diol + IBX (2 equiv), TFA, 1.0 h, 30 ºC.

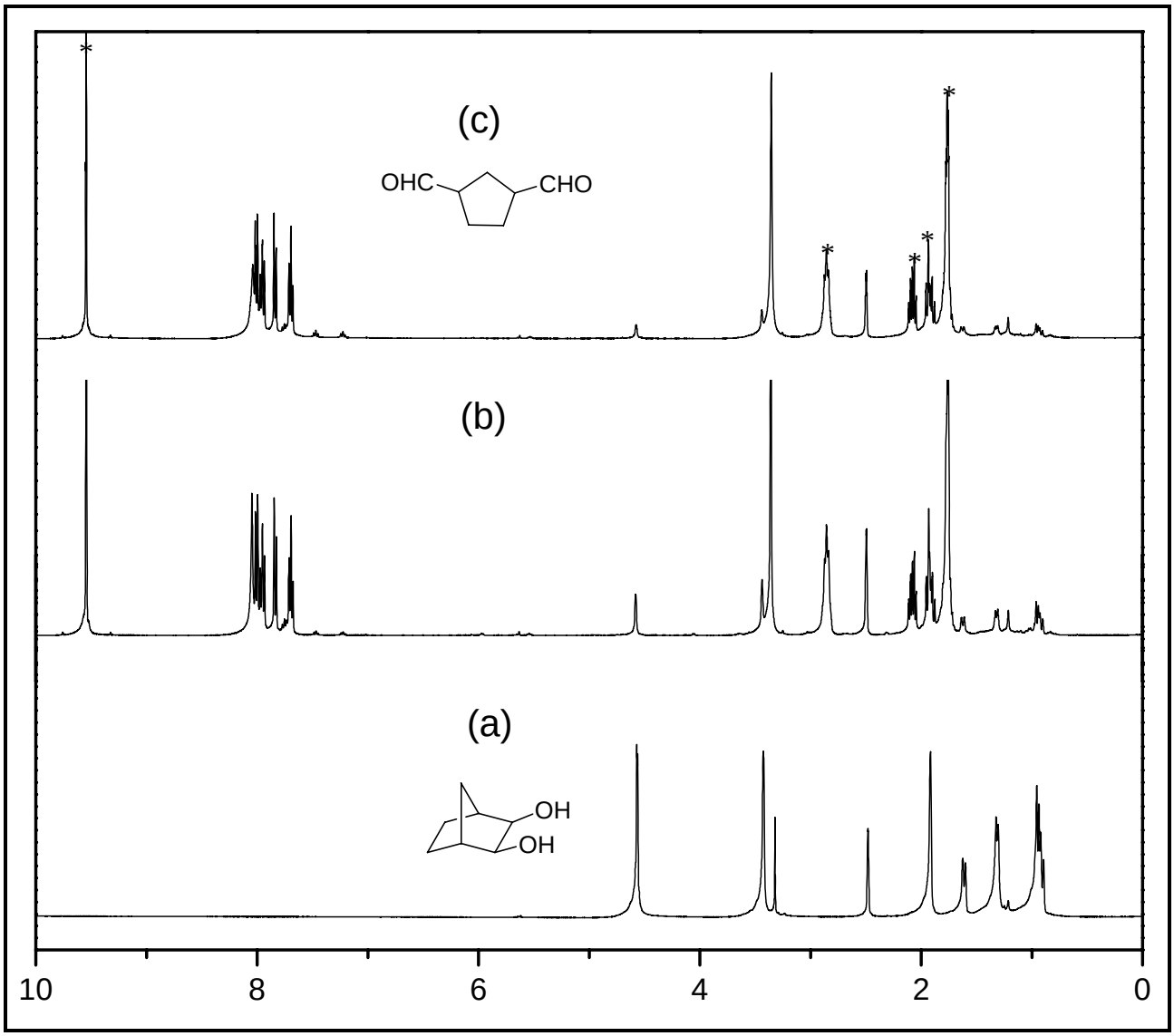


Figure S32. ^{1}H NMR monitoring of reaction of 2-exo-3-exo-bicyclo[2.2.1]heptane-diol with IBX in DMSO-d_6 (a) diol in DMSO (b) diol + IBX (1.2 equiv) in DMSO, 0.5 h, 30 ºC (c) diol + IBX (1.2 equiv) in DMSO, 2.0 h, 30 ºC. (* = dialdehyde)