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Efficient access to *cis*-decalinol frameworks: Copper(I)-catalyzed borylative cyclization of allene cyclohexanediones

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^{1}H NMR, ^{13}C NMR COPIES

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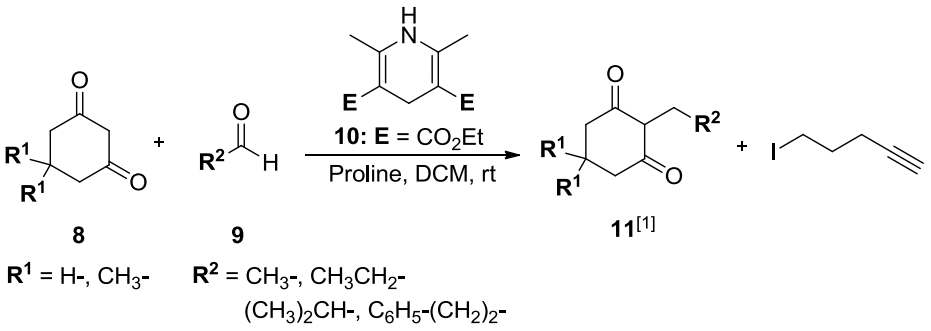
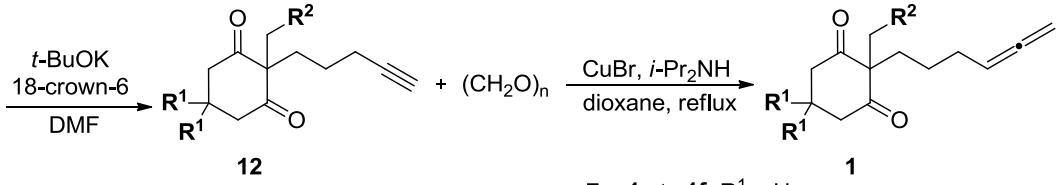
1. GENERAL INFORMATION

All solvents were dried before use following the standard procedures. Unless otherwise indicated, all starting materials purchased from commercial suppliers were used without further purification. The ^{1}H and ^{13}C NMR spectra were recorded on Bruker AV-400 MHz in the indicated solvents. Chemical shifts are reported in δ (ppm) referenced to an internal TMS standard for ^{1}H NMR and $CDCl_3$ (δ = 77.10 ppm) for ^{13}C NMR. Coupling constants (J) are quoted in Hz. Optical rotations were measured on a JASCO P-1030 polarimeter. IR spectra were recorded on Nicolet iN 10 MX. ESI mass spectra were recorded on Agilent1200/G6100A, Microwave heating was performed on a Milestone MicroSYNTH.

2. SUBSTRATE PREPARATION

2.1 General Procedures for the Preparation of 1a-1k （except 1e，1j）[1]





For **1a** to **1f**, R^1 = H-;

1a: R^2 = H- **1b**: R^2 = CH_3-

1c: R^2 = CH_3CH_2- **1d**: R^2 = $(CH_3)_2CH$-

1f: R^2 = C_6H_5-$(CH_2)_2$-

For **1g**–**1k**, R^1 = CH_3-;

1g: R^2 = CH_3- **1h**: R^2 = CH_3CH_2-

1i: R^2 = $(CH_3)_2CH$- **1k**: R^2 = C_6H_5-$(CH_2)_2$-

To a well-stirred solution of cyclohexane-1,3-diones **8** (10 mmol), Hantzsch ester **10 (**10 mmol) and the catalyst proline (20 mol%) in DCM (50 mL) was added

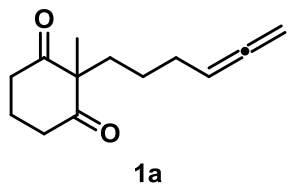
[1] 2-methylcyclohexane-1,3-dione (**11a**, CAS: 1193-55-1) was purchased from Energy Chemical (China)

aldehyde **9 (**20 mmol) under argon atmosphere at room temperature. The resulting solution was stirred for 12–20 hours. Then the reaction mixture was diluted with water (100 mL) and extracted with DCM (50 mL × 3). The combined organic phases were washed with brine (50 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was used in the next step without any further purification.

To a well-stirred solution of the previous residue, 18-crown-6 (10 mmol) in DMF (50 mL) was added *t*-BuOK (10 mmol) in several portions under argon atmosphere at 0℃ and allowed to stir for 30 minutes, then 5-iodine-1-pentyne (10 mmol) was added slowly in 10 min. The resulting solution was warmed to room temperature (80 ℃ for **11g–11k**) and allowed to stir for 20 hours. The reaction mixture was quenched with water (150 mL) and extracted with diethyl ether (50 mL × 3). The combined organic phases were washed with brine (50 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to afford the crude compound **12**. The crude compound **12** was used in the next step without any further purification.

To a well-stirred solution of the previous crude compound **12**, paraformaldehyde (15 mmol) and CuBr (1 mmol) in dioxane (25 mL) was added *i*-Pr_2NH (20 mmol) under argon atmosphere at room temperature. The reaction mixture was refluxed at 110℃ for 2.0 h. The resulting mixture was cooled to rt, quenched with saturated aqueous NaCl (10 mL), then extracted with ethyl acetate (10 mL × 3). The combined organic phases were dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by silica gel (300–400 mesh) column chromatography to afford the desired product **1a-1k (**except **1e, 1j)**.

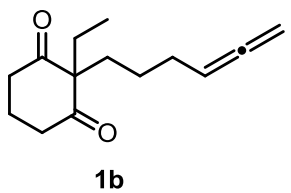
2-(Hexa-4,5-dien-1-yl)-2-methylcyclohexane-1,3-dione (1a)



1a

Pale yellow oil. 597.4 mg, 29% yield; ^{1}H NMR (400 MHz, CD_3OD) δ (ppm) 5.10−5.02 (m, 1H), 4.86−4.63 (m, 2H), 2.81−2.72 (m, 2H), 2.64−2.56 (m, 2H), 2.04−1.93 (m, 3H), 1.87−1.79 (m, 3H), 1.30−1.19 (m, 2H), 1.18 (s, 3H); ^{13}C NMR (100 MHz, CD_3OD) δ (ppm) 212.39, 209.97, 89.94, 75.03, 66.76, 38.75, 37.94, 29.24, 25.24, 19.21, 18.80; IR (KBr) ν (cm^{-1}) 2933, 2294, 1725, 1694, 1458, 1374, 1317, 1269, 1171, 1132, 1103, 1025, 846, 557, 417; HRMS (EI) for $[C_{13}H_{18}O_2]^{\cdot+}$: calcd. 206.1301, found: 206.1299.

2-Ethyl-2-(hexa-4,5-dien-1-yl)cyclohexane-1,3-dione (1b)

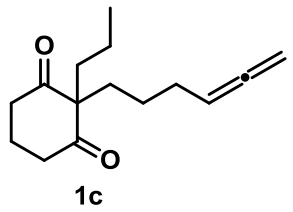


1b

Pale yellow oil. 462.2 mg, 21% yield; ^{1}H NMR (400 MHz, CD_3OD) δ (ppm) 5.01−4.96 (m, 1H), 4.63−4.59 (m, 2H), 2.60−2.55 (m, 4H), 1.96−1.87 (m, 4H), 1.80−1.71 (m, 4H), 1.23−1.14 (m, 2H), 0.75-0.70 (m, 3H); ^{13}C NMR (100 MHz, CD_3OD) δ (ppm) 211.19, 208.53, 89.29, 75.04, 69.22, 39.54, 35.31, 29.57, 28.52, 24.65, 16.99, 9.60; IR (KBr) ν (cm^{-1}) 2959, 2931, 2863, 1955, 1722, 1694, 1455, 1366, 1268,

1171, 1021, 847, 721, 556, 417; HRMS (EI) for $[C_{14}H_{20}O_2]^{\cdot+}$: calcd. 220.1458, found: 220.1463.

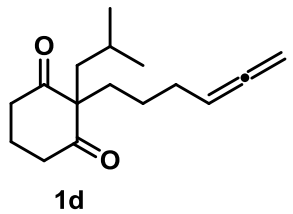
2-(Hexa-4,5-dien-1-yl)-2-propylcyclohexane-1,3-dione (1c)



1c

Pale yellow oil. 220.1 mg, 9.4% yield; ^{1}H NMR (400 MHz, CD_3OD) δ (ppm) 5.07−5.02 (m, 1H), 4.67−4.62 (m, 2H), 2.65−2.61 (m, 4H), 1.96−1.89 (m, 4H), 1.77−1.67 (m, 4H), 1.23−1.12 (m, 2H), 1.11−1.06 (m, 2H), 0.87−0.85 (m, 3H); ^{13}C NMR (100 MHz, CD_3OD) δ (ppm) 212.95, 209.89, 89.98, 75.01, 70.02, 40.14, 39.54, 36.51, 29.52, 25.63, 19.38, 18.07, 14.86; IR (KBr) ν (cm^{-1}) 2960, 2932, 2873, 1955, 1723, 1693, 1458, 1317, 1258, 1211, 1031, 845, 727, 555, 418; HRMS (EI) for $[C_{15}H_{22}O_2]^{\cdot+}$: calcd. 234.1614, found: 234.1620.

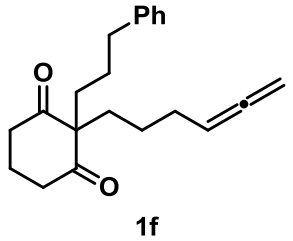
2-(Hexa-4,5-dien-1-yl)-2-isobutylcyclohexane-1,3-dione (1d)



1d

Pale yellow oil. 134 mg, 5.4% yield; ^{1}H NMR (400 MHz, CD_3OD) δ (ppm) 5.06−5.02 (m, 1H), 4.66−4.62 (m, 2H), 2.73−2.60 (m, 4H), 1.98−1.88 (m, 4H), 1.76−1.71 (m, 4H), 1.56−1.52 (m, 1H), 1.22−1.17 (m, 2H), 0.81−0.78 (m, 6H); ^{13}C NMR (100 MHz, CD_3OD) δ (ppm) 213.35, 209.96, 89.93, 74.96, 69.26, 46.21, 40.30, 38.15, 29.50, 26.31, 25.58, 24.48, 18.18; IR (KBr) ν (cm^{-1}) 2925, 2854, 1955, 1819, 1786, 1723, 1693, 1641, 1597, 1467, 1369, 1256, 1107, 1032, 846, 555, 411; HRMS (EI) for $[C_{16}H_{24}O_2]^{\cdot+}$: calcd. 248.1771, found: 248.1776.

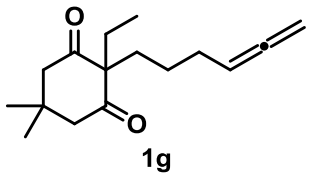
2-(Hexa-4,5-dien-1-yl)-2-(3-phenylpropyl)cyclohexane-1,3-dione (1f)



1f

Pale yellow oil. 459.1 mg, 14.8% yield; ^{1}H NMR (400 MHz, CD_3OD) δ (ppm) 5.62−5.52 (m, 1H), 5.08−4.98 (m, 3H), 4.66−4.62 (m, 2H), 2.69−2.55 (m, 4H), 1.95−1.90 (m, 2H), 1.81−1.76 (m, 2H), 1.24−1.16 (m, 2H); ^{13}C NMR (100 MHz, CD_3OD) δ (ppm) 212.85, 209.95, 143.00, 129.37, 129.34, 126.87, 89.95, 74.97, 70.05, 40.00, 37.04, 36.41, 36.35, 29.46, 27.94, 25.55, 18.09; IR (KBr) ν (cm^{-1}) 3285, 2957, 2872, 2112, 1955, 1725, 1691, 1459, 1332, 1250, 1203, 1147, 1096, 1052, 964, 932, 634, 590, 526, 435; HRMS (EI) for $[C_{21}H_{26}O_2]^{\cdot+}$: calcd. 310.1927, found: 310.1933.

2-Ethyl-2-(hexa-4,5-dien-1-yl)-5,5-dimethylcyclohexane-1,3-dione (1g)

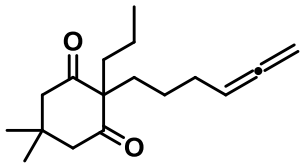


1g

Pale yellow oil. 119.1 mg, 4.8% yield; ^{1}H NMR (400 MHz, CD_3OD) δ (ppm) 5.09−5.05 (m, 1H), 4.66−4.62 (m, 2H), 2.67−2.56 (m, 4H), 1.97−1.92 (m, 2H), 1.83−1.72 (m, 4H), 1.26−1.19 (m, 2H), 1.19−0.96 (m, 6H), 0.78−0.75 (m, 3H);

^{13}C NMR (100 MHz, CD_3OD) δ (ppm) 211.72, 209.96, 90.13, 74.93, 70.18, 52.15, 34.24, 31.46, 29.53, 28.87, 28.60, 25.21, 9.42; IR (KBr) ν (cm^{-1}) 3026, 2933, 2857, 1955, 1722, 1693, 1496, 1454, 1264, 1208, 1163, 1083, 1030, 847, 750, 700, 555, 457; HRMS (EI) for $[C_{16}H_{24}O_2]^{\bullet+}$: calcd. 248.1771, found: 248.1776.

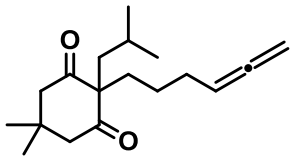
2-(Hexa-4,5-dien-1-yl)-5,5-dimethyl-2-propylcyclohexane-1,3-dione (1h)



1h

Pale yellow oil. 427.4 mg, 16.3% yield; ^{1}H NMR (400 MHz, CD_3OD) δ (ppm) 5.11−5.03 (m, 1H), 4.66−4.62 (m, 2H), 2.67−2.56 (m, 4H), 1.99−1.91 (m, 2H), 1.78−1.67 (m, 4H), 1.27−1.19 (m, 2H), 1.15−1.07 (m, 2H), 0.98 (s, 3H), 0.96 (s, 3H), 0.90-0.86 (m, 3H); ^{13}C NMR (100 MHz, CD_3OD) δ (ppm) 211.81, 209.98, 90.12, 74.91, 69.98, 52.16, 38.17, 34.83, 31.48, 29.51, 28.64, 25.25, 18.91, 14.77; IR (KBr) ν (cm^{-1}) 2927, 2373, 2320, 1955, 1890, 1772, 1695, 1636, 1457, 1437, 1418, 1373, 1338, 1251, 1020, 843, 457, 419; HRMS (EI) for $[C_{17}H_{26}O_2]^{\bullet+}$: calcd. 262.1927, found: 262.1933.

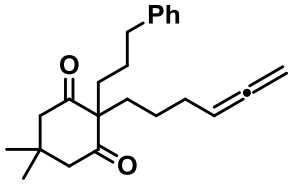
2-(Hexa-4,5-dien-1-yl)-2-isobutyl-5,5-dimethylcyclohexane-1,3-dione (1i)



1i

Pale yellow oil. 250.8 mg, 12.7% yield; ^{1}H NMR (400 MHz, CD_3OD) δ (ppm) 5.09−5.05 (m, 1H), 4.65−4.60 (m, 2H), 2.86−2.82 (m, 2H), 2.45−2.41 (m, 2H), 2.00−1.93 (m, 2H), 1.81−1.77 (m, 2H), 1.71−1.65 (m, 2H), 1.64−1.60 (m, 1H), 1.25−1.16 (m, 2H), 1.09 (s, 3H), 0.88−0.85 (m, 9H); ^{13}C NMR (100 MHz, CD_3OD) δ (ppm) 212.05, 210.02, 90.23, 74.75, 70.25, 52.38, 47.32, 33.06, 31.60, 29.85, 27.60, 25.94, 25.64, 24.76; IR (KBr) ν (cm^{-1}) 2957, 2313, 2210, 1965, 1844, 1792, 1655, 1556, 1497, 1472, 1436, 1387, 1338, 1252, 1020, 845, 557, 410; HRMS (EI) for $[C_{18}H_{28}O_2]^{\bullet+}$: calcd. 276.2084, found: 276.2089.

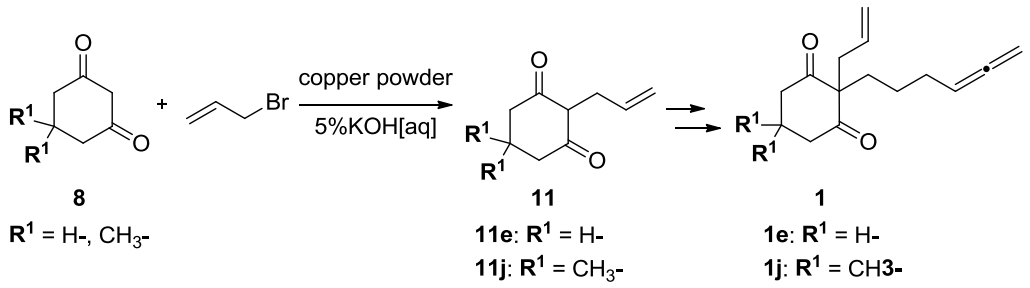
2-(Hexa-4,5-dien-1-yl)-5,5-dimethyl-2-(3-phenylpropyl)cyclohexane-1,3-dione (1k)



1k

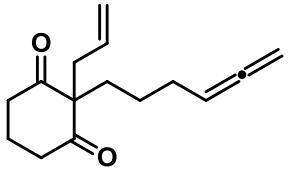
Pale yellow oil. 882.7 mg, 26.1% yield; ^{1}H NMR (400 MHz, CD_3OD) δ (ppm) 7.27−7.22 (m, 2H), 7.17−7.12 (m, 3H), 5.07−5.03 (m, 1H), 4.65−4.61 (m, 2H), 2.61−2.50 (m, 6H), 1.95−1.91 (m, 2H), 1.78−1.71 (m, 4H), 1.44−1.39 (m, 2H), 1.22−1.17 (m, 2H), 0.95−0.92 (m, 6H); ^{13}C NMR (100 MHz, CD_3OD) δ (ppm) 211.65, 209.95, 143.11, 129.40, 129.34, 126.87, 90.09, 74.96, 69.87, 52.08, 36.97, 35.08, 34.89, 31.45, 29.43, 28.76, 27.50, 25.15; IR (KBr) ν (cm^{-1}) 3282, 2956, 2873, 2312, 1955, 1725, 1711, 1439, 1372, 1253, 1213, 1167, 1076, 1022, 924, 832, 656, 591, 520, 425; HRMS (EI) for $[C_{23}H_{30}O_2]^{\bullet+}$: calcd. 338.2240, found: 338.2246.

2.2 Preparation of 1e, 1j



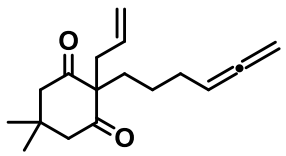
To a well-stirred solution of cyclohexane-1,3-diones **1** (10 mmol), copper powder (50 mol%) in 5% KOH (200 mL) was added allyl bromide (12 mmol), under argon atmosphere at room temperature. The resulting solution was stirred for 12 hours. Then the reaction mixture was extracted with ethyl acetate (200 mL × 3). The combined organic phases were washed with brine, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was used in the next step without any further purification. Then followed the general procedure for preparation of **1a-1k** to afford the desired product **1e, 1j.**

2-Allyl-2-(hexa-4,5-dien-1-yl)cyclohexane-1,3-dione (1e)


1e

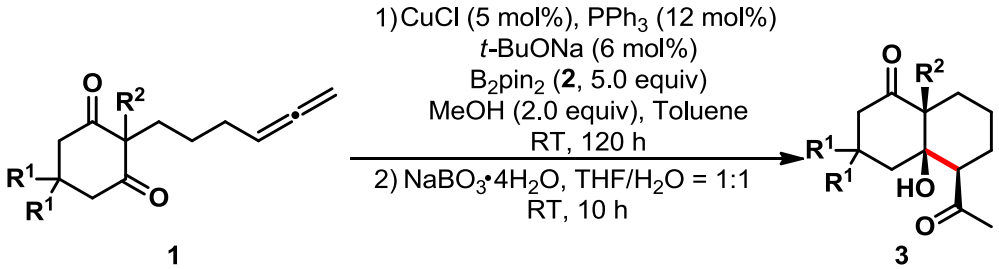
Pale yellow oil. 290.4 mg, 12.4% yield; ^{1}H NMR (400 MHz, CD_3OD) δ (ppm) 5.62−5.52 (m, 1H), 5.08−4.98 (m, 3H), 4.66−4.62 (m, 2H), 2.69−2.55 (m, 4H), 1.95−1.90 (m, 2H), 1.81−1.76 (m, 2H), 1.24−1.16 (m, 2H); ^{13}C NMR (100 MHz, CD_3OD) δ (ppm) 212.36, 209.92, 134.27, 119.22, 89.92, 75.02, 69.78, 41.30, 40.29, 36.49, 29.44, 25.51, 17.89; IR (KBr) ν (cm^{-1}) 2929,1955, 1723, 1694, 1639, 1439, 1322, 1258, 1210, 1102, 1033, 999, 922, 846, 556; HRMS (EI) for $[C_{15}H_{22}O_2]^{\bullet+}$: calcd. 234.1458, found: 234.1459.

2-Allyl-2-(hexa-4,5-dien-1-yl)-5,5-dimethylcyclohexane-1,3-dione (1j)


1j

Pale yellow oil. 260.2 mg, 10% yield; ^{1}H NMR (400 MHz, CD_3OD) δ (ppm) 5.61−5.56 (m, 1H), 5.09−4.99 (m, 3H), 4.66−4.62 (m, 2H), 2.67−2.56 (m, 4H), 2.51−2.49 (m, 2H), 1.98−1.92 (m, 2H), 1.80−1.75 (m, 2H), 1.29−1.19 (m, 2H), 0.99−0.94 (m, 6H); ^{13}C NMR (100 MHz, CD_3OD) δ (ppm) 211.16, 209.99, 134.31, 119.34, 90.05, 74.95, 52.32, 39.27, 35.11, 31.61, 29.38, 28.89, 28.63, 25.04; IR (KBr) ν (cm^{-1}) 2955, 2870, 2395,1955, 1725, 1427, 1371, 1329, 1251, 1217, 1178, 1078, 1000, 921, 845, 588, 437; HRMS (EI) for $[C_{17}H_{24}O_2]^{\bullet+}$: calcd. 260.1771, found: 260.1776.

3. SCOPE OF THE SUBSTRATES IN TABLE 2



For **1a** to **1f**, R^1 = H;

1a: R^2 = CH_3- **1b**: R^2 = CH_3CH_2- **1c**: R^2 = $CH_3CH_2CH_2$-

1d: R^2 = $(CH_3)_2CH$-CH_2- **1e**: R^2 = CH_2=CH-CH_2- **1f**: R^2 = C_6H_5-$(CH_2)_3$-

For **1g**–**1k**, R^1 = Me.

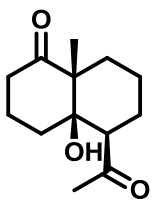
1g: R^2 = CH_3CH_2- **1h**: R^2 = $CH_3CH_2CH_2$- **1i**: R^2 = $(CH_3)_2CH$-CH_2-

1j: R^2 = CH_2=CH-CH_2- **1k**: R^2 = C_6H_5-$(CH_2)_3$-

GENERAL PROCEDURE:

A dried Schlenk flask was charged with CuCl (0.01mmol, 5 mol%), *t*-BuONa (0.012 mmol, 6 mol%), PPh_3 (0.024 mmol, 12 mol%), and freshly distilled dry toluene (1 mL) under argon atmosphere. The reaction mixture was stirred at room temperature for 0.5 h. Then bis(pinacolato)diboron **2** (1 mmol, 5.0 equiv) was added and the mixture was allowed to stir for another 0.5 h under argon atmosphere at room temperature. A solution of allenes **1** (0.2 mmol) in freshly distilled toluene (1 mL) and MeOH (16 μL, 2.0 equiv) was then added to the Schlenk flask. The mixture was allowed to stir for 120 h at room temperature under argon atmosphere. The resulting mixture was filtered and concentrated *in vacuo*. Then sodium perborate tetrahydrate (1 mmol, 5.0 equiv), THF (0.5mL) and H_2O (0.5 mL) was added and the mixture was allowed to stir for 3h at room temperature. Then quenched with saturated aqueous NaCl (2 mL), extracted with ethyl acetate (4 mL × 3). The combined organic phases were dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by silica gel (300-400 mesh) column chromatography to afford the desired product **3**.

(4a*R*,5*R*,8a*R*)-rel-5-Acetyl-4a-hydroxy-8a-methyloctahydronaphthalen-1(2*H*)-one (3a)

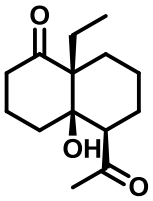


3a

Colorless oil, 43.1 mg, 96% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 4.28 (s, 1H), 2.64−2.55 (m, 2H), 2.28−2.14 (m, 5H), 1.94−1.86 (m, 2H), 1.78−1.70 (m, 1H), 1.67−1.64 (m, 1H), 1.59−1.48 (m, 4H), 1.24 (s, 1H), 1.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 215.67, 213.65, 75.16, 54.45, 52.69, 36.57, 32.01, 31.47, 29.16, 25.58, 22.35, 22.07, 19.87; IR (KBr) ν (cm^{-1}) 3467, 2958, 2878, 1695,

1653, 1636, 1558, 1540, 1507, 1458, 1395, 1337, 1229, 1172, 1018, 969, 823, 603, 543; HRMS (ESI) for $[C_{13}H_{19}O_3]^{\ominus}$: calcd. 223.1340, found: 223.1338.

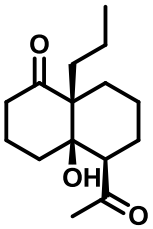
(4a*R*,5*R*,8a*R*)-rel-5-Acetyl-8a-ethyl-4a-hydroxyoctahydronaphthalen-1(2*H*)-one (3b)



3b

Colorless oil. 43.8 mg, 92% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 4.28 (s, 1H), 2.66−2.61 (m, 1H), 2.49−2.39 (m, 1H), 2.34−2.23 (m, 1H), 2.20−2.15 (m, 4H), 1.99−1.87 (m, 2H), 1.82−1.70 (m, 2H), 1.67−1.62 (m, 3H), 1.53−1.48 (m, 1H), 1.36−1.27 (m, 3H), 0.66 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 215.89, 212.85, 75.92, 58.24, 53.06, 37.65, 31.73, 31.57, 29.79, 26.78, 25.42, 25.22, 20.16, 7.43; IR (KBr) ν (cm^{-1}) 3473, 2926, 2853, 2360, 1692, 1463, 1335, 1299, 1228, 1188, 1089, 1068, 1002, 968, 906, 863, 822, 668, 578; HRMS (EI) for $[C_{14}H_{22}O_3]^{\cdot+}$: calcd. 238.1563, found: 238.1568.

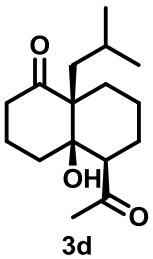
(4a*R*,5*R*,8a*R*)-rel-5-Acetyl-4a-hydroxy-8a-propyloctahydronaphthalen-1(2*H*)-one (3c)



3c

Colorless oil. 46.9 mg, 93% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 4.30 (s, 1H), 2.65−2.60 (m, 1H), 2.50−2.39 (m, 1H), 2.36−2.22 (m, 2H), 2.20 (s, 3H), 2.19−2.14 (m, 1H), 1.95−1.88 (m, 1H), 1.87−1.80 (m, 1H), 1.78−1.69 (m, 2H), 1.66−1.61 (m, 4H), 1.54−1.49 (m, 1H), 1.41−1.32 (m, 1H), 1.29−1.18 (m, 2H), 0.87 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 215.89, 212.94, 75.92, 58.09, 52.96, 37.70, 36.52, 31.74, 31.57, 25.95, 25.38, 21.98, 20.21, 16.35, 14.87; IR (KBr) ν (cm^{-1}) 3465, 2925, 2851, 2360, 1692, 1463, 1387, 1335, 1229, 1210, 1188,1171, 1142, 1018, 968, 823, 688, 543; HRMS (ESI) for $[C_{15}H_{24}O_3Na]^{\oplus}$: calcd. 275.1618, found: 275.1620.

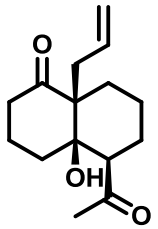
(4a*R*,5*R*,8a*S*)-rel-5-Acetyl-4a-hydroxy-8a-isobutyloctahydronaphthalen-1(2*H*)-one (3d)



3d

Colorless oil. 51.6 mg, 97% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 4.30 (s, 1H), 2.67−2.61 (m, 2H), 2.30−2.18 (m, 6H), 1.93−1.70 (m, 4H), 1.64−1.50 (m, 6H), 1.46−1.37 (m, 1H), 0.89 (d, J = 6.8 Hz, 3H), 0.77 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 215.85, 214.08, 76.14, 57.96, 52.78, 42.60, 37.84, 31.65, 31.55, 26.17, 25.78, 25.28, 23.57, 21.81, 20.37; IR (KBr) ν (cm^{-1}) 3469, 2955, 270, 1722, 1693, 1572, 1564, 1536, 1461, 1365, 1335, 1188, 1095, 1004, 973, 793, 601; HRMS (EI) for $[C_{16}H_{26}O_3]^{\cdot+}$: calcd. 266.1876, found: 266.1878.

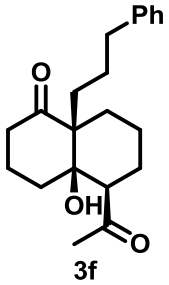
(4a*R*,5*R*,8a*S*)-rel-5-Acetyl-8a-allyl-4a-hydroxyoctahydronaphthalen-1(2*H*)-one (3e)



3e

Colorless oil. 51.3 mg, 94% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 5.53−5.44 (m, 1H), 5.05−4.99 (m, 2H), 4.34 (s, 1H), 2.67−2.61 (m, 2H), 2.51−2.42 (m, 2H), 2.32−2.24 (m, 2H), 2.20 (br, s, 3H), 2.13−2.09 (m, 1H), 1.96−1.89 (m, 1H), 1.78−1.71 (m, 1H), 1.71−1.61 (m, 3H), 1.59−1.50 (m, 2H), 1.46−1.38 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 215.71, 211.85, 132.74, 118.21, 75.66, 58.01, 52.78, 38.93, 37.83, 31.52, 26.43, 25.44, 21.88, 20.16; IR (KBr) ν (cm^{-1}) 3204, 3075, 2925, 2872, 2377, 1690, 1639, 1460, 1335, 1314, 1206, 1187, 1169, 1095, 916, 815, 766, 652, 602; HRMS (ESI) for $[C_{15}H_{22}O_3Na]^{\oplus}$: calcd. 273.1461, found: 273.1463.

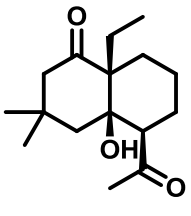
(4a*R*,5*R*,8a*S*)-rel-5-Acetyl-4a-hydroxy-8a-(3-phenylpropyl)octahydro-naphthalen-1(2*H*)-one (3f)



3f

Colorless oil. 43.1 mg, 96% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.27−7.23 (m, 2H), 7.18−7.10 (m, 3H), 4.30 (s, 1H), 2.67−2.58 (m, 2H), 2.53−2.45 (m, 1H), 2.26−2.13 (m, 7H), 1.91−1.68 (m, 4H), 1.66−1.58 (m, 4H), 1.56−1.46 (m, 2H), 1.41−1.30 (m, 1H), 1.11−1.05 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 215.81, 212.77, 141.94, 128.48, 128.38, 125.91, 76.78, 75.89, 57.95, 52.93, 37.51, 36.22, 33.35, 31.69, 31.53, 25.89, 25.34, 24.77, 21.93, 20.11; IR (KBr) ν (cm^{-1}) 3464, 3060, 2953, 2359, 1693, 1454, 1430, 1337, 1189, 1104, 1088, 906, 812, 749, 700, 603, 543, 492; HRMS (EI) for $[C_{21}H_{28}O_3]^{\bullet+}$: calcd. 328.2033, found: 328.2034.

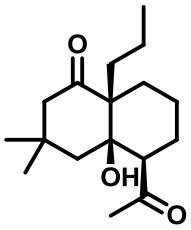
(4a*R*,5*R*,8a*R*)-rel-5-Acetyl-8a-ethyl-4a-hydroxy-3,3-dimethyloctahydro-naphthalen-1(2*H*)-one (3g)



3g

Colorless oil. 47.4 mg, 89% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 4.65 (s, 1H), 2.73−2.70 (m, 1H), 2.46−2.42 (m, 1H), 2.29−2.25 (m, 1H), 2.18 (br, s, 3H), 2.06−2.02 (m, 1H), 2.01−1.91 (m, 1H), 1.81−1.63 (m, 6H), 1.32−1.25 (m, 2H), 1.09 (s, 3H), 1.03 (s, 3H), 0.67 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 215.77, 213.41, 109.90, 75.59, 56.63, 55.44, 50.72, 45.54, 34.77, 31.29, 30.05, 27.89, 25.66, 22.39, 7.34; IR (KBr) ν (cm^{-1}) 3566, 2924, 2853, 2349, 1991, 1749, 1698, 1615, 1464, 1387, 1337, 1296, 1179, 1018, 945, 777, 663, 592; HRMS (EI) for $[C_{16}H_{26}O_3]^{\bullet+}$: calcd. 266.1876, found: 266.1878.

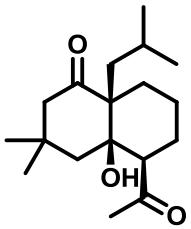
(4a*R*,5*R*,8a*R*)-rel-5-Acetyl-4a-hydroxy-3,3-dimethyl-8a-propyloctahydro-naphthalen-1(2*H*)-one (3h)



3h

Colorless oil. 50.4 mg, 90% yield; ^{1}H NMR (400 MHz, CD_3OD) δ (ppm) 2.75−2.67 (m, 1H), 2.52−2.44 (m, 1H), 2.27−2.11 (m, 5H), 2.00−1.92 (m, 1H),1.91−1.79 (m, 1H), 1.78−1.56 (m, 5H), 1.37−1.15 (m, 3H), 1.09 (s, 3H), 1.05 (s, 3H), 0.95−0.86 (m, 3H), 0.85−0.71 (m, 1H); ^{13}C NMR (100 MHz, CD_3OD) δ (ppm) 216.92, 215.46, 76.88, 57.60, 51.96, 46.30, 39.22, 35.18, 32.51, 30.31, 30.18, 27.92, 26.65, 23.51, 17.43, 15.14 ; IR (KBr) ν (cm^{-1}) 3466, 2957, 2870, 2369, 1868, 1699, 1578, 1506, 1489, 1471, 1419, 1397, 1337, 1292, 1180, 1074, 1021, 892, 813, 776, 592; HRMS (EI) for $[C_{17}H_{28}O_3]^{\cdot+}$: calcd. 280.2033, found: 280.2031.

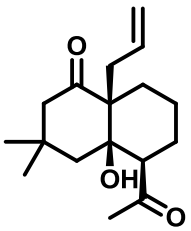
(4a*R*,5*R*,8a*S*)-rel-5-Acetyl-4a-hydroxy-8a-isobutyl-3,3-dimethyloctahydro-naphthalen-1(2*H*)-one (3i)



3i

Colorless oil. 48.8 mg, 83% yield; ^{1}H NMR (400 MHz, CD_3OD) δ (ppm) 2.76−2.67 (m, 2H), 2.23−2.14 (m, 5H), 2.04−1.96 (m, 1H), 1.91−1.75 (m, 2H), 1.74−1.60 (m, 4H), 1.55−1.29 (m, 3H), 1.10 (s, 3H), 1.05 (s, 3H), 0.92 (d, J = 6.4 Hz, 3H), 0.80 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, CD_3OD) δ (ppm) 216.84, 216.69, 77.02, 57.38, 52.16, 46.22, 44.79, 35.32, 32.55, 30.52, 30.08, 28.20, 26.53, 26.03, 24.93, 23.40 ; IR (KBr) ν (cm^{-1}) 3466, 2957, 2930, 2871, 2369, 2322, 1868, 1699, 1569, 1471, 1397, 1337, 1292, 1220, 1180, 997, 892, 776, 592; HRMS (EI) for $[C_{18}H_{30}O_3]^{\cdot+}$: calcd. 294.2189, found: 294.2191.

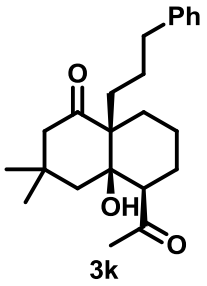
(4a*R*,5*R*,8a*S*)-rel-5-Acetyl-8a-Allyl-4a-Hydroxy-3,3-Dimethyloctahydro-naphthalen-1(2*H*)-one (3j)



3j

Colorless oil. 51.2 mg, 92% yield; ^{1}H NMR (400 MHz, CD_3OD) δ (ppm) 5.56−5.43 (m, 1H), 5.12−4.97 (m, 2H), 2.79−2.64 (m, 2H), 2.60−2.51 (m, 1H), 2.47−2.36 (m, 1H), 2.27−2.17 (m, 4H), 2.15−2.06 (m, 1H), 2.03−1.96 (m, 1H), 1.75−1.66 (m, 3H), 1.65−1.54 (m, 2H), 1.42−1.22 (m, 1H), 1.11 (s, 3H), 1.06 (s, 3H); ^{13}C NMR (100 MHz, CD_3OD) δ (ppm) 216.78, 214.40, 134.16, 118.65, 76.64, 57.91, 57.48 52.19, 46.34, 41.48, 35.15, 32.52, 30.41, 28.47, 26.70, 23.41; IR (KBr) ν (cm^{-1}) 3467, 3076, 2923, 2850, 2349, 1694, 1633, 1462, 1397, 1335, 1298, 1179, 1023, 997, 917, 811, 776, 591, 562; HRMS (EI) for $[C_{17}H_{26}O_3]^{\cdot+}$: calcd. 278.1876, found: 278.1878.

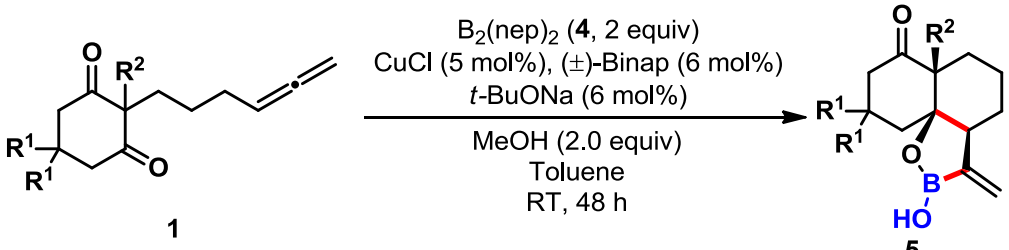
(4a*R*,5*R*,8a*S*)-rel-5-Acetyl-4a-Hydroxy-3,3-Dimethyl-8a-(3-Phenylpropyl)octa-hydronaphthalen-1(2*H*)-one (3k)



3k

White solid. 65.5 mg, 92% yield; Mp 120–124 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.30−7.22 (m, 2H), 7.20−7.08 (m, 3H), 4.64 (s, 1H), 2.75−2.62 (m, 2H), 2.50−2.38 (m, 1H), 2.20−2.08 (m, 5H), 2.07−1.84 (m, 2H), 1.83−1.71 (m, 2H), 1.69−1.57 (m, 6H),1.40−1.28 (m, 1H), 1.07−0.97 (m, 1H), 0.96 (s, 3H), 0.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 215.91, 213.64, 141.86, 128.70, 128.39, 125.96, 75.72, 56.54, 55.46, 50.64, 45.57, 36.00, 34.75, 33.98, 31.26, 30.28, 26.58, 25.77, 24.87, 22.52 ; IR (KBr) ν (cm^{-1}) 3467, 2922, 2850, 2360, 2341, 1712, 1690, 1644, 1552, 1462, 1424, 1370, 1249, 1156, 1083, 948, 748, 699, 668, 586; HRMS (EI) for $[C_{23}H_{32}O_3]^{\cdot+}$: calcd. 356.2346, found: 356.2343.

4. Scope Of The Substrates In Table 3



1 5

For **1a** to **1f**, R^1 = H;

1a: R^2 = CH_3- **1b**: R^2 = CH_3CH_2- **1c**: R^2 = $CH_3CH_2CH_2$-

1d: R^2 = $(CH_3)_2CH$-CH_2- **1e**: R^2 = CH_2=CH-CH_2- **1f**: R^2 = C_6H_5-$(CH_2)_3$-

For **1g**–**1k**, R^1 = Me.

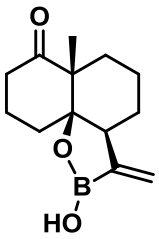
1g: R^2 = CH_3CH_2- **1h**: R^2 = $CH_3CH_2CH_2$- **1i**: R^2 = $(CH_3)_2CH$-CH_2-

1j: R^2 = CH_2=CH-CH_2- **1k**: R^2 = C_6H_5-$(CH_2)_3$-

General Procedure:

A dried Schlenk flask was charged with CuCl (0.01 mmol, 5 mol%), *t*-BuONa (0.012 mmol, 6 mol%), (±)-BINAP (0.012 mmol, 6 mol%), and freshly distilled dry toluene (1 mL) under argon atmosphere. The reaction mixture was stirred at room temperature for 0.5 h. Then bis(neopentyl glycolato)diboron **4** (0.4 mmol, 2.0 equiv) was added and the mixture was allowed to stir for another 0.5 h under argon atmosphere at room temperature. A solution of allenes **1** (0.2 mmol) in freshly distilled toluene (1 mL) and MeOH (16 μL, 2.0 equiv) was then added to the Schlenk flask. The mixture was allowed to stir for 48 h at room temperature under argon atmosphere. The resulting mixture was quenched with H_2O (2 mL) then extracted with ethyl acetate (4 mL × 3). The combined organic phases were dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by silica gel (300−400 mesh) column chromatography to afford the desired product **5**.

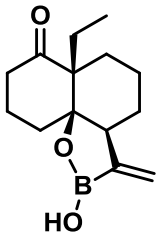
(3a*S*,6a*R*,10a*R*)-rel-2-Hydroxy-6a-methyl-3-methyleneoctahydro-2H-naphtho[1,8a-d][1,2]oxaborol-7(8*H*)-one (5a)



5a

Colorless oil. 46.1 mg, 99% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 5.64 (br, s, 1H), 5.48 (br, s, 1H), 4.91 (br, s, 1H), 2.65−2.34 (m, 3H), 2.11−1.99 (m, 1H), 1.98−1.84 (m, 3H), 1.79−1.58 (m, 3H), 1.52−1.38 (m, 2H), 1.31−1.16 (m, 2H), 1.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 214.31, 120.23, 86.56, 53.68, 49.60, 37.14, 34.99, 30.39, 26.66, 21.43, 19.64, 17.97; IR (KBr) ν (cm^{-1}) 3358, 2921, 2851, 1841, 1659, 1632, 1582, 1470, 1376, 1011, 940, 877, 646, 582; HRMS (EI) for $[C_{13}H_{19}{}^{10}BO_3]^{\cdot+}$: calcd. 233.1464, found: 233.1467.

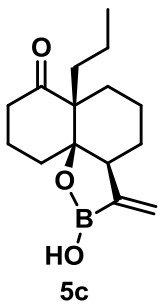
(3a*S*,6a*R*,10a*R*)-rel-6a-Ethyl-2-hydroxy-3-methyleneoctahydro-2H-naphtho[1,8a-d][1,2]oxaborol-7(8*H*)-one (5b)



5b

Colorless oil. 47.5 mg, 96% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 5.62 (br, s, 1H), 5.51 (br, s, 1H), 4.38 (br, s, 1H), 2.56−2.51 (m, 1H), 2.43−2.39 (m, 2H), 2.38−2.13 (m, 2H), 1.99−1.89 (m, 1H), 1.88−1.80 (m, 1H), 1.78−1.70 (m, 1H), 1.69−1.58 (m, 2H), 1.51−1.35 (m, 4H), 1.00−0.91 (m, 1H), 0.67 (t, J = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 212.28, 121.37, 86.82, 56.91, 49.07, 38.13, 34.61, 28.81, 27.48, 24.43, 19.49, 18.73, 7.81; IR (KBr) ν (cm^{-1}) 3361, 2935, 2877, 2360, 2341, 1693, 1461, 1317, 1291, 1228, 1144, 1018, 943, 824, 668, 544; HRMS (EI) for $[C_{14}H_{21}{}^{10}BO_3]^{\cdot+}$: calcd. 247.1620, found: 247.1623.

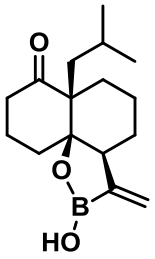
(3a*S*,6a*R*,10a*R*)-rel-2-Hydroxy-3-methylene-6a-propyloctahydro-2H-naphtho[1,8a-d][1,2]oxaborol-7(8*H*)-one (5c)



5c

Colorless oil. 49.6 mg, 95% yield; ^{1}H NMR (400 MHz, CD_3OD) δ (ppm) 5.54 (br, s, 1H), 5.46 (br, s, 1H), 2.59−2.44 (m, 2H), 2.32−2.12 (m, 2H), 1.98−1.82 (m, 2H), 1.74−1.59 (m, 3H), 1.52−1.29 (m, 4H), 1.27−1.13 (m, 1H), 1.06−0.93 (m, 1H), 0.92−0.88 (m, 3H), 0.87−0.79 (m, 2H); ^{13}C NMR (100 MHz, CD_3OD) δ (ppm) 214.65, 121.02, 87.60, 58.06, 56.49, 50.28, 39.08, 38.25, 35.57, 29.82, 26.38, 20.43, 17.72, 15.06; IR (KBr) ν (cm^{-1}) 3334, 2926, 2870, 2375, 1701, 1455, 1402, 1286, 1186, 1144, 1074, 994, 829, 744, 672, 543; HRMS (EI) for $[C_{15}H_{23}{}^{10}BO_3]^{\cdot+}$: calcd. 261.1777, found: 261.1778.

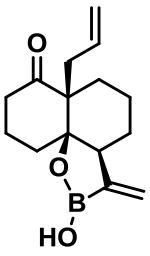
(3a*R*,6a*S*,10a*R*)-rel-2-Hydroxy-6a-isobutyl-3-methyleneoctahydro-2H-naphtho[1,8a-d][1,2]oxaborol-7(8*H*)-one (5d)



5d

Colorless oil. 50.1 mg, 91% yield; ^{1}H NMR (400 MHz, CD_3OD) δ (ppm) 5.54 (t, J = 2.4 Hz, 1H), 5.46 (br, s, 1H), 2.69−2.58 (m, 1H), 2.57−2.48 (m, 1H), 2.32−2.22 (m, 3H), 1.96−1.86 (m, 2H), 1.81−1.73 (m, 1H), 1.52−1.38 (m, 4H), 1.34−1.28 (m, 3H), 1.08−0.98 (m, 1H), 0.90 (d, J = 9.6 Hz, 3H), 0.82 (d, J = 9.6 Hz, 3H); ^{13}C NMR (100 MHz, CD_3OD) δ (ppm) 215.14, 121.18, 87.67, 58.17, 50.31, 44.87, 39.43, 35.61, 29.88, 26.75, 26.05, 24.73, 20.49, 19.96; IR (KBr) v (cm^{-1}) 3371, 2925, 2869, 2375, 1848, 1699, 1455, 1286, 1198, 1144, 1029, 928, 891, 774, 672, 599; HRMS (EI) for $[C_{16}H_{25}{}^{10}BO_3]^{\cdot+}$: calcd. 275.1933, found: 275.1935.

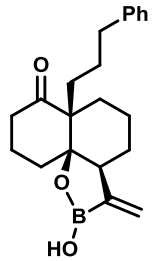
(3a*R*,6a*S*,10a*R*)-rel-6a-Allyl-2-hydroxy-3-methyleneoctahydro-2H-naphtho[1,8a-d][1,2]oxaborol-7(8*H*)-one (5e)



5e

White solid. 50.2 mg, 97% yield, Mp 97–103 ℃. ^{1}H NMR (400 MHz, CD_3OD) δ (ppm) 5.65−5.51 (m, 2H), 5.50−5.42 (m, 1H), 2.76−2.66 (m, 1H), 2.61−2.42 (m, 3H), 2.33−2.22 (m, 2H), 2.17−2.07 (m, 1H), 1.95−1.84 (m, 1H), 1.80−1.25 (m, 8H), 1.07−1.01 (m, 1H); ^{13}C NMR (100 MHz, CD_3OD) δ (ppm) 213.71, 134.80, 121.05, 117.94, 87.37, 58.14, 50.37, 40.49, 39.25, 35.69, 29.52, 26.96, 20.45, 19.66; IR (KBr) v (cm^{-1}) 3391, 2927, 2869, 2850, 2361, 2342, 1699, 1632, 1496, 1367, 1244, 1197, 1072, 998, 933, 882, 776, 673, 567; HRMS (EI) for $[C_{15}H_{21}{}^{10}BO_3]^{\cdot+}$: calcd. 259.1620, found: 259.1621.

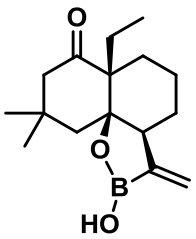
(3a*R*,6a*S*,10a*R*)-rel-2-Hydroxy-3-methylene-6a-(3-phenylpropyl)octahydro-2H-naphtho[1,8a-d][1,2]oxaborol-7(8*H*)-one (5f)



5f

Colorless oil. 63.4 mg, 94% yield; ^{1}H NMR (400 MHz, CD_3OD) δ (ppm) 7.29−7.21 (m, 2H), 7.19−7.10 (m, 3H), 5.52 (br, s, 1H), 5.43 (br, s, 1H), 2.64−2.48 (m, 3H), 2.38−2.26 (m, 1H), 2.24−2.08 (m, 3H), 1.99−1.87 (m, 1H), 1.86−1.71 (m, 2H), 1.69−1.57 (m, 2H), 1.56−1.44 (m, 2H), 1.42−1.28 (m, 2H), 1.19−1.08 (m, 1H), 1.01−0.86 (m, 2H); ^{13}C NMR (100 MHz, CD_3OD) δ (ppm) 214.75, 143.36, 129.49, 129.31, 126.84, 121.02, 87.62, 57.90, 50.31, 38.93, 37.10, 35.55, 34.89, 29.53, 26.45, 26.28, 20.39, 19.76; IR (KBr) v (cm^{-1}) 3392, 3060, 2930, 2870, 2360, 2341, 1701, 1602, 1495, 1343, 1291, 1198, 1029, 933, 881, 747, 668, 551, 454; HRMS (EI) for $[C_{21}H_{27}{}^{10}BO_3]^{\cdot+}$: calcd. 337.2090, found: 337.2093.

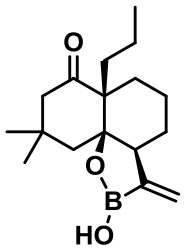
(3a*R*,6a*R*,10a*R*)-rel-6a-Ethyl-2-hydroxy-9,9-dimethyl-3-methyleneoctahydro-2H-naphtho[1,8a-d][1,2]oxaborol-7(8*H*)-one (5g)



5g

Colorless oil. 52.8 mg, 96% yield; ^{1}H NMR (400 MHz, CD_3OD) δ (ppm) 5.53 (t, J = 2.8 Hz, 1H), 5.38 (br, s, 1H), 2.63−2.55 (m, 1H), 2.48−2.27 (m, 2H), 2.12−2.05 (m, 1H), 1.87−1.67 (m, 4H), 1.56−1.28 (m, 5H), 1.12 (s, 3H), 1.01 (s, 3H), 0.73 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, CD_3OD) δ (ppm) 211.91, 127.41, 73.03, 69.58, 52.18, 35.95, 35.47, 31.48, 31.20, 28.63, 25.34, 21.95, 21.62, 9.50; IR (KBr) ν (cm^{-1}) 3353, 2936, 2878, 2361, 2344, 1701, 1401, 1317, 1229, 1172, 1144, 1090, 945, 828, 669, 544; HRMS (EI) for $[C_{16}H_{25}{}^{10}BO_3]^{\cdot+}$: calcd.275.1933, found: 275.1935.

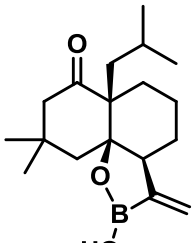
(3a*S*,6a*R*,10a*R*)-rel-2-Hydroxy-9,9-dimethyl-3-methylene-6a-propyloctahydro-2 H-naphtho[1,8a-d][1,2]oxaborol-7(8*H*)-one (5h)



5h

Colorless oil. 54.4 mg, 94% yield; ^{1}H NMR (400 MHz, CD_3OD) δ (ppm) 5.54 (t, J = 2.8 Hz, 1H), 5.43-5.34 (br, s, 1H), 2.64−2.54 (m, 1H), 2.45−2.28 (m, 2H), 2.12−2.02 (m, 1H), 1.86−1.65 (m, 4H), 1.64−1.50 (m, 2H), 1.49−1.31 (m, 4H), 1.15−1.08 (m, 4H), 1.01 (s, 3H), 0.88−0.81 (m, 3H); ^{13}C NMR (100 MHz, CD_3OD) δ (ppm) 211.89, 124.11, 73.03, 69.56, 52.15, 38.08, 36.05, 35.49, 31.50, 30.89, 28.77, 25.36, 21.62, 18.93, 14.78; IR (KBr) ν (cm^{-1}) 3334, 2930, 2871, 2855, 2376, 2349, 1701, 1457, 1401, 1287, 1189, 1039, 930, 892, 805, 745, 665, 564; HRMS (EI) for $[C_{17}H_{27}{}^{10}BO_3]^{\cdot+}$: calcd. 289.2090, found: 289.2094.

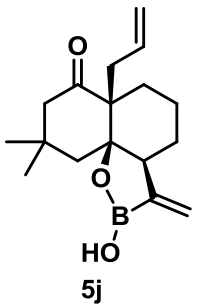
(3a*R*,6a*S*,10a*R*)-rel-2-Hydroxy-6a-isobutyl-9,9-dimethyl-3-methyleneoctahydro-2 H-naphtho[1,8a-d][1,2]oxaborol-7(8*H*)-one (5i)



5i

Colorless oil. 53.4 mg, 88% yield; ^{1}H NMR (400 MHz, CD_3OD) δ (ppm) 5.54 (t, J = 2.4 Hz, 1H), 5.46−5.35 (m, 1H), 2.76−2.67 (m, 1H), 2.65−2.55 (m, 1H), 2.18−2.08 (m, 1H), 1.85−1.74 (m, 3H), 1.70−1.51 (m, 6H), 1.47−1.40 (m, 2H), 1.14 (s, 3H), 0.98 (s, 3H), 0.95−0.84 (m, 3H), 0.83−0.78 (m, 3H); ^{13}C NMR (100 MHz, CD_3OD) δ (ppm) 210.73, 125.89, 71.57, 68.83, 68.09, 50.93, 45.45, 36.64, 32.62, 30.15, 28.48, 26.36, 24.53, 23.39, 20.17; IR (KBr) ν (cm^{-1}) 3357, 2927, 2870, 2852, 2350, 2307, 1990, 1784, 1700, 1456, 1401, 1240, 1187, 1230, 929, 892, 774, 734, 645, 598; HRMS (EI) for $[C_{18}H_{29}{}^{10}BO_3]^{\cdot+}$: calcd. 303.2246, found: 303.2251.

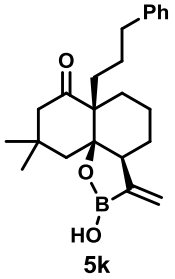
(3a*R*,6a*S*,10a*R*)-rel-6a-Allyl-2-hydroxy-9,9-dimethyl-3-methyleneoctahydro-2H-naphtho[1,8a-d][1,2]oxaborol-7(8*H*)-one (5j)



5j

Colorless oil. 52.8 mg, 92% yield; ^{1}H NMR (400 MHz, CD_3OD) δ (ppm) 5.78−5.64 (m, 1H), 5.61−5.55 (m, 1H), 5.46−5.38 (m, 1H), 4.98−4.87 (m, 2H), 2.64−2.57 (m, 1H), 2.49−2.42 (m, 2H), 2.36−2.29 (m, 1H), 2.23−2.15 (m, 2H), 1.99−1.88 (m, 1H), 1.81−1.70 (m, 2H), 1.60−1.34 (m, 4H), 1.12 (s, 3H), 1.04 (s, 3H); ^{13}C NMR (100 MHz, CD_3OD) δ (ppm) 216.18, 136.58, 118.12, 117.33, 88.88, 56.80, 53.22, 51.36, 37.09, 34.90, 32.00, 30.47, 30.09, 25.34, 17.90; IR (KBr) ν (cm^{-1}) 3371, 2925, 2862, 2382, 2350, 2017, 1869, 1844, 1771, 1647, 1540, 1436, 1396, 1286, 1086, 912, 800, 674, 663, 587; HRMS (EI) for $[C_{17}H_{25}{}^{10}BO_3]^{\cdot+}$: calcd. 287.1933, found: 287.1934.

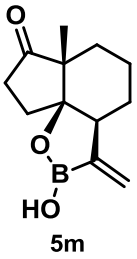
(3a*R*,6a*S*,10a*R*)-rel-2-Hydroxy-9,9-dimethyl-3-methylene-6a-(3-phenyl propyl)octahydro-2H-naphtho[1,8a-d][1,2]oxaborol-7(8*H*)-one (5k)



5k

White solid. 66.5 mg, 91% yield, Mp 106–111 ℃. ^{1}H NMR (400 MHz, CD_3OD) δ (ppm) 7.24−7.20 (m, 2H), 7.14−7.08 (m, 3H), 5.45−5.40 (m, 1H), 5.30−5.24 (m, 1H), 2.62−2.47 (m, 3H), 2.31−2.26 (m, 1H), 2.10−2.04 (m, 1H), 1.86−1.77 (m, 1H), 1.73−1.64 (m, 3H), 1.59−1.45 (m, 3H), 1.44−1.33 (m, 5H), 1.07 (s, 3H), 0.99 (s, 3H); ^{13}C NMR (100 MHz, CD_3OD) δ (ppm) 216.92, 143.36, 129.54, 129.27, 129.71, 118.18, 89.08, 56.55, 53.13, 51.26, 37.29, 34.68, 31.77, 30.75, 30.67, 29.52, 27.00, 25.81, 18.42; IR (KBr) ν (cm^{-1}) 3391, 3061, 3022, 2928, 2867, 2359, 2340, 1701, 1604, 1497, 1402, 1345, 1242, 1195, 1091, 935, 899, 882, 749, 667, 551, 435; HRMS (EI) for $[C_{23}H_{31}{}^{10}BO_3]^{\cdot+}$: calcd. 365.2403, found: 365.2401.

(3a*R*,6a*R*,9a*R*)-rel-2-hydroxy-6a-methyl-3-methyleneoctahydroindeno[4,3a-d][1,2]oxaborol-7(2*H*)-one (5m)

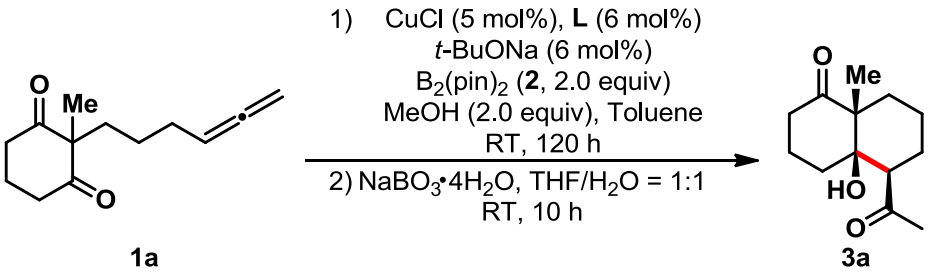


5m

Colorless oil. 41.6 mg, 95% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 5.71 (t, J = 2.4 Hz, 1H), 5.59−5.48 (m, 1H), 4.90 (br, s, 1H), 2.63−2.47 (m, 2H), 2.39−2.28 (m, 1H), 2.19−2.03 (m, 2H), 1.82−1.72 (m, 1H), 1.69−1.54 (m, 2H), 1.49−1.39 (m, 1H), 1.36−1.27 (m, 2H), 0.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 221.17, 120.69, 89.07, 53.52, 52.78, 48.82, 34.80, 31.59, 29.78, 25.88, 17.79, 14.21; IR (KBr) ν (cm^{-1}) 3361, 2932, 2857, 1847, 1664, 1637, 1593, 1477, 1382, 1009, 957, 867, 655, 573; HRMS (EI) for $[C_{12}H_{17}{}^{10}BO_3]^{\cdot+}$: calcd. 219.1307, found: 219.1311.

5 Initial Evaluation of Various Chiral Ligands

5.1 Evaluation of Various Chiral Ligands for Cu-catalyzed asymmetric cyclization of allene diketone 1a using $B_2(pin)_2$ (2) as boron source.



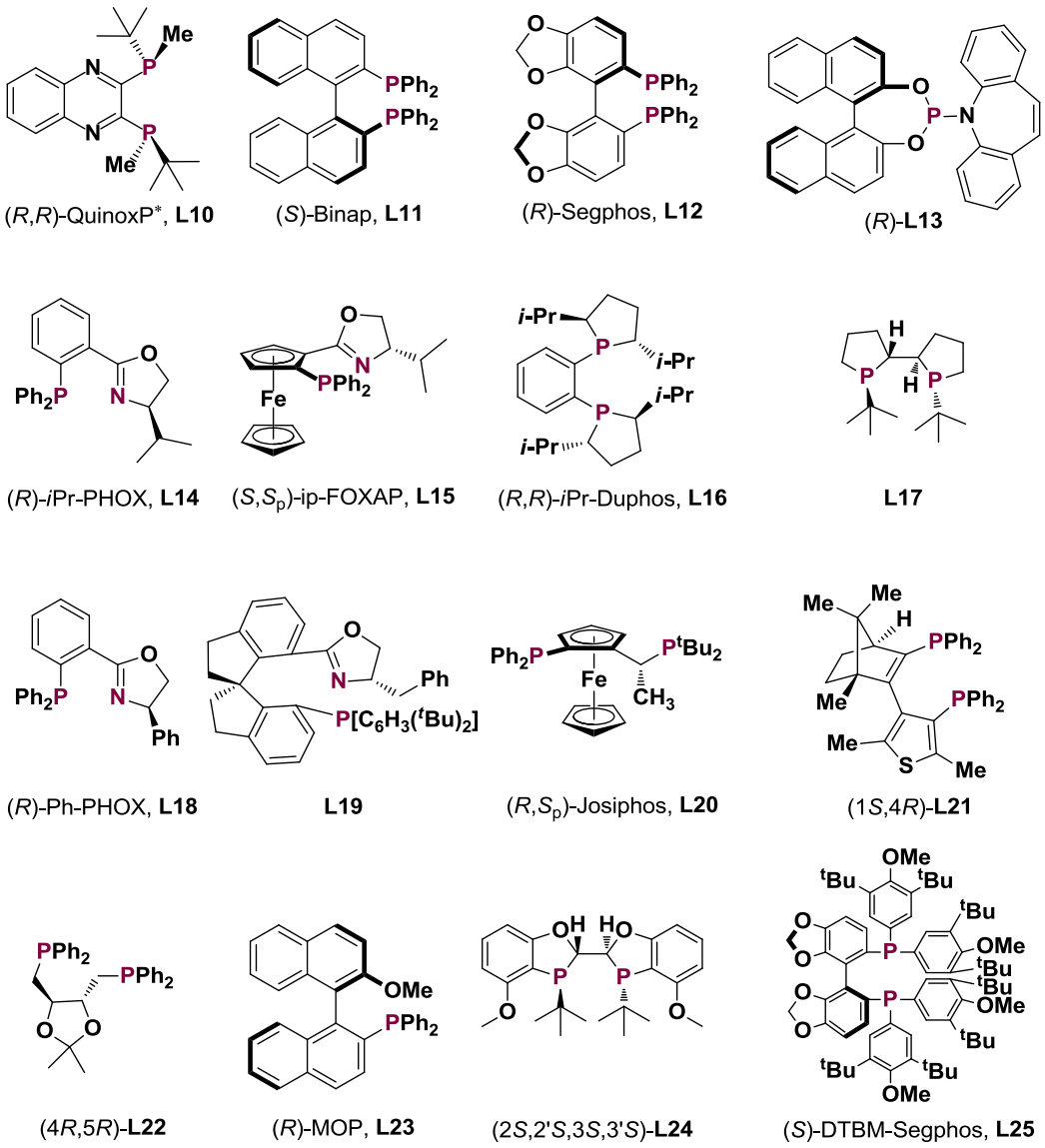
Entry	ligand	yield(%)[a]	d.r.[b]	ee (%)[c]
1	**L10**	77	>20:1	<10
2	**L11**	75	>20:1	33
3	**L12**	64	>20:1	<10
4 [d]	**L13**	45	>20:1	<10
5	**L14**	95	>20:1	<10
6	**L15**	60	>20:1	<10
7	**L16**	80	>20:1	<10
8	**L17**	98	>20:1	<10
9	**L18**	79	>20:1	<10
10	**L19**	93	>20:1	32
11	**L20**	76	>20:1	<10
12	**L21**	97	>20:1	<10
13	**L22**	68	>20:1	27
14[d]	**L23**	98	>20:1	<10
15	**L24**	80	>20:1	20
16	**L25**	85	>20:1	53

a:Yield of isolated and purified product **3a**.

b: Determined by ^{1}H NMR

c: Determined by HPLC analysis using a chiral stationary phase

d: 12% mmol Ligand was used



L10, **L18**, **L21, L22**: purchased from Sigma-Aldrich and used as received.

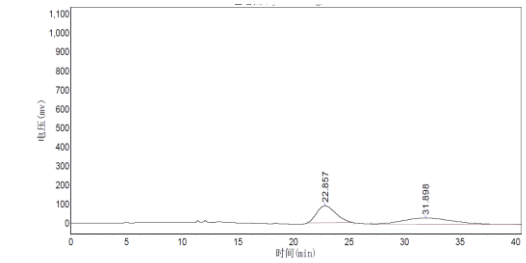
L12, L14, L16, L17, L19, L20, L23, L24: purchased from Strem Chemicals Inc. and used as received.

L11, **L15, L25**: purchased from TCI and used as received.

L13: made by ourselves according to literatures[2]

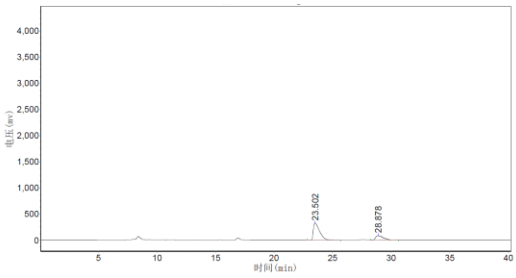
[2] M. A. Schafroth, D. Sarlah, S. Krautwald and E. M. Carreira, *J. Am. Chem. Soc.*, **2012**, *134*, 20276. (**L13**)

(–)-**3a** $[\alpha]_D^{24.2}$ –26.8 (*c* 0.63, $CHCl_3$) for 53% *ee*



分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		22.857	88754.039	10543974.000	50.4403
2		31.898	32844.742	10359897.000	49.5597
总计			121598.781	20903871.000	100.0000

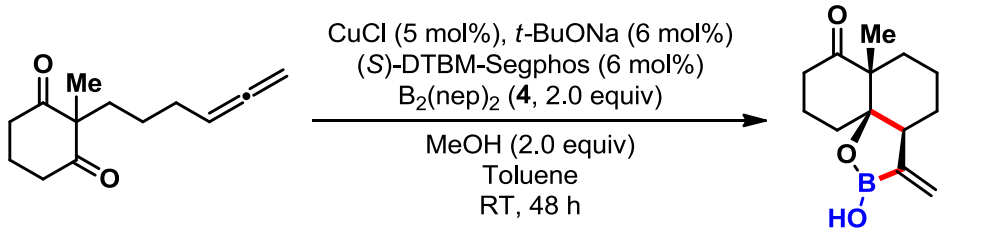


分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		23.502	325031.500	11960612.000	76.3280
2		28.878	82306.602	3709414.000	23.6720
总计			407338.102	15670026.000	100.0000

HPLC: Phenomenex Lux 5u Cellulose-2 (PC-2) Column in series with Chiracel OD-H Column (250 mm); detected at 214 nm; n-hexane / i-propanol = 99.5/0.5; flow = 0.5 ml/min; Retention time: 23.5 min (major), 28.9 min (minor).

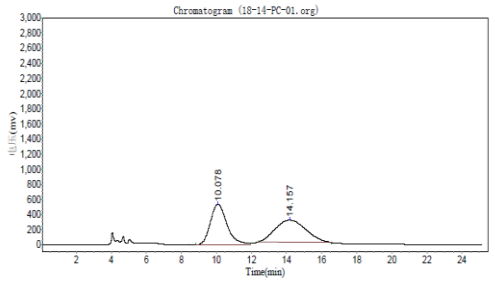
5.2 Chiral Ligands((*S*)-DTBM-Segphos) for Cu-catalyzed asymmetric cyclization of allene diketone 1a using $B_2(nep)_2$ (4) as boron source.



(–)-5a, d.r.>20:1
80% yield, 73% *ee*

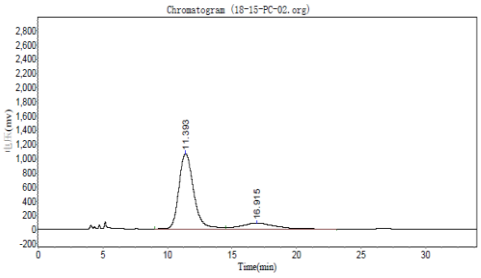
The procedure was followed the general procedure for scope of the substrates in table 2

(–)-**5a**: $[\alpha]_D^{24.2}$–56.1 (*c* 0.5, CH_3OH) for 73% *ee*



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.078	529856.000	34425292.000	49.1740
2		14.157	292056.500	35581860.000	50.8260
Total			821912.500	70007152.000	100.0000

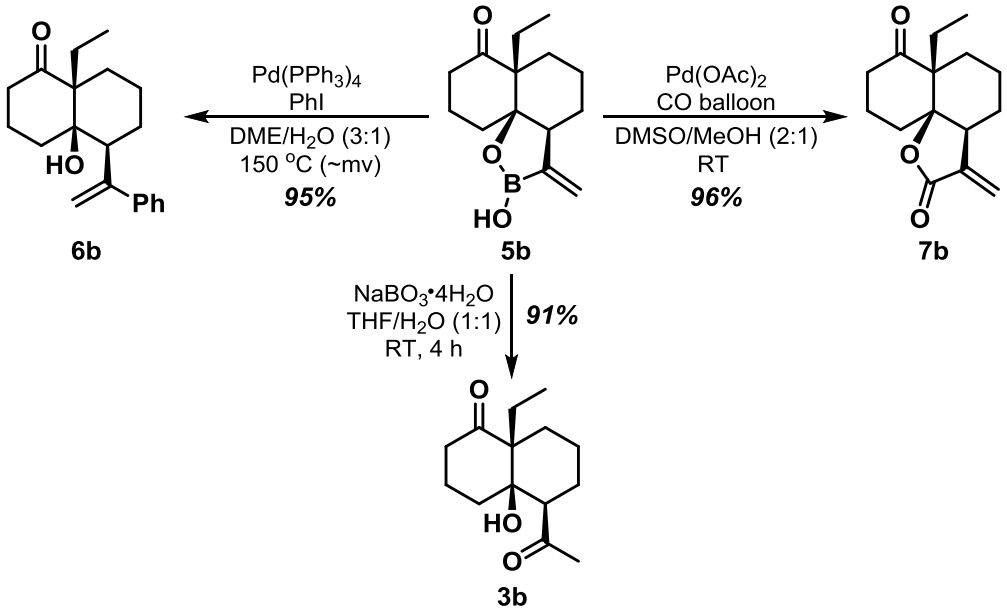


Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.393	1053768.750	82796288.000	86.1393
2		16.915	79082.336	13322804.000	13.8607
Total			1132851.086	96119092.000	100.0000

HPLC: Phenomenex Lux 5u Cellulose-2 (PC-2) Column in series with Chiracel OD-H Column (250 mm); detected at 214 nm; n-hexane / i-propanol = 99/1; flow = 0.7 ml/min; Retention time: 11.4 min (major), 16.9 min (minor).

6. TRANSFORMATIONS OF THE CYCLIZATION PRODUCTS 5b



(4a*R*,5*R*,8a*R*)-rel-8a-Ethyl-4a-hydroxy-5-(1-phenylvinyl)octahydronaphthalen-1(2*H*)-one (6b) [3]. Into a 5 mL microwave reactor containing DME/H_2O (2 mL, 3:1 v/v) were added **5b** (24.8 mg, 0.1 mmol), 3-methoxyphenyl iodide (24.5 mg, 0.12 mmol), K_2CO_3 (27.6 mg, 0.2 mmol) and [$Pd(PPh_3)_4$] (5.8 mg, 0.005 mmol). The mixture was de-gassed with Ar for 10 min. The reactor was then capped and placed in the microwave oven. The temperature was ramped to 150 ℃ over 15 min, and kept at 150 ℃ for 15 min. After the reaction mixture was cooled to 25 ℃, EtOAc/H_2O was added, and the organic layer was separated. The aqueous layer was extracted with EtOAc (2 mL × 3). The combined organic phases were washed with brine, and dried over anhydrous $MgSO_4$. The residue was purified by column chromatography resulting in **6b** as a colorless oil (28.3 mg, 95% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.35−7.17 (m, 5H), 5.28−5.23 (m, 2H), 2.62−2.52 (m, 1H), 2.33−2.15 (m, 2H), 2.12−2.03 (m, 1H), 2.01−1.87 (m, 3H), 1.75−1.66 (m, 2H), 1.65−1.55 (m, 3H), 1.35−1.23 (m, 3H), 1.02−0.89 (m, 1H), 0.63 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 213.33, 151.87, 144.75, 128.53, 127.40, 126.47, 115.87, 77.37, 58.88, 47.45, 37.41, 31.42, 28.02, 25.72, 22.57, 19.10, 14.19, 7.62; IR (KBr) ν (cm^{-1}) 3524, 2954, 2927, 2877, 2855, 1701, 1621, 1492, 1463, 1144, 1017, 977, 906, 823, 762, 717, 702, 552, 428; HRMS (TOF-EI) for $[C_{20}H_{26}O_2]^{\cdot+}$: calcd. 298.1933, found 298.1930.

(3a*R*,6a*R*,10a*R*)-rel-6a-Ethyl-3-methyleneoctahydro-2H-naphtho[8a,1-b]furan-2,7(8*H*)-dione (7b)[3]. A dried Schlenk flask was charged with **5b** (24.8 mg, 0.1 mmol), DMSO (2 mL). MeOH (1 mL) and $Pd(OAc)_2$ (22.5 mg, 0.1 mmol), then the reaction mixture was evacuated and filled with CO three times. The reaction mixture was stirred at 25 ℃ for 3 h until the brown catalyst turned to a black precipitate. The

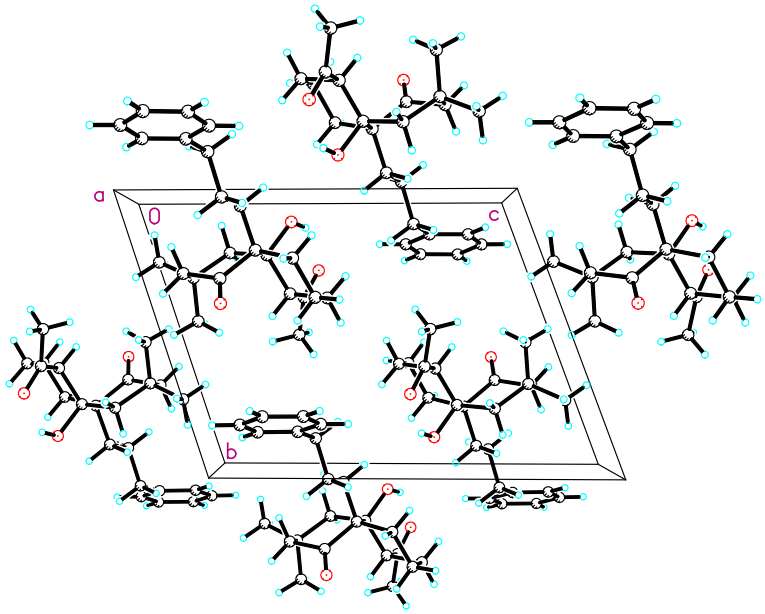
[3] Q. J. Zhou, K. Worm and R. E. Dolle, *J. Org. Chem*. **2004**, *69*, 5147-5149

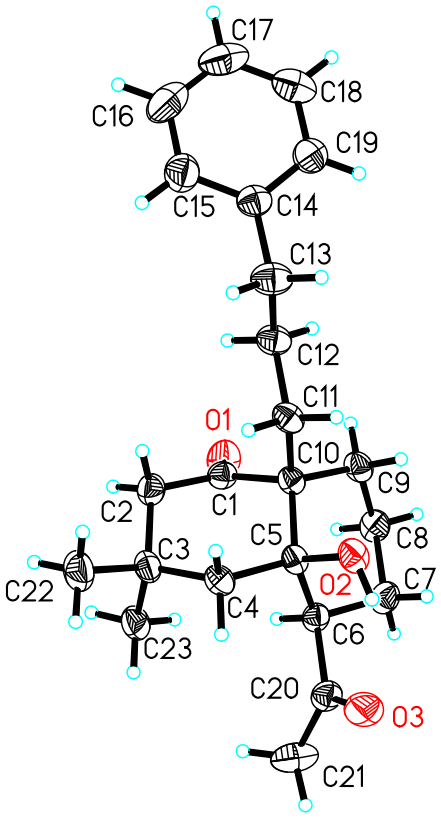
mixture was poured into an Erlenmeyer flask containing 15 mL of H_2O, which was then extracted with EtOAc (3 × 10 mL). The organic phases were combined and washed with H_2O, brine, and dried over $MgSO_4$. The solvent was removed *in vacuo* and the residue was purified by column chromatography (hexane/EtOAc = 10/1) to give a white solid **7b** (23.8 mg, 96% yield). Mp 124–129 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.23 (d, J = 2.0 Hz, 1H), 5.54 (d, J = 2.0 Hz, 1H), 2.87−2.84 (m, 1H), 2.49−2.31 (m, 3H), 2.28 (dt, J = 14.0 Hz, 4.8 Hz, 1H), 2.01−1.93 (m, 2H), 1.82−1.70 (m, 2H), 1.67−1.54 (m, 2H), 1.53−1.47 (m, 3H), 0.99−0.90 (m, 1H), 0.69 (t, J = 7.6 Hz, 3H); ^{13}CNMR (100 MHz, $CDCl_3$) δ (ppm) 210.30, 169.44, 140.50, 121.23, 87.76, 56.19, 43.79, 37.76, 33.39, 27.42, 27.26, 23.15, 18.90, 17.16, 7.68; IR (KBr) ν (cm^{-1}) 3473, 2940, 2848, 1763, 1706, 1644, 1463, 1289, 1260, 1230, 1186, 1134, 1042, 1008, 942, 828; HRMS (TOF-EI) for $[C_{15}H_{20}O_3]^{\cdot+}$: calcd. 248.1412, found: 248.1406.

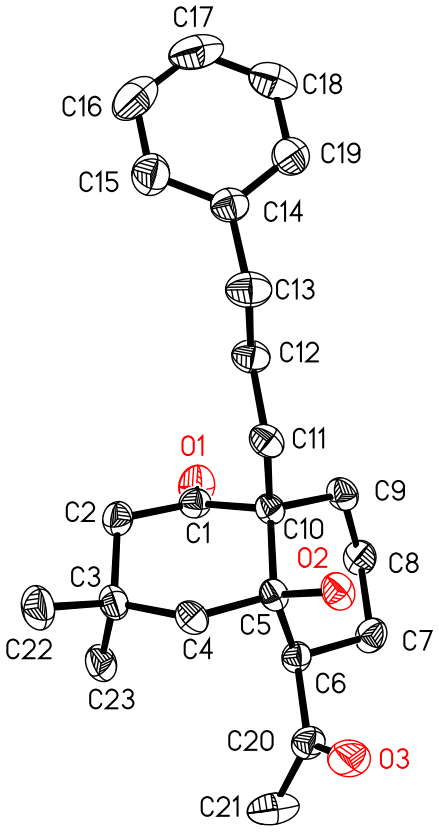
(4a*R*,5*R*,8a*R*)-rel-5-Acetyl-8a-ethyl-4a-hydroxyoctahydronaphthalen-1(2*H*)-one (3b). A dried Schlenk flask was charged with **5b** (24.8 mg, 0.1 mmol), Sodium perborate tetrahydrate (77 mg, 0.5 mmol), THF (0.5 mL) and H_2O (0.5 mL) was added and the mixture was allowed to stir for 3h at room temperature. Then quenched with saturated aqueous NaCl (2 mL), extracted with ethyl acetate (4 mL × 3). The combined organic phases were dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by silica gel (300−400 mesh) column chromatography to afford the desired product **3b** as colorless oil (21.7 mg, 91% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 4.28 (s, 1H), 2.66−2.61 (m, 1H), 2.49−2.39 (m, 1H), 2.34−2.23 (m, 1H), 2.20−2.15 (m, 4H), 1.99−1.87 (m, 2H), 1.82−1.70 (m, 2H), 1.67−1.62 (m, 3H), 1.53−1.48 (m, 1H), 1.36−1.27 (m, 3H), 0.66 (t, J = 8.0 Hz, 3H).

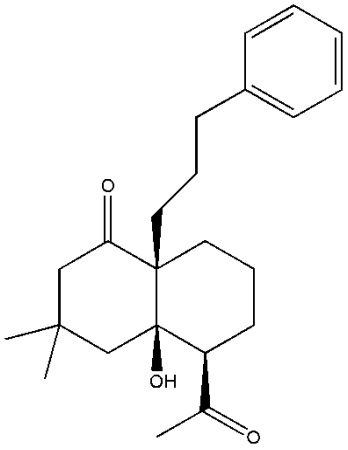
7. Relative Configuration Confirmation

7.1 Relative Configuration Confirmation of 3K







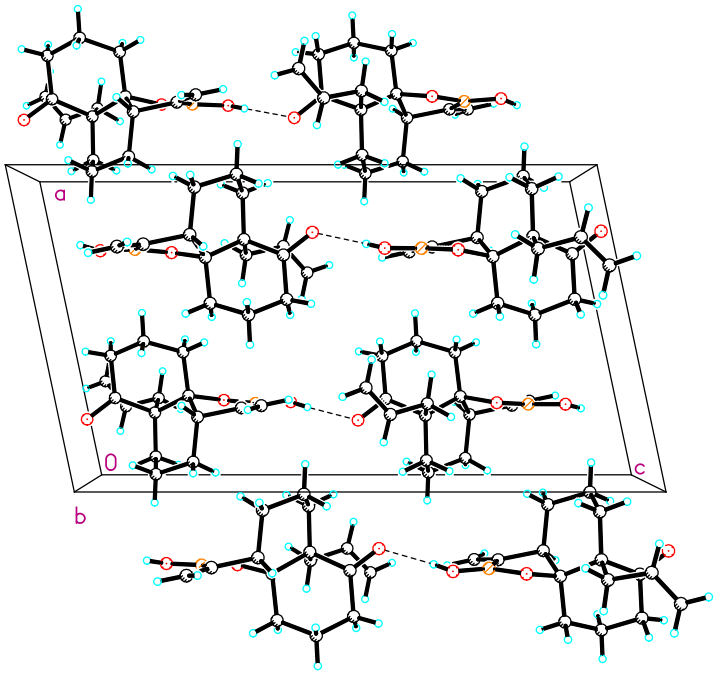


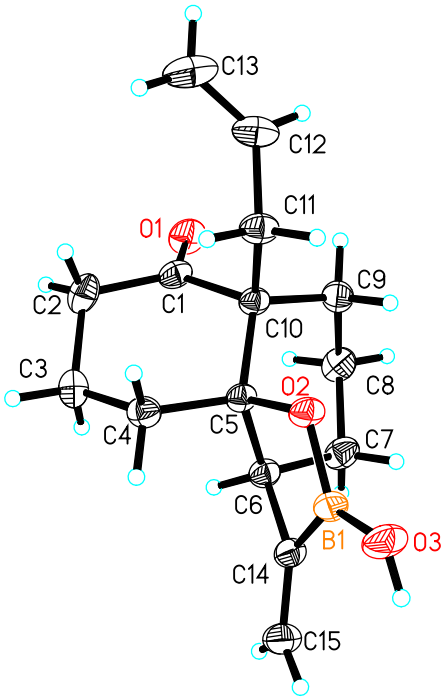
The relative configuration of **3k**

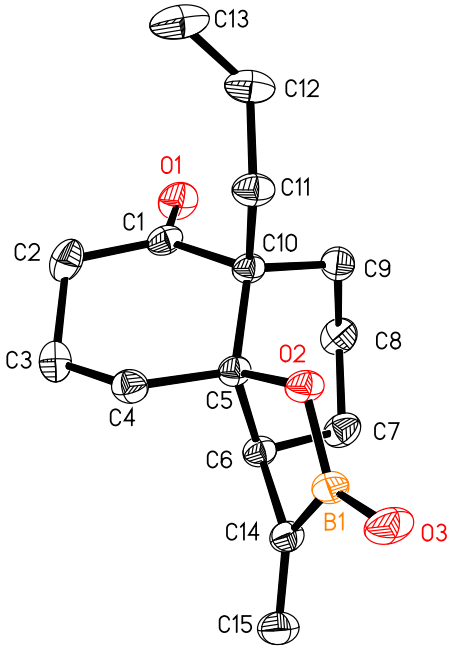
Crystal data and structure refinement for 3k.

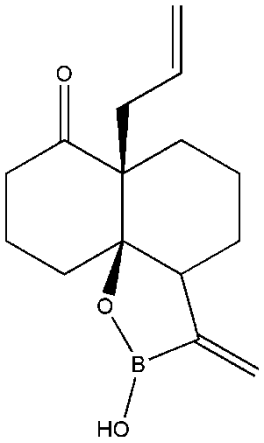
Identification code	3k
Empirical formula	C23 H32 O3
Formula weight	356.49
Temperature	296(2) K
Wavelength	1.54178 A
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 8.0136(16) A alpha = 70.38(3) deg. b = 10.278(2) A beta = 86.42(3) deg. c = 13.463(3) A gamma = 78.55(3) deg.
Volume	1023.7(4) A^3
Z, Calculated density	2, 1.157 Mg/m^3
Absorption coefficient	0.586 mm^-1
F(000)	388
Crystal size	0.31 x 0.20 x 0.16 mm
Theta range for data collection	4.65 to 65.93 deg.
Limiting indices	-9<=h<=9, -12<=k<=12, -14<=l<=15
Reflections collected / unique	5726 / 3136 [R(int) = 0.0163]
Completeness to theta = 65.93	88.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7529 and 0.6742
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3136 / 0 / 236
Goodness-of-fit on F^2	1.053
Final R indices [I>2sigma(I)]	R1 = 0.0441, wR2 = 0.1229
R indices (all data)	R1 = 0.0459, wR2 = 0.1250
Extinction coefficient	0.0152(14)
Largest diff. peak and hole	0.178 and -0.174 e.A^-3

7.2 Relative Configuration Confirmation of 5e







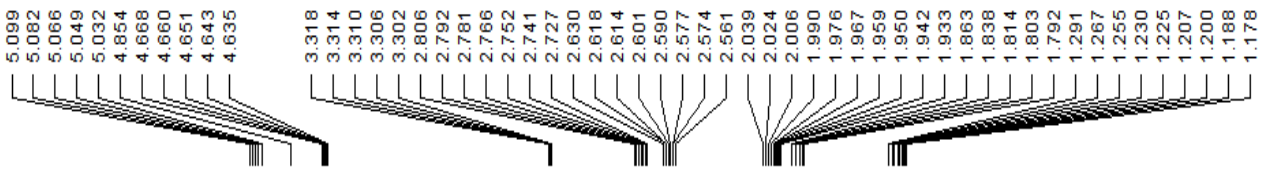


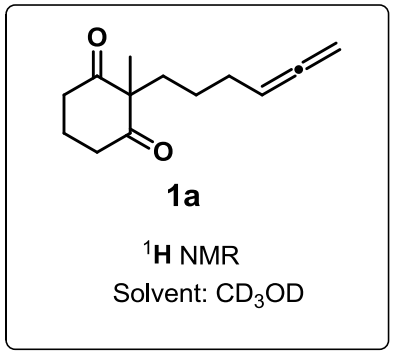
The relative configuration of **5e**

Crystal data and structure refinement for 5e.

Identification code	5e
Empirical formula	C15 H21 B O3
Formula weight	260.13
Temperature	296(2) K
Wavelength	1.54178 A
Crystal system, space group	Monoclinic, P 21/c
Unit cell dimensions	a = 10.555(2) A alpha = 90 deg. b = 7.2517(15) A beta = 101.90(3) deg. c = 18.652(4) A gamma = 90 deg.
Volume	1397.0(5) A^3
Z, Calculated density	4, 1.237 Mg/m^3
Absorption coefficient	0.663 mm^-1
F(000)	560
Crystal size	0.32 x 0.21 x 0.15 mm
Theta range for data collection	4.85 to 67.57 deg.
Limiting indices	-12<=h<=12, -7<=k<=8, -20<=l<=22
Reflections collected / unique	6044 / 2375 [R(int) = 0.0213]
Completeness to theta = 67.57	94.2 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7529 and 0.6526
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2375 / 0 / 173
Goodness-of-fit on F^2	1.052
Final R indices [I>2sigma(I)]	R1 = 0.0398, wR2 = 0.1055
R indices (all data)	R1 = 0.0405, wR2 = 0.1061
Extinction coefficient	0.0100(8)
Largest diff. peak and hole	0.184 and -0.171 e.A^-3

8. ^{1}H NMR, ^{13}C NMR COPIES

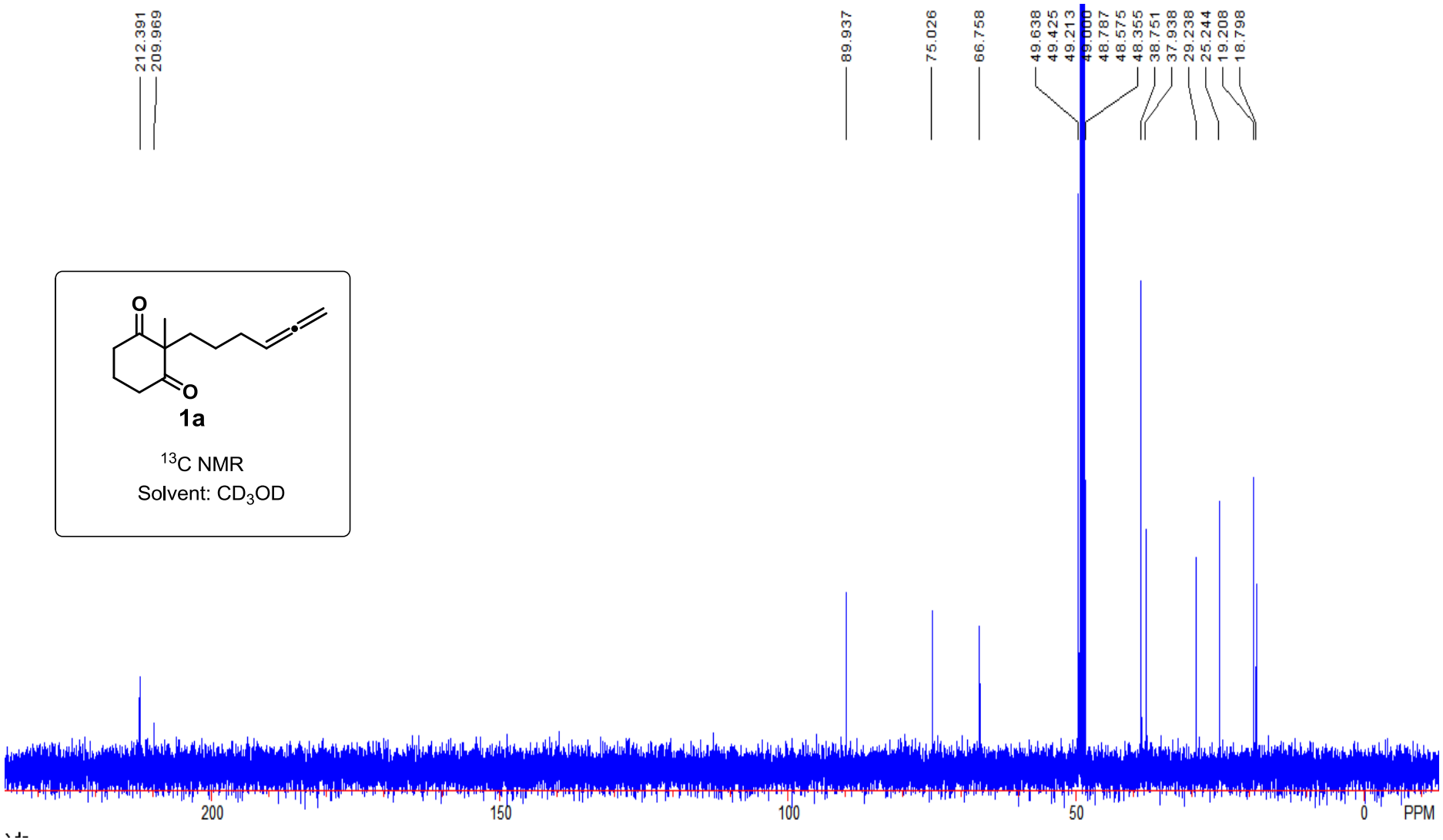


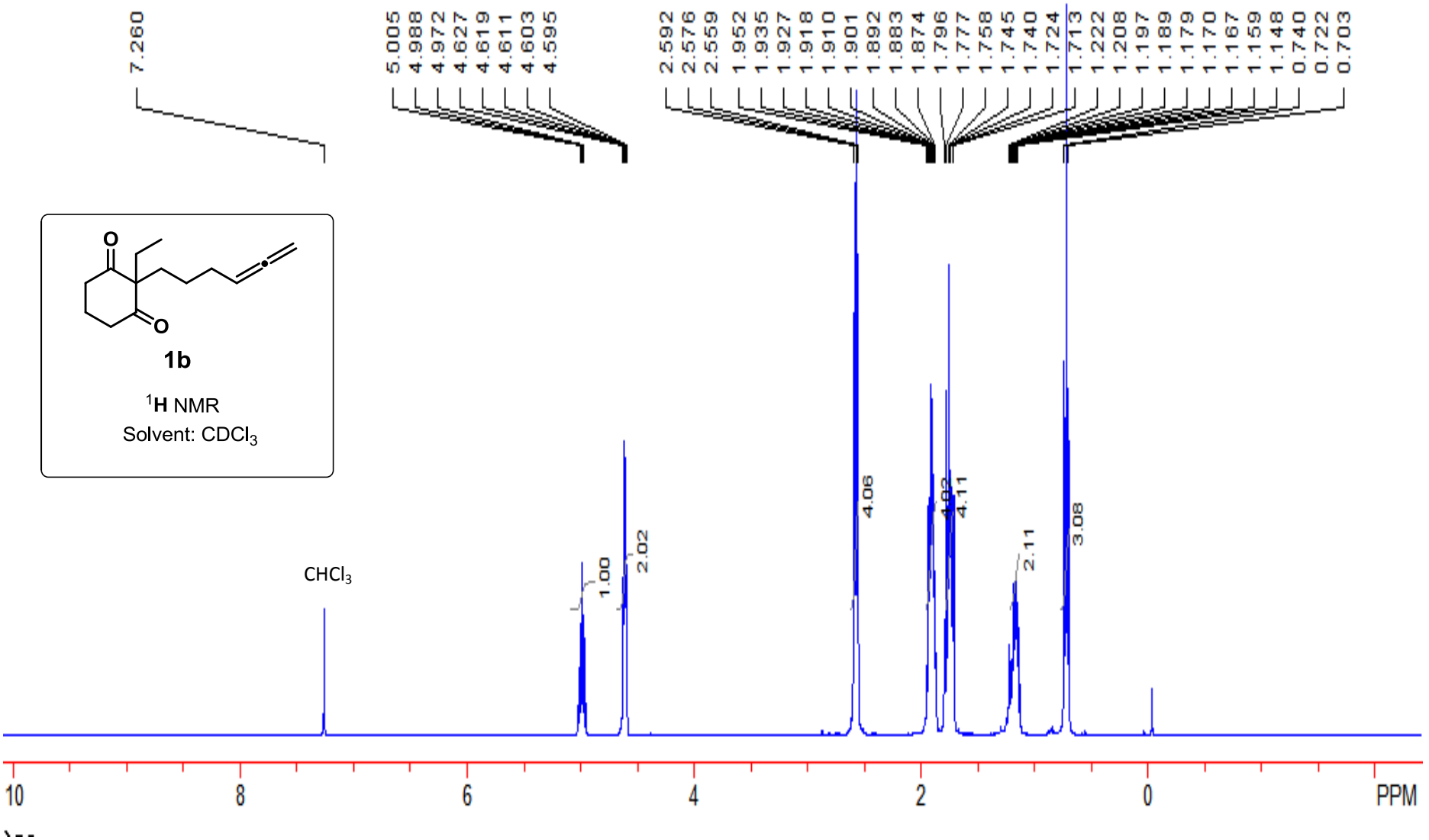


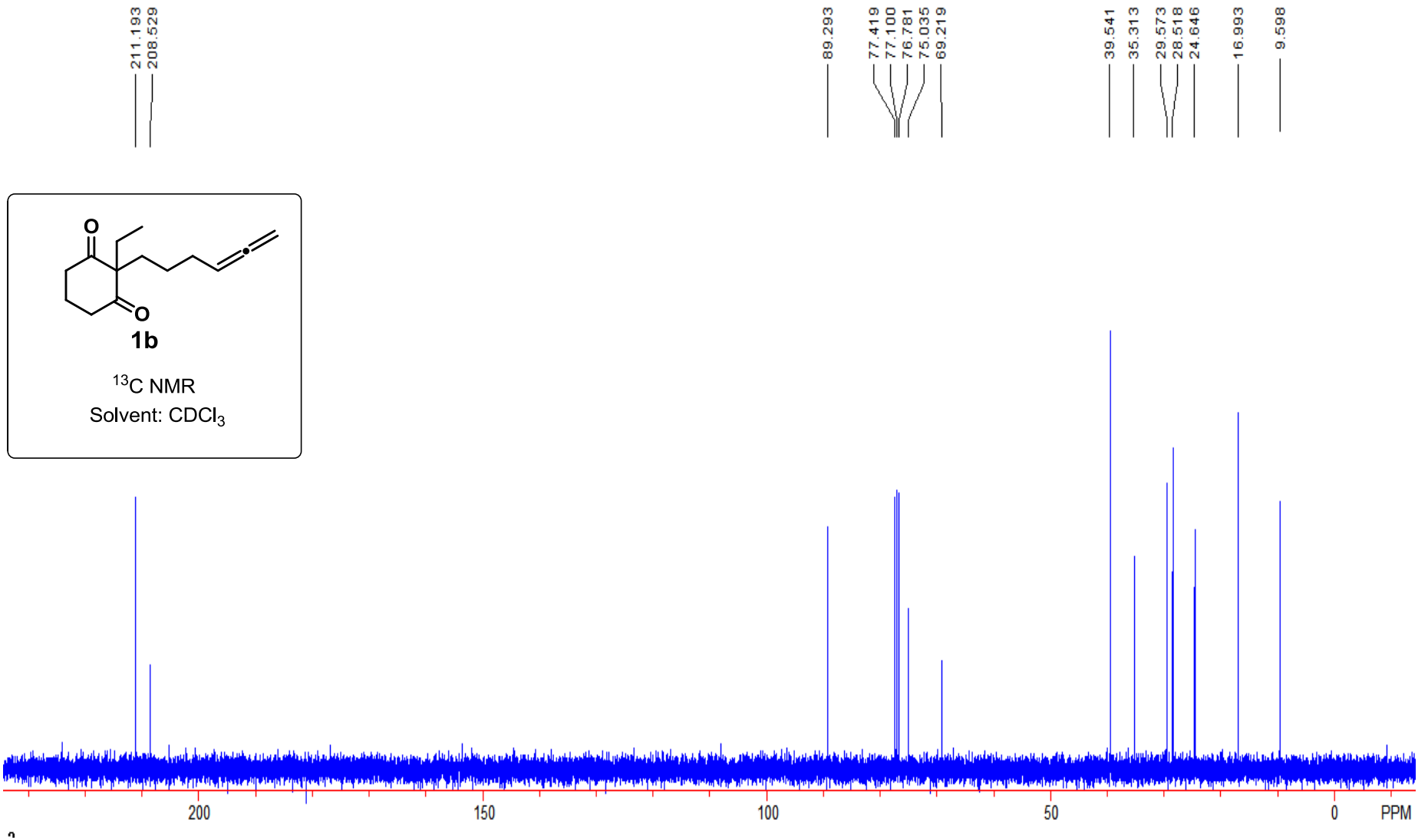
1a

^{1}**H** NMR

Solvent: CD_3OD


212.391
209.969
89.937
75.026
66.758
49.638
49.425
49.213
49.000
48.787
48.575
48.355
38.751
37.938
29.238
25.244
19.208
18.798
O
O
1a
^{13}C NMR
Solvent: CD_3OD
200
150
100
50
0
PPM


7.260
5.005
4.988
4.972
4.627
4.619
4.611
4.603
4.595
2.592
2.576
2.559
1.952
1.935
1.927
1.918
1.910
1.901
1.892
1.883
1.874
1.796
1.777
1.758
1.745
1.740
1.724
1.713
1.222
1.208
1.197
1.189
1.179
1.170
1.167
1.159
1.148
0.740
0.722
0.703
O
O
1b
1H NMR
Solvent: CDCl3
CHCl3
1.00
2.02
4.06
4.02
4.11
2.11
3.08
10
8
6
4
2
0
PPM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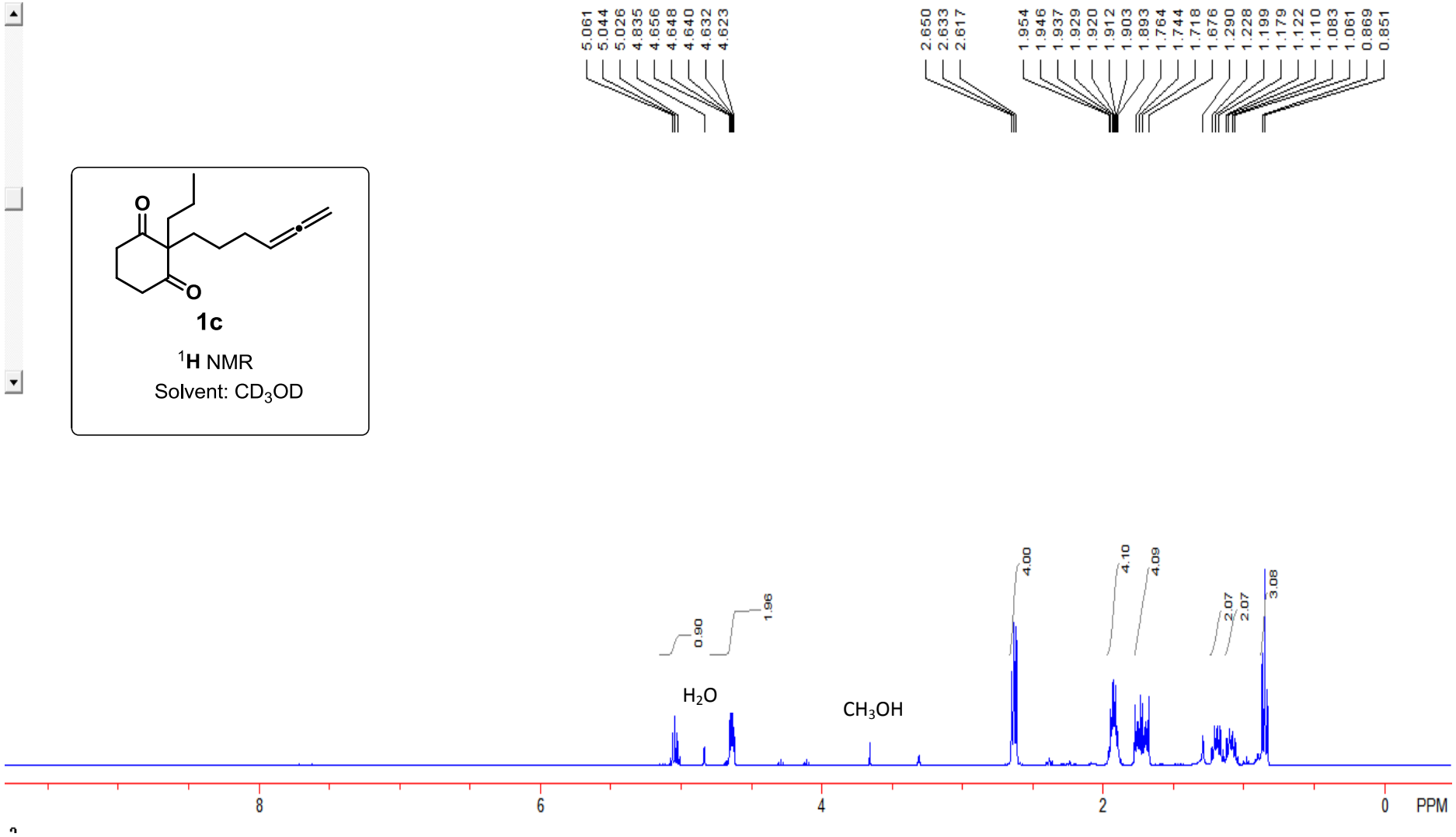
208.529
89.293
77.419
77.100
76.781
75.035
69.219
39.541
35.313
29.573
28.518
24.646
16.993
9.598
O
O
1b
^{13}C NMR
Solvent: $CDCl_3$
200
150
100
50
0
PPM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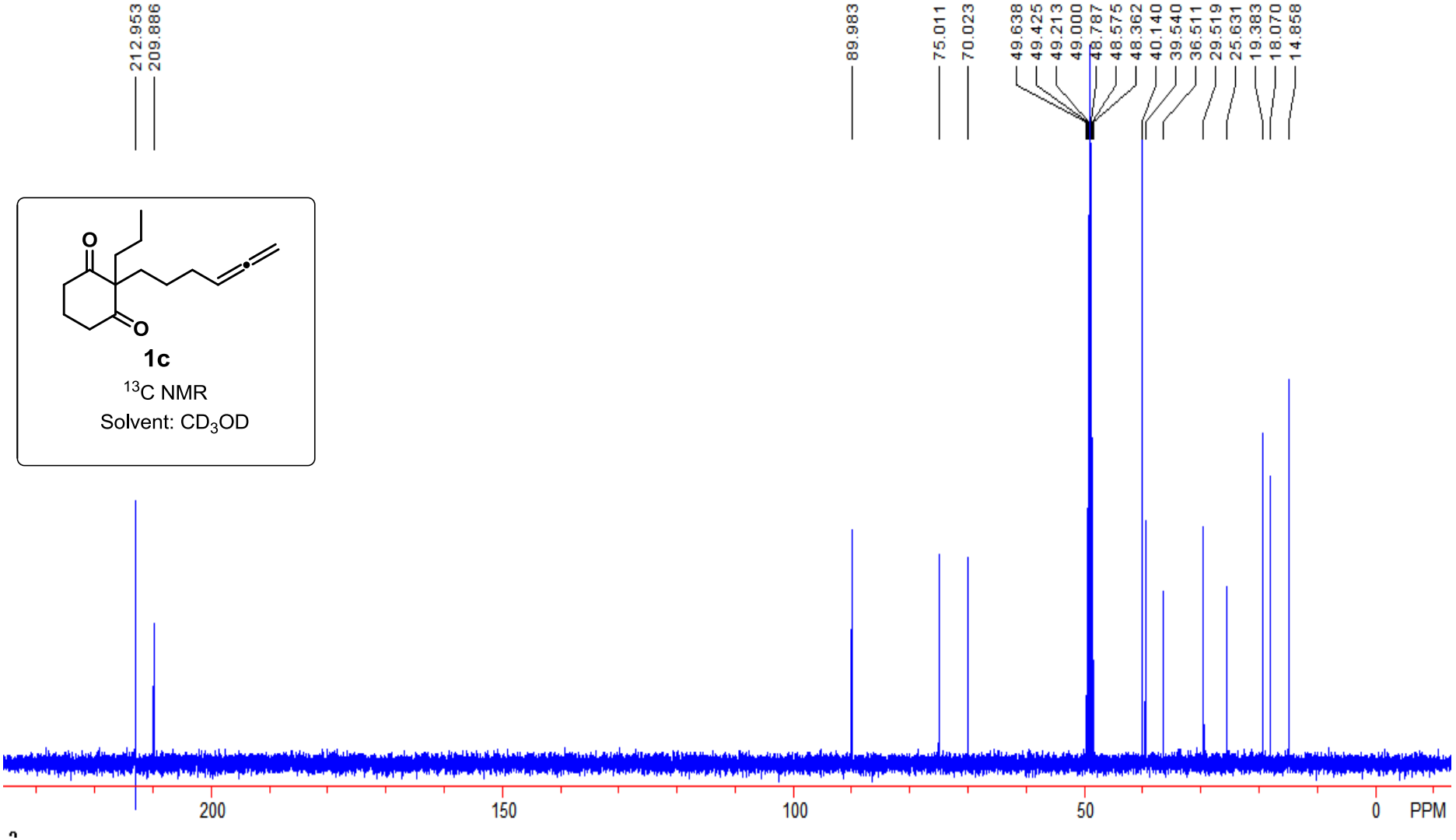
5.026
4.835
4.656
4.648
4.640
4.632
4.623
2.650
2.633
2.617
1.954
1.946
1.937
1.929
1.920
1.912
1.903
1.893
1.764
1.744
1.718
1.676
1.290
1.228
1.199
1.179
1.122
1.110
1.083
1.061
0.869
0.851
O
O
1c
1H NMR
Solvent: CD3OD
0.90
1.96
4.00
4.10
4.09
2.07
2.07
3.08
H2O
CH3OH
8
6
4
2
0
PPM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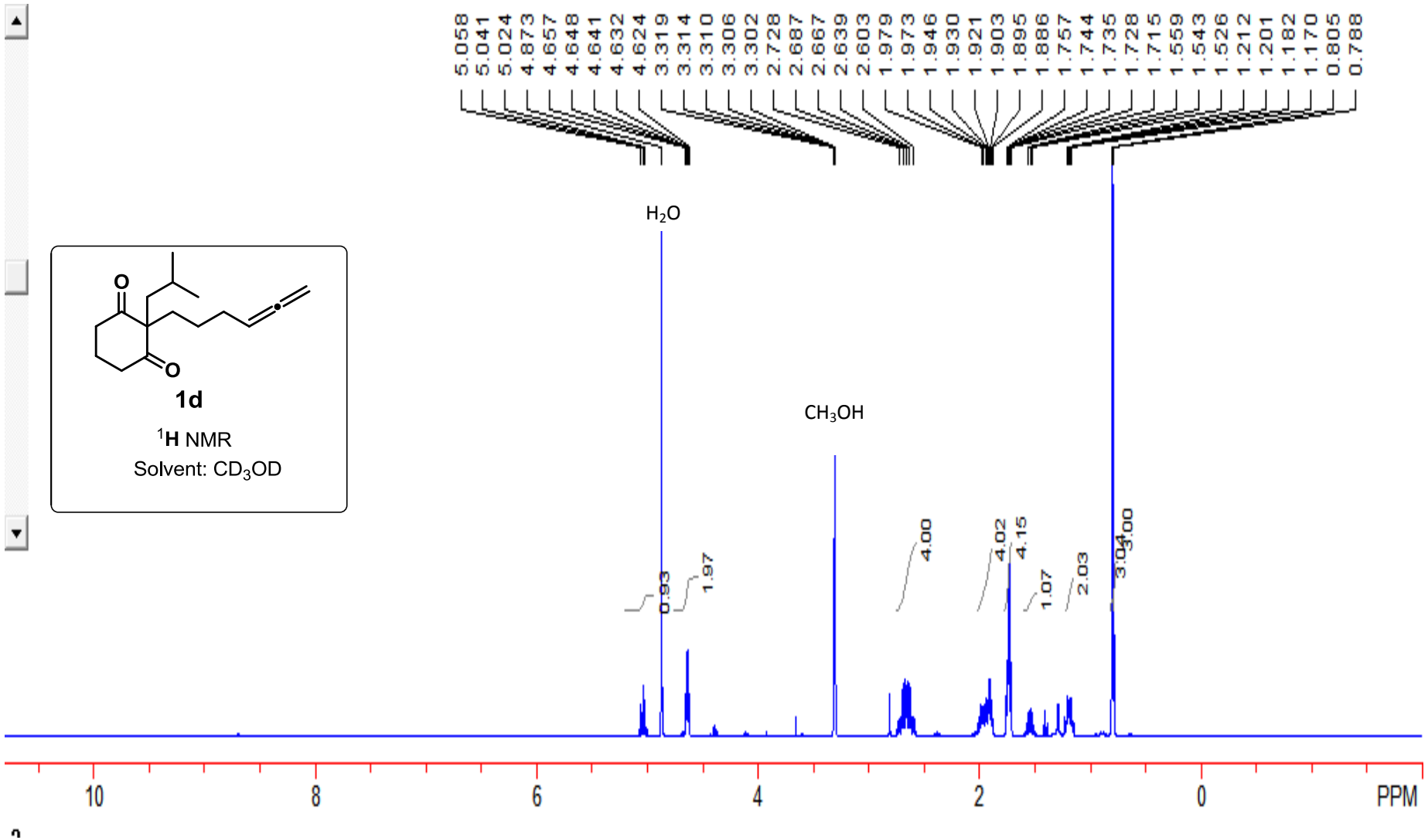
209.886
89.983
75.011
70.023
49.638
49.425
49.213
49.000
48.787
48.575
48.362
40.140
39.540
36.511
29.519
25.631
19.383
18.070
14.858
O
O
1c
13C NMR
Solvent: CD3OD
200
150
100
50
0
PPM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5.024
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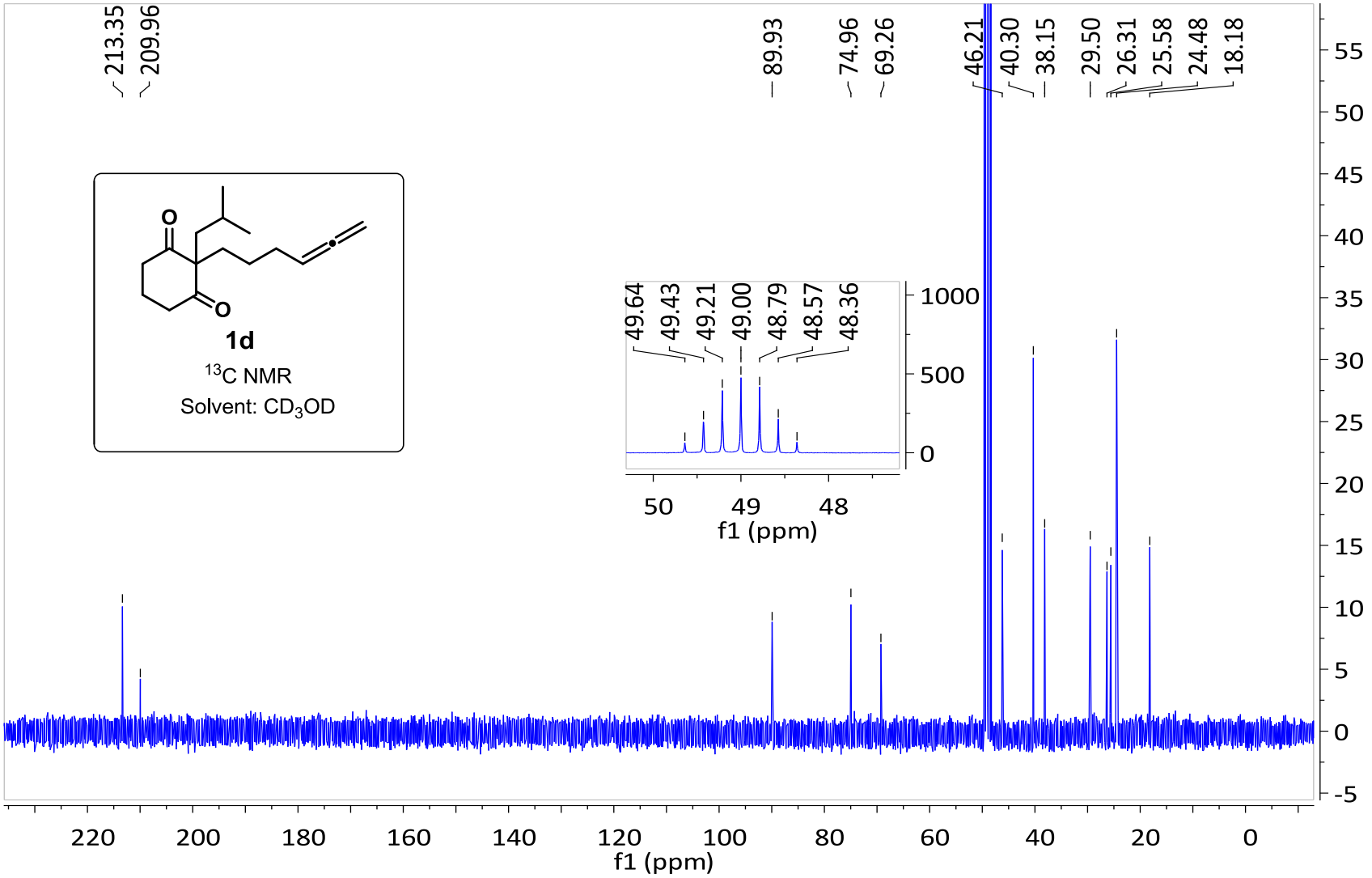
4.657
4.648
4.641
4.632
4.624
3.319
3.314
3.310
3.306
3.302
2.728
2.687
2.667
2.639
2.603
1.979
1.973
1.946
1.930
1.921
1.903
1.895
1.886
1.757
1.744
1.735
1.728
1.715
1.559
1.543
1.526
1.212
1.201
1.182
1.170
0.805
0.788
H2O
CH3OH
0.93
1.97
4.00
4.02
4.15
1.07
2.03
3.04
3.00
O
O
1d
1H NMR
Solvent: CD3OD
10
8
6
4
2
0
PPM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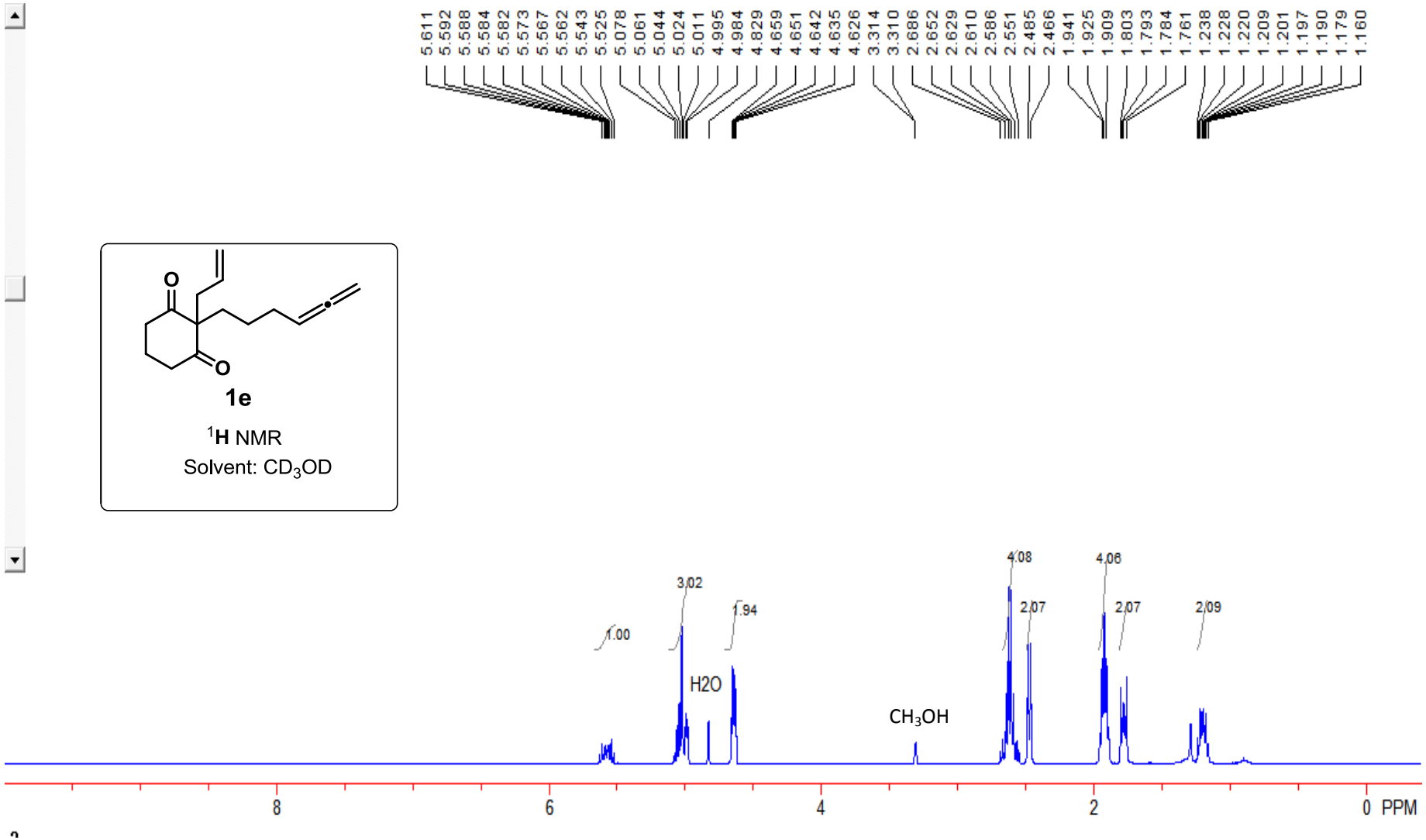
209.96
89.93
74.96
69.26
46.21
40.30
38.15
29.50
26.31
25.58
24.48
18.18
1d
13C NMR
Solvent: CD3OD
49.64
49.43
49.21
49.00
48.79
48.57
48.36
f1 (ppm)
f1 (ppm)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5.592
5.588
5.584
5.582
5.573
5.567
5.562
5.543
5.525
5.078
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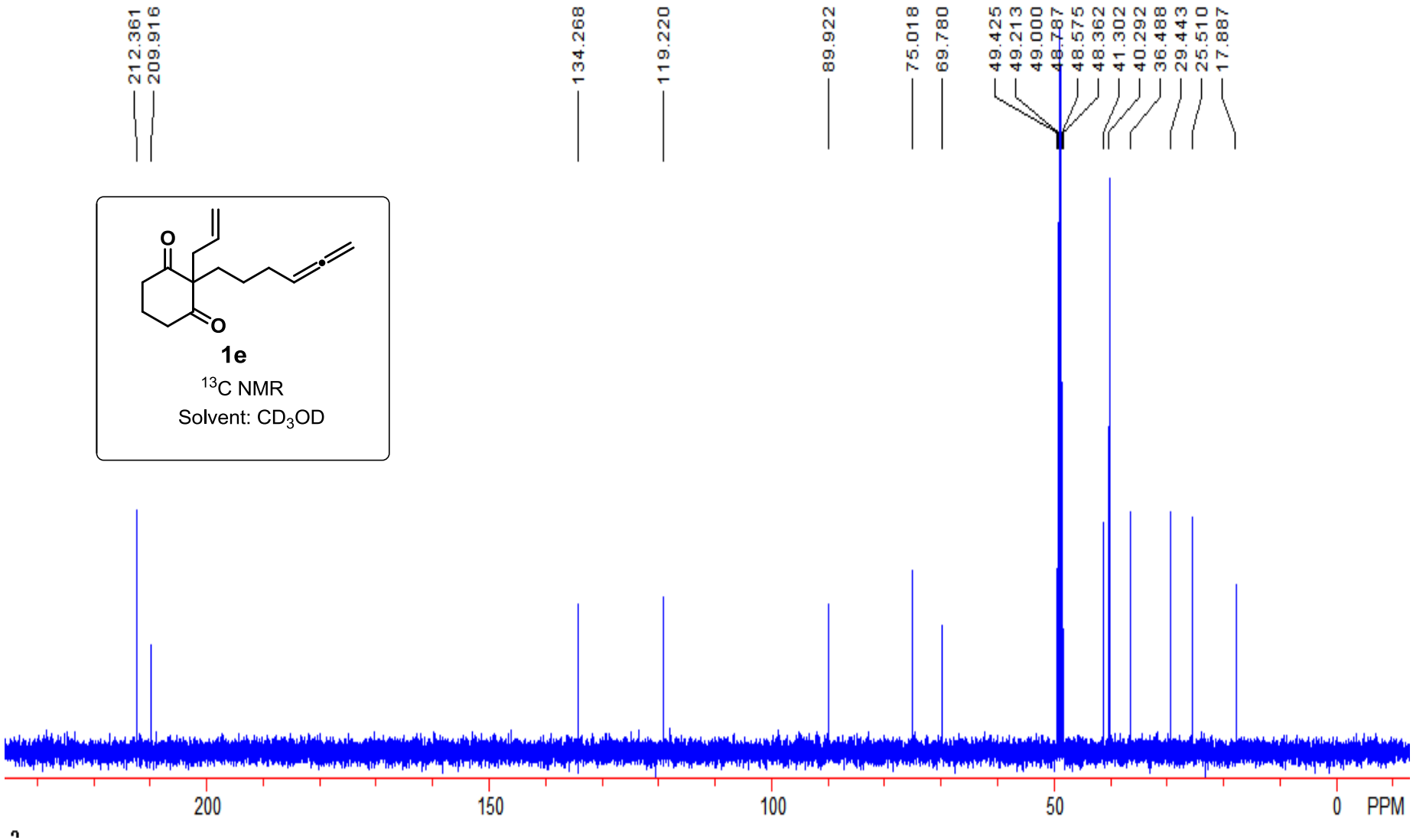
5.044
5.024
5.011
4.995
4.984
4.829
4.659
4.651
4.642
4.635
4.626
3.314
3.310
2.686
2.652
2.629
2.610
2.586
2.551
2.485
2.466
1.941
1.925
1.909
1.803
1.793
1.784
1.761
1.238
1.228
1.220
1.209
1.201
1.197
1.190
1.179
1.160
O
O
1e
1H NMR
Solvent: CD3OD
1.00
3.02
1.94
4.08
2.07
4.06
2.07
2.09
H2O
CH3OH
8
6
4
2
0 PPM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75.018
69.780
49.425
49.213
49.000
48.787
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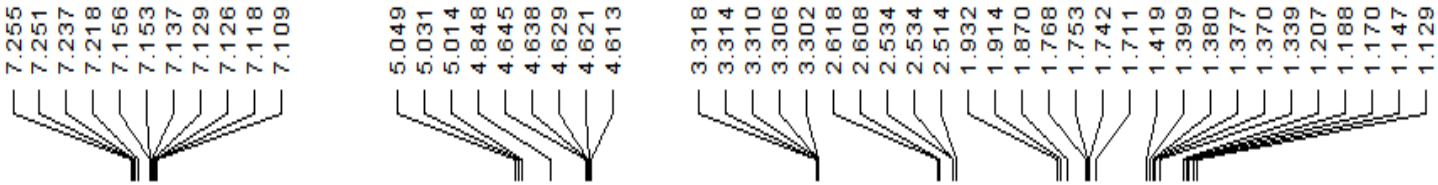
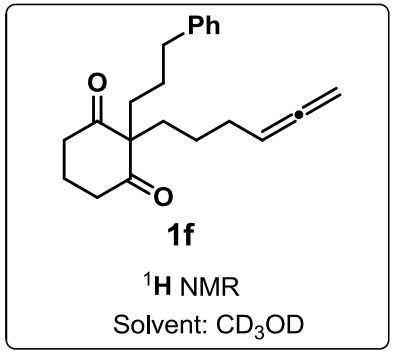
48.362
41.302
40.292
36.488
29.443
25.510
17.887
O
O
1e
13C NMR
Solvent: CD3OD
200
150
100
50
0
PPM

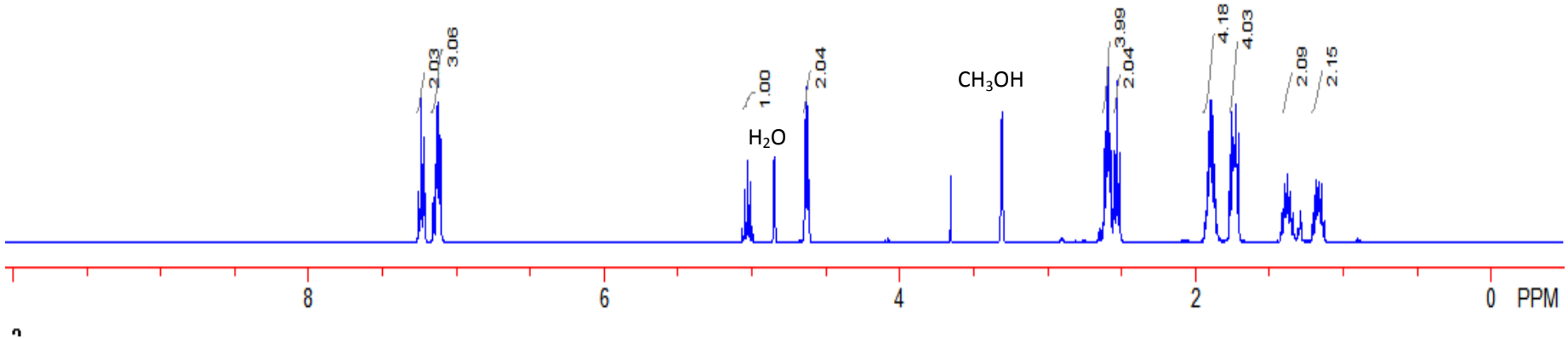


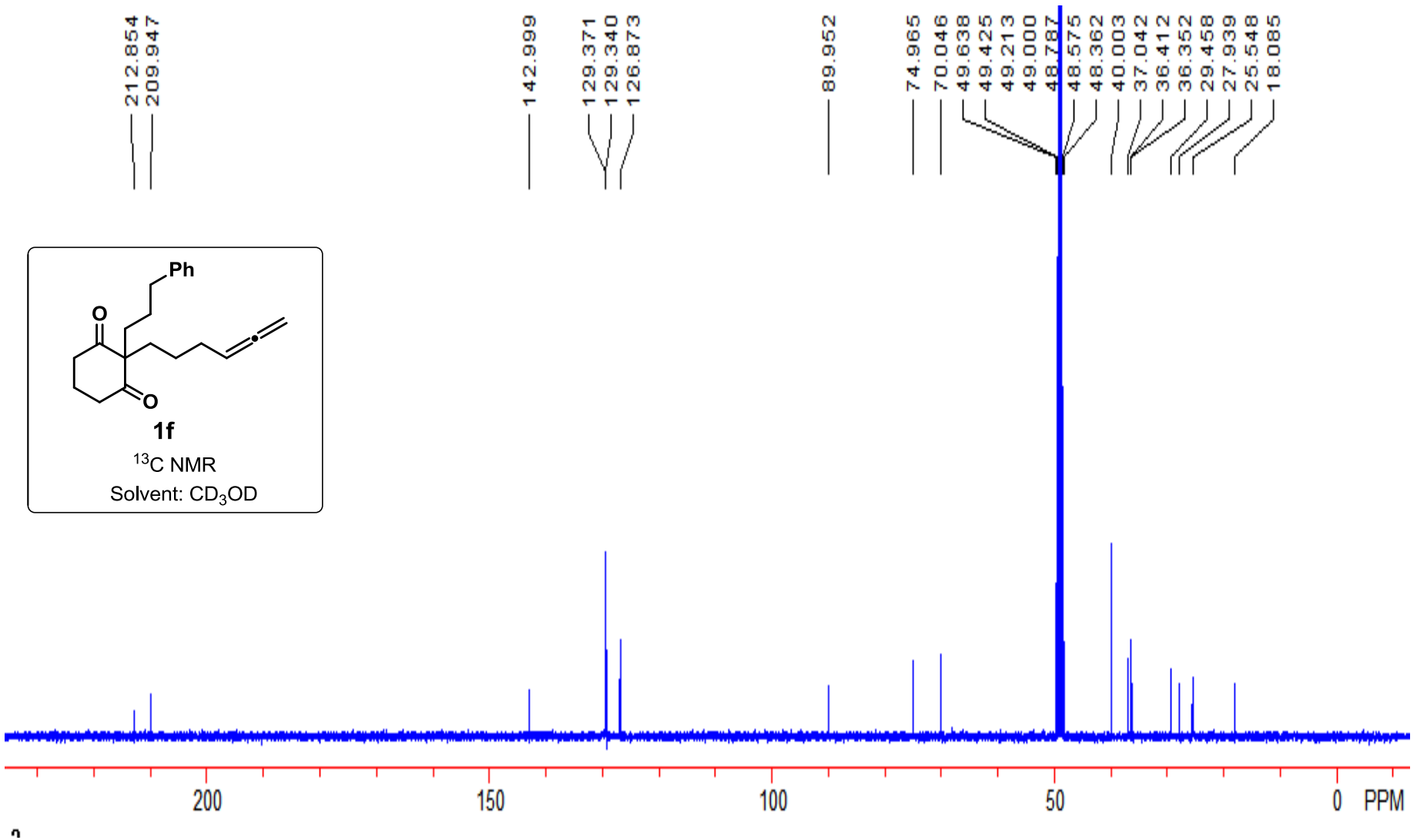


1f

^{1}**H** NMR

Solvent: CD_3OD

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129.371
129.340
126.873
89.952
74.965
70.046
49.638
49.425
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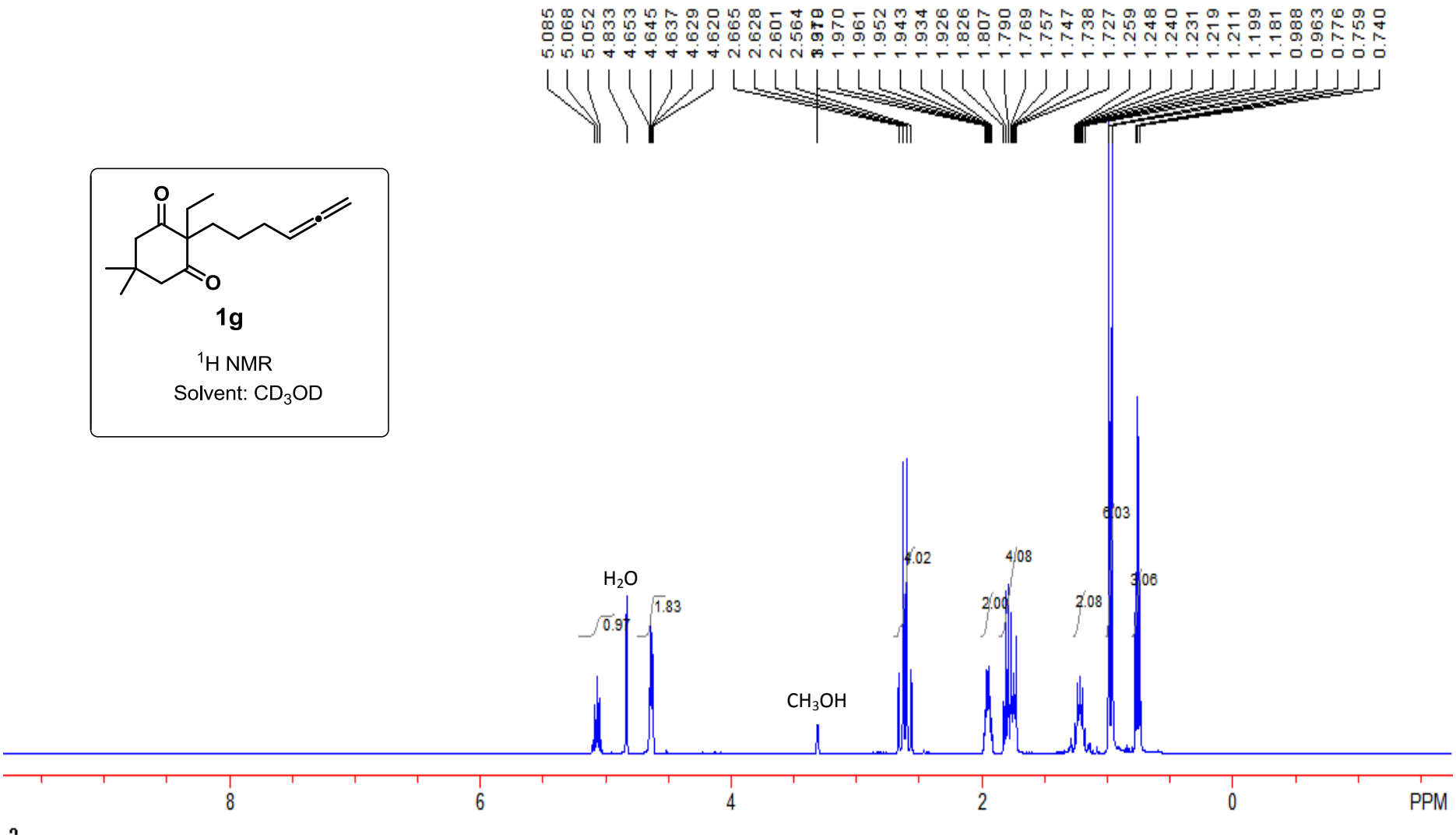
48.787
48.575
48.362
40.003
37.042
36.412
36.352
29.458
27.939
25.548
18.085
Ph
O
O
1f
13C NMR
Solvent: CD3OD
200
150
100
50
0
PPM


1g
1H NMR
Solvent: CD3OD
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5.068
5.052
4.833
4.653
4.645
4.637
4.629
4.620
2.665
2.628
2.601
2.564
1.970
1.961
1.952
1.943
1.934
1.926
1.826
1.807
1.790
1.769
1.757
1.747
1.738
1.727
1.259
1.248
1.240
1.231
1.219
1.211
1.199
1.181
0.988
0.963
0.776
0.759
0.740
H2O
CH3OH
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2.08
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3.06
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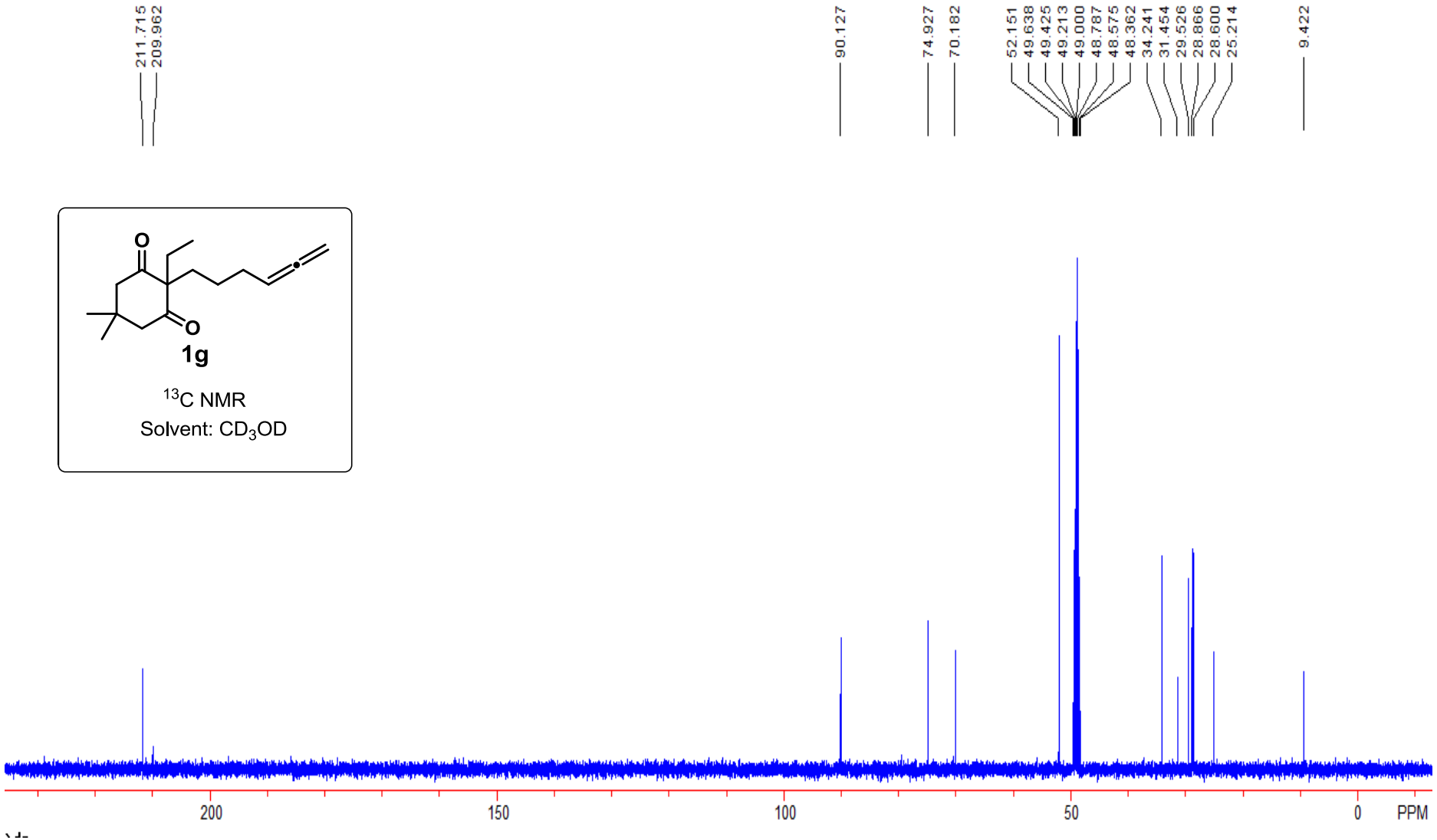
0
PPM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48.575
48.362
34.241
31.454
29.526
28.866
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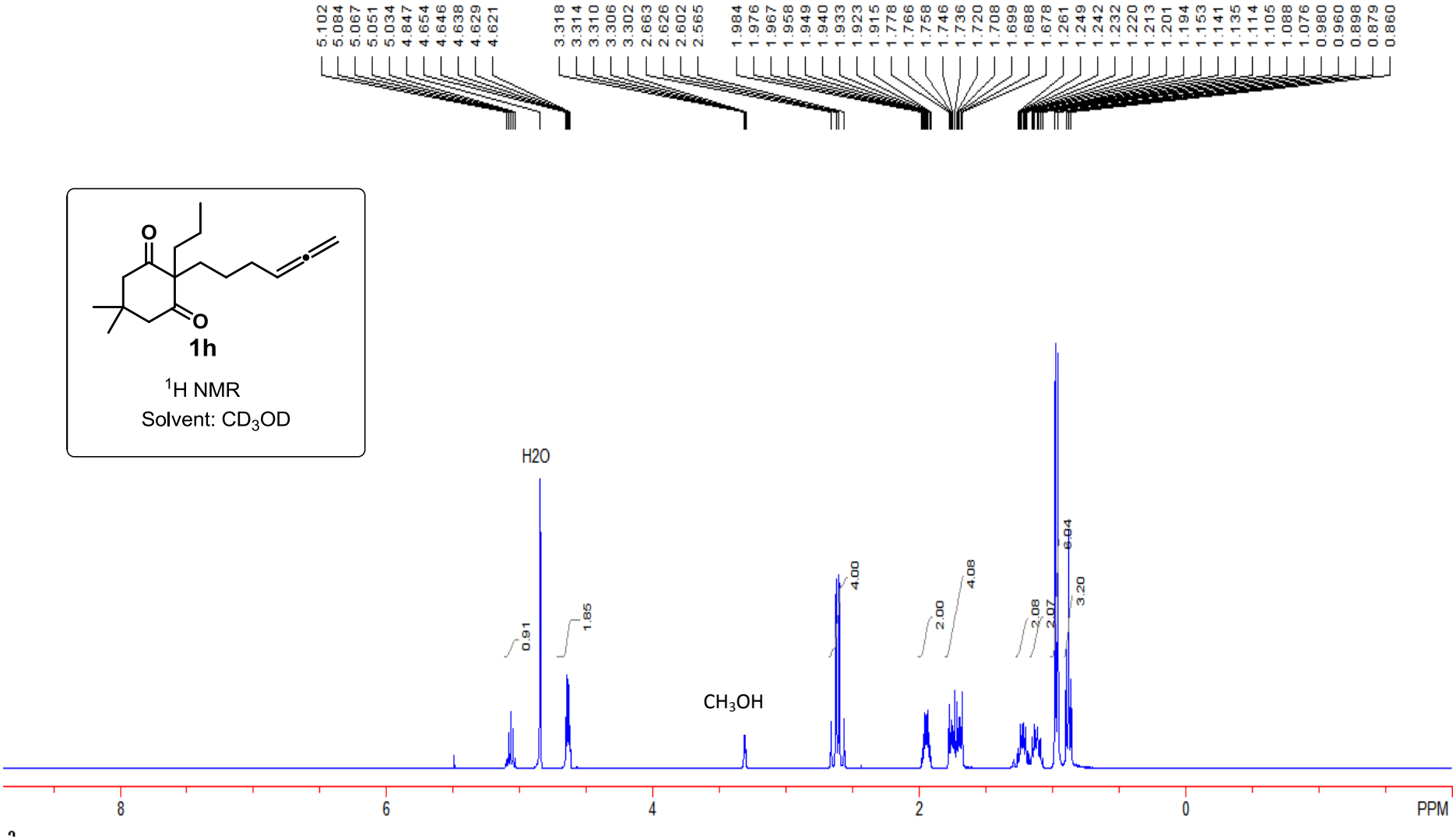
O
O
1g
13C NMR
Solvent: CD3OD
200
150
100
50
0
PPM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4.646
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4.629
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3.314
3.310
3.306
3.302
2.663
2.626
2.602
2.565
1.984
1.976
1.967
1.958
1.949
1.940
1.933
1.923
1.915
1.778
1.766
1.758
1.746
1.736
1.720
1.708
1.699
1.688
1.678
1.261
1.249
1.242
1.232
1.220
1.213
1.201
1.194
1.153
1.141
1.135
1.114
1.105
1.088
1.076
0.980
0.960
0.898
0.879
0.860
O
O
1h
1H NMR
Solvent: CD3OD
H2O
CH3OH
0.91
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3.20
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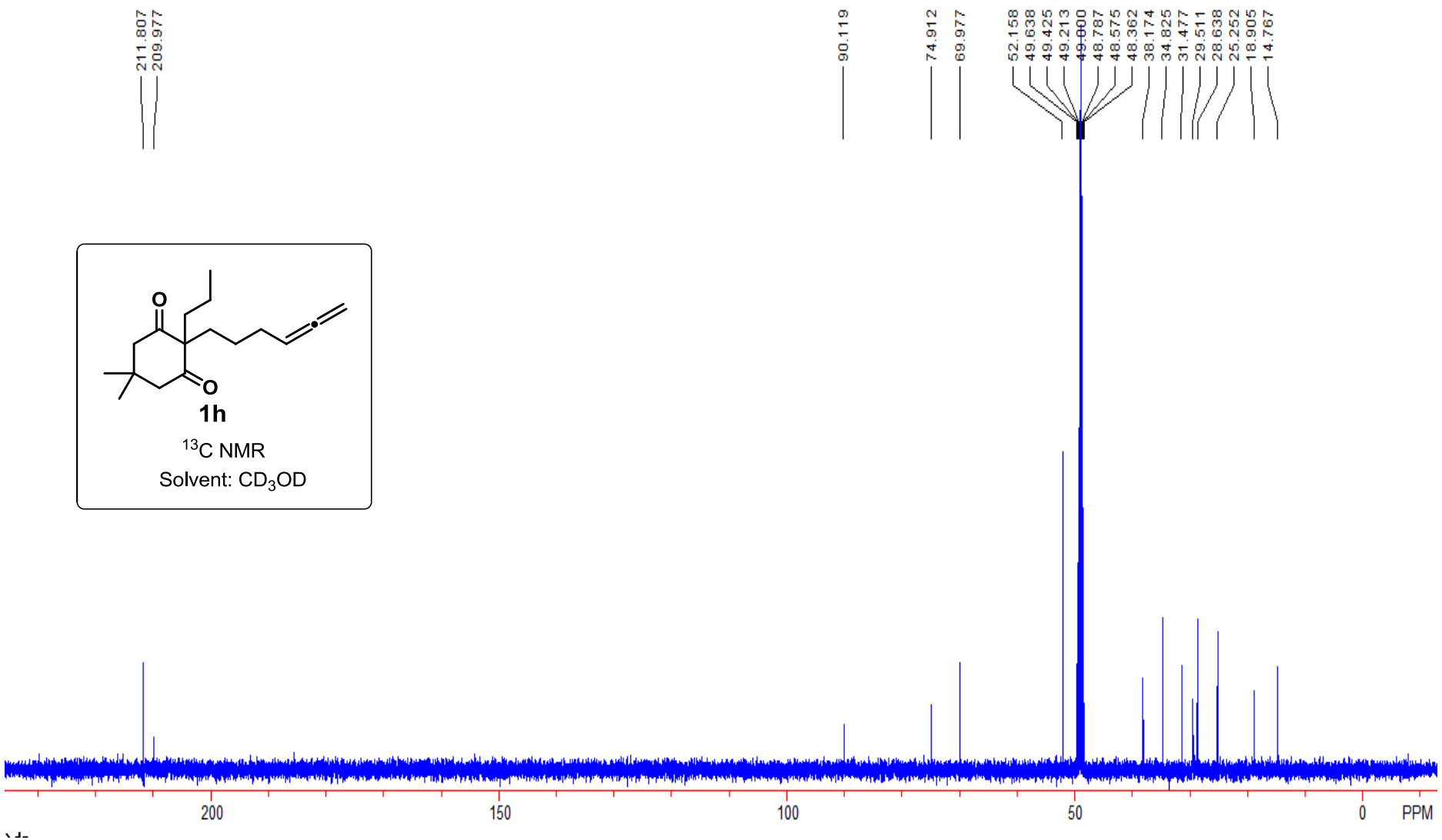
PPM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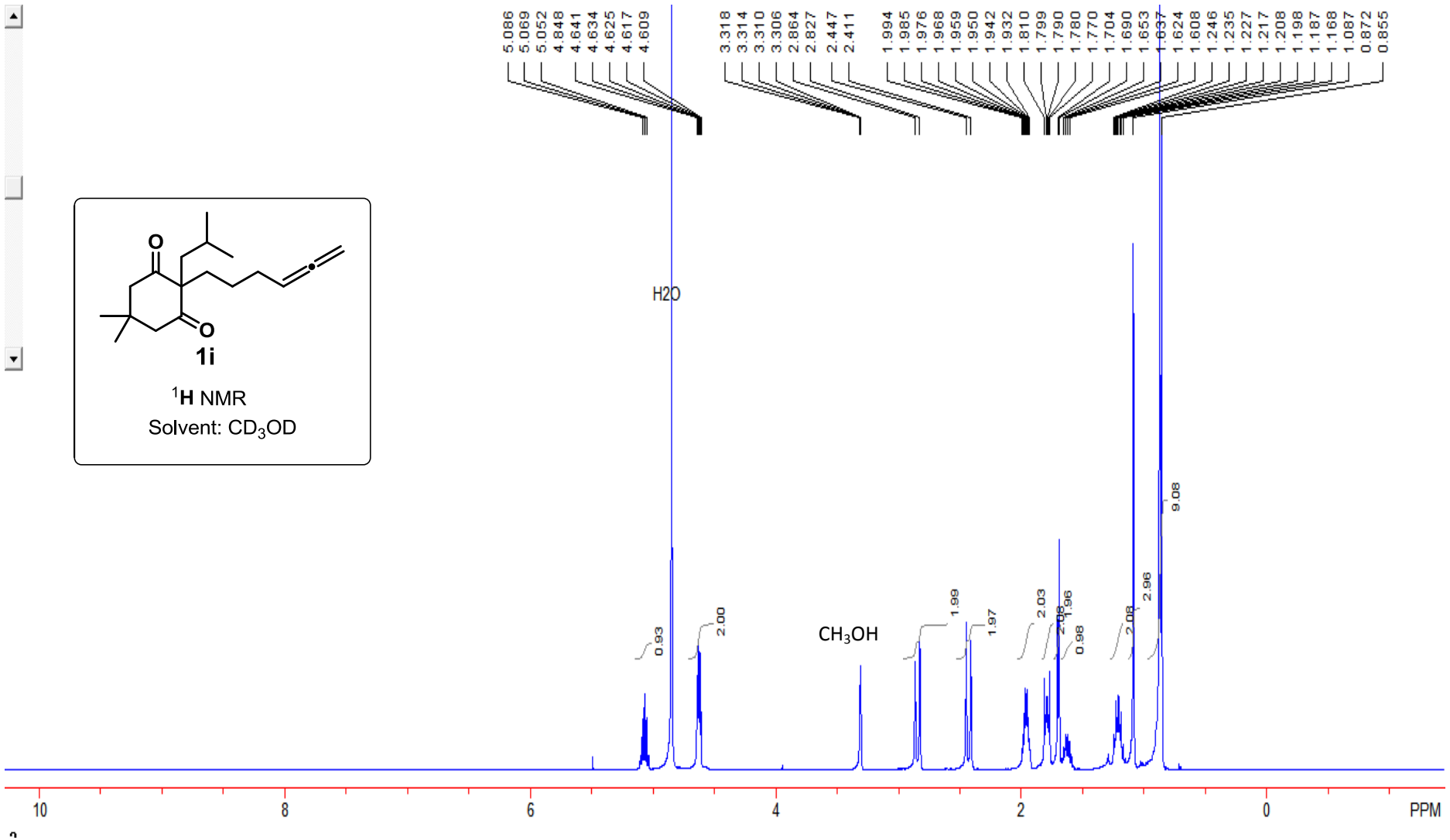
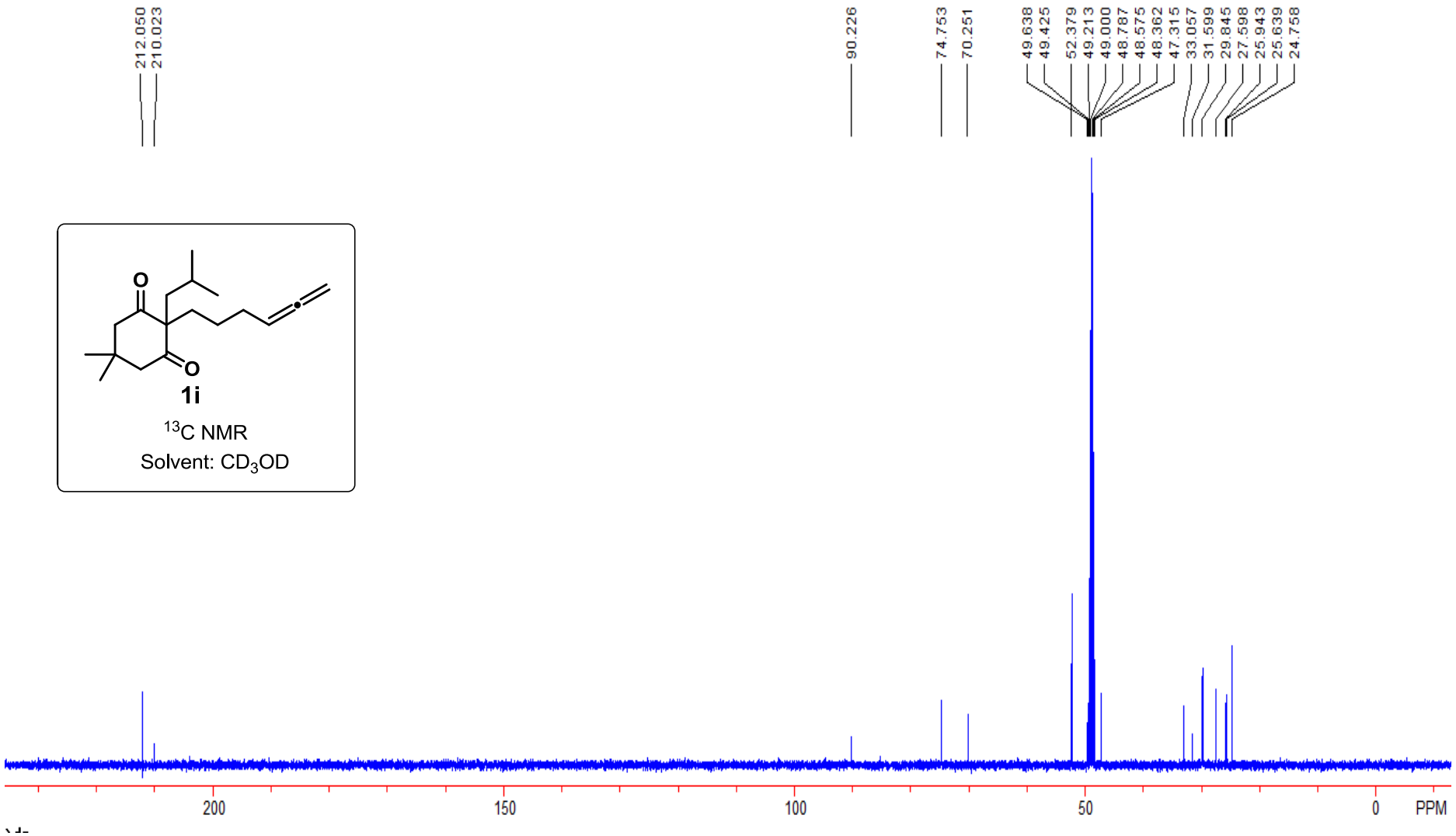
209.977
90.119
74.912
69.977
52.158
49.638
49.425
49.213
49.000
48.787
48.575
48.362
38.174
34.825
31.477
29.511
28.638
25.252
18.905
14.767
O
O
1h
13C NMR
Solvent: CD3OD
200
150
100
50
0
PPM


1i
1H NMR
Solvent: CD3OD
H2O
CH3OH
PPM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70.251
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49.425
52.379
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49.000
48.787
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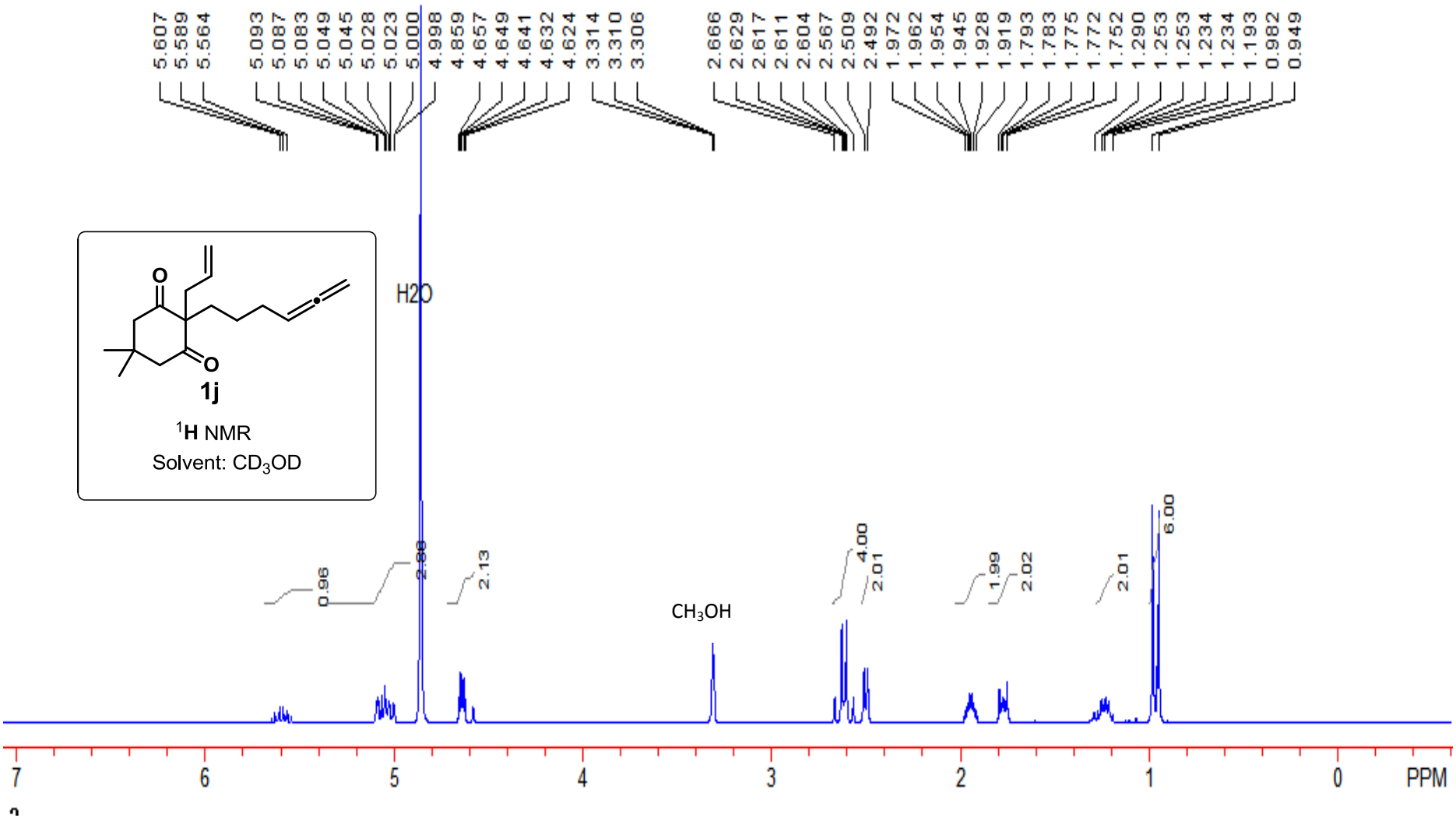
48.362
47.315
33.057
31.599
29.845
27.598
25.943
25.639
24.758
O
O
1i
^{13}C NMR
Solvent: CD_3OD
200
150
100
50
0
PPM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5.045
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4.998
4.859
4.657
4.649
4.641
4.632
4.624
3.314
3.310
3.306
2.666
2.629
2.617
2.611
2.604
2.567
2.509
2.492
1.972
1.962
1.954
1.945
1.928
1.919
1.793
1.783
1.775
1.772
1.752
1.290
1.253
1.253
1.234
1.234
1.193
0.982
0.949
O
O
1j
1H NMR
Solvent: CD3OD
H2O
CH3OH
0.96
2.88
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1.99
2.02
2.01
6.00
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6
5
4
3
2
1
0
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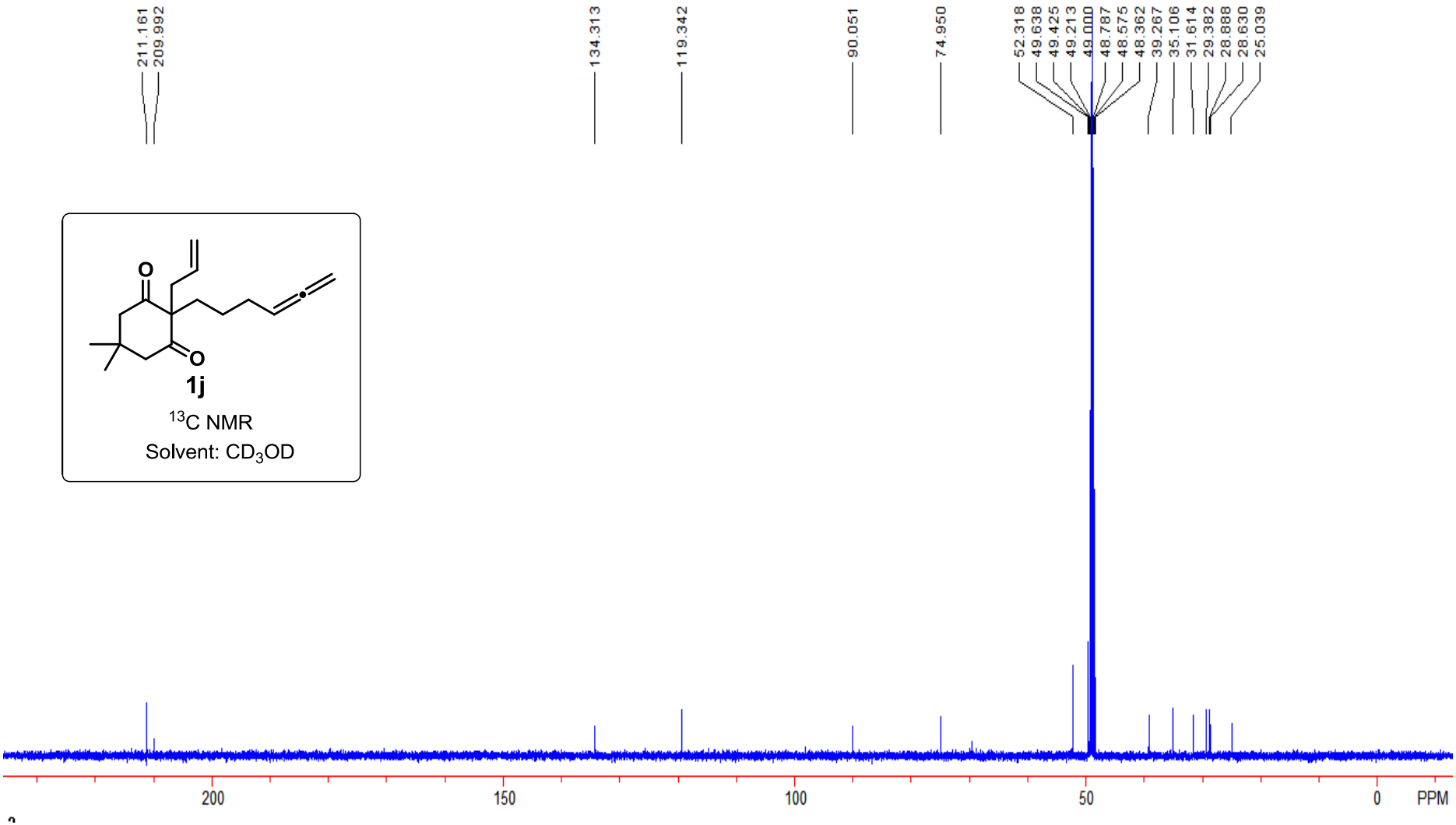
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134.313
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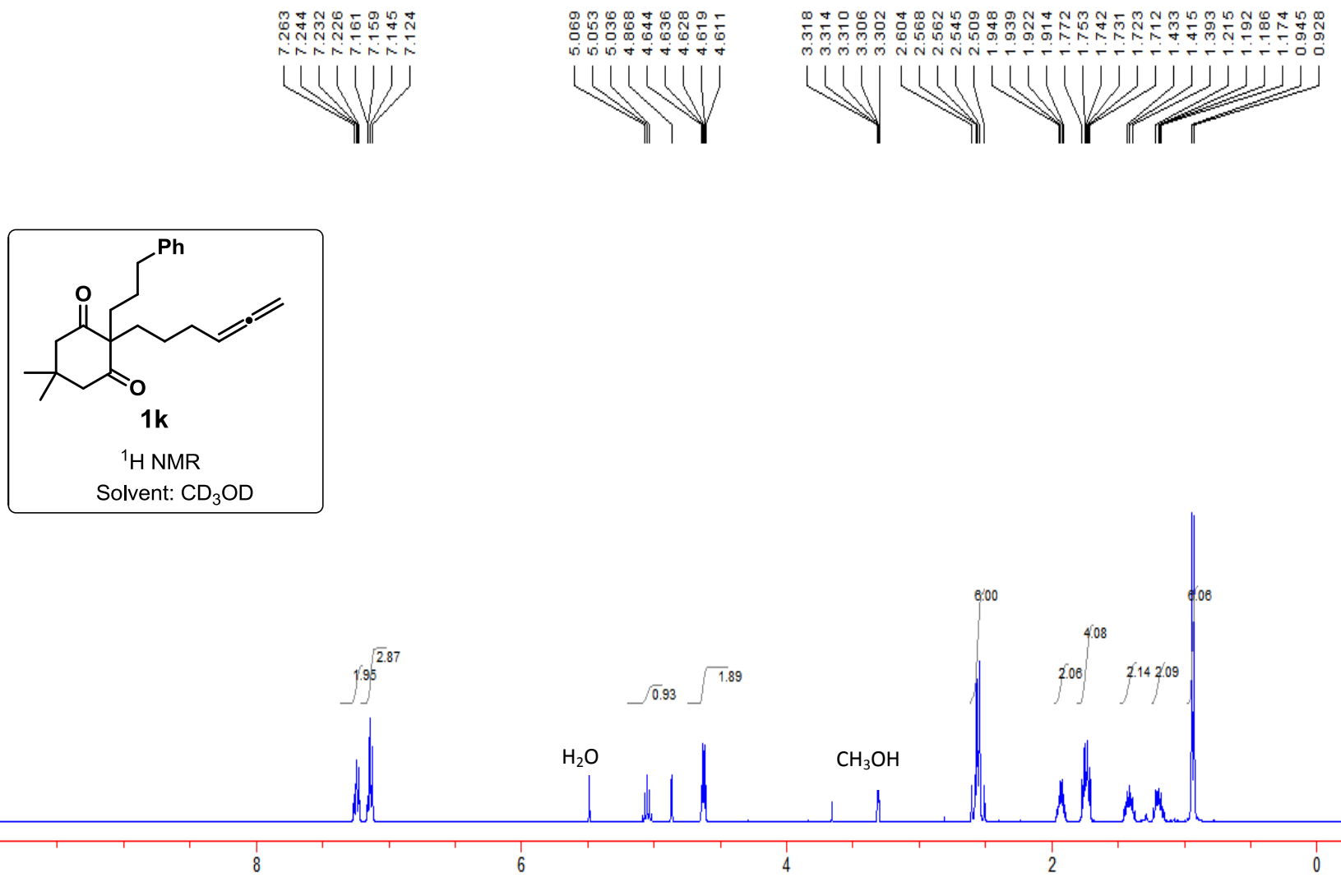
49.638
49.425
49.213
49.000
48.787
48.575
48.362
39.267
35.106
31.614
29.382
28.888
28.630
25.039
O
O
1j
13C NMR
Solvent: CD3OD
200
150
100
50
0
PPM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7.232
7.226
7.161
7.159
7.145
7.124
5.069
5.053
5.036
4.868
4.644
4.636
4.628
4.619
4.611
3.318
3.314
3.310
3.306
3.302
2.604
2.568
2.562
2.545
2.509
1.948
1.939
1.922
1.914
1.772
1.753
1.742
1.731
1.723
1.712
1.433
1.415
1.393
1.215
1.192
1.186
1.174
0.945
0.928
Ph
O
O
1k
1H NMR
Solvent: CD3OD
1.95
2.87
0.93
1.89
H2O
CH3OH
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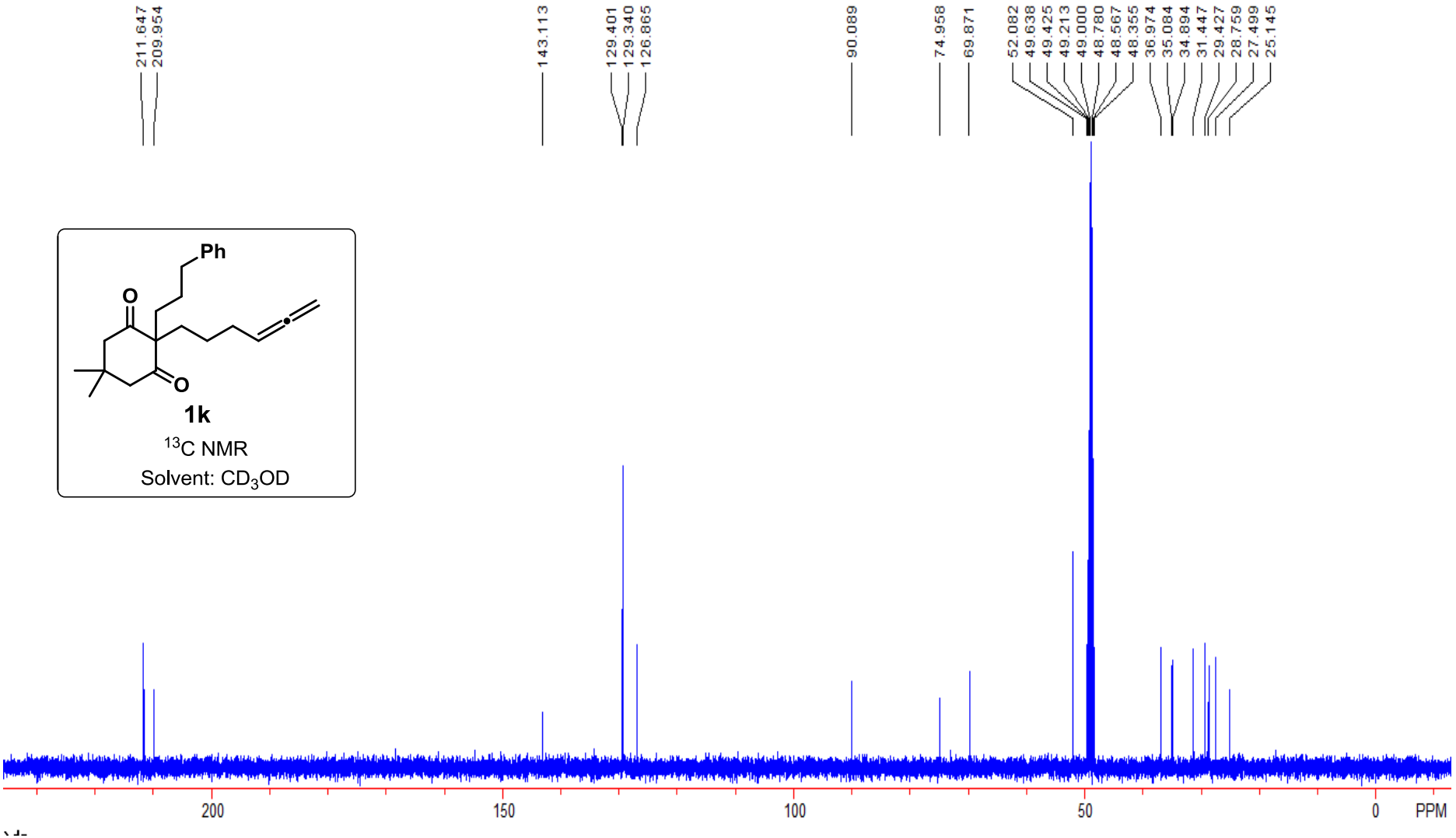
4.08
2.14
2.09
6.06
10
8
6
4
2
0
PPM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74.958
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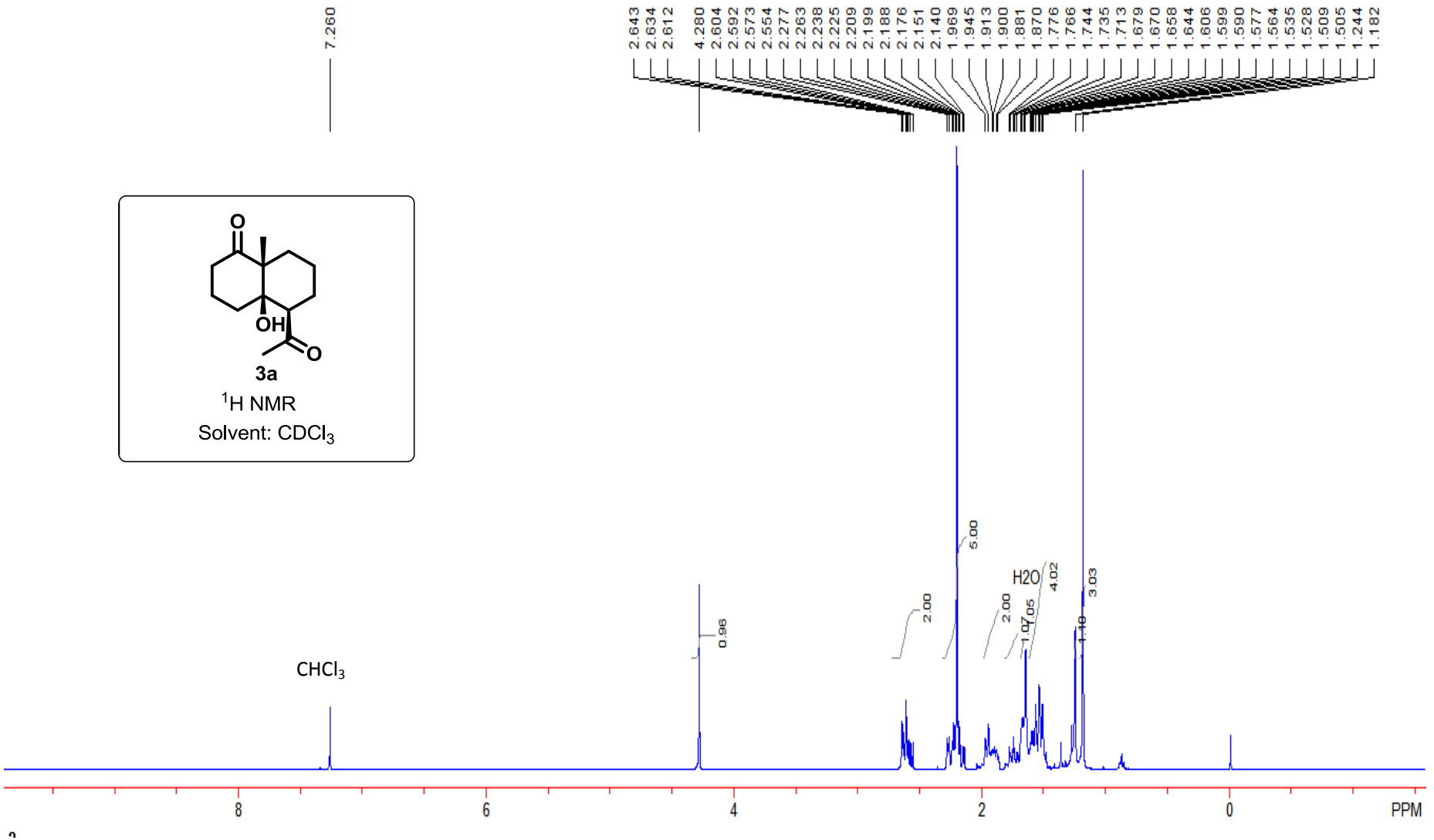
49.213
49.000
48.780
48.567
48.355
36.974
35.084
34.894
31.447
29.427
28.759
27.499
25.145
Ph
O
O
1k
13C NMR
Solvent: CD3OD
200
150
100
50
0
PPM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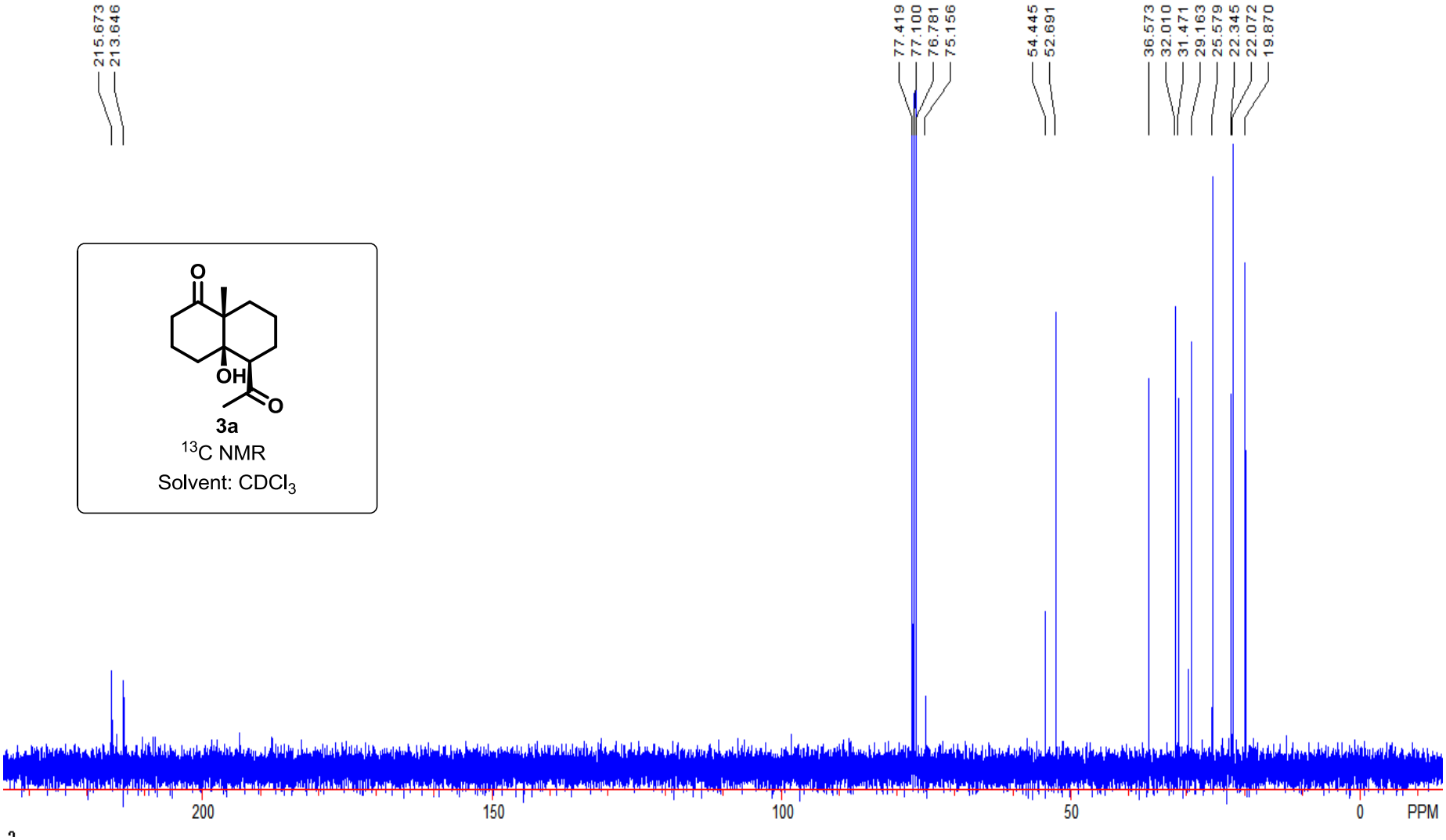
2.634
2.612
4.280
2.604
2.592
2.573
2.554
2.277
2.263
2.238
2.225
2.209
2.199
2.188
2.176
2.151
2.140
1.969
1.945
1.913
1.900
1.881
1.870
1.776
1.766
1.744
1.735
1.713
1.679
1.670
1.658
1.644
1.606
1.599
1.590
1.577
1.564
1.535
1.528
1.509
1.505
1.244
1.182
O
OH
O
3a
1H NMR
Solvent: CDCl3
CHCl3
0.96
2.00
5.00
H2O
4.02
2.00
1.05
1.07
1.10
3.03
8
6
4
2
0
PPM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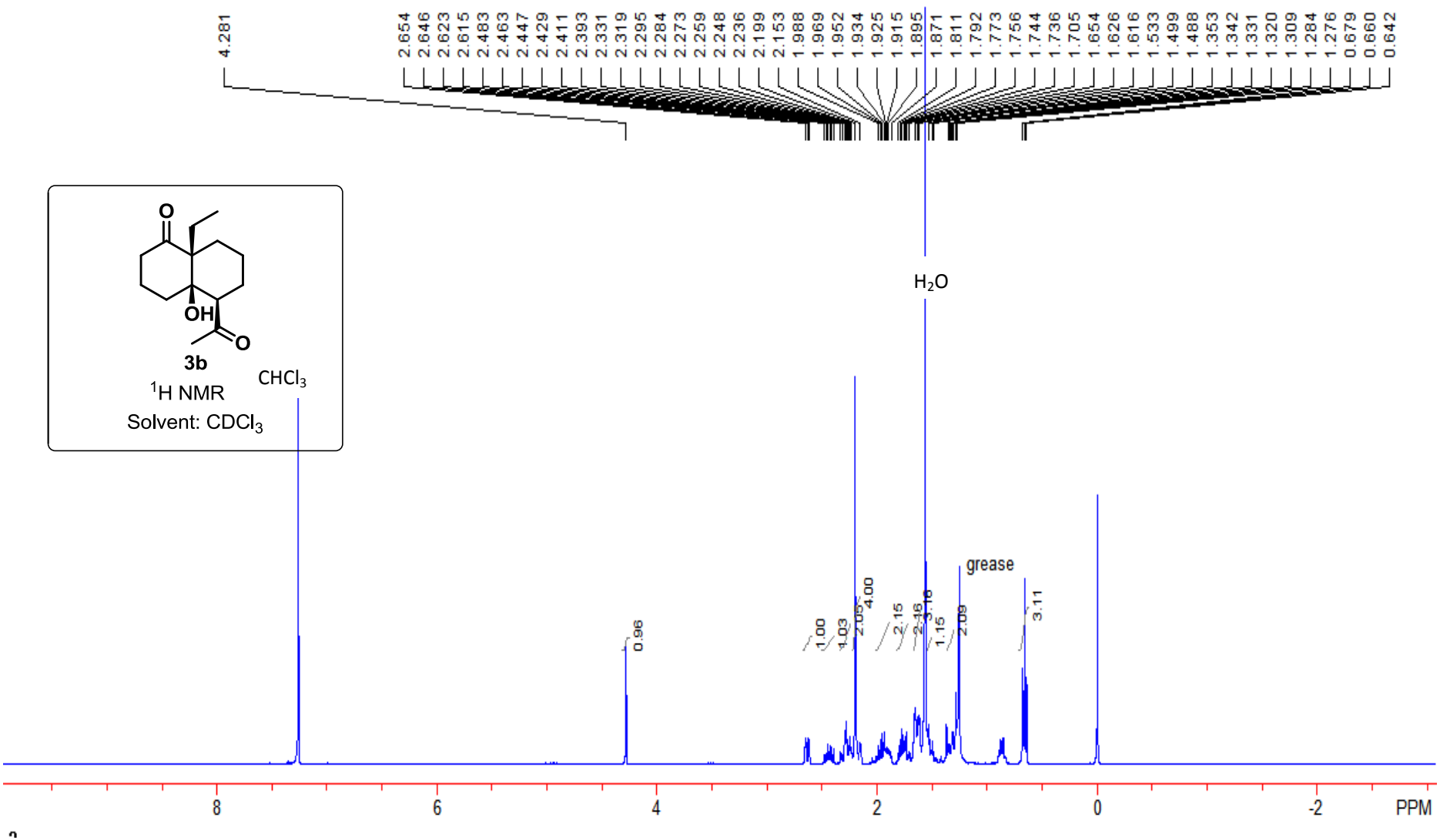
213.646
77.419
77.100
76.781
75.156
54.445
52.691
36.573
32.010
31.471
29.163
25.579
22.345
22.072
19.870
O
OH
O
3a
13C NMR
Solvent: CDCl3
200
150
100
50
0
PPM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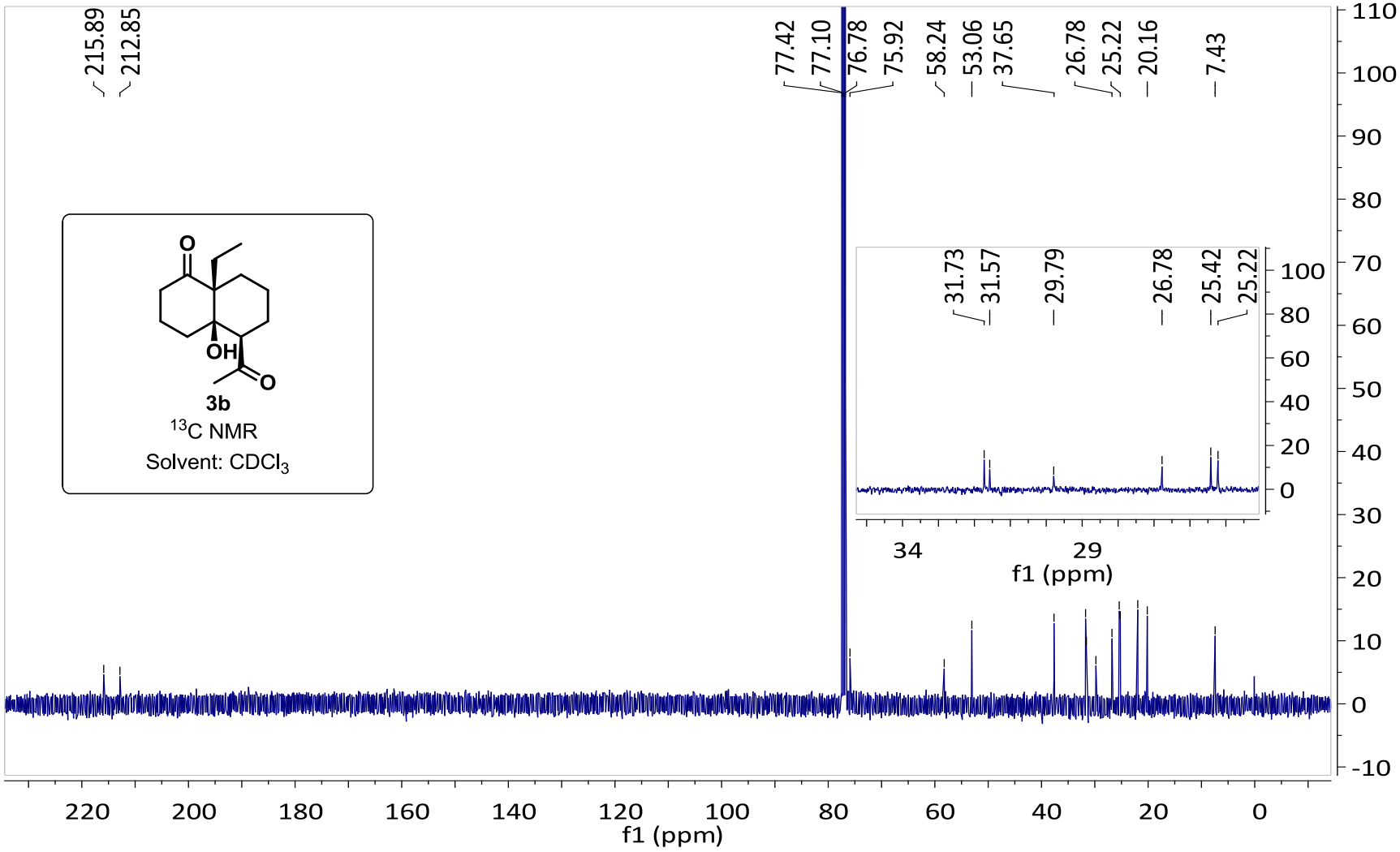
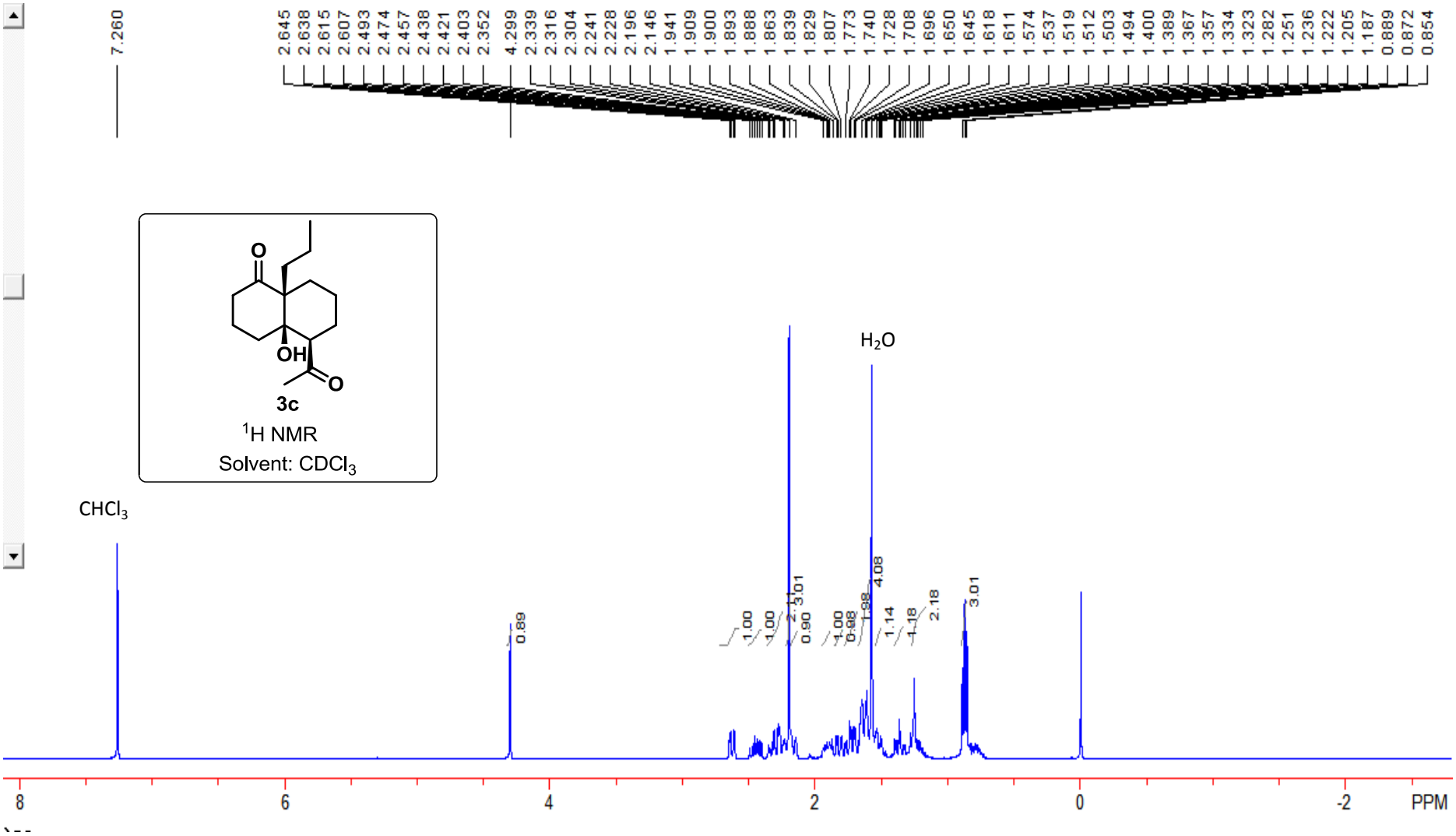
2.654
2.646
2.623
2.615
2.483
2.463
2.447
2.429
2.411
2.393
2.331
2.319
2.295
2.284
2.273
2.259
2.248
2.236
2.199
2.153
1.988
1.969
1.952
1.934
1.925
1.915
1.895
1.871
1.811
1.792
1.773
1.756
1.744
1.736
1.705
1.654
1.626
1.616
1.533
1.499
1.488
1.353
1.342
1.331
1.320
1.309
1.284
1.276
0.679
0.660
0.642
O
OH
O
3b
1H NMR
Solvent: CDCl3
CHCl3
H2O
grease
0.96
1.00
1.03
2.05
4.00
2.15
2.18
3.16
1.15
2.09
3.11
8
6
4
2
0
-2
PPM


215.89
212.85
77.42
77.10
76.78
75.92
58.24
53.06
37.65
26.78
25.22
20.16
7.43
O
OH
O
3b
13C NMR
Solvent: CDCl3
31.73
31.57
29.79
26.78
25.42
25.22
34
29
f1 (ppm)
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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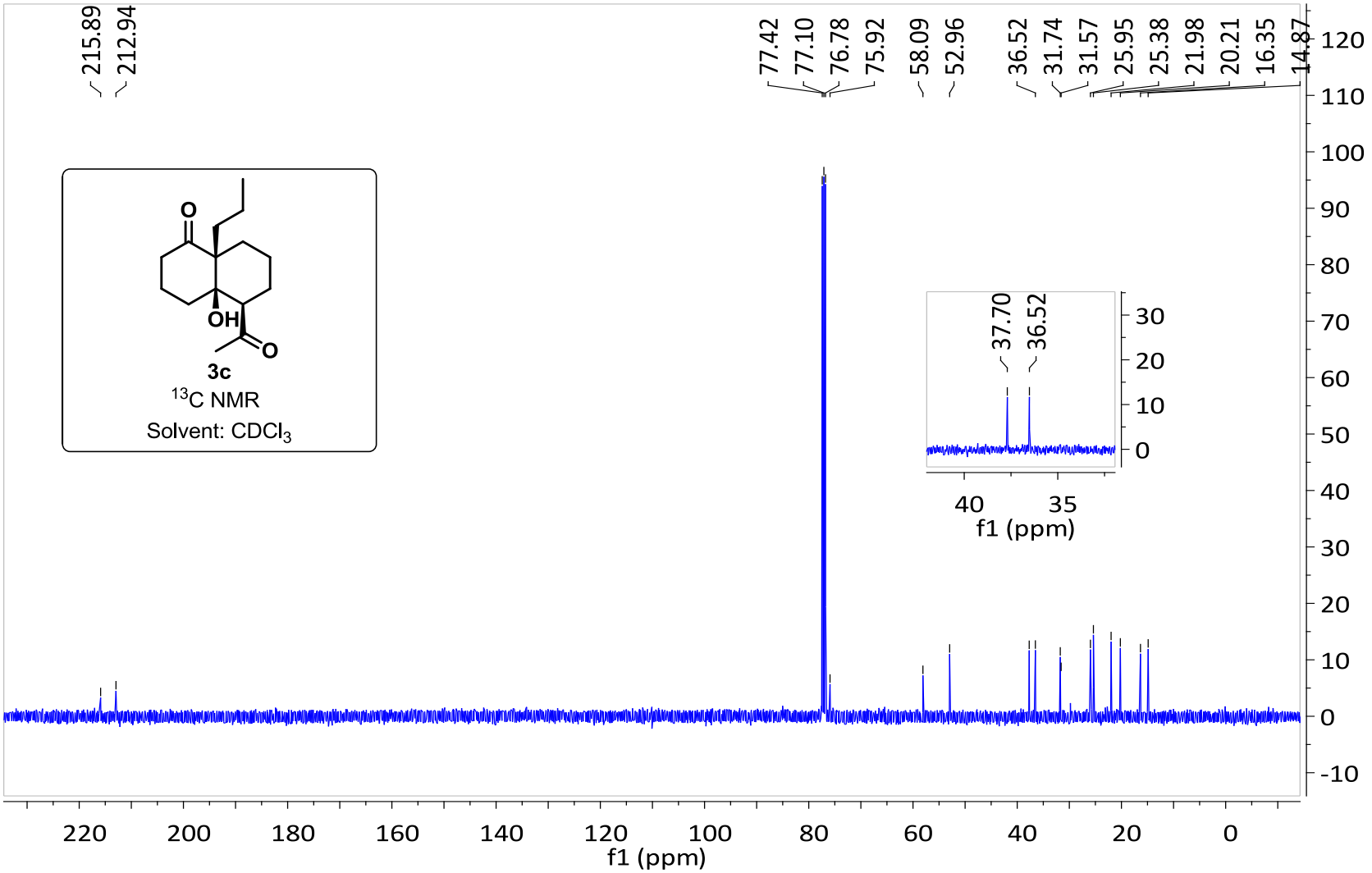
O
OH
O
3c
1H NMR
Solvent: CDCl3
CHCl3
H2O
0.89
1.00 1.00 2.11 3.01 0.90 1.00 0.98 1.98 4.08 1.14 1.18 2.18 3.01
8
6
4
2
0
-2
PPM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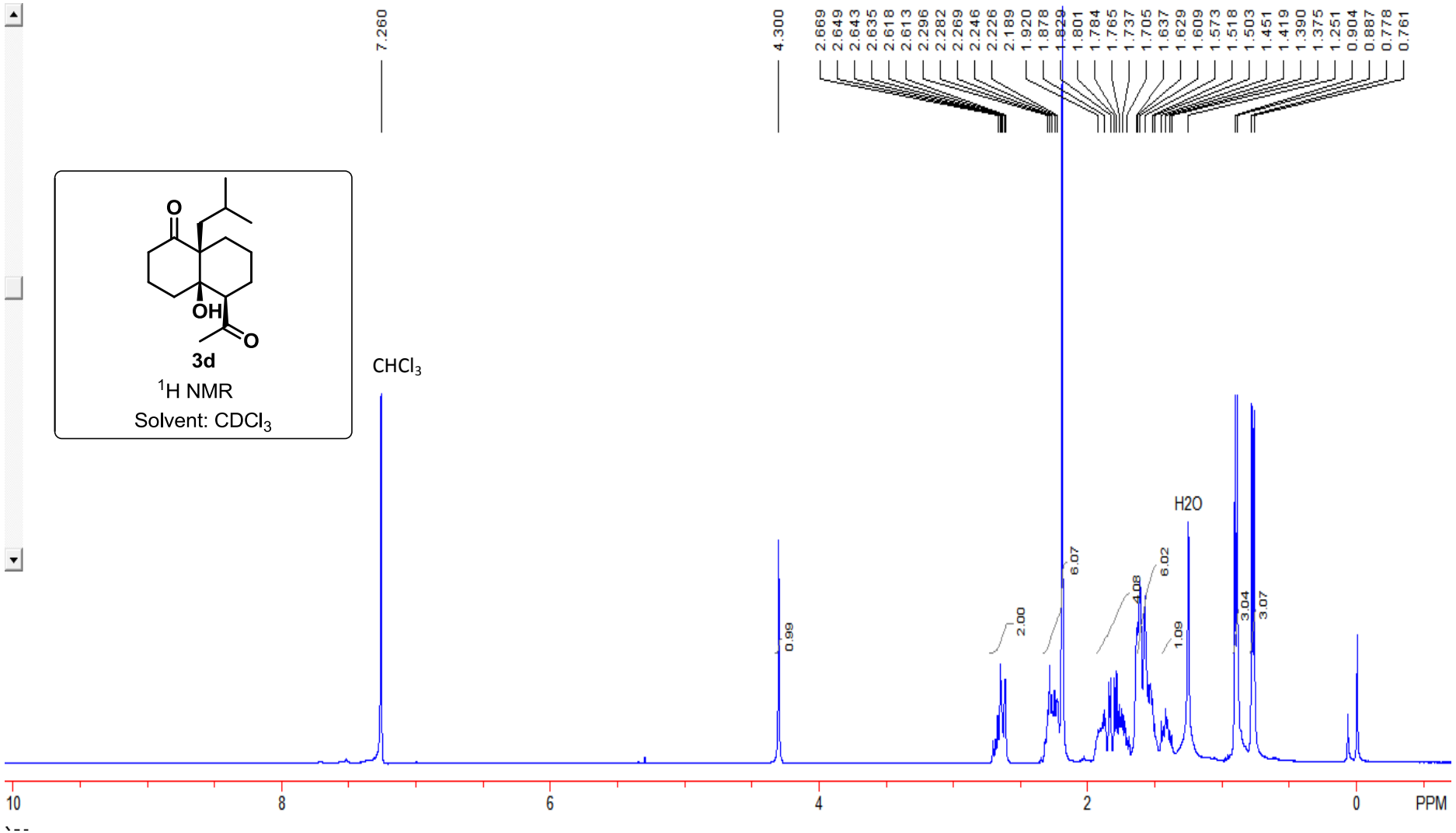
77.10
76.78
75.92
58.09
52.96
36.52
31.74
31.57
25.95
25.38
21.98
20.21
16.35
14.87
O
OH
O
3c
13C NMR
Solvent: CDCl3
37.70
36.52
40
35
f1 (ppm)
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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4.300
2.669
2.649
2.643
2.635
2.618
2.613
2.296
2.282
2.269
2.246
2.226
2.189
1.920
1.878
1.829
1.801
1.784
1.765
1.737
1.705
1.637
1.629
1.609
1.573
1.518
1.503
1.451
1.419
1.390
1.375
1.251
0.904
0.887
0.778
0.761
O
OH
O
3d
1H NMR
Solvent: CDCl3
CHCl3
H2O
0.99
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4.08
6.02
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10
8
6
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2
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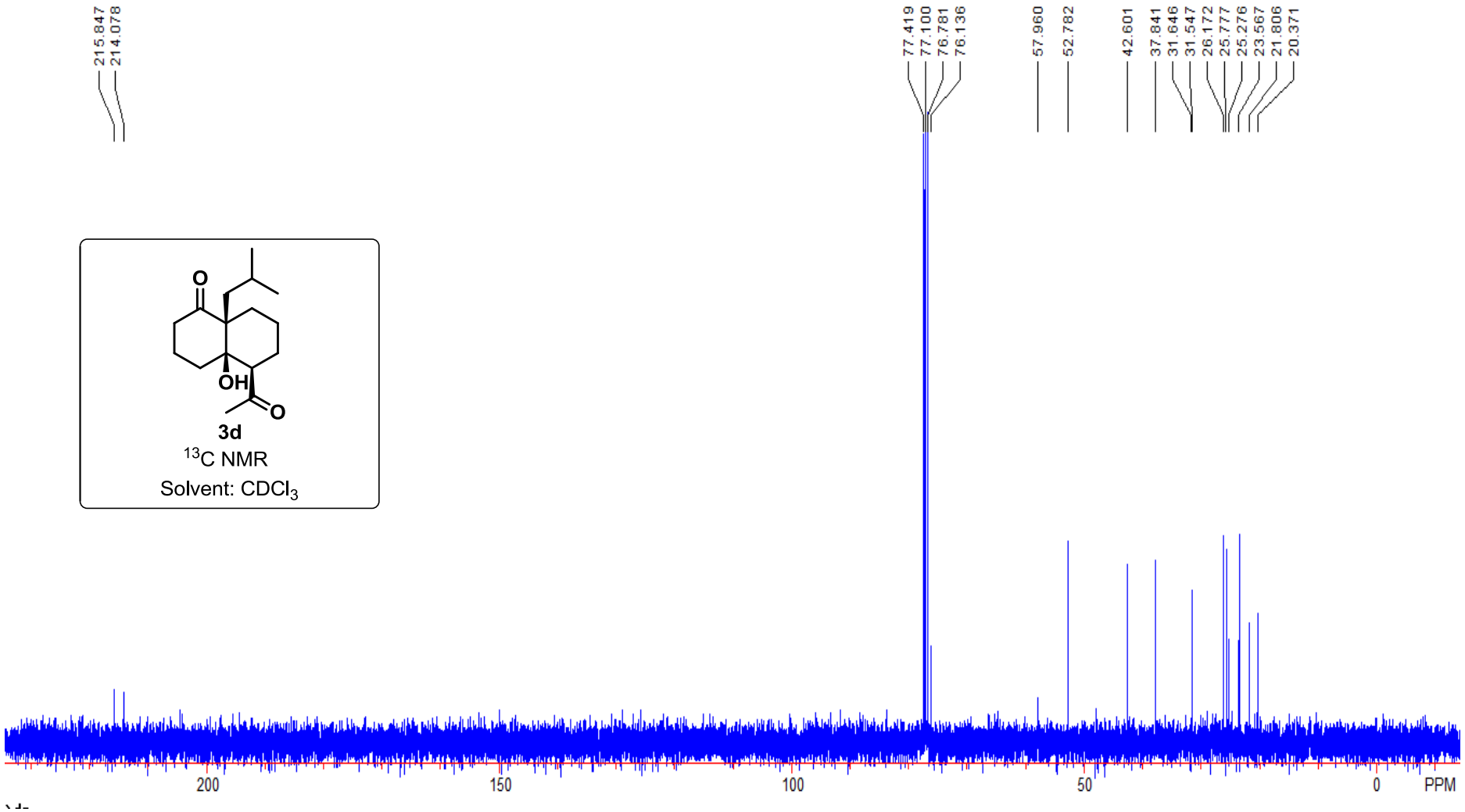
PPM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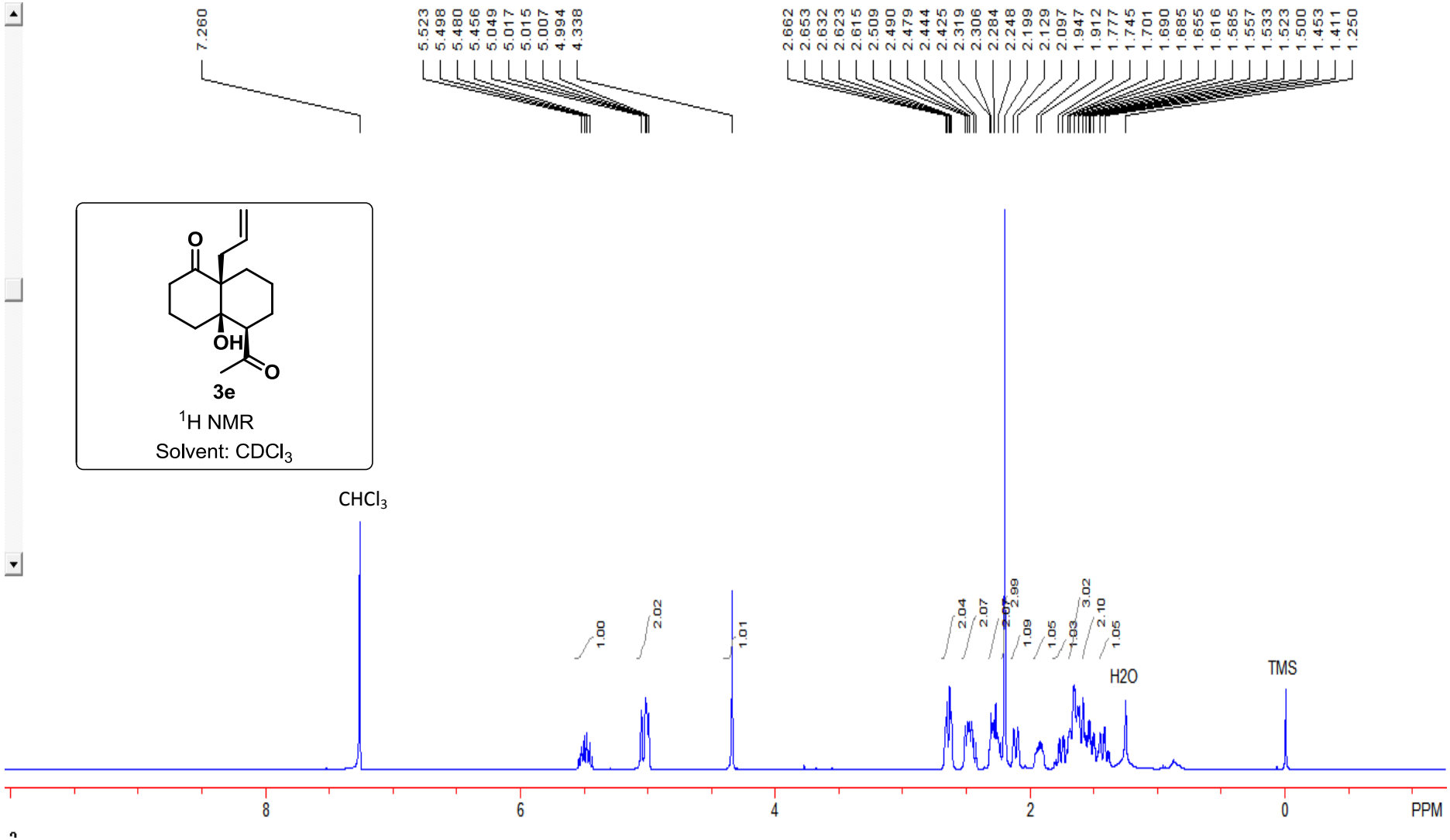
214.078
77.419
77.100
76.781
76.136
57.960
52.782
42.601
37.841
31.646
31.547
26.172
25.777
25.276
23.567
21.806
20.371
O
OH
O
3d
13C NMR
Solvent: CDCl3
200
150
100
50
0
PPM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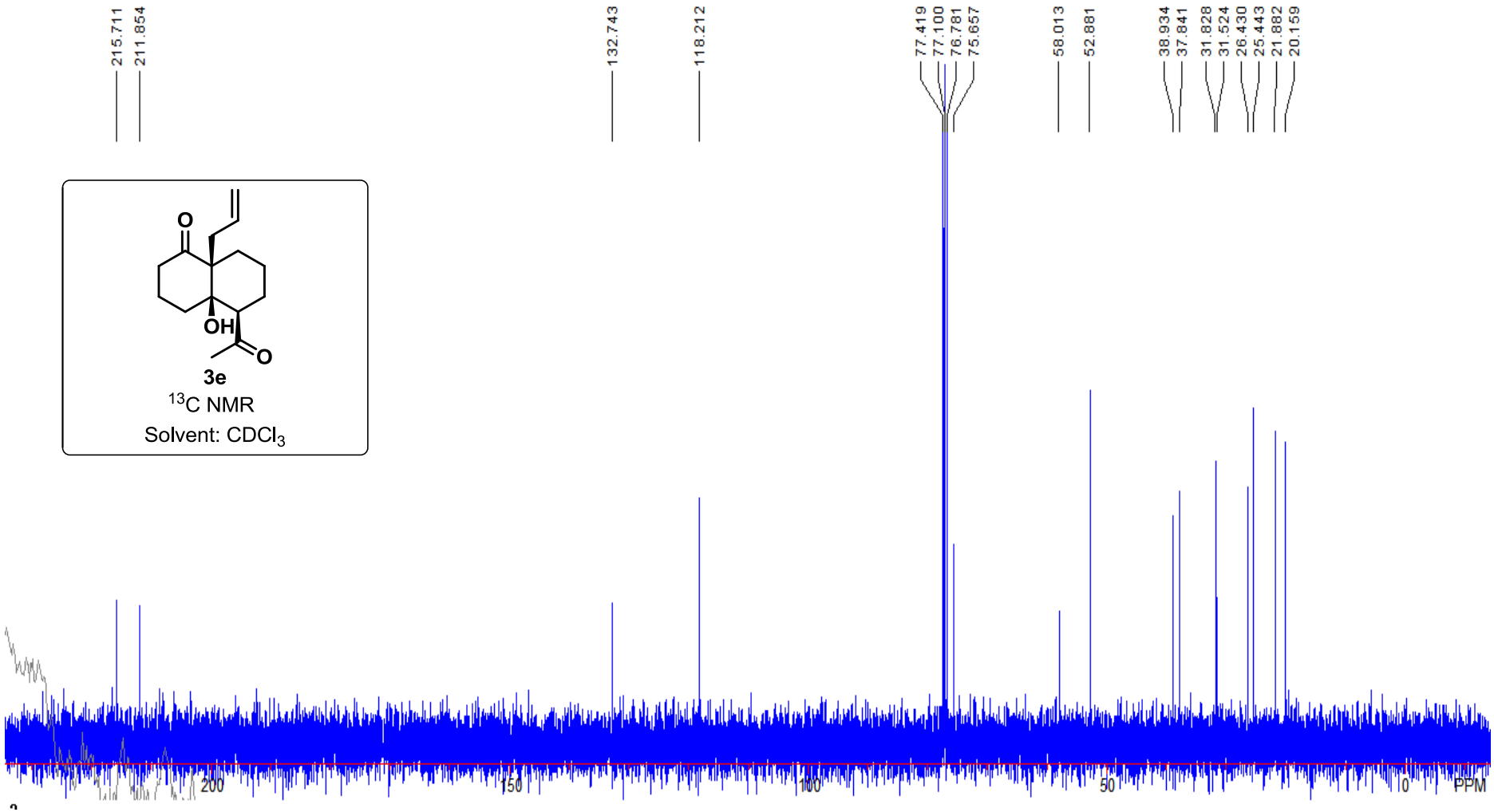
5.480
5.456
5.049
5.017
5.015
5.007
4.994
4.338
2.662
2.653
2.632
2.623
2.615
2.509
2.490
2.479
2.444
2.425
2.319
2.306
2.284
2.248
2.199
2.129
2.097
1.947
1.912
1.777
1.745
1.701
1.690
1.685
1.655
1.616
1.585
1.557
1.533
1.523
1.500
1.453
1.411
1.250
O
OH
O
3e
1H NMR
Solvent: CDCl3
CHCl3
1.00
2.02
1.01
2.04
2.07
2.01
2.99
1.09
1.05
1.03
3.02
2.10
1.05
H2O
TMS
8
6
4
2
0
PPM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77.100
76.781
75.657
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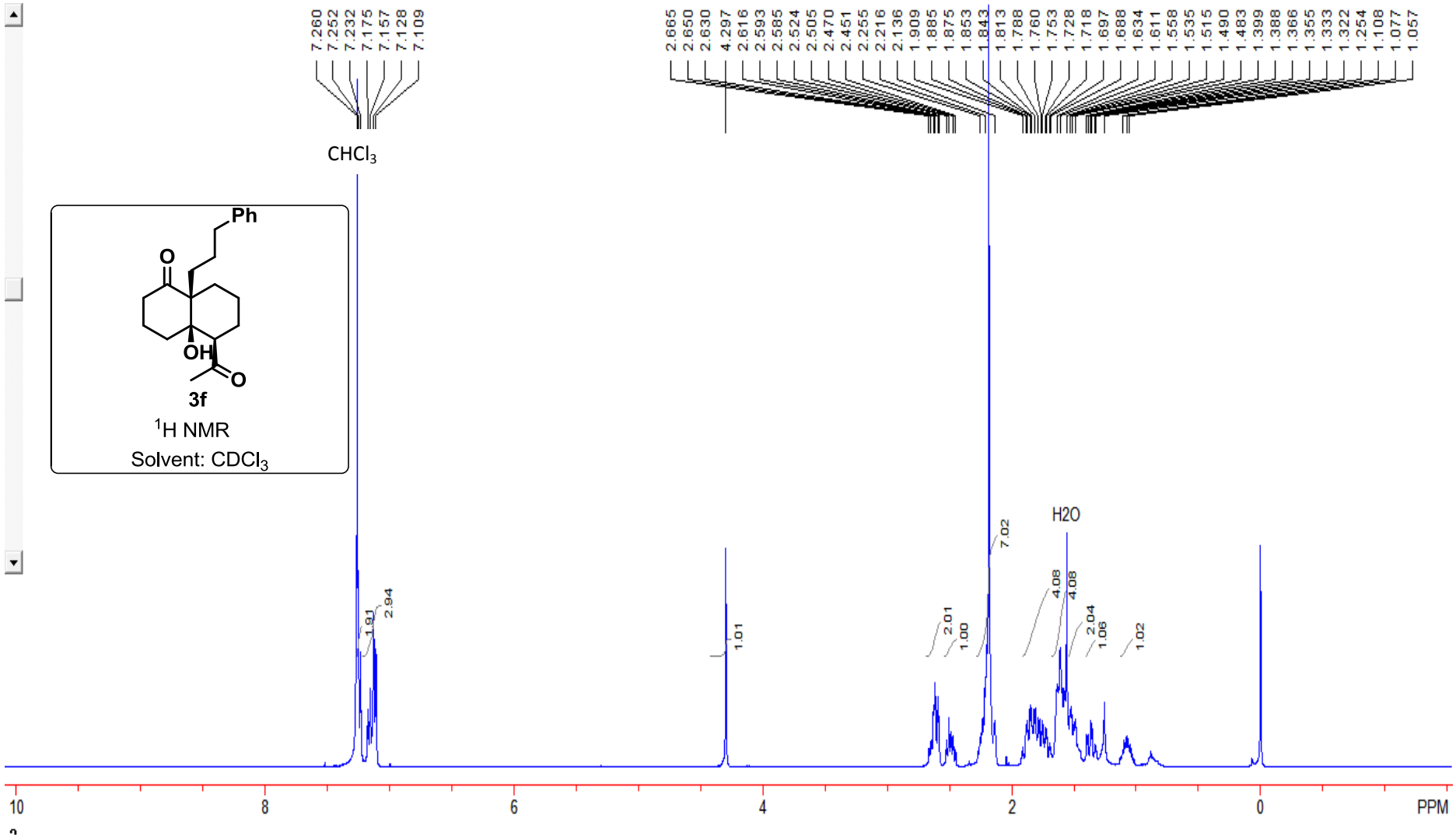
52.881
38.934
37.841
31.828
31.524
26.430
25.443
21.882
20.159
O
OH
O
3e
13C NMR
Solvent: CDCl3
200
150
100
50
0
PPM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7.157
7.128
7.109
CHCl3
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2.650
2.630
4.297
2.616
2.593
2.585
2.524
2.505
2.470
2.451
2.255
2.216
2.136
1.909
1.885
1.875
1.853
1.843
1.813
1.788
1.760
1.753
1.728
1.718
1.697
1.688
1.634
1.611
1.558
1.535
1.515
1.490
1.483
1.399
1.388
1.366
1.355
1.333
1.322
1.254
1.108
1.077
1.057
Ph
O
OH
O
3f
1H NMR
Solvent: CDCl3
H2O
7.02
4.08
4.08
2.01
1.00
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1.06
1.02
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10
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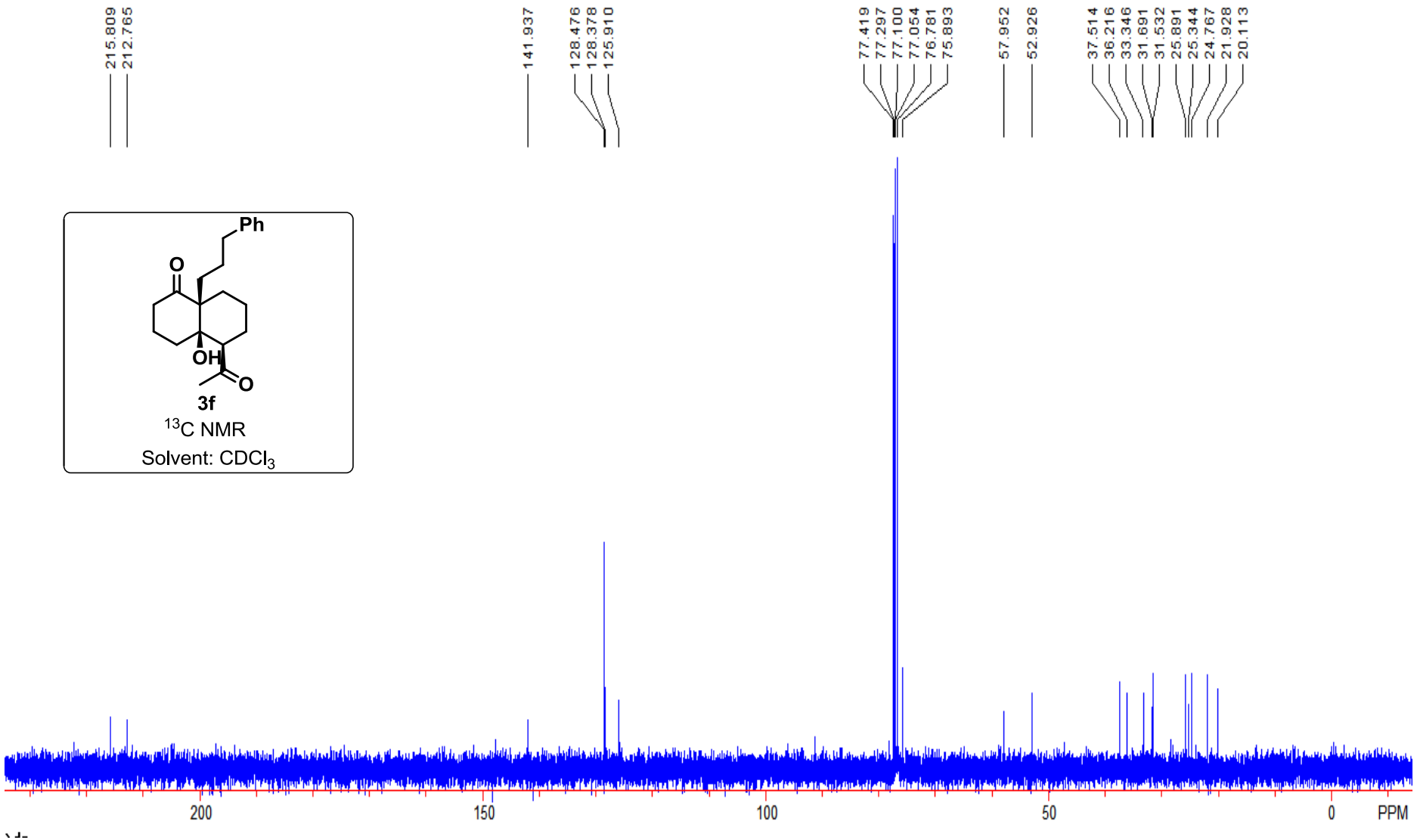
PPM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125.910
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77.054
76.781
75.893
57.952
52.926
37.514
36.216
33.346
31.691
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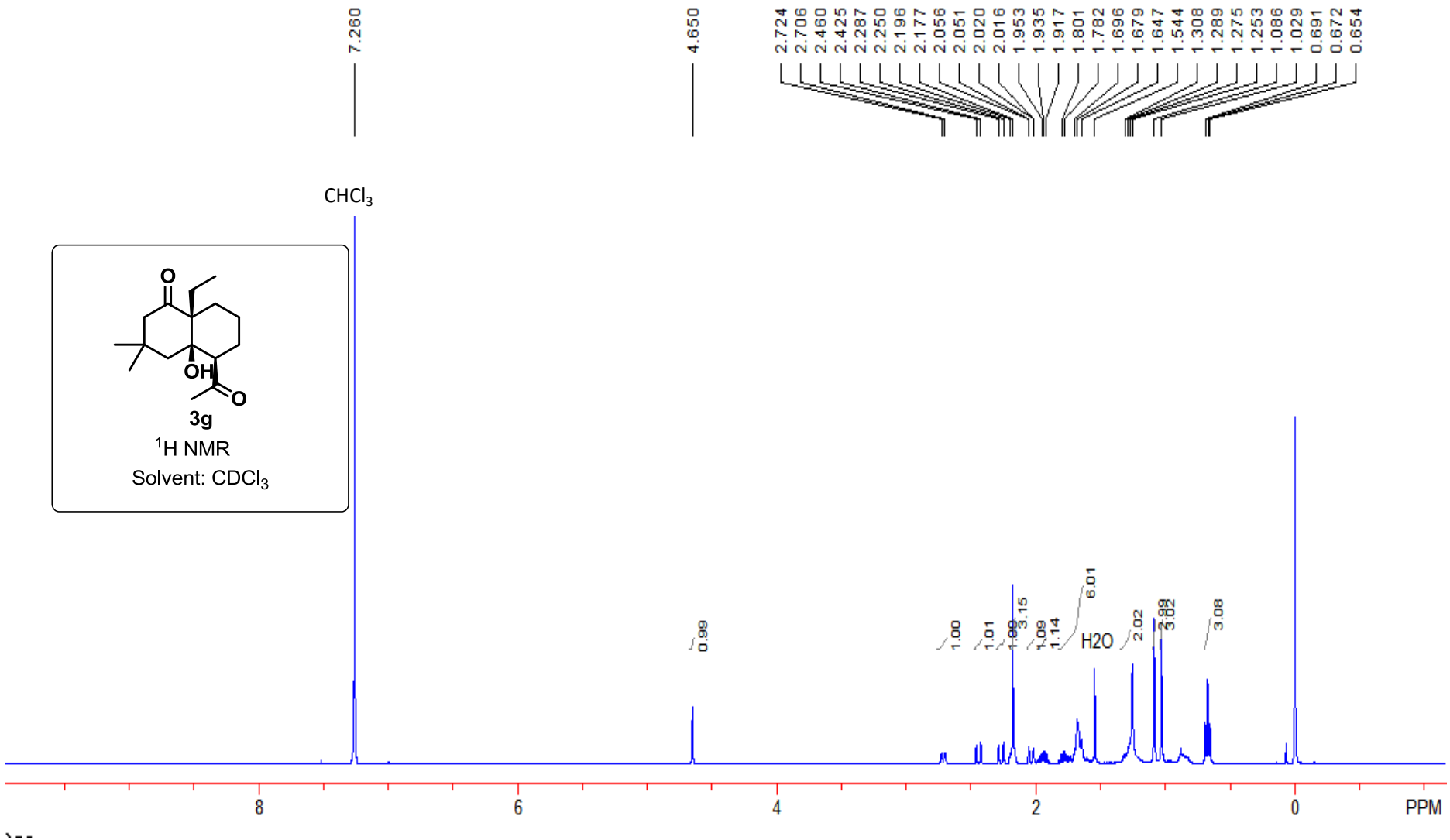
25.891
25.344
24.767
21.928
20.113
Ph
O
OH
O
3f
13C NMR
Solvent: CDCl3
200
150
100
50
0
PPM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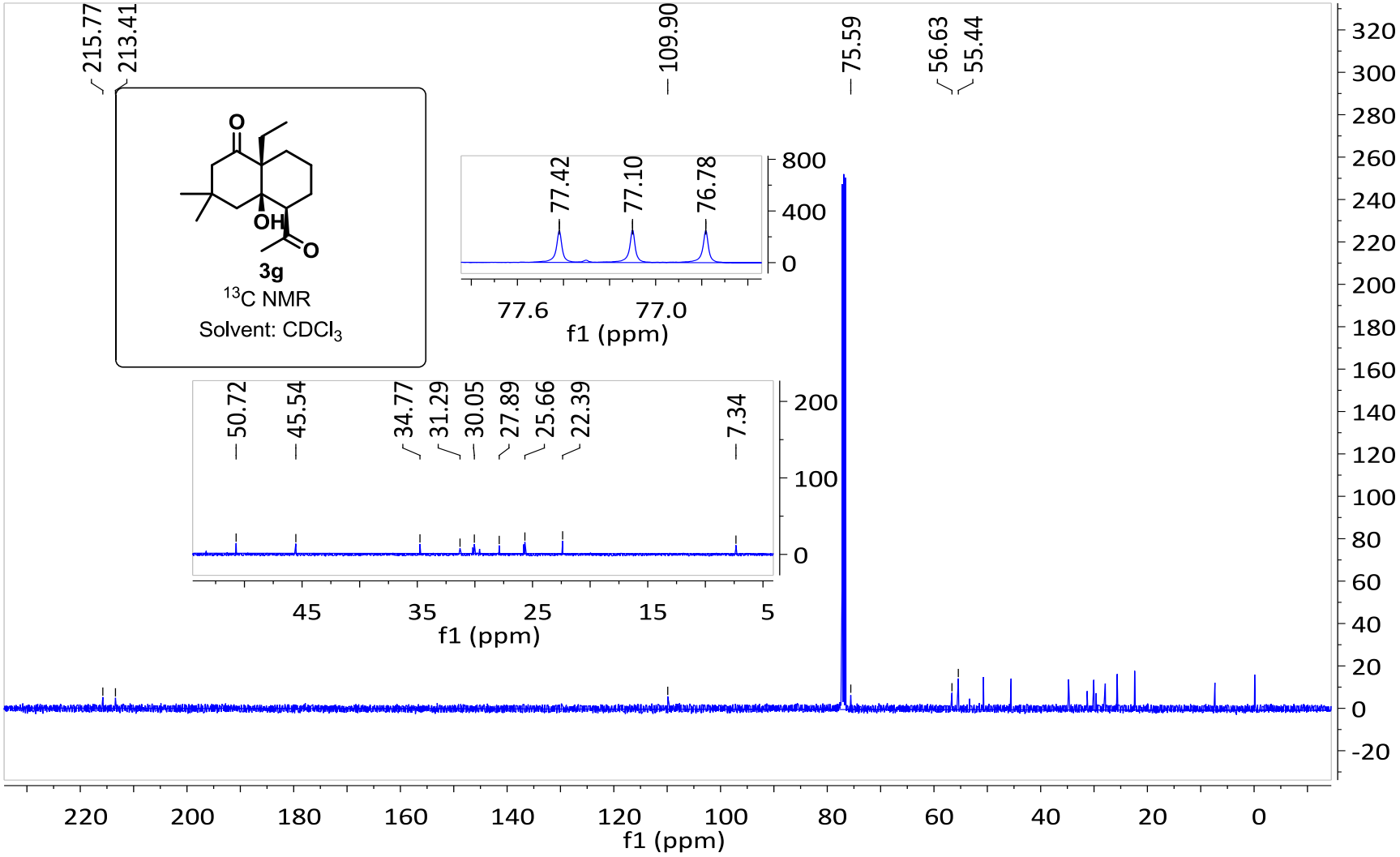
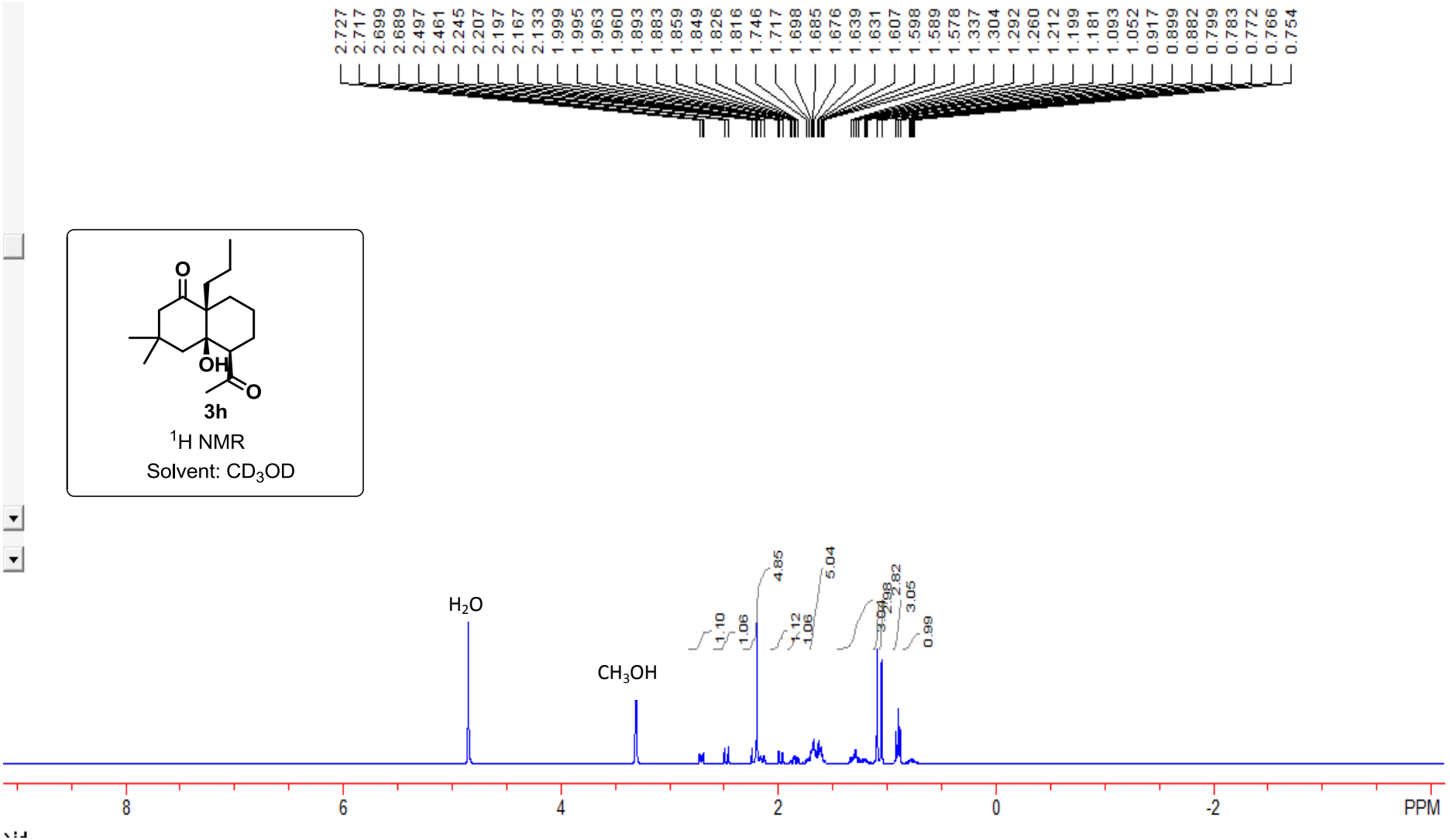
2.051
2.020
2.016
1.953
1.935
1.917
1.801
1.782
1.696
1.679
1.647
1.544
1.308
1.289
1.275
1.253
1.086
1.029
0.691
0.672
0.654
CHCl3
O
OH
O
3g
1H NMR
Solvent: CDCl3
0.99
1.00
1.01
1.09
1.14
3.15
6.01
H2O
2.02
3.08
8
6
4
2
0
PPM


215.77
213.41
109.90
75.59
56.63
55.44
O
OH
O
3g
13C NMR
Solvent: CDCl3
77.42
77.10
76.78
77.6
77.0
f1 (ppm)
50.72
45.54
34.77
31.29
30.05
27.89
25.66
22.39
7.34
45
35
25
15
5
f1 (ppm)
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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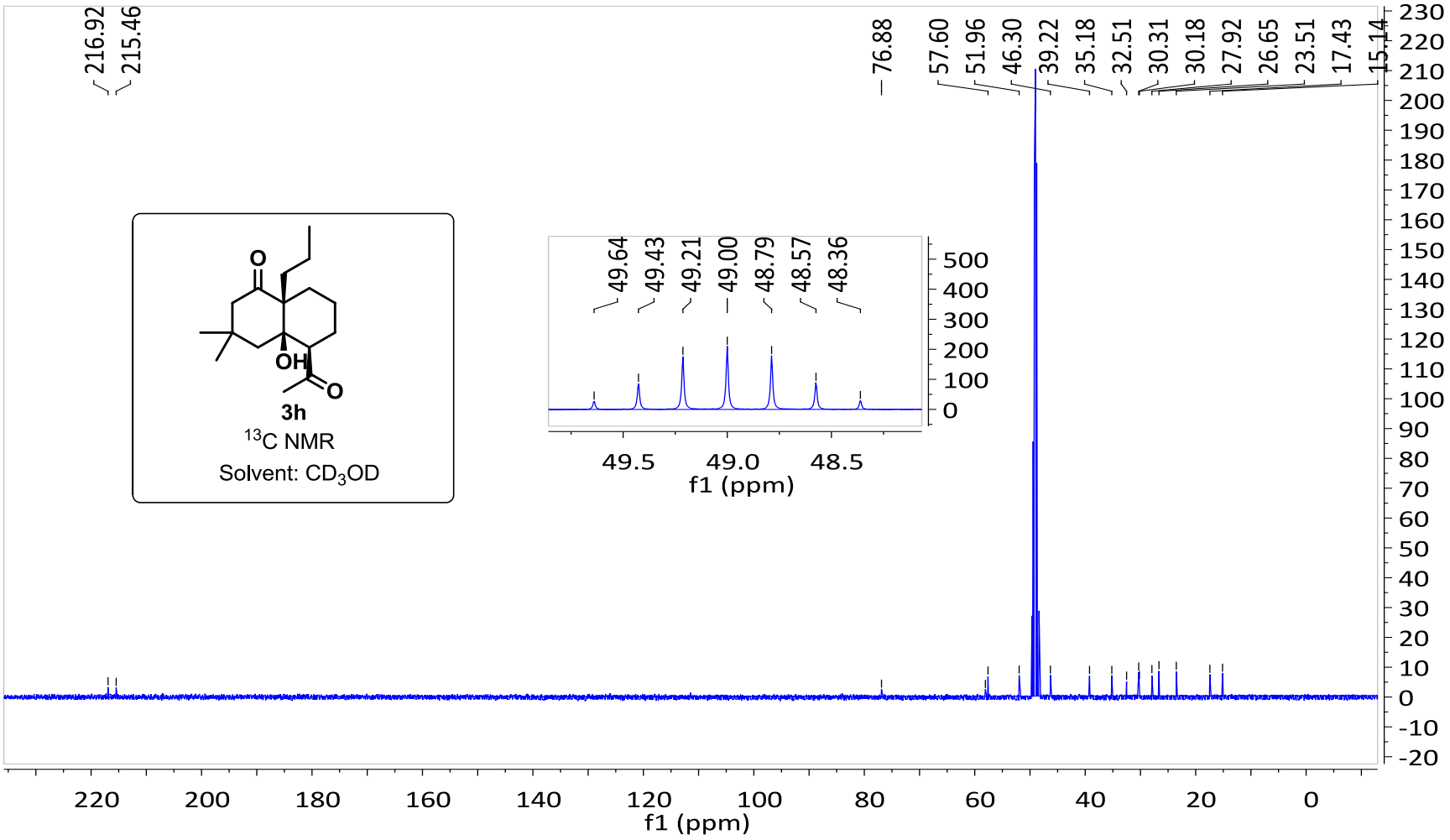
2.717
2.699
2.689
2.497
2.461
2.245
2.207
2.197
2.167
2.133
1.999
1.995
1.963
1.960
1.893
1.883
1.859
1.849
1.826
1.816
1.746
1.717
1.698
1.685
1.676
1.639
1.631
1.607
1.598
1.589
1.578
1.337
1.304
1.292
1.260
1.212
1.199
1.181
1.093
1.052
0.917
0.899
0.882
0.799
0.783
0.772
0.766
0.754
O
OH
O
3h
1H NMR
Solvent: CD3OD
H2O
CH3OH
1.10
1.06
4.85
1.12
1.06
5.04
3.98
2.82
3.05
0.99
8
6
4
2
0
-2
PPM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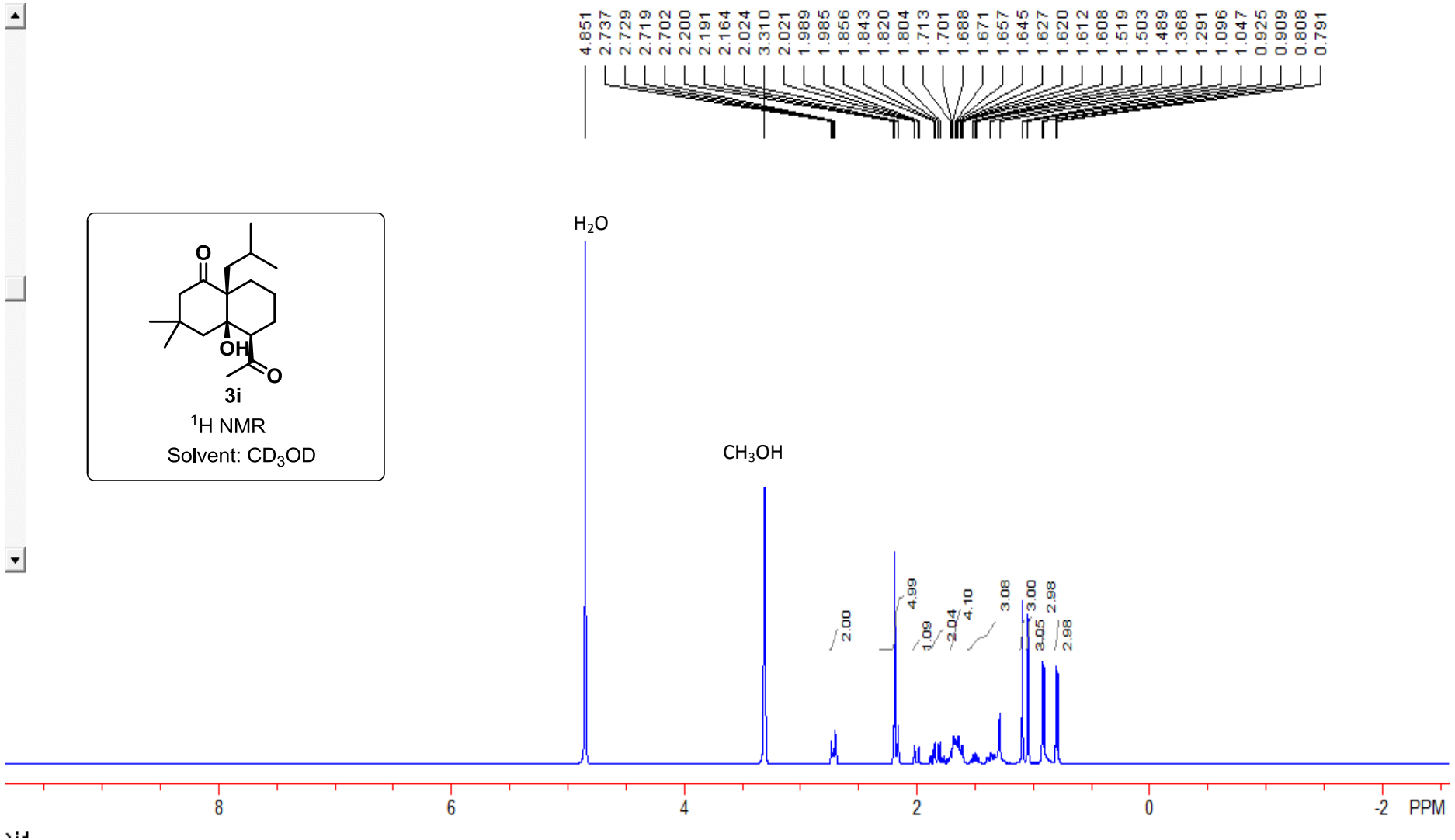
215.46
76.88
57.60
51.96
46.30
39.22
35.18
32.51
30.31
30.18
27.92
26.65
23.51
17.43
15.14
O
OH
O
3h
13C NMR
Solvent: CD3OD
49.64
49.43
49.21
49.00
48.79
48.57
48.36
49.5
49.0
48.5
f1 (ppm)
f1 (ppm)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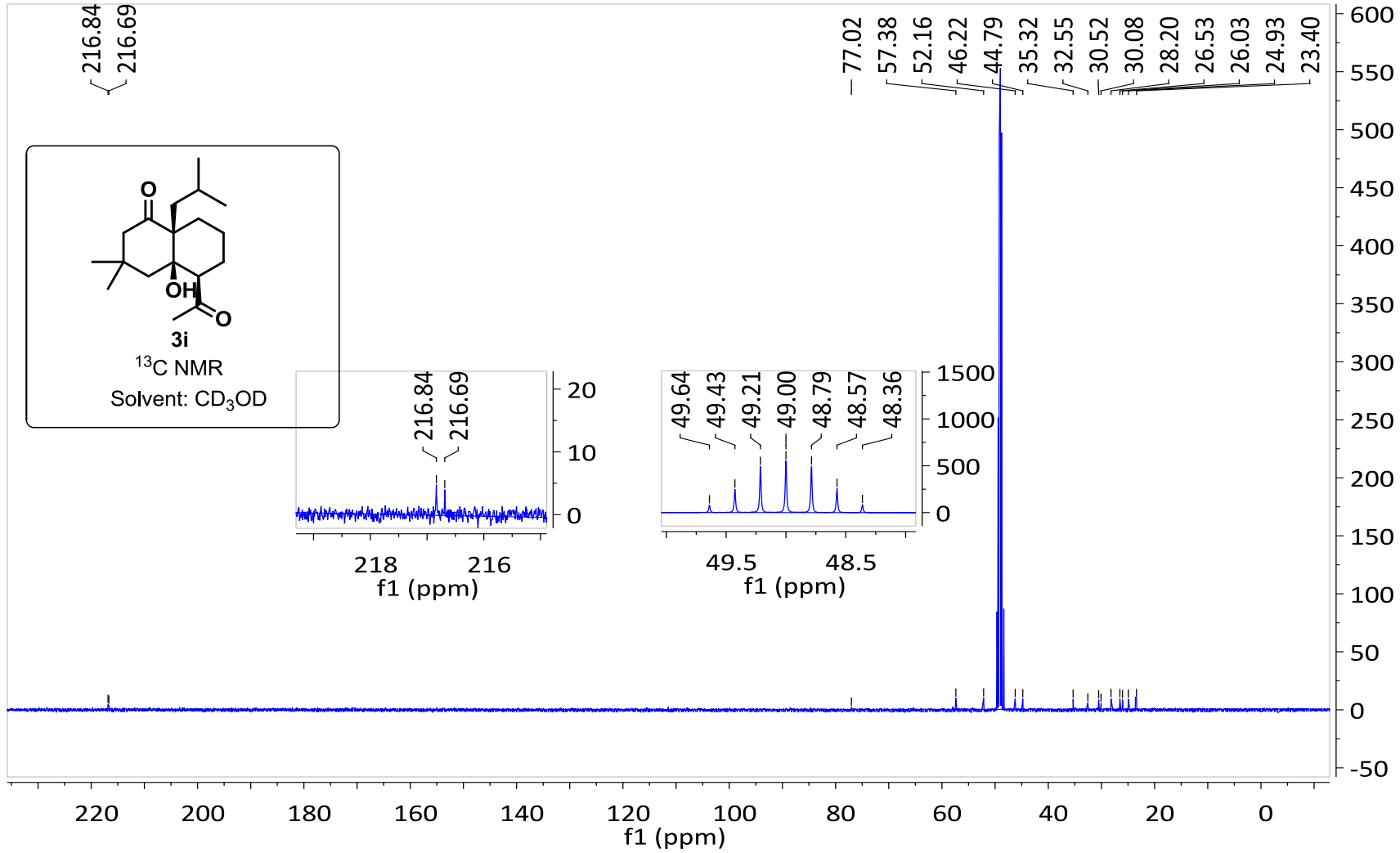
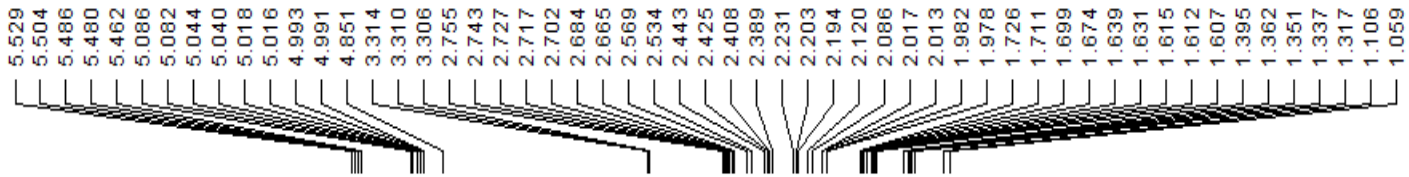
2.737
2.729
2.719
2.702
2.200
2.191
2.164
2.024
3.310
2.021
1.989
1.985
1.856
1.843
1.820
1.804
1.713
1.701
1.688
1.671
1.657
1.645
1.627
1.620
1.612
1.608
1.519
1.503
1.489
1.368
1.291
1.096
1.047
0.925
0.909
0.808
0.791
O
OH
O
3i
1H NMR
Solvent: CD3OD
H2O
CH3OH
2.00
4.99
1.09
2.04
4.10
3.08
3.00
3.05
2.98
2.98
8
6
4
2
0
-2
PPM


216.84
216.69
77.02
57.38
52.16
46.22
44.79
35.32
32.55
30.52
30.08
28.20
26.53
26.03
24.93
23.40
O
OH
O
3i
13C NMR
Solvent: CD3OD
216.84
216.69
49.64
49.43
49.21
49.00
48.79
48.57
48.36
f1 (ppm)
f1 (ppm)
f1 (ppm)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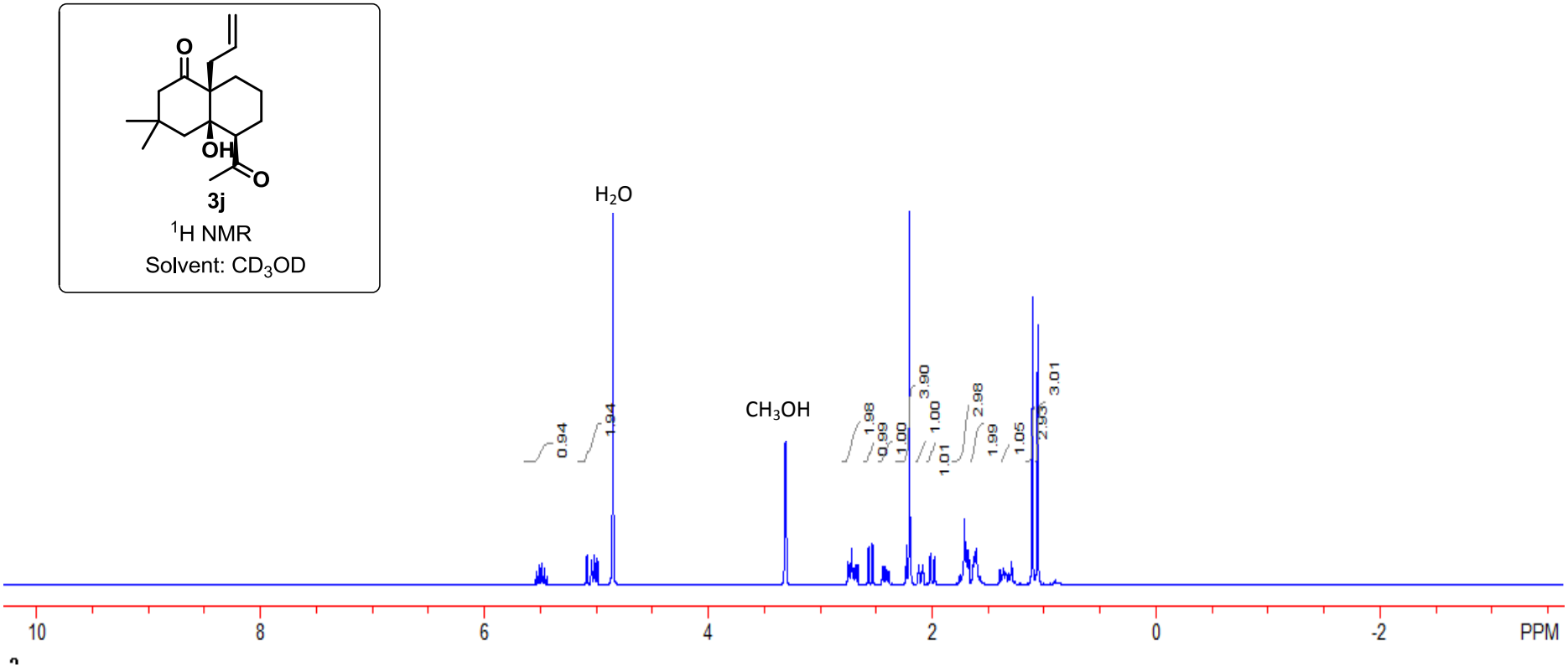
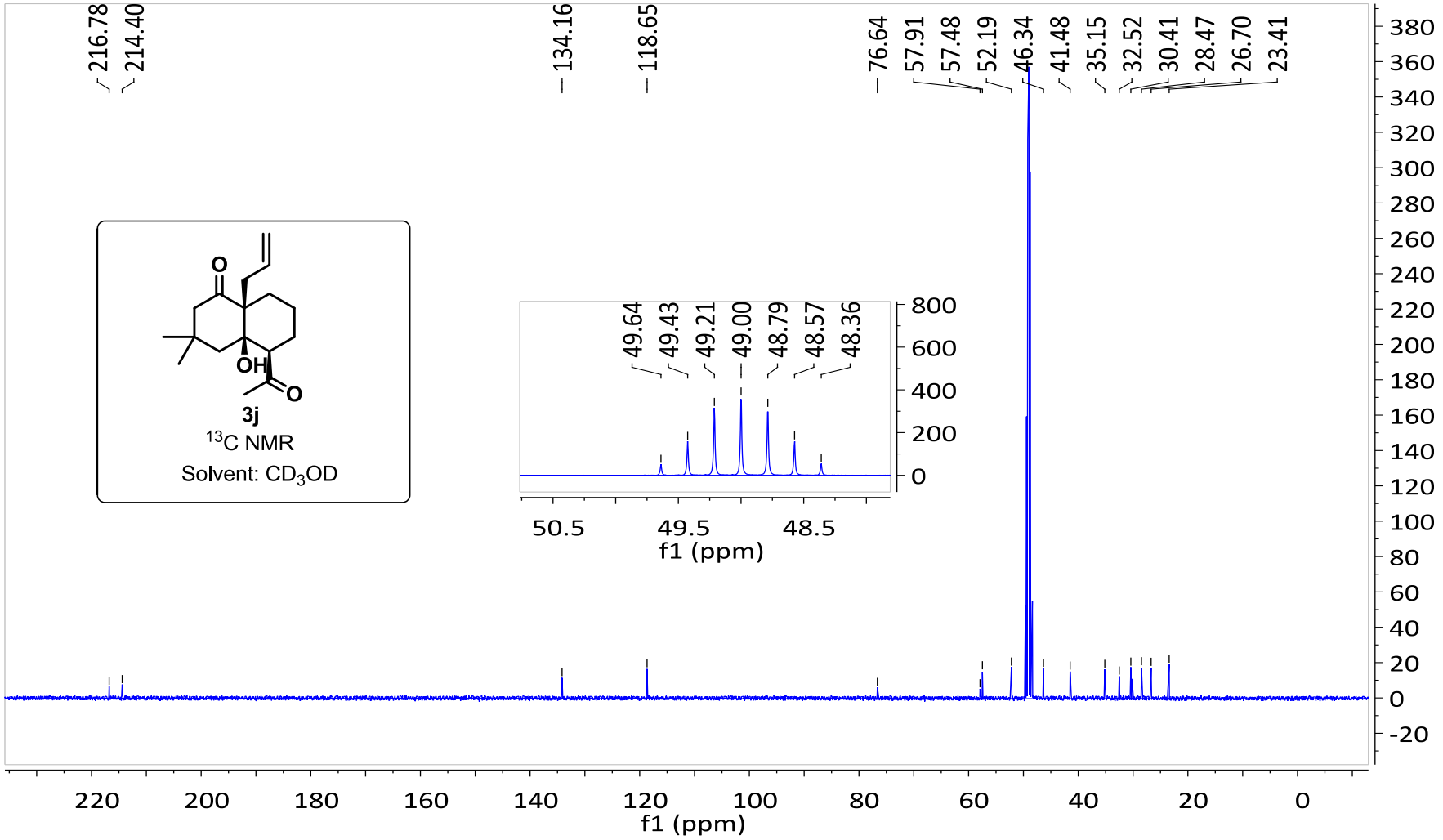
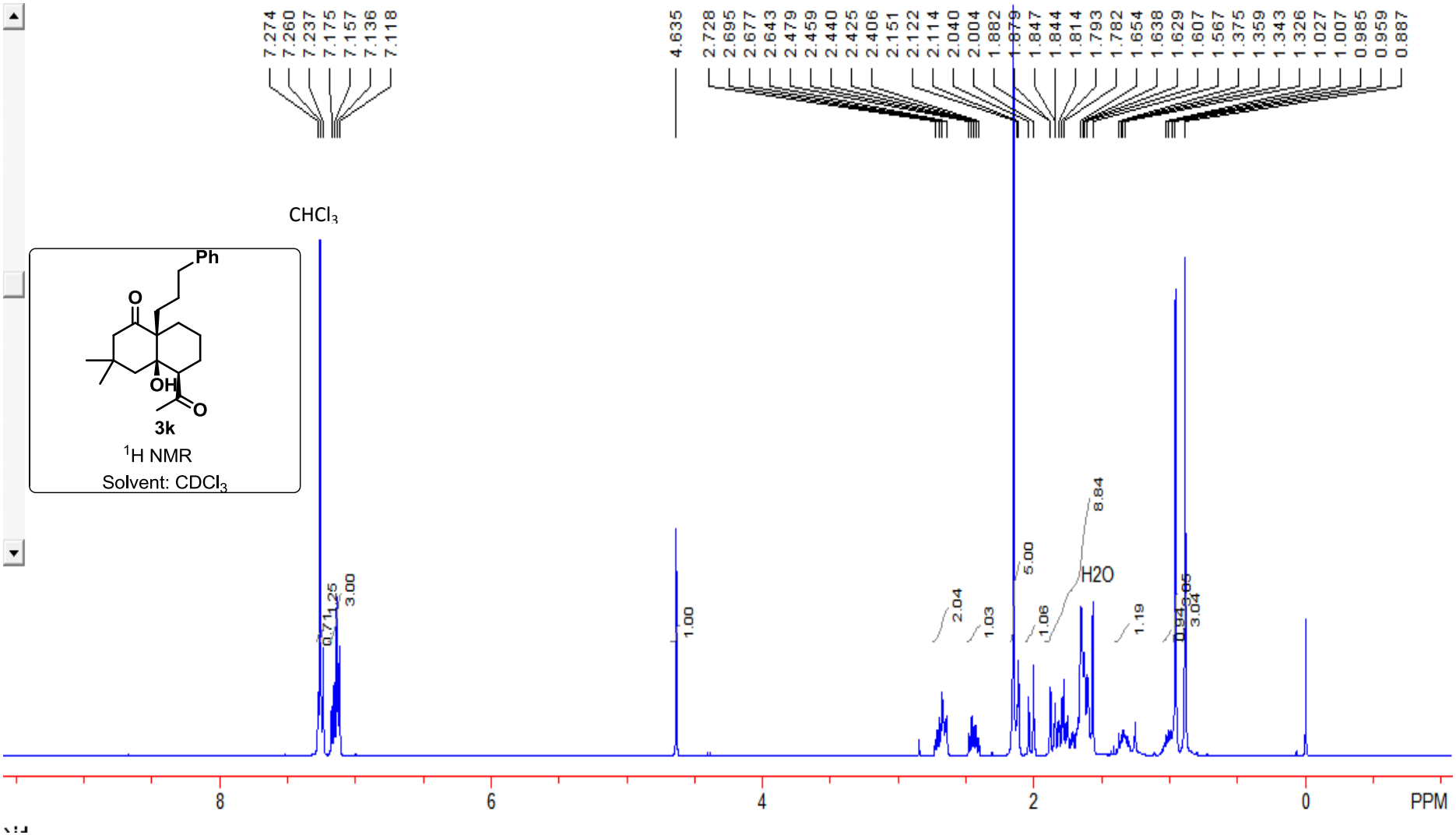
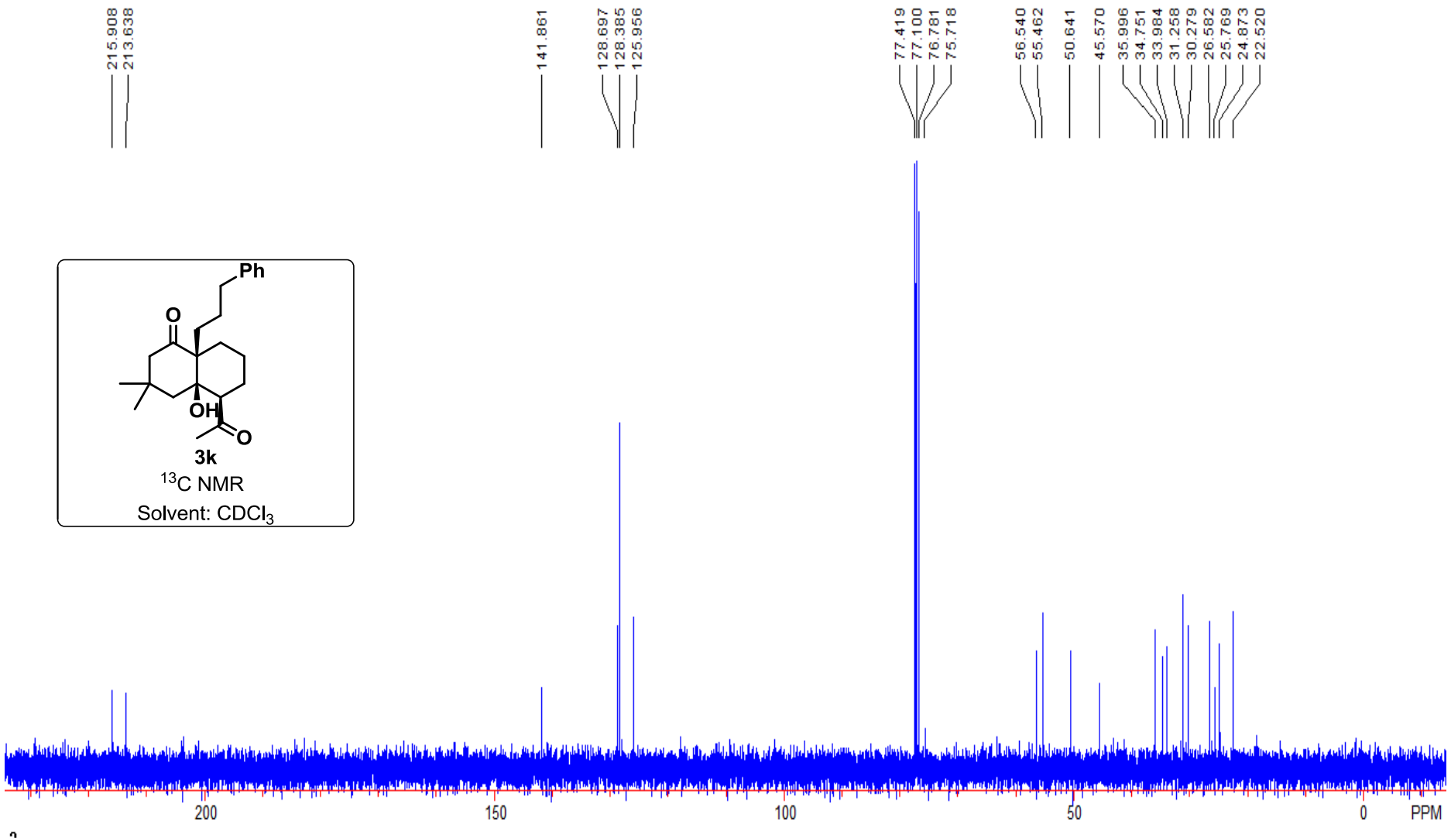
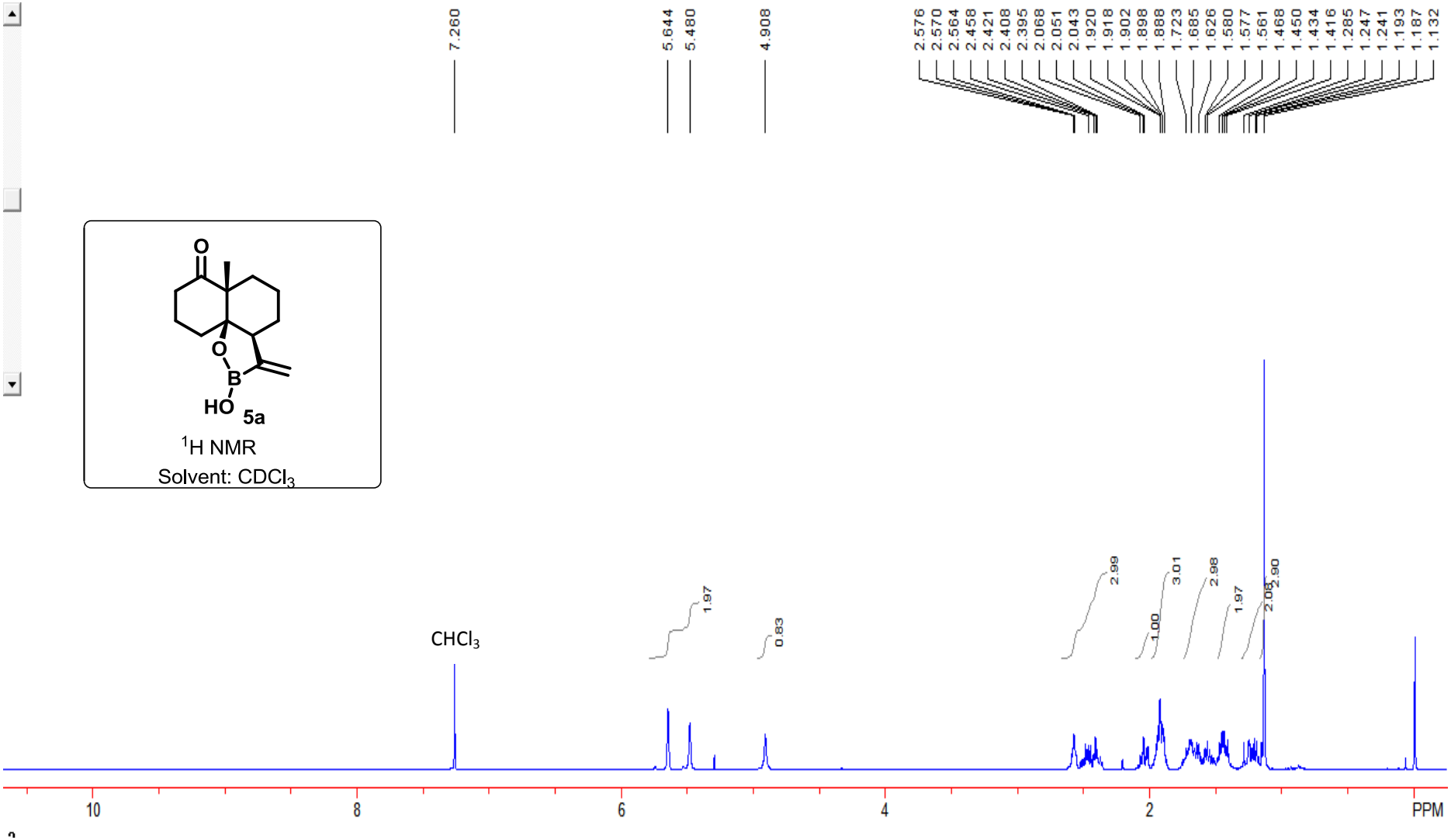
5.504
5.486
5.480
5.462
5.086
5.082
5.044
5.040
5.018
5.016
4.993
4.991
4.851
3.314
3.310
3.306
2.755
2.743
2.727
2.717
2.702
2.684
2.665
2.569
2.534
2.443
2.425
2.408
2.389
2.231
2.203
2.194
2.120
2.086
2.017
2.013
1.982
1.978
1.726
1.711
1.699
1.674
1.639
1.631
1.615
1.612
1.607
1.395
1.362
1.351
1.337
1.317
1.106
1.059

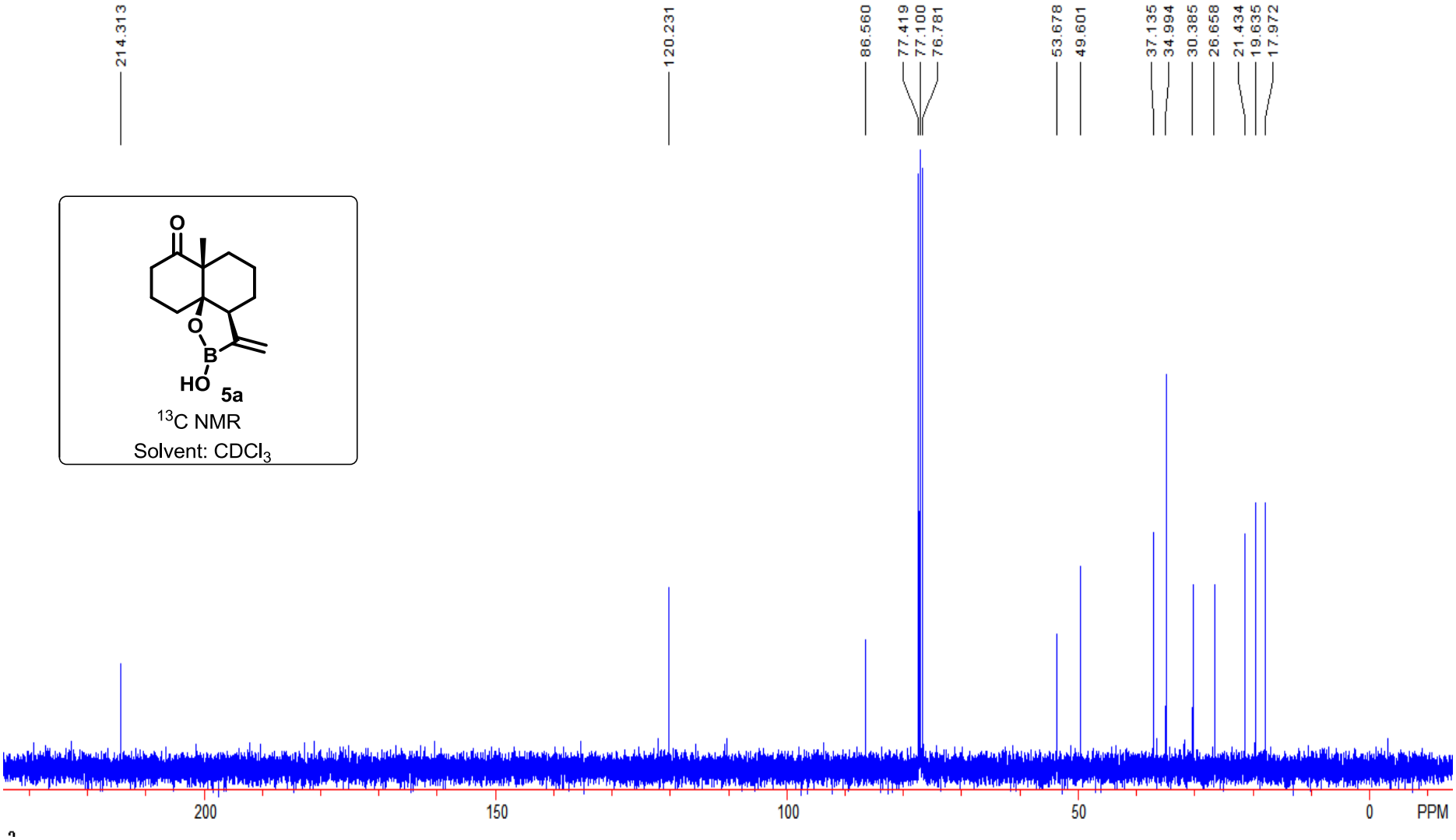

O
OH
O
3j
^{1}H NMR
Solvent: CD_3OD
H_2O
CH_3OH
0.94
1.94
1.98
0.99
1.00
3.90
1.00
1.01
2.98
1.99
1.05
2.93
3.01
10
8
6
4
2
0
-2
PPM

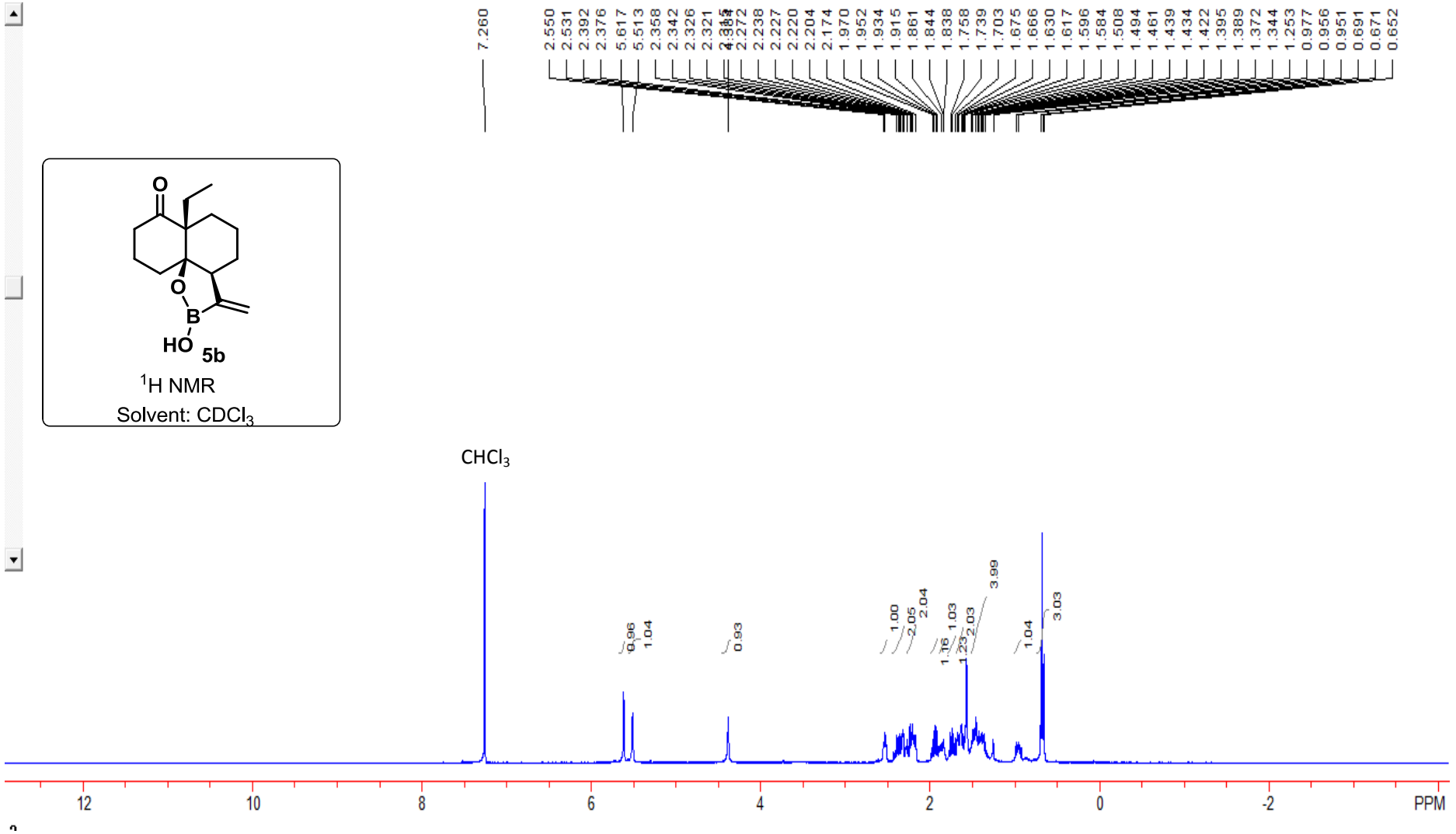

216.78
214.40
134.16
118.65
76.64
57.91
57.48
52.19
46.34
41.48
35.15
32.52
30.41
28.47
26.70
23.41
O
OH
O
3j
13C NMR
Solvent: CD3OD
49.64
49.43
49.21
49.00
48.79
48.57
48.36
50.5
49.5
48.5
f1 (ppm)
f1 (ppm)

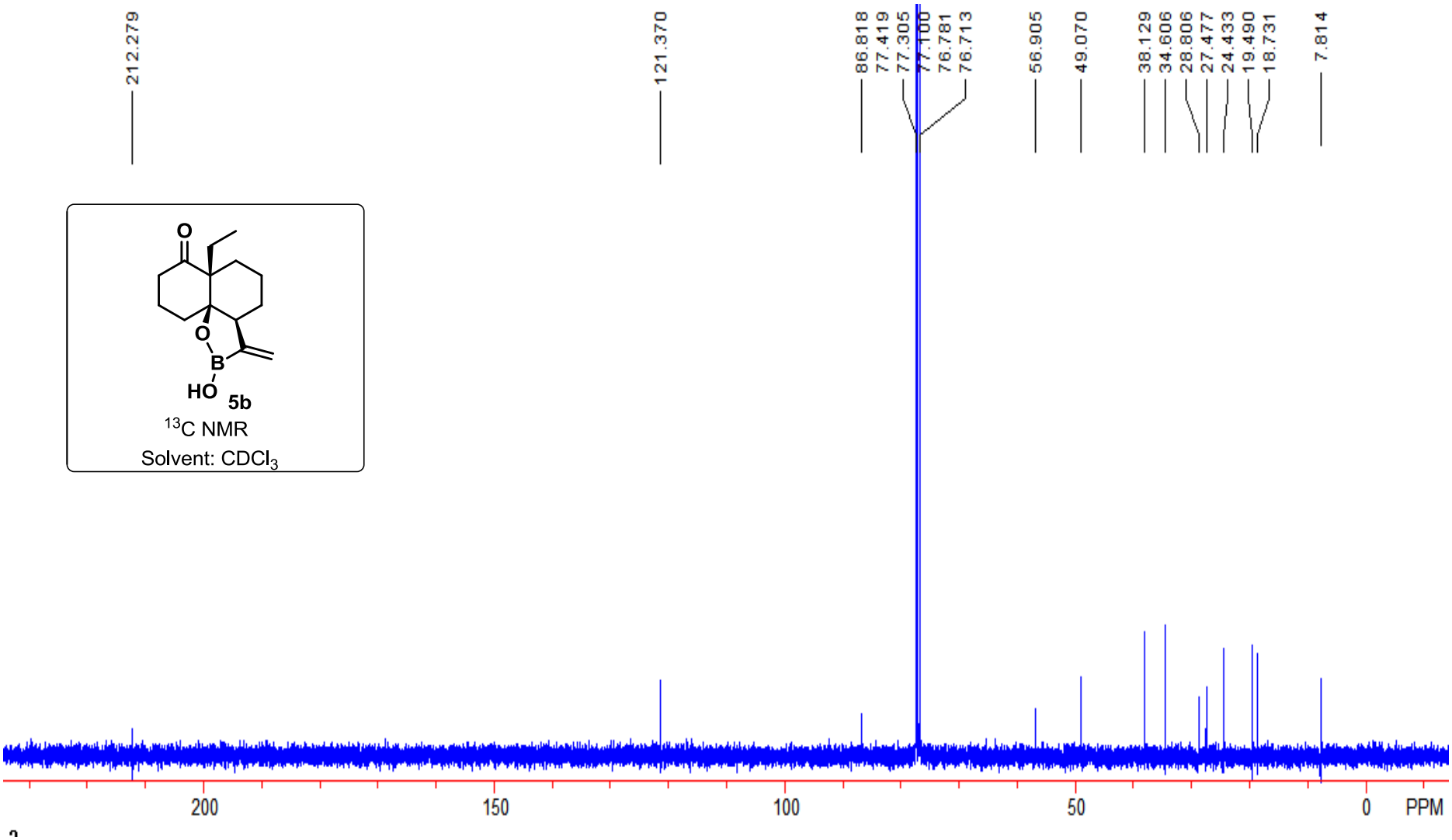

7.274
7.260
7.237
7.175
7.157
7.136
7.118
4.635
2.728
2.695
2.677
2.643
2.479
2.459
2.440
2.425
2.406
2.151
2.122
2.114
2.040
2.004
1.882
1.879
1.847
1.844
1.814
1.793
1.782
1.654
1.638
1.629
1.607
1.567
1.375
1.359
1.343
1.326
1.027
1.007
0.985
0.959
0.887
CHCl3
Ph
O
OH
O
3k
1H NMR
Solvent: CDCl3
0.71
1.25
3.00
1.00
2.04
1.03
5.00
1.06
8.84
H2O
1.19
0.94
3.05
3.04
8
6
4
2
0
PPM


215.908
213.638
141.861
128.697
128.385
125.956
77.419
77.100
76.781
75.718
56.540
55.462
50.641
45.570
35.996
34.751
33.984
31.258
30.279
26.582
25.769
24.873
22.520
Ph
O
OH
O
3k
13C NMR
Solvent: CDCl3
200
150
100
50
0
PPM


7.260
5.644
5.480
4.908
2.576
2.570
2.564
2.458
2.421
2.408
2.395
2.068
2.051
2.043
1.920
1.918
1.902
1.898
1.888
1.723
1.685
1.626
1.580
1.577
1.561
1.468
1.450
1.434
1.416
1.285
1.247
1.241
1.193
1.187
1.132
O
O
B
HO
5a
1H NMR
Solvent: CDCl3
CHCl3
1.97
0.83
2.99
1.00
3.01
2.98
1.97
2.08
2.90
10
8
6
4
2
PPM


214.313
120.231
86.560
77.419
77.100
76.781
53.678
49.601
37.135
34.994
30.385
26.658
21.434
19.635
17.972
O
O
B
HO
5a
13C NMR
Solvent: CDCl3
200
150
100
50
0
PPM


7.260
2.550
2.531
2.392
2.376
5.617
5.513
2.358
2.342
2.326
2.321
2.272
2.238
2.227
2.220
2.204
2.174
1.970
1.952
1.934
1.915
1.861
1.844
1.838
1.758
1.739
1.703
1.675
1.666
1.630
1.617
1.596
1.584
1.508
1.494
1.461
1.439
1.434
1.422
1.395
1.389
1.372
1.344
1.253
0.977
0.956
0.951
0.691
0.671
0.652
O
O
B
HO
5b
^{1}H NMR
Solvent: $CDCl_3$
$CHCl_3$
0.96
1.04
0.93
1.00
2.05
2.04
1.16
1.03
1.23
2.03
3.99
1.04
3.03
12
10
8
6
4
2
0
-2
PPM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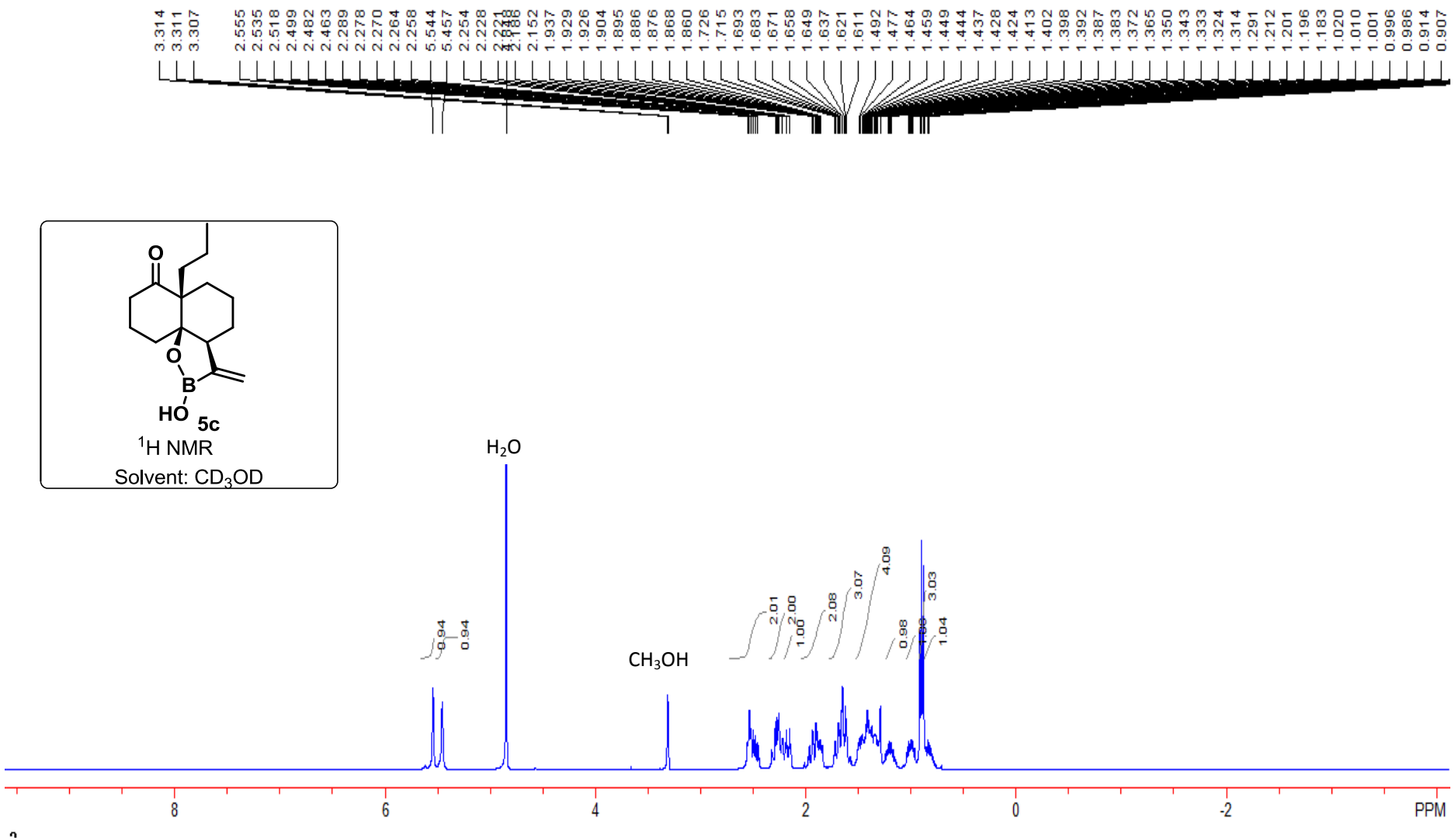
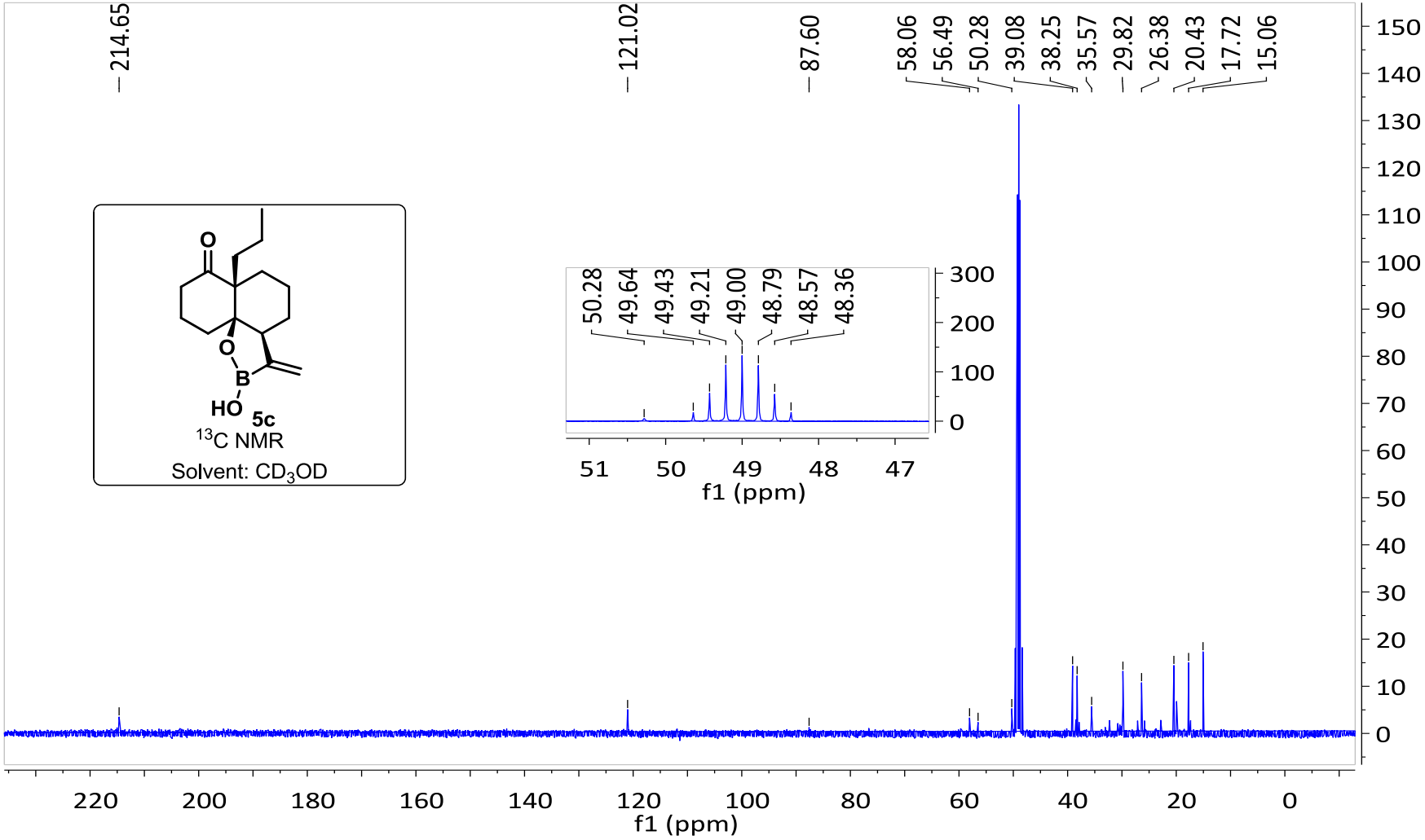
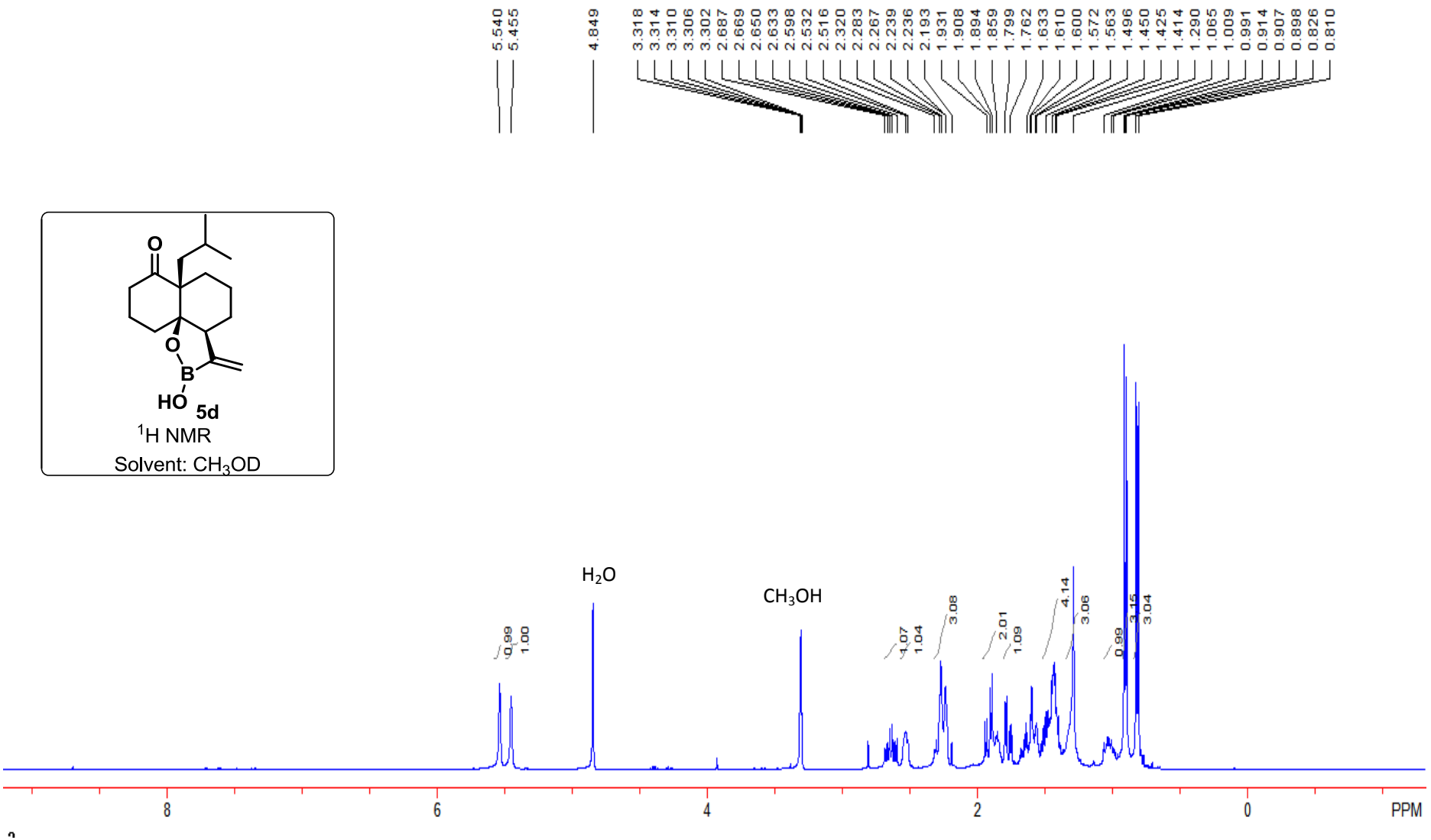
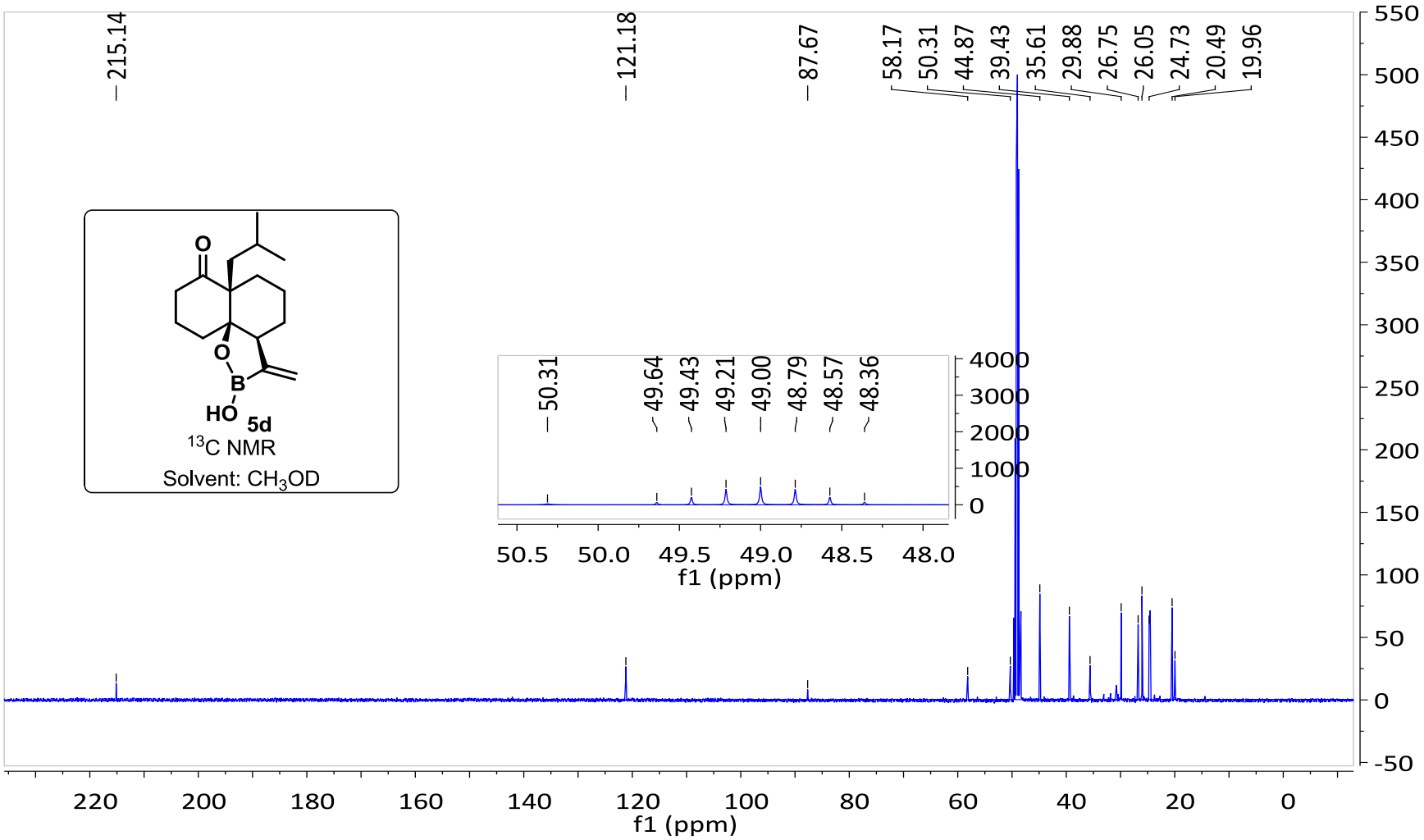
86.818
77.419
77.305
77.100
76.781
76.713
56.905
49.070
38.129
34.606
28.806
27.477
24.433
19.490
18.731
7.814
O
O
B
HO
5b
13C NMR
Solvent: CDCl3
200
150
100
50
0
PPM


3.314
3.311
3.307
2.555
2.535
2.518
2.499
2.482
2.463
2.289
2.278
2.270
2.264
2.258
5.544
5.457
2.254
2.228
2.221
2.186
2.152
1.937
1.929
1.926
1.904
1.895
1.886
1.876
1.868
1.860
1.726
1.715
1.693
1.683
1.671
1.658
1.649
1.637
1.621
1.611
1.492
1.477
1.464
1.459
1.449
1.444
1.437
1.428
1.424
1.413
1.402
1.398
1.392
1.387
1.383
1.372
1.365
1.350
1.343
1.333
1.324
1.314
1.291
1.212
1.201
1.196
1.183
1.020
1.010
1.001
0.996
0.986
0.914
0.907
O
O
B
HO
5c
1H NMR
Solvent: CD3OD
H2O
CH3OH
0.94
0.94
2.01
2.00
1.00
2.08
3.07
4.09
0.98
3.03
1.04
8
6
4
2
0
-2
PPM


214.65
121.02
87.60
58.06
56.49
50.28
39.08
38.25
35.57
29.82
26.38
20.43
17.72
15.06
O
O
B
HO
5c
13C NMR
Solvent: CD3OD
50.28
49.64
49.43
49.21
49.00
48.79
48.57
48.36
f1 (ppm)
f1 (ppm)


5.540
5.455
4.849
3.318
3.314
3.310
3.306
3.302
2.687
2.669
2.650
2.633
2.598
2.532
2.516
2.320
2.283
2.267
2.239
2.236
2.193
1.931
1.908
1.894
1.859
1.799
1.762
1.633
1.610
1.600
1.572
1.563
1.496
1.450
1.425
1.414
1.290
1.065
1.009
0.991
0.914
0.907
0.898
0.826
0.810
O
O
B
HO
5d
1H NMR
Solvent: CH3OD
H2O
CH3OH
0.99
1.00
4.07
1.04
3.08
2.01
1.09
4.14
3.06
0.99
3.15
3.04
8
6
4
2
0
PPM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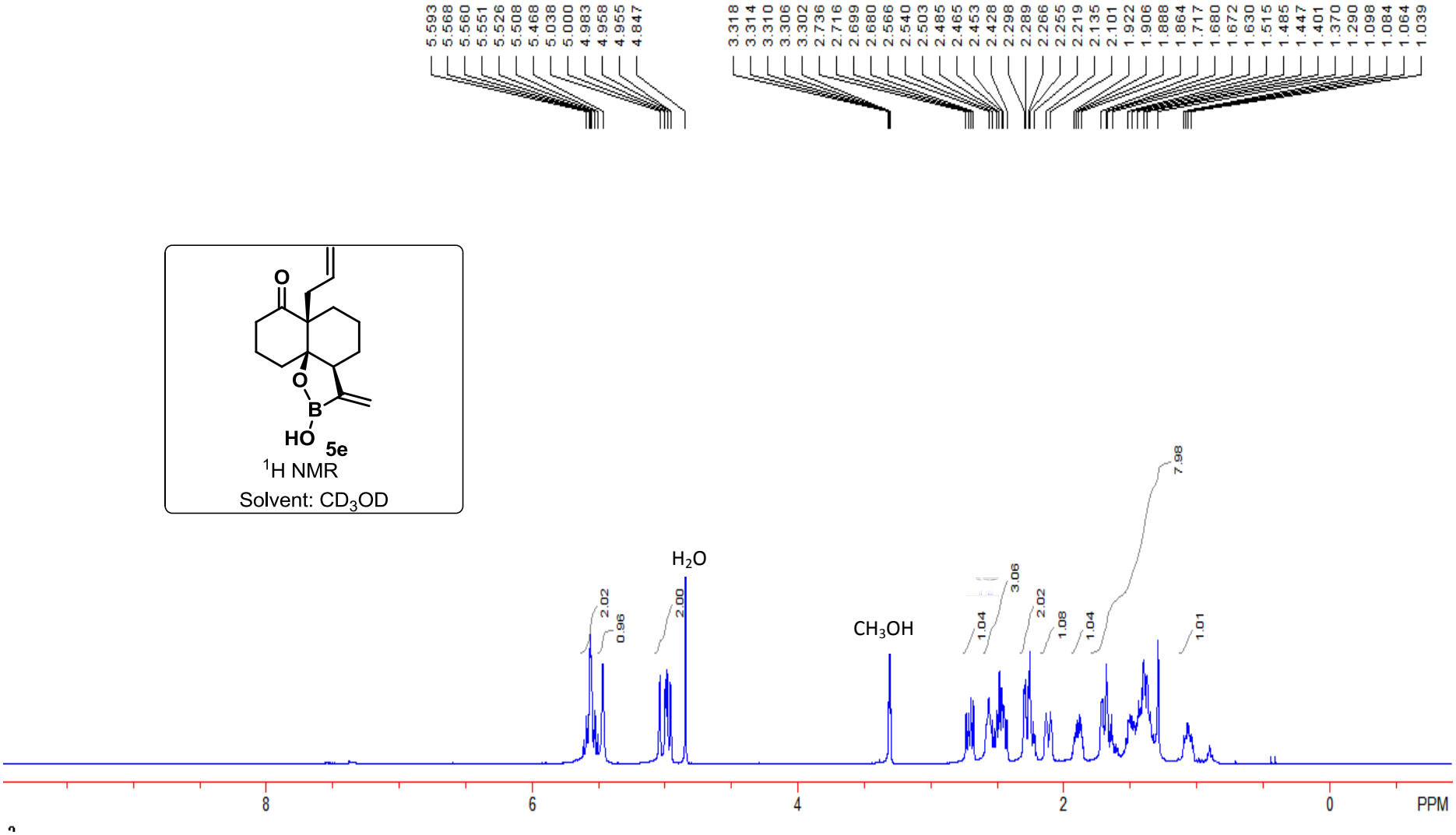
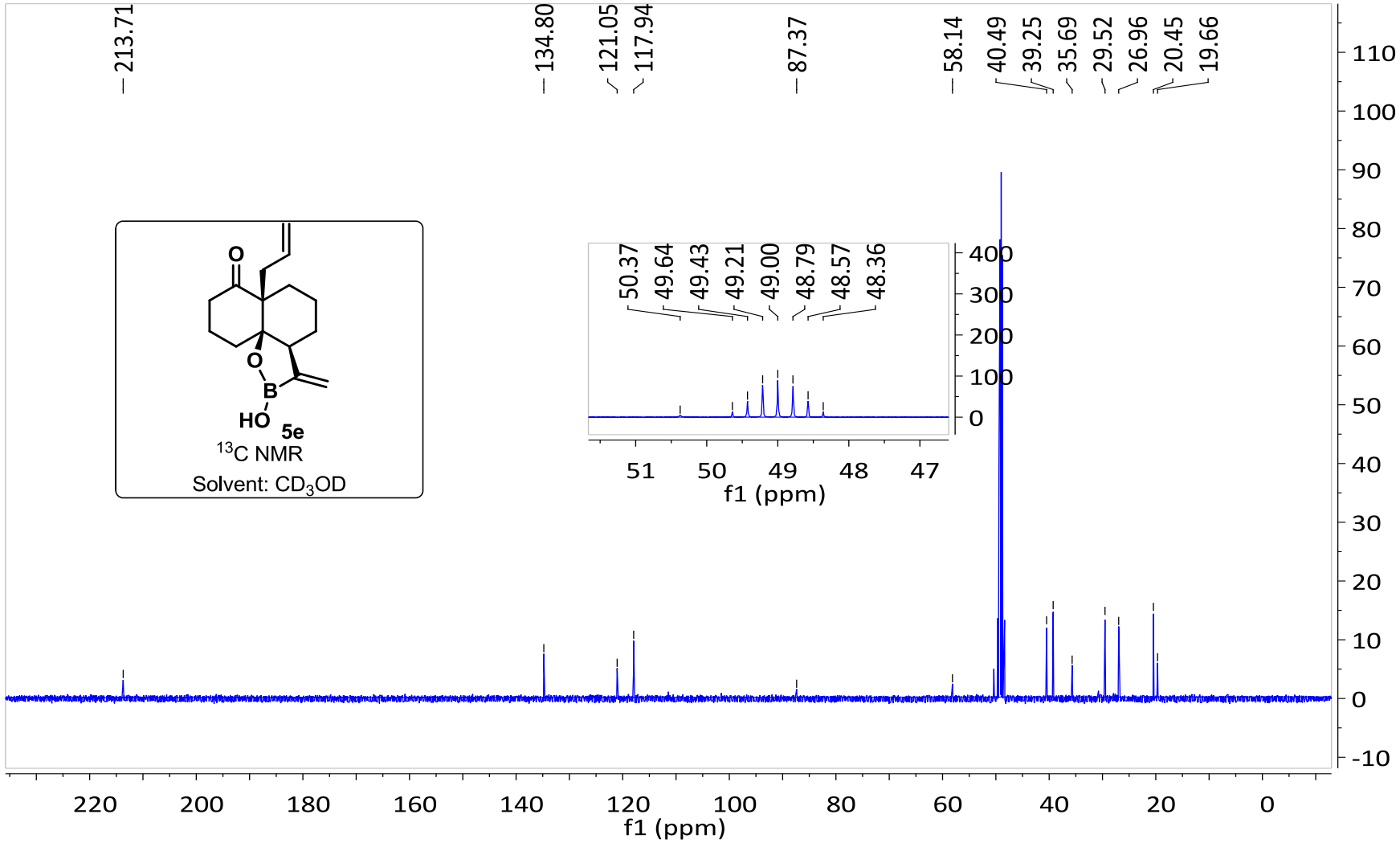
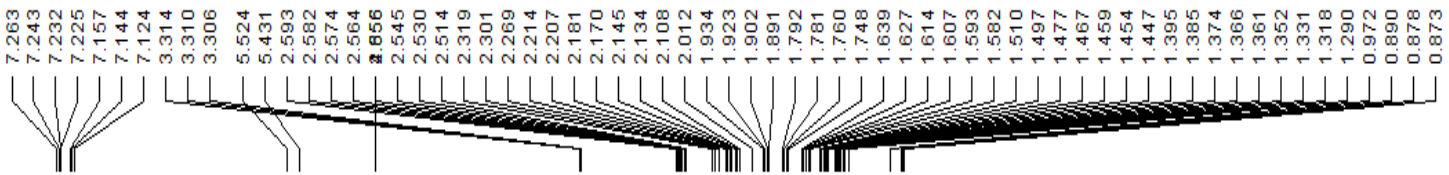
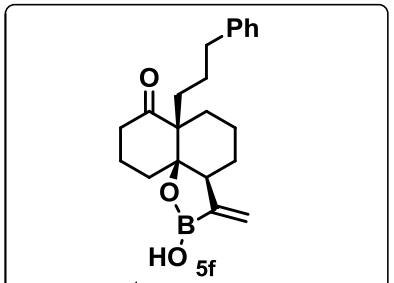
121.18
87.67
58.17
50.31
44.87
39.43
35.61
29.88
26.75
26.05
24.73
20.49
19.96
O
O
B
HO
5d
13C NMR
Solvent: CH3OD
50.31
49.64
49.43
49.21
49.00
48.79
48.57
48.36
f1 (ppm)
f1 (ppm)


5.593
5.568
5.560
5.551
5.526
5.508
5.468
5.038
5.000
4.983
4.958
4.955
4.847
3.318
3.314
3.310
3.306
3.302
2.736
2.716
2.699
2.680
2.566
2.540
2.503
2.485
2.465
2.453
2.428
2.298
2.289
2.266
2.255
2.219
2.135
2.101
1.922
1.906
1.888
1.864
1.717
1.680
1.672
1.630
1.515
1.485
1.447
1.401
1.370
1.290
1.098
1.084
1.064
1.039
O
O
B
HO
5e
1H NMR
Solvent: CD3OD
H2O
CH3OH
2.02
0.96
2.00
1.04
3.06
2.02
1.08
1.04
7.98
1.01
8
6
4
2
0
PPM

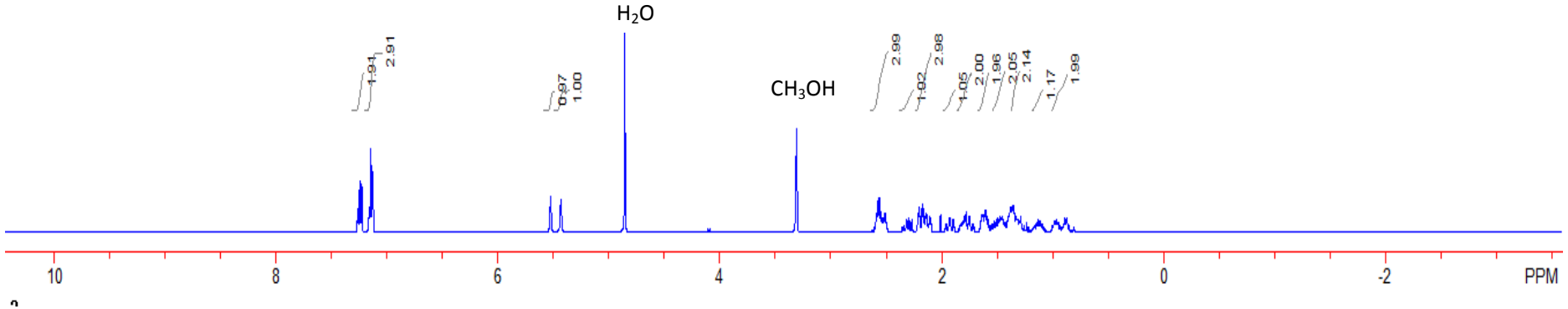

213.71
134.80
121.05
117.94
87.37
58.14
40.49
39.25
35.69
29.52
26.96
20.45
19.66
O
O
B
HO
5e
13C NMR
Solvent: CD3OD
50.37
49.64
49.43
49.21
49.00
48.79
48.57
48.36
f1 (ppm)
f1 (ppm)

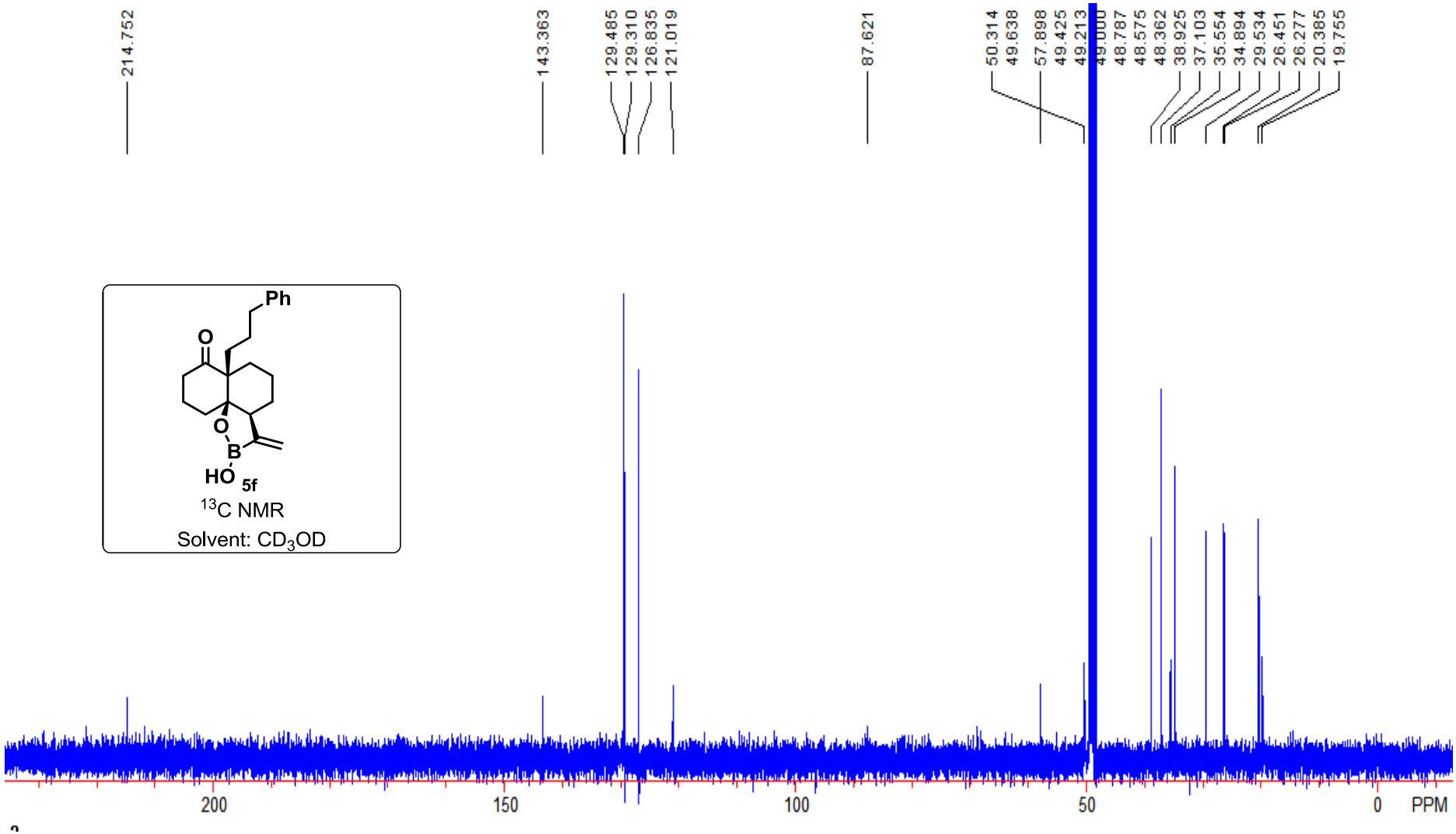


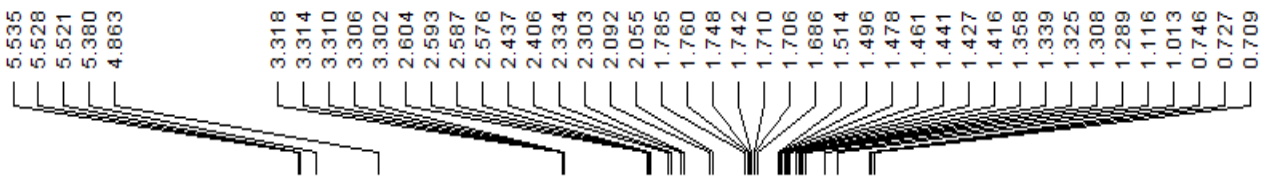


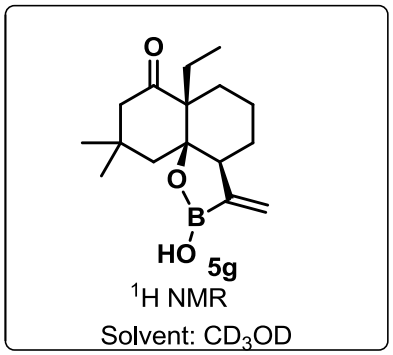
^{1}H NMR

Solvent: CD_3OD




214.752
143.363
129.485
129.310
126.835
121.019
87.621
50.314
49.638
57.898
49.425
49.213
49.000
48.787
48.575
48.362
38.925
37.103
35.554
34.894
29.534
26.451
26.277
20.385
19.755
Ph
O
O
B
HO
5f
13C NMR
Solvent: CD3OD
200
150
100
50
0
PPM

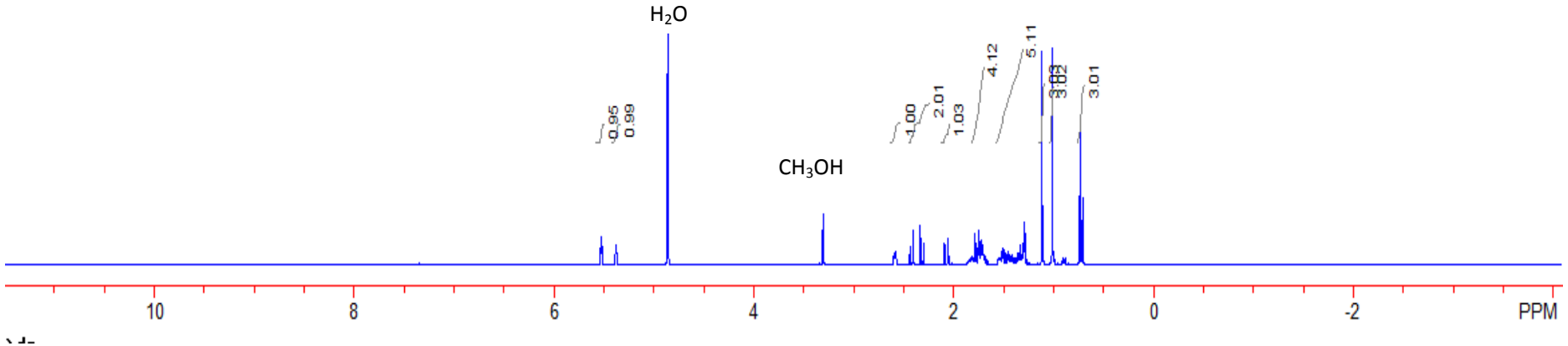


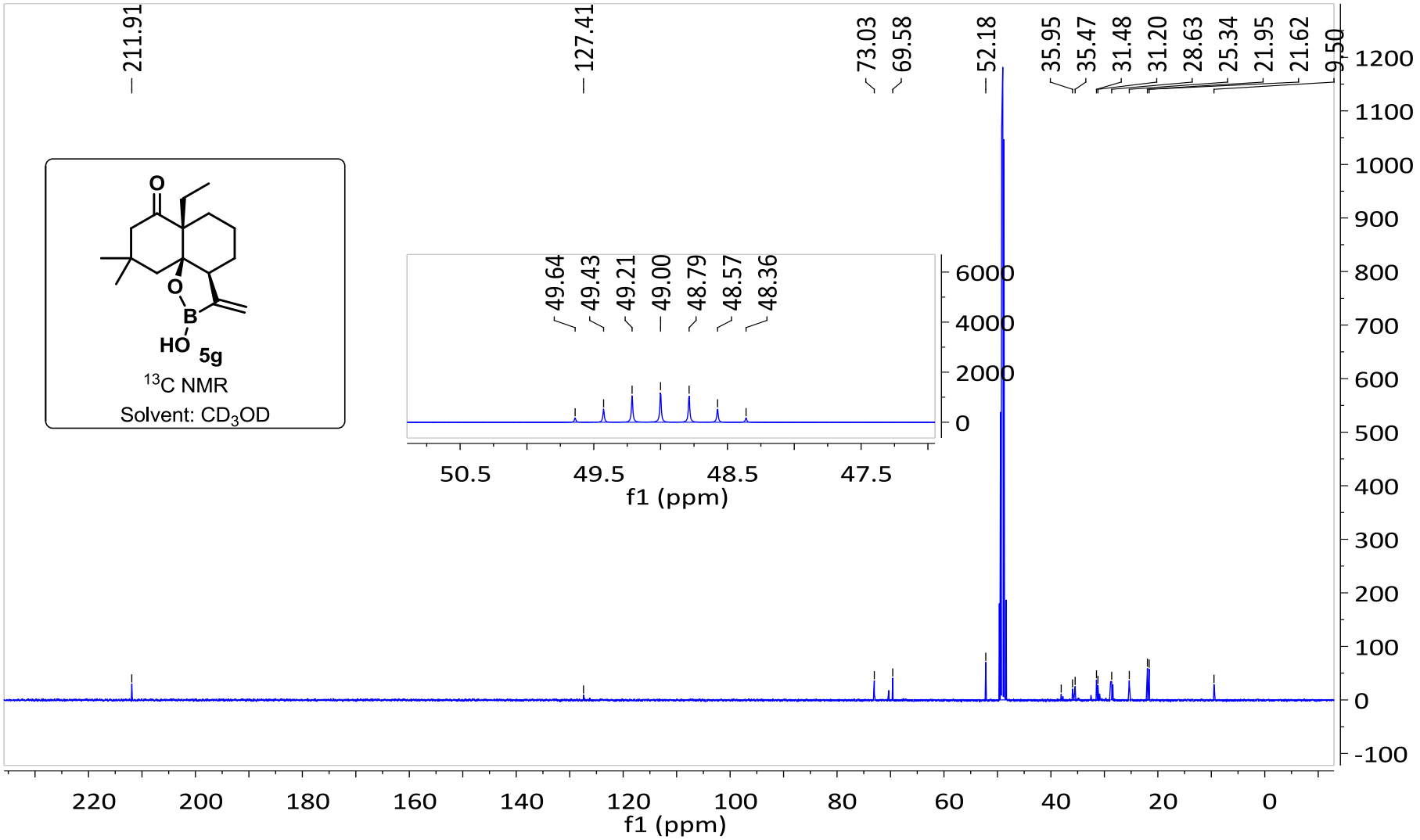


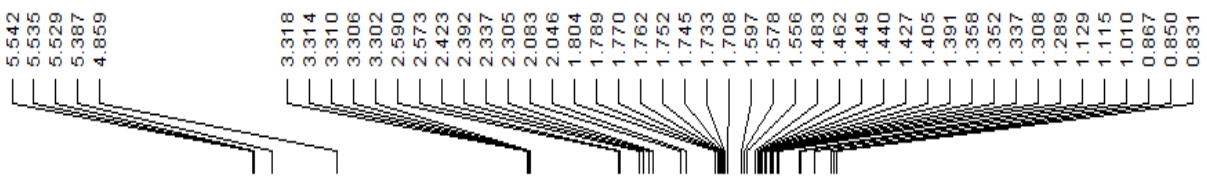
5g

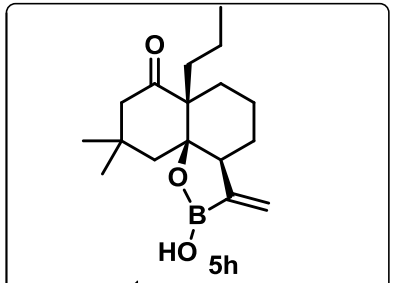
^{1}H NMR

Solvent: CD_3OD




211.91
127.41
73.03
69.58
52.18
35.95
35.47
31.48
31.20
28.63
25.34
21.95
21.62
9.50
49.64
49.43
49.21
49.00
48.79
48.57
48.36
5g
13C NMR
Solvent: CD3OD
f1 (ppm)
f1 (ppm)

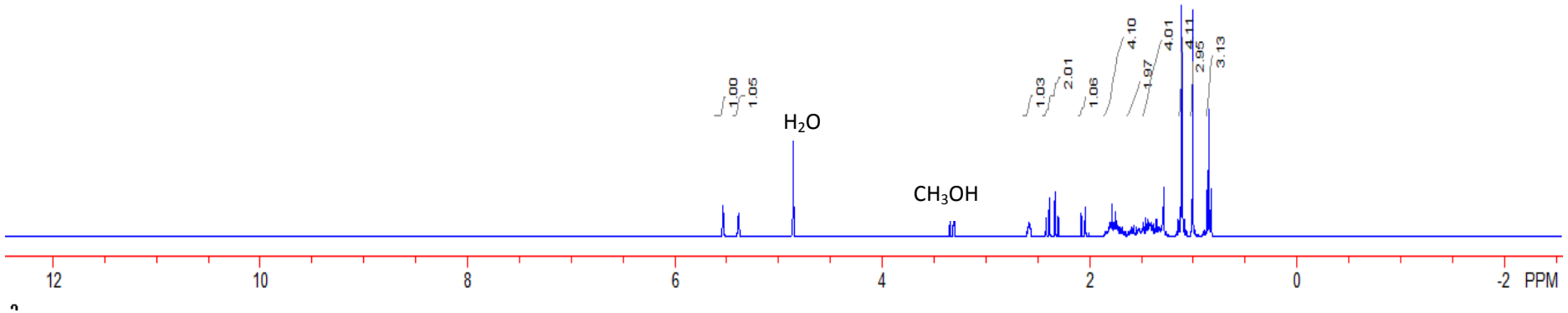


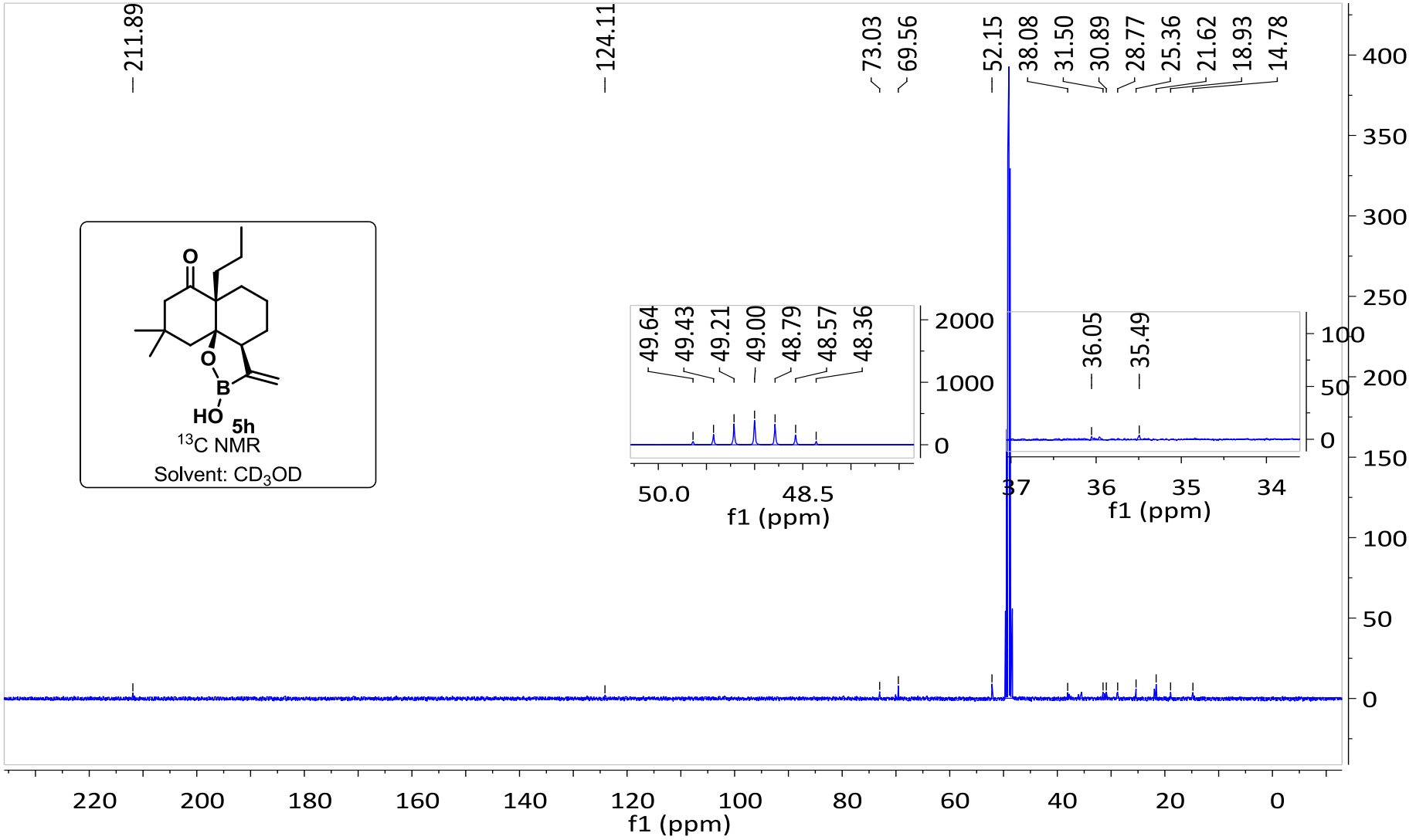


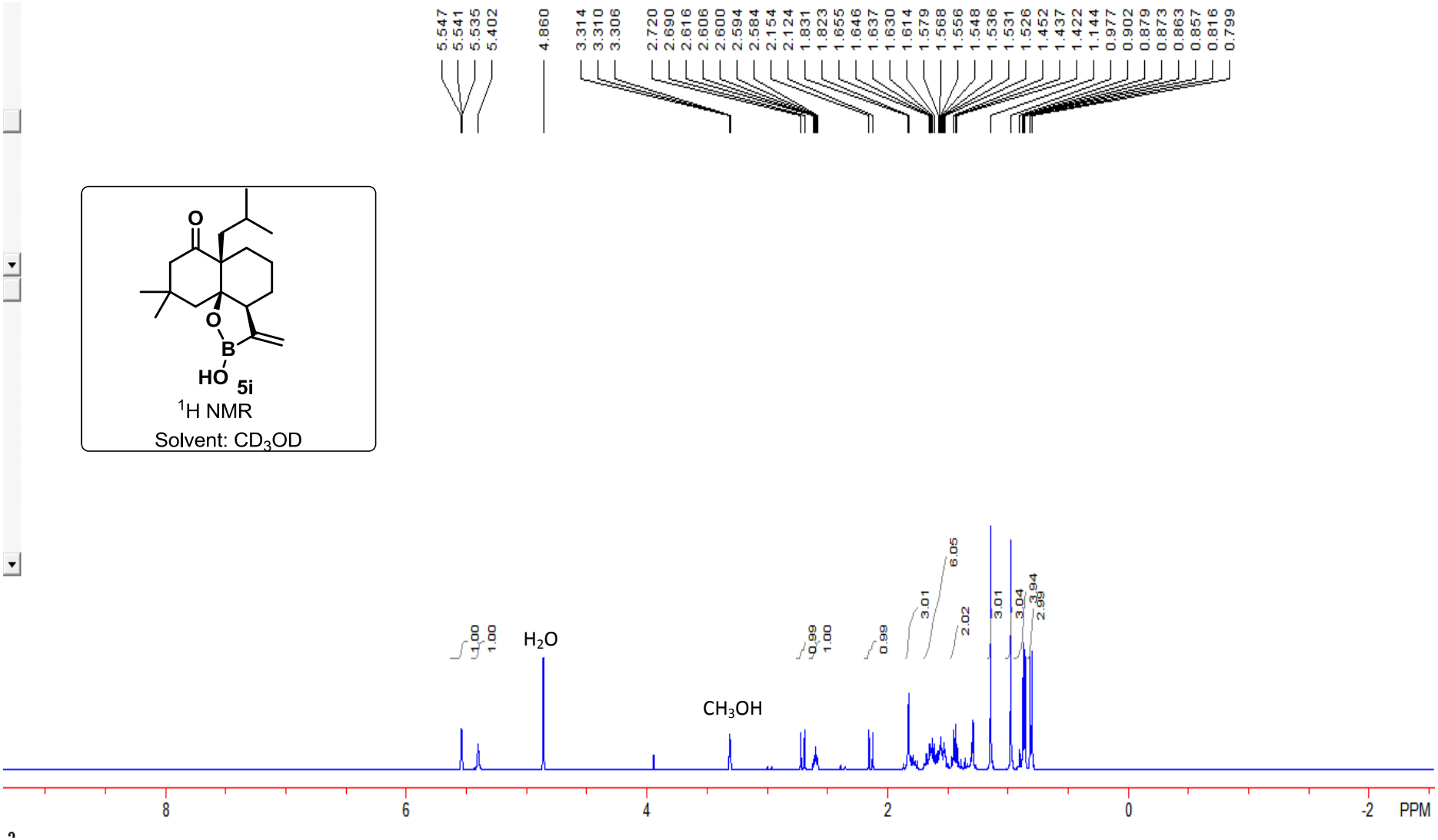
5h

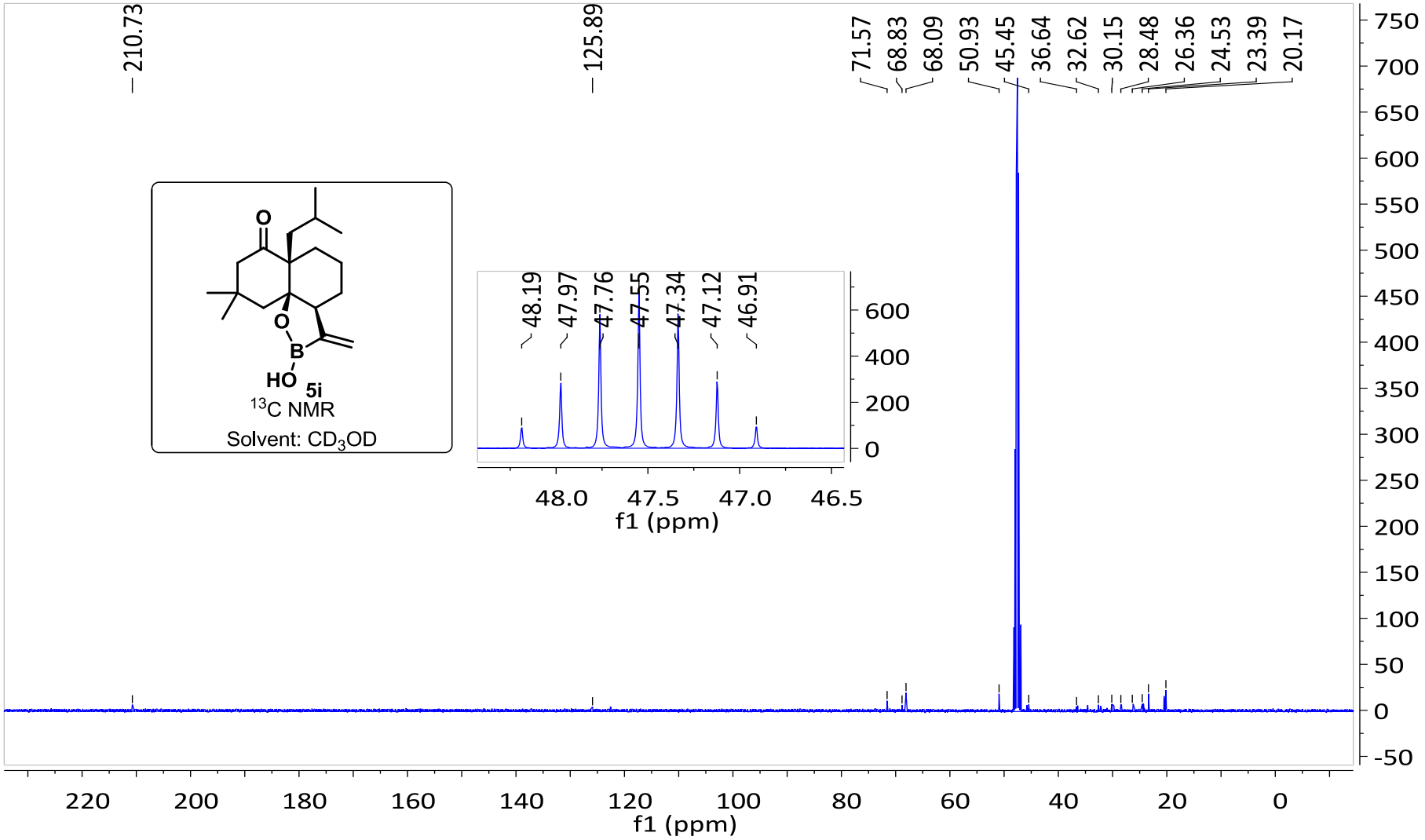
^{1}H NMR

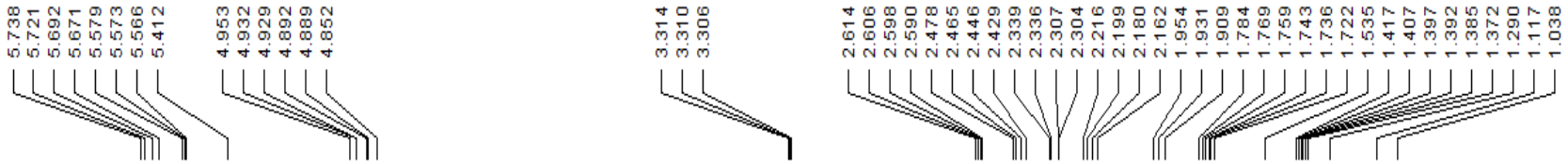
Solvent: CD_3OD

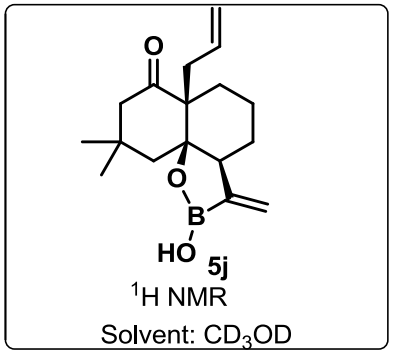



211.89
124.11
73.03
69.56
52.15
38.08
31.50
30.89
28.77
25.36
21.62
18.93
14.78
49.64
49.43
49.21
49.00
48.79
48.57
48.36
36.05
35.49
5h
13C NMR
Solvent: CD3OD
f1 (ppm)


5.547
5.541
5.535
5.402
4.860
3.314
3.310
3.306
2.720
2.690
2.616
2.606
2.600
2.594
2.584
2.154
2.124
1.831
1.823
1.655
1.646
1.637
1.630
1.614
1.579
1.568
1.556
1.548
1.536
1.531
1.526
1.452
1.437
1.422
1.144
0.977
0.902
0.879
0.873
0.863
0.857
0.816
0.799
O
O
B
HO
5i
1H NMR
Solvent: CD3OD
1.00
1.00
H2O
0.99
1.00
0.99
3.01
6.05
2.02
3.01
3.04
3.94
2.99
CH3OH
8
6
4
2
0
-2
PPM

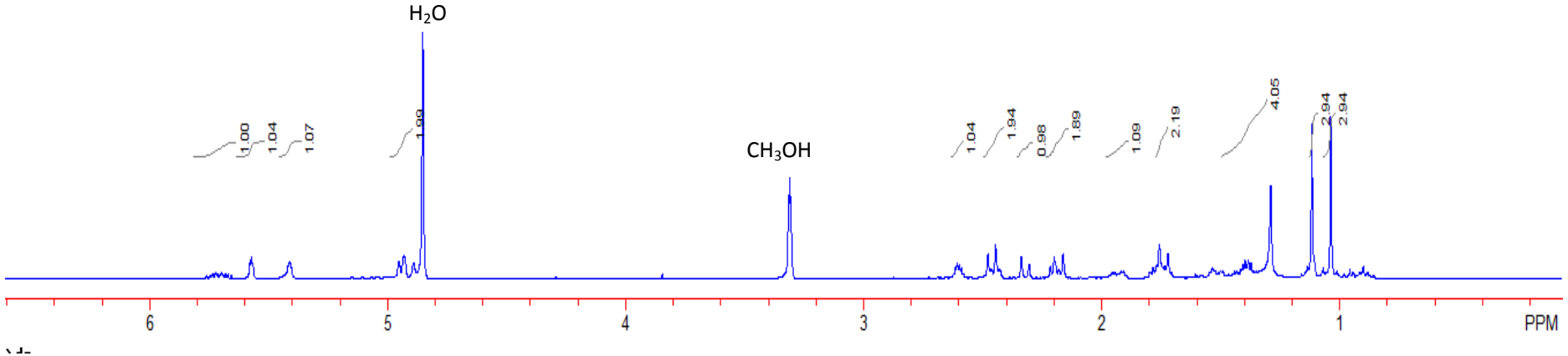

210.73
125.89
71.57
68.83
68.09
50.93
45.45
36.64
32.62
30.15
28.48
26.36
24.53
23.39
20.17
O
O
B
HO
5i
13C NMR
Solvent: CD3OD
48.19
47.97
47.76
47.55
47.34
47.12
46.91
48.0
47.5
47.0
46.5
f1 (ppm)
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

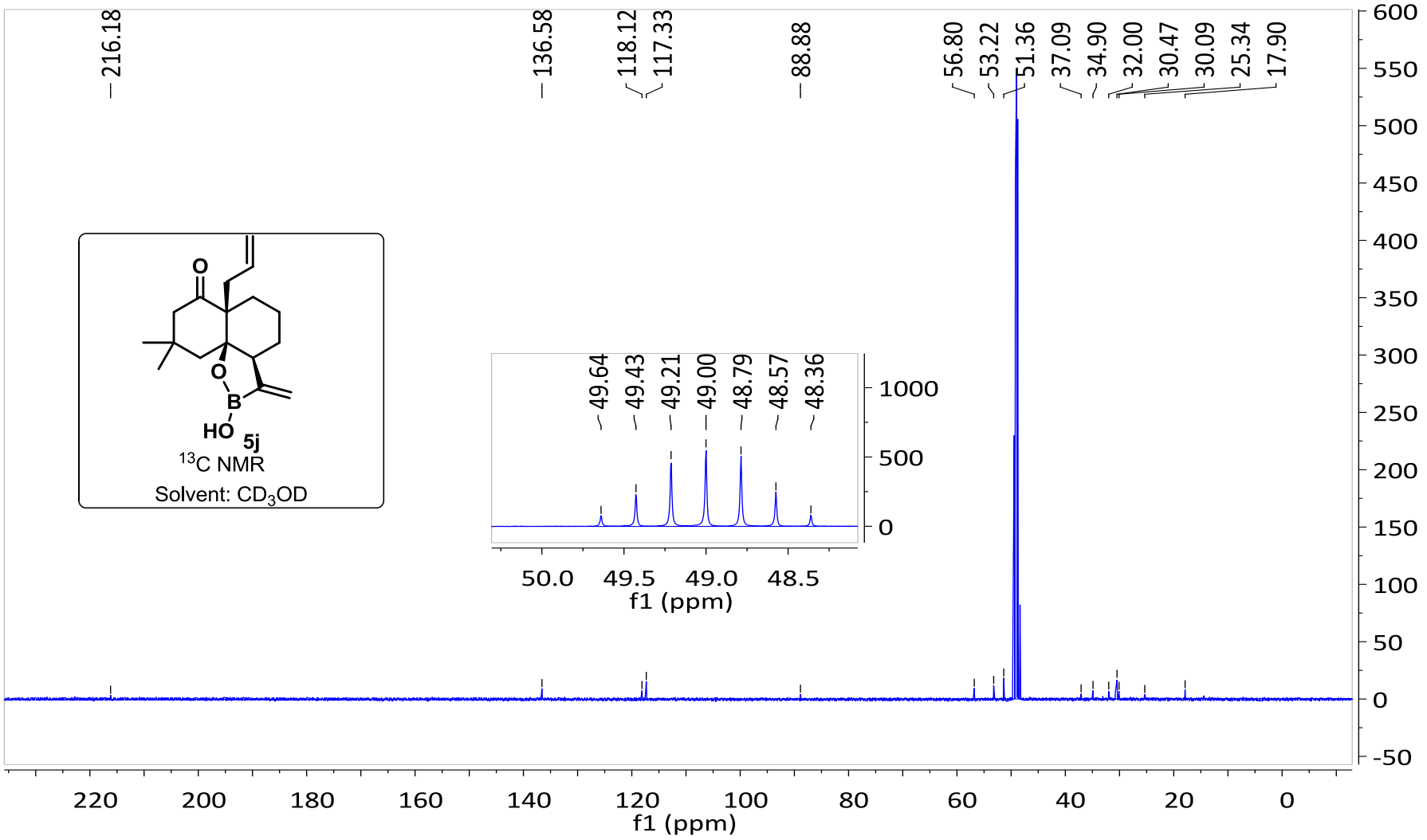


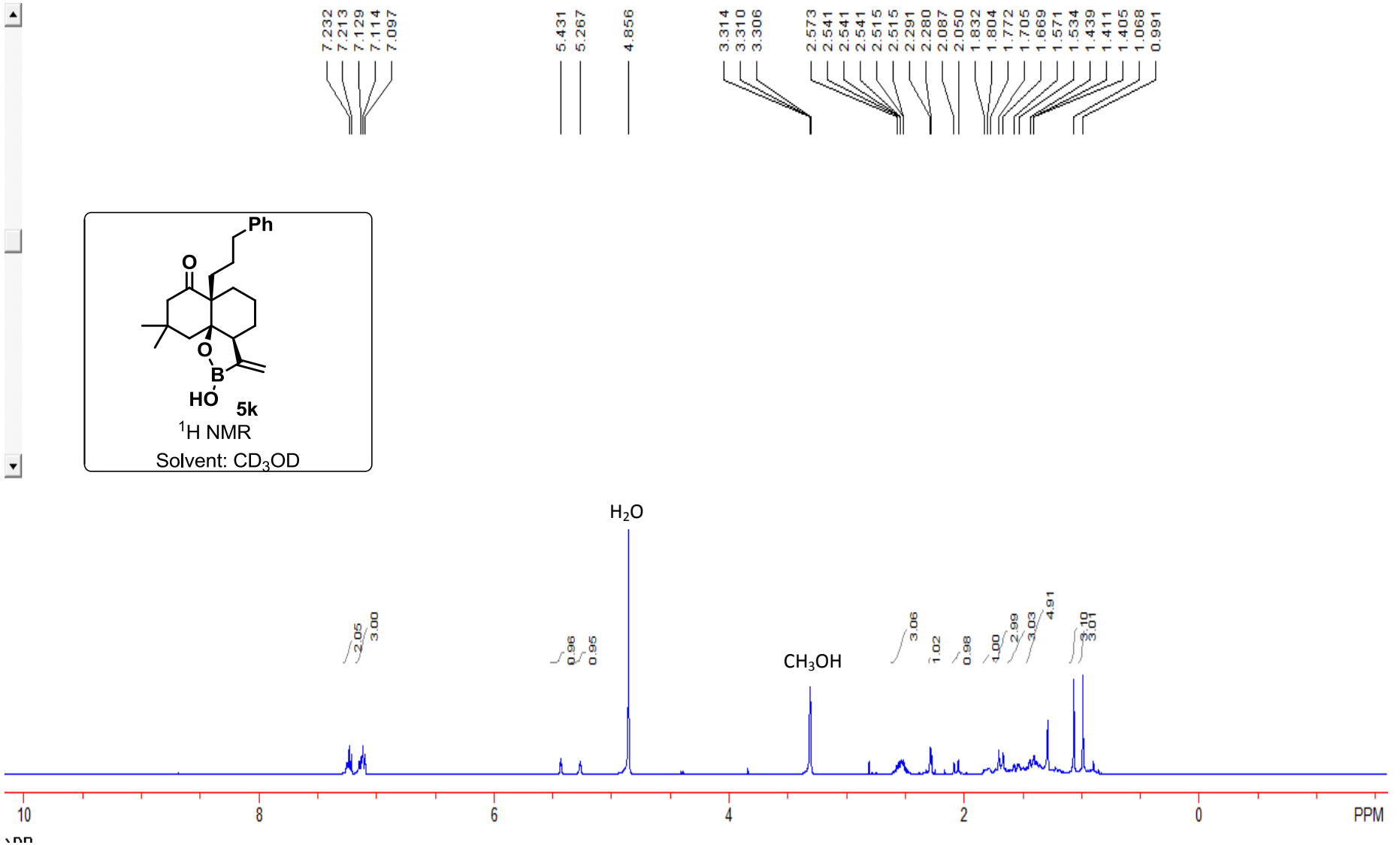


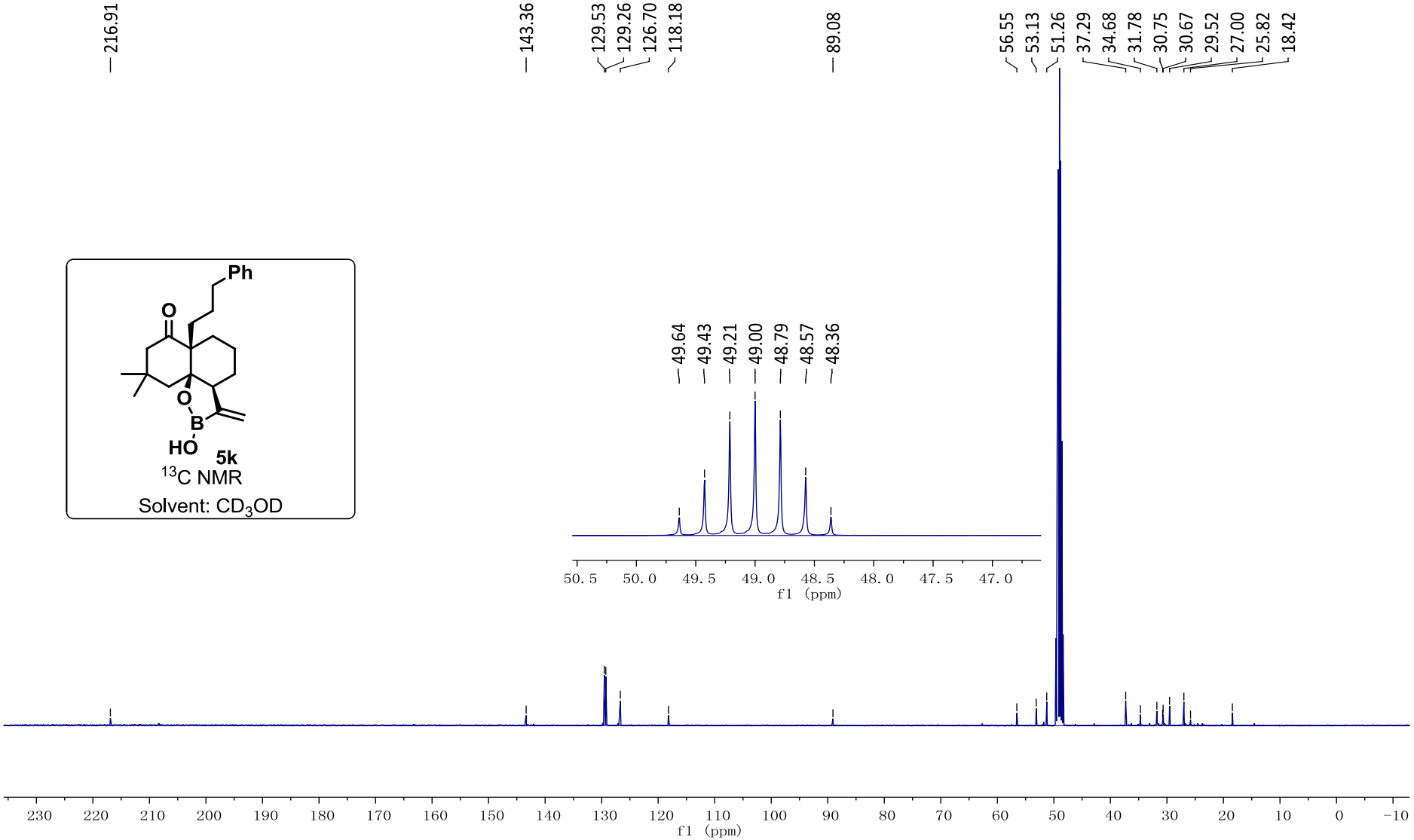
^{1}H NMR

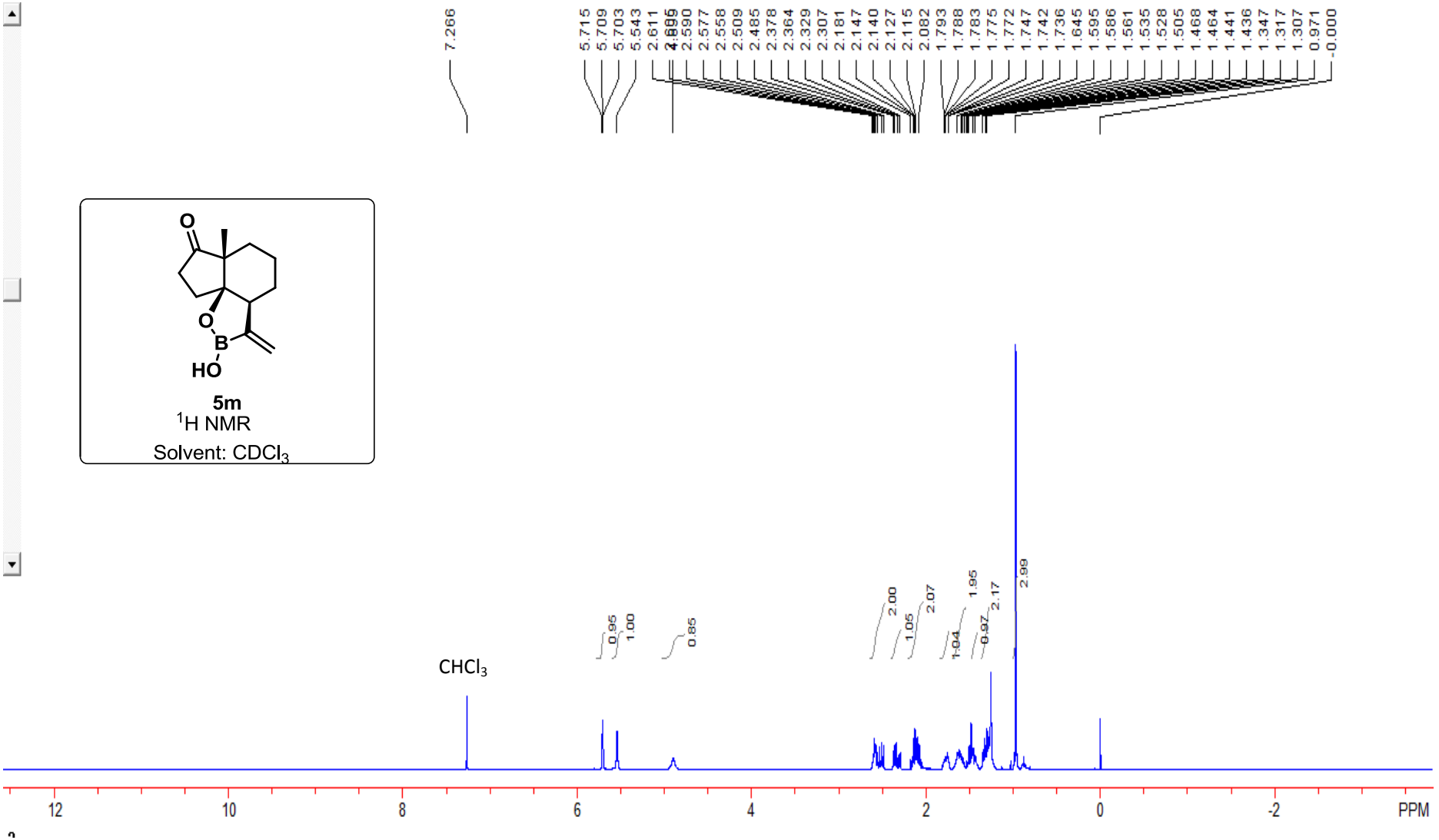
Solvent: CD_3OD

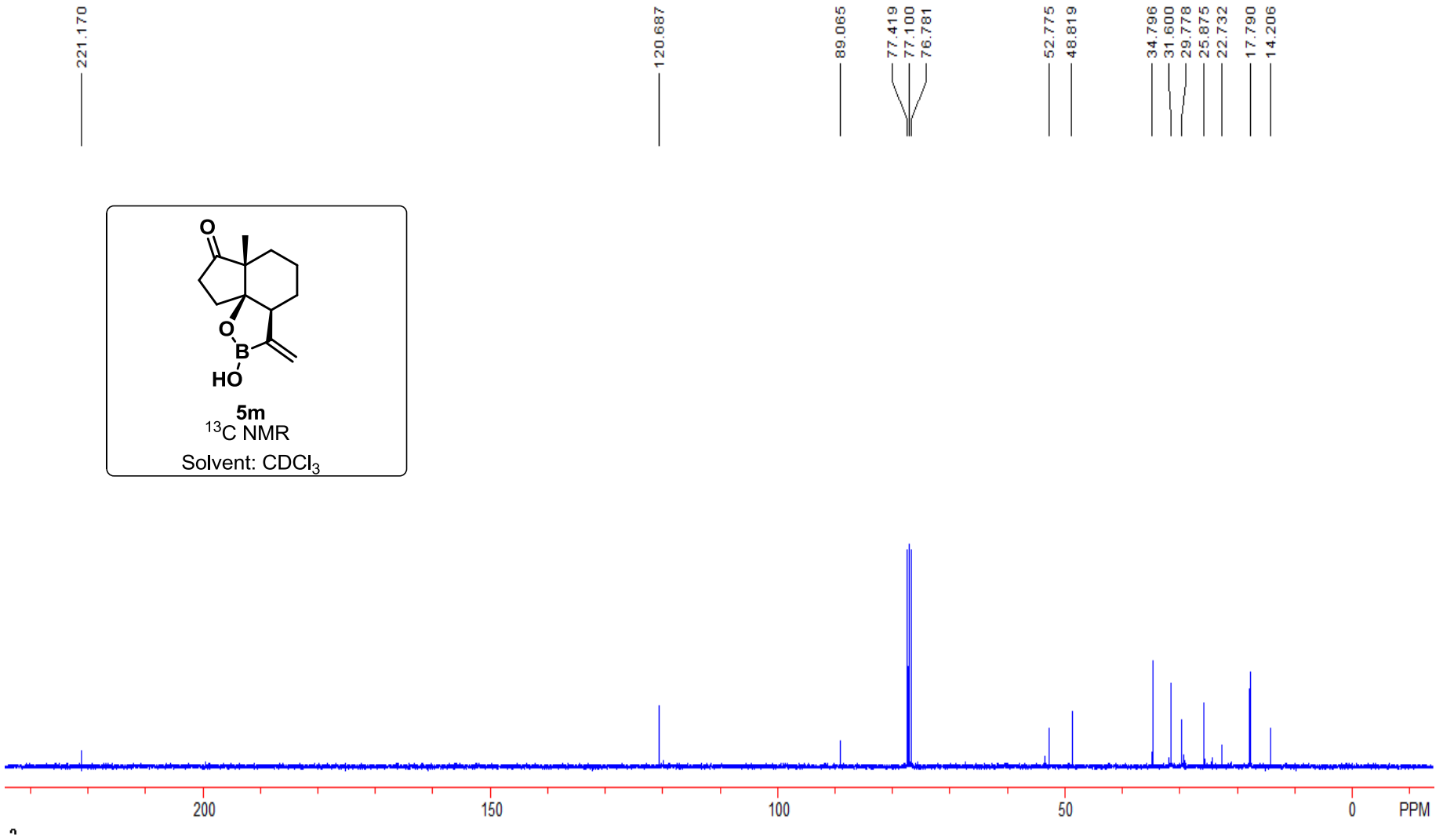


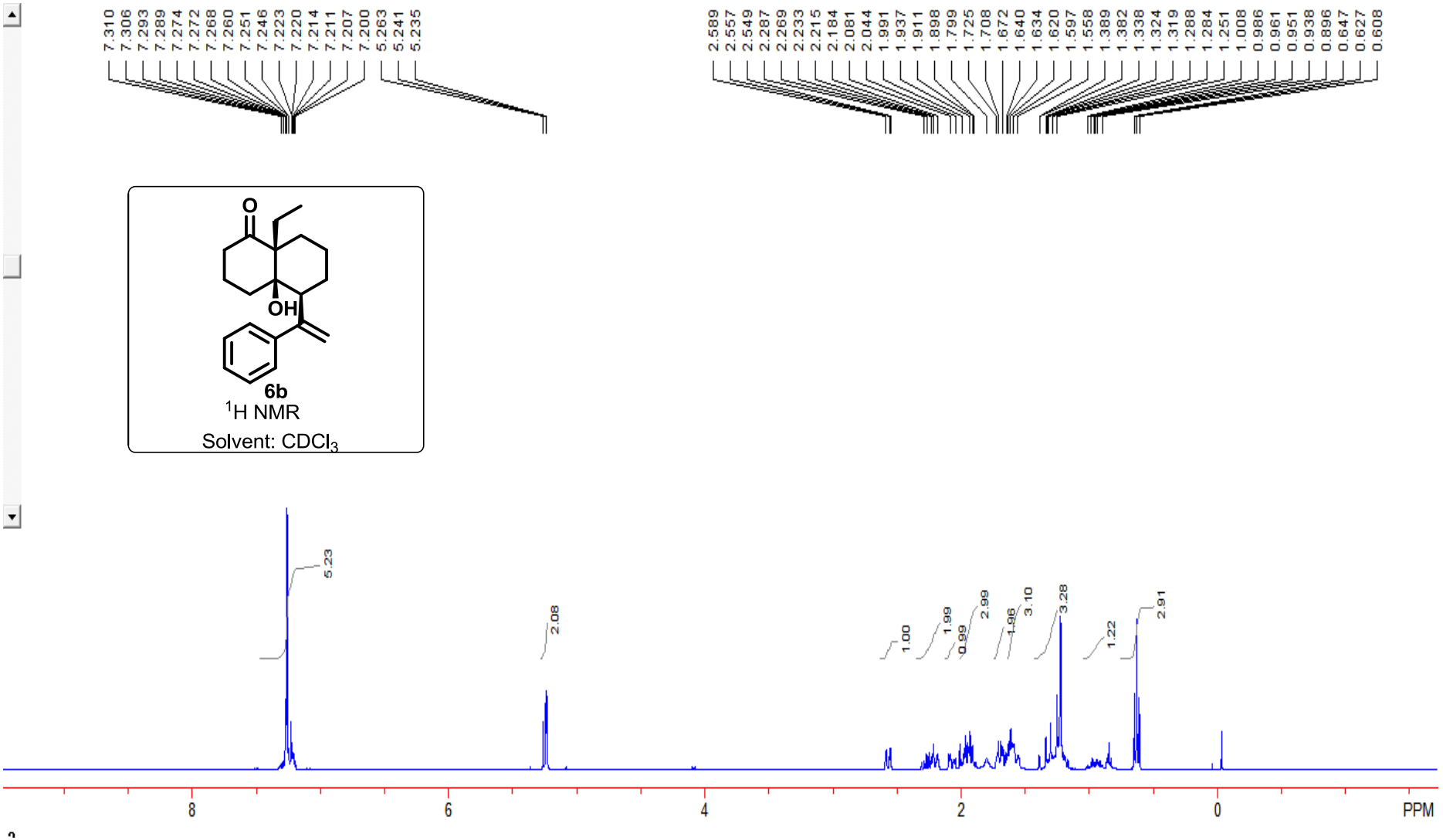

216.18
136.58
118.12
117.33
88.88
56.80
53.22
51.36
37.09
34.90
32.00
30.47
30.09
25.34
17.90
O
O
B
HO
5j
13C NMR
Solvent: CD3OD
49.64
49.43
49.21
49.00
48.79
48.57
48.36
1000
500
0
50.0
49.5
49.0
48.5
f1 (ppm)
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

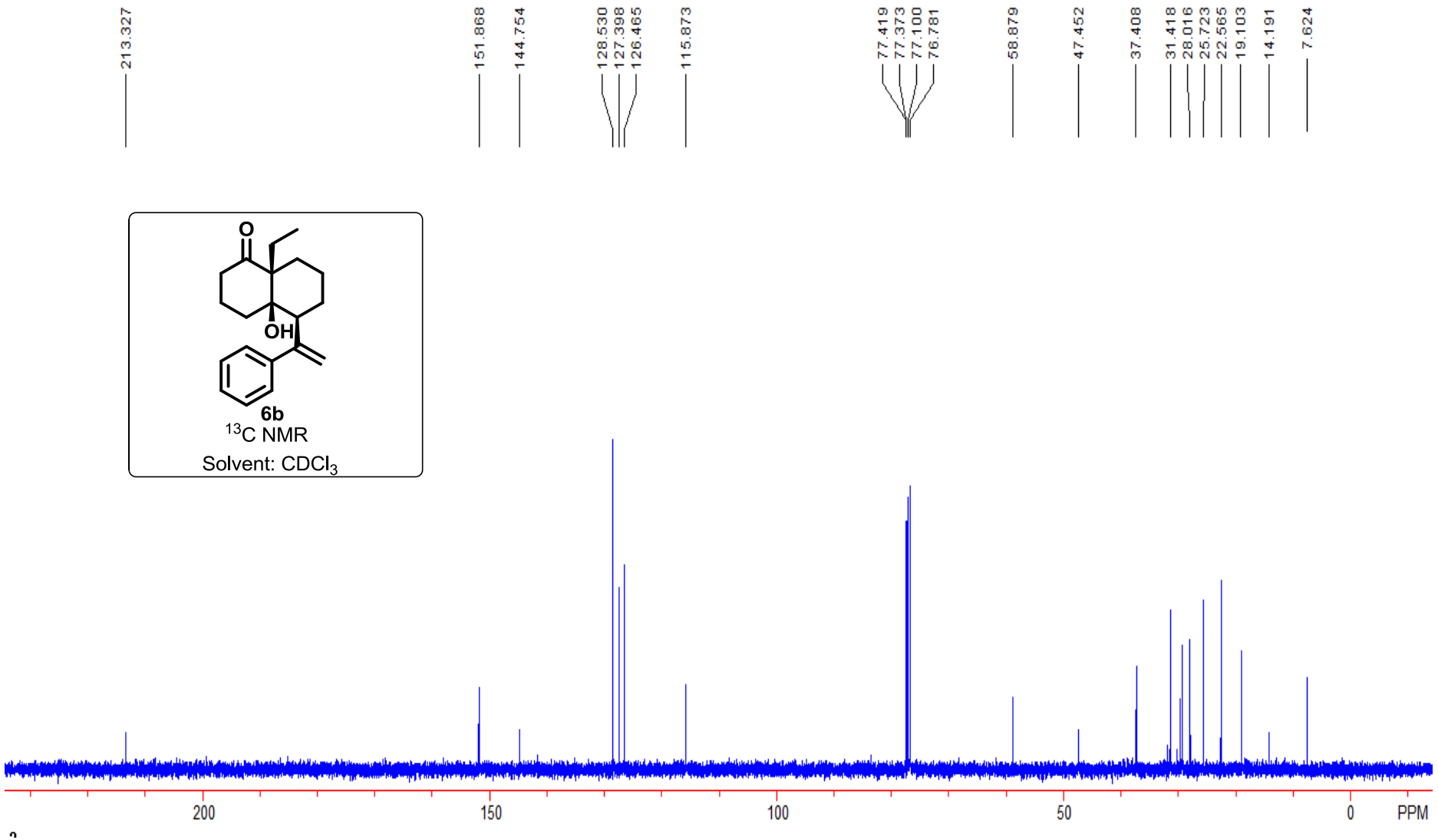

7.232
7.213
7.129
7.114
7.097
5.431
5.267
4.856
3.314
3.310
3.306
2.573
2.541
2.541
2.541
2.515
2.515
2.291
2.280
2.087
2.050
1.832
1.804
1.772
1.705
1.669
1.571
1.534
1.439
1.411
1.405
1.068
0.991
Ph
O
O
B
HO
5k
1H NMR
Solvent: CD3OD
H2O
CH3OH
2.05
3.00
0.96
0.95
3.06
1.02
0.98
1.00
2.99
3.03
4.91
3.10
3.01
10
8
6
4
2
0
PPM

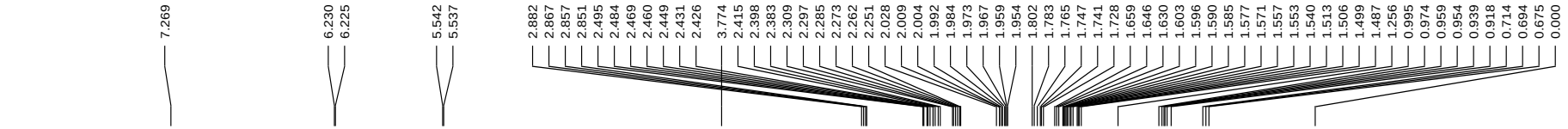

216.91
143.36
129.53
129.26
126.70
118.18
89.08
56.55
53.13
51.26
37.29
34.68
31.78
30.75
30.67
29.52
27.00
25.82
18.42
Ph
O
O
B
HO
5k
13C NMR
Solvent: CD3OD
49.64
49.43
49.21
49.00
48.79
48.57
48.36
50.5 50.0 49.5 49.0 48.5 48.0 47.5 47.0
f1 (ppm)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

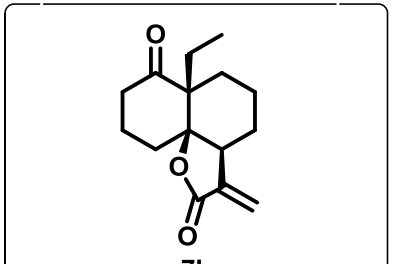

7.266
5.715
5.709
5.703
5.543
2.611
2.590
2.577
2.558
2.509
2.485
2.378
2.364
2.329
2.307
2.181
2.147
2.140
2.127
2.115
2.082
1.793
1.788
1.783
1.775
1.772
1.747
1.742
1.736
1.645
1.595
1.586
1.561
1.535
1.528
1.505
1.468
1.464
1.441
1.436
1.347
1.317
1.307
0.971
-0.000
O
O
B
HO
5m
1H NMR
Solvent: CDCl3
CHCl3
0.95
1.00
0.85
2.00
1.05
2.07
1.94
1.95
0.97
2.17
2.99
12
10
8
6
4
2
0
-2
PPM


221.170
120.687
89.065
77.419
77.100
76.781
52.775
48.819
34.796
31.600
29.778
25.875
22.732
17.790
14.206
O
O
B
HO
5m
13C NMR
Solvent: CDCl3
200
150
100
50
0
PPM


7.310
7.306
7.293
7.289
7.274
7.272
7.268
7.260
7.251
7.246
7.223
7.220
7.214
7.211
7.207
7.200
5.263
5.241
5.235
2.589
2.557
2.549
2.287
2.269
2.233
2.215
2.184
2.081
2.044
1.991
1.937
1.911
1.898
1.799
1.725
1.708
1.672
1.640
1.634
1.620
1.597
1.558
1.389
1.382
1.338
1.324
1.319
1.288
1.284
1.251
1.008
0.986
0.961
0.951
0.938
0.896
0.647
0.627
0.608
O
OH
6b
1H NMR
Solvent: CDCl3
5.23
2.08
1.00
1.99
0.99
2.99
1.96
3.10
3.28
1.22
2.91
8
6
4
2
0
PPM


213.327
151.868
144.754
128.530
127.398
126.465
115.873
77.419
77.373
77.100
76.781
58.879
47.452
37.408
31.418
28.016
25.723
22.565
19.103
14.191
7.624
O
OH
6b
13C NMR
Solvent: CDCl3
200
150
100
50
0
PPM

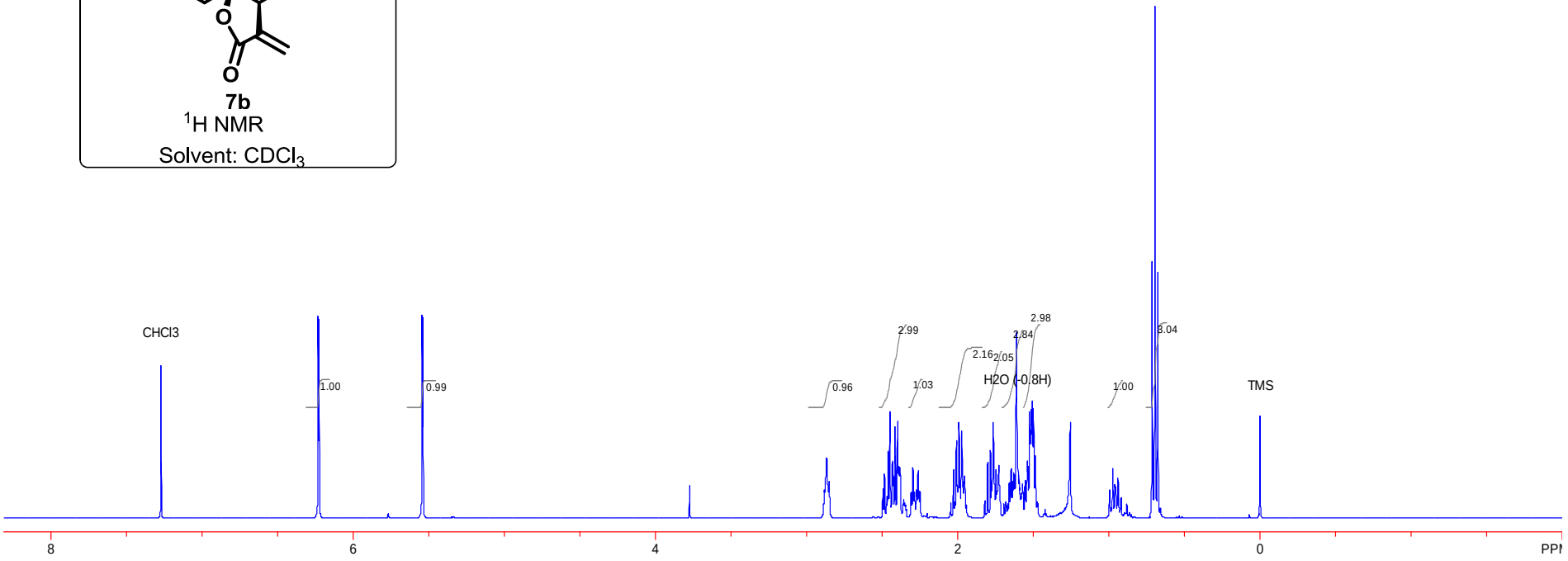


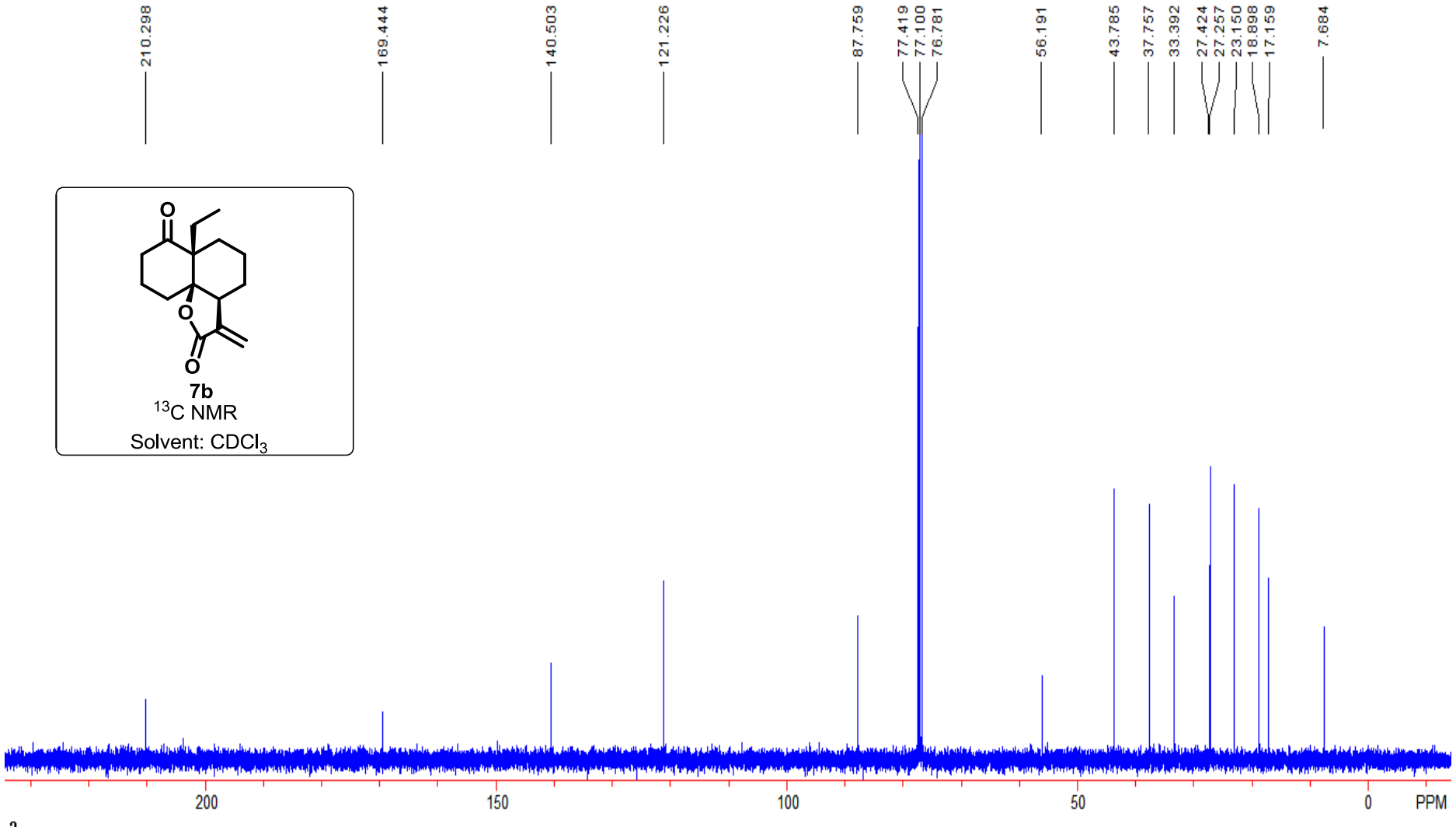


7b

^{1}H NMR

Solvent: $CDCl_3$




210.298
169.444
140.503
121.226
87.759
77.419
77.100
76.781
56.191
43.785
37.757
33.392
27.424
27.257
23.150
18.898
17.159
7.684
7b
13C NMR
Solvent: CDCl3
200
150
100
50
0
PPM