Supporting information for

A Mild Two-Step Propargylation of Aromatic Bioactive Small Molecules

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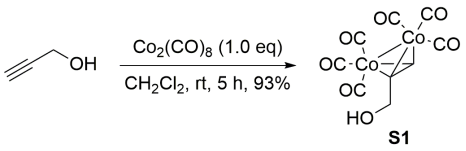
Table of Contexts

1. General procedure

All reactions were carried out under an argon atmosphere with dehydrated solvents under anhydrous conditions, unless otherwise noted. Dehydrated THF and CH_2Cl_2 were purchased from Kanto Chemical Co., Inc. Other solvents were dehydrated and distilled according to standard protocols. Reagents were obtained from commercial suppliers, unless otherwise noted. Reactions were monitored by thin-layer chromatography (TLC) carried out on Silica gel plates (Merck). Column chromatography was performed on Silica gel 60N (Kanto Chemical Co., Inc., spherical, neutral, 63-210 μm) or (Kanto Chemical Co., Inc., spherical, neutral, 40-50 μm). High performance column chromatography was performed on Mightysil Si60 250-20 mm (Kanto Chemical Co., Inc., spherical, neutral, 5 μm). IR spectra were recorded on a JASCO *FT/IR*-410 Fourier Transform Infrared Spectrophotometer. ^{1}H-NMR (400 and 600 MHz) and ^{13}C-NMR spectra (100 and 150 MHz) were recorded on JEOL JNM-AL-400 and JEOL JNM-ECA-600 spectrometers, respectively. For ^{1}H-NMR spectra, chemical shifts (δ) are given from TMS (0.00 ppm) or $CHCl_3$ (7.26 ppm) in $CDCl_3$, CHD_2COCD_3 (2.05 ppm) in CD_3COCD_3 and CHD_2SOCD_3 (2.50 ppm) in CD_3SOCD_3 as internal standards. For ^{13}C-NMR spectra, chemical shifts (δ) are given from $CDCl_3$ (77.0 ppm), CD_3COCD_3 (29.84 ppm and 206.26 ppm) and CD_3SOCD_3 (39.52 ppm) as internal standards. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, dd, = double doublet, ddt = double double triplet, m = multiplet, br = broad. EI mass spectra were recorded on JEOL JMS-DX303, JEOL JMS-700 and JEOL JMS-T 100 GC. FAB mass spectra were recorded on JEOL JMS-700. ESI mass spectra were recorded on Thermo Scientific Exactive Mass Spectrometer. HPLC was performed on Gilson Model 305 and 306 as pumps and Gilson Model 118 as a UV detector (254 nm) using Mightysil Si60 ϕ20-250 mm (Kanto Chemical Co., Inc., spherical, neutral, 5 μm).. Microwave irradiation was performed by using a Discover^{TM} system (CEM Japan Inc).

2. Synthesis of complex 1a

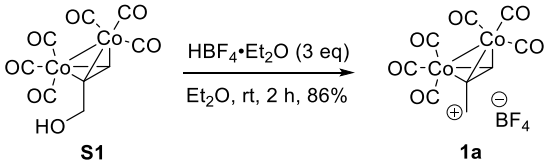
Synthesis of (prop-2-yn-1-ol)dicobalt hexacarbonyl (S1)[1]



S1

A mixture of prop-2-yn-1-ol (0.90 mL, 15.6 mmol) and $Co_2(CO)_8$ (5.22 g, 15.6 mmol) in CH_2Cl_2 (38 mL) was stirred at room temperature for 5 h. The solution was concentrated in vacuo. Column chromatography of the residue on silica gel (EtOAc / Hexane = 1 / 4) yielded cobalt complex **S1**[1] as a red solid (4.76 g, 13.9 mmol, 93%).

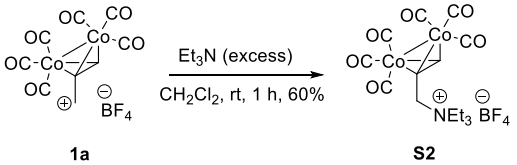
Synthesis of hexacarbonyl(2-propynylium)dicobalt tetrafluoroborate (1a)[1]



S1 1a

To a solution of HBF_4•Et_2O (1.10 mL, 6.99 mmol) in Et_2O (6.0 mL) was added a solution of cobalt complex **S1** (798 mg, 2.33 mmol) in Et_2O (5.5 mL) dropwise over 15 min. The resulting mixture was stirred at room temperature for 2 h, causing precipitation of a red solid. The solid was filtered and rinsed three times with ether to remove fluoroboric acid. After vacuum drying, complex **1a**[1] was obtained as a fine red powder (828 mg, 2.01 mmol, 86%).

3. Synthesis of ammonium complex S2

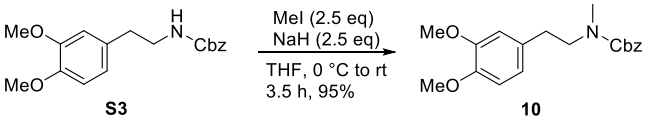


1a S2

To a suspension of complex **1a** (100 mg, 0.243 mmol) in CH_2Cl_2 (4.0 mL) was added Et_3N (2.0 ml). The reaction mixture was stirred at room temperature for 1 h and then concentrated in vacuo. The residue was purified by silica gel column chromatography (MeOH : $CHCl_3$ = 1 : 4) to give complex **S2** (74.5 mg, 0.145 mmol, 60%) as a red amorphous.

S2: red amorphous; IR (neat): 2055 cm^{-1}; ^{1}H-NMR (400 MHz, CD_3COCD_3): δ 7.06 (s, 1H), 5.22 (s, 2H), 3.69 (q, *J* = 7.1 Hz, 6H), 1.47 (t, *J* = 7.1 Hz, 9H); ^{13}C-NMR (100 MHz, CD_3COCD_3): δ 199.7, 77.2, 75.7, 60.6, 53.6, 8.1; HRMS (ESI): calcd for $C_{15}H_{18}NO_6Co_2$ (M^+): 425.9793, found: 425.9778.

4. Preparation of substrate 10



To a solution of carbamate **S3**[2] (1.00 g, 3.17 mmol) in THF (16 mL) was added 60% NaH (387 mg, 9.68 mmol) at 0 °C and the resulting mixture was stirred for 30 min at room temperature. Then the reaction mixture was cooled at 0 °C and MeI (0.5 mL, 0.80 mmol) was added. The reaction mixture was allowed to warm to room temperature and stirred for 3.5 h. The reaction was quenched with sat. NH_4Cl (5 mL) and extracted with Et_2O (20 ml × 2). The combined organic layers were washed with brine, dried over Mg_2SO_4, filtered, and concentrated in vacuo. The residue was purified by silica gel column chromatography (AcOEt : Hexane = 1:1) to give **10** (998 mg, 3.03 mm, 95%) as a yellow oil.

10: yellow oil; IR (neat): 1701 cm^{-1}; ^{1}H-NMR (400 MHz, CD_3SOCD_3): δ 7.37-7.29 (m, 5H), 6.84 (d, *J* = 8.0 Hz, 1H), 6.77 (d, *J* = 1.7 Hz, 1H), 6.79 (dd, *J* = 8.0 Hz, 1.7 Hz, 1H), 5.04 (s, 2H), 3.73 (s, 3H), 3.72 (s, 3H), 3.46 (t, *J* = 7.2 Hz, 2H), 2.83 (s, 3H), 2.73 (t, *J* = 7.2 Hz, 2H); ^{13}C-NMR (100 MHz, CD_3SOCD_3): δ 154.9, 148.8, 147.4, 136.7, 131.4, 127.7, 127.1, 126.8, 120.4, 113.3, 112.7, 65.6, 55.6, 55.5, 49.5, 33.7, 32.6; HRMS (ESI): calcd for $C_{19}H_{23}NO_4Na$ ($[M+Na]^+$): 352.1519, found 352.1505.

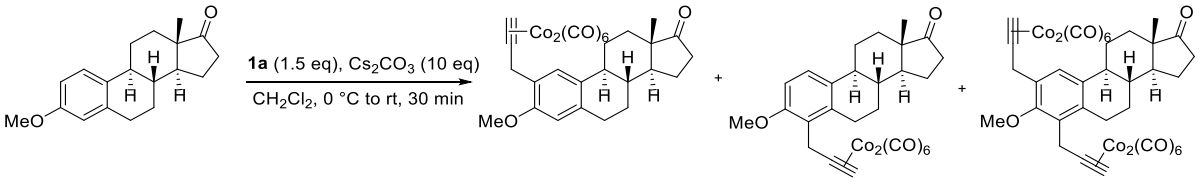
5. Functionalization of aromatic bioactive small molecules

General procedure for the functionalization of aromatic bioactive small molecules

Procedure A: To a suspension of complex **1a** (0.150 mmol) and Cs_2CO_3 (1.0 mmol) in CH_2Cl_2 (1.0 mL) was added neat substrate (0.100 mmol) or a solution of substrate (0.100 mmol) in CH_2Cl_2 (1.0 mL) at -20 °C or 0 °C. The solution was allowed to warm to 0 °C or room temperature and stirred until completion of the reaction as monitored by TLC. The reaction mixture was diluted with water (2.0 mL) and extracted with CH_2Cl_2 (4.0 mL × 2). The combined organic layers were dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by silica gel column chromatography or HPLC.

Procedure B: The suspension of complex **1a** (0.150 mmol), Cs_2CO_3 (0.100 mmol) and substrate (0.100 mmol) in CH_2Cl_2 (2.0 mL) was heated at 40 °C by microwave irradiation. After reaction was complete, the mixture was diluted with water (2.0 mL) and extracted with CH_2Cl_2 (4.0 mL × 2). The combined oragnic layers were dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by silica gel column chromatography.

Functionalization of estrone 3-methyl ether (2)



2 **3** (45%) **4** (40%) **5** (7%)

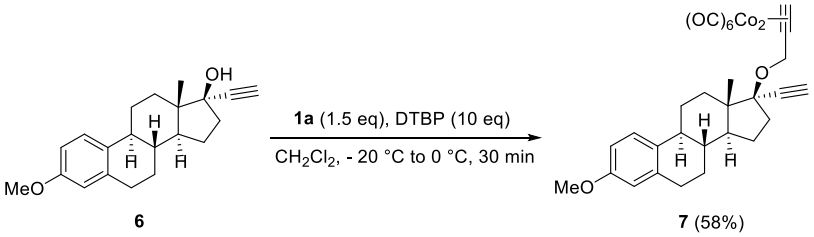
The procedure A was followed with a reaction time of 30 min at room temperature to provide a mixture (57.8 mg) of **3** (0.0451 mmol, 45%), **4** (0.0397 mmol, 40%) and **5** (6.60 μmol, 7%). The product ratio was determined by ^{1}H-NMR. The analytical samples were obtained by HPLC separation (AcOEt : Hexane = 15 : 85, 9 mL/min).

3 (retention time: 13.5 min): red oil; IR (neat): 2018 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.07 (s, 1H), 6.57 (s, 1H), 6.00 (s, 1H), 4.07 (s, 2H), 3.79 (s, 3H), 2.89-2.86 (m, 2H), 2.50 (dd, *J* = 19.1 Hz, 8.5 Hz, 1H), 2.40-2.37 (m, 1H), 2.23-1.95 (m, 4H), 1.64-1.36 (m, 6H), 0.91 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 221.0, 199.9, 155.0, 136.4, 131.5, 127.6, 126.0, 110.6, 98.4, 73.7, 54.8, 50.4, 48.0, 43.8, 38.4, 35.9, 33.9, 31.6, 29.6, 26.6, 25.8, 21.6, 13.8; HRMS (ESI): calcd for $C_{28}H_{27}O_8Co_2$ ($[M+H]^+$): 609.0364, found: 609.0361.

4 (retention time: 14.3 min): red oil; IR (neat): 2014 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.19 (d, *J* = 8.8 Hz, 1H), 6.71 (d, *J* = 8.8 Hz, 1H), 5.94 (s, 1H), 4.26 (d, *J* = 15.1 Hz, 1H), 4.14 (d, *J* = 15.1 Hz, 1H), 3.81 (s, 3H), 3.06 (dd, *J* = 16.7 Hz, 5.8 Hz, 1H), 2.93-2.84 (m, 1H), 2.51 (dd, *J* = 18.5 Hz, 8.8 Hz, 1H), 2.39 (br s, 1H), 2.27 (br s, 1H), 2.20-2.05 (m, 4H), 1.66-1.40 (m, 6H), 0.90 (s, 3H);^{13}C-NMR (100 MHz, $CDCl_3$): δ 220.9, 199.8, 155.0, 135.5, 132.5, 126.7, 124.8, 107.8, 95.9, 73.6, 54.7, 50.5, 47.9, 44.2, 37.7, 35.9, 31.6, 29.8, 27.0, 26.5, 26.1, 21.6, 13.8; HRMS (ESI): calcd for $C_{28}H_{26}O_8Co_2Na$ ($[M+Na]^+$): 631.0184, found: 631.0184.

5 (retention time: 11.7 min): red oil; IR (neat): 2017 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.18 (s, 1H), 6.09 (s, 1H), 5.92 (s, 1H), 4.19 (s, 2H), 4.17 (s, 2H), 3.81 (s, 3H), 3.02 (dd, *J* = 17.1 Hz, 5.4 Hz, 1H), 2.90-2.81 (m, 1H), 2.51 (dd, *J* = 18.4 Hz, 8.6 Hz, 1H), 2.36 (br s, 1H), 2.21-2.04 (m, 4H), 1.97 (d, *J* = 9.6 Hz, 1H), 1.65-1.43 (m, 6H), 0.88 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 220.7, 199.7, 154.3, 136.4, 134.8, 131.9, 130.2, 126.5, 96.2, 95.2, 74.2, 61.4, 50.5, 47.9, 44.3, 37.4, 35.9, 34.7, 31.6, 31.2, 27.0, 26.4, 25.9, 21.6, 13.7; HRMS (ESI): calcd for $C_{37}H_{27}O_{14}Co_4$ ($[M-H]^-$): 930.8723, found: 930.8743.

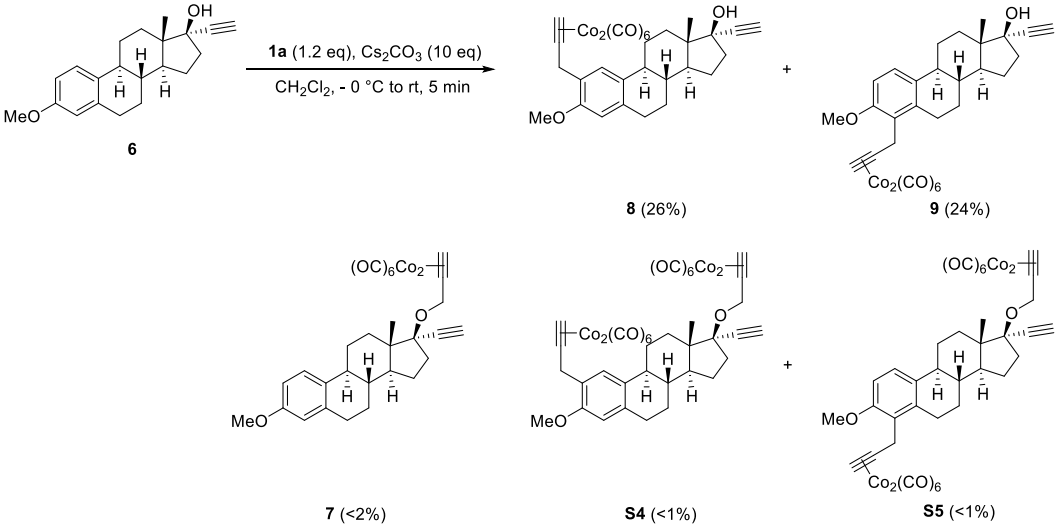
Functionalization of mestranol (6) using *2,6*-di-*tert*-butylpyridine as a base



The procedure A was followed, employing *2,6*-di-*tert*-butylpyridine instead of Cs_2CO_3 as a base, with a reaction time of 30 min. The crude product was purified by silica gel column chromatography (AcOEt : hexane = 1 : 20) to provide **7** (36.7 mg, 0.0579 mmol, 58%) and recovered **6** (11.2 mg, 0.0361 mmol, 36%).

7: red oil; IR (neat): 2033 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.21 (d, *J* = 8.6 Hz, 1H), 6.71 (dd, *J* = 8.6 Hz, 2.6 Hz, 1H), 6.63 (d, *J* = 2.6 Hz, 1H), 5.99 (s, 1H), 4.86 (d, *J* = 13.0 Hz, 1H), 4.72 (d, *J* = 13.0 Hz, 1H), 3.78 (s, 3H), 2.85-2.84 (m, 2H), 2.63 (s, 1H), 2.32-2.24 (m, 3H), 2.12-2.02 (m, 2H), 1.99-1.77 (m, 4H), 1.51-1.35 (m, 4H), 0.93 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 199.7, 157.4, 137.9, 132.6, 126.4, 113.8, 111.5, 93.3, 85.7, 84.8, 76.1, 70.8, 65.8, 55.2, 49.4, 47.8, 43.5, 39.2, 36.7, 33.9, 29.8, 27.3, 26.5, 22.9, 12.8; HRMS (FAB): calcd for $C_{30}H_{29}O_8Co_2$ ($[M+H]^+$): 635.0526, found: 635.0537.

Functionalization of mestranol (6) using Cs_2CO_3 as a base



The procedure A was followed with a reaction time of 30 min to provide a mixture (35.4 mg) of **8** (0.0260 mmol, 26%), **9** (0.0237 mmol, 24%) and recovered **6** (0.0148 mmol, 15%), and a mixture (4.50 mg) of **7** (<1.58 μmol, <2%), **S4** (<0.689 μmol, <1%) and **S5** (<0.896 μmol, <1%) containing unseparatable and unknown byproduct. The ratio was determined by ^{1}H-NMR. In this case, 1.2 equivalent of **1a** was added.

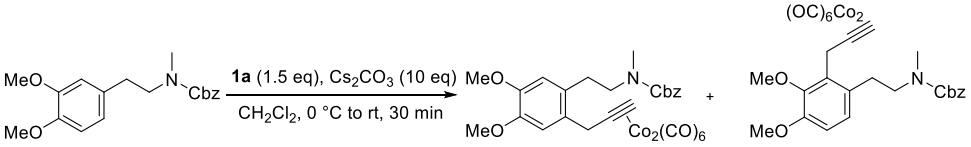
The analytical samples were obtained by extensive silica gel column chromatography separation (AcOEt : hexane = 1 : 8 to 1 : 4).

8: red oil; IR (neat): 2018 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.07 (s, 1H), 6.56 (s, 1H), 5.99 (s, 1H), 4.07 (s, 2H), 3.79 (s, 3H), 2.83 (br s, 2H), 2.60 (s, 1H), 2.37-2.30 (m, 2H), 2.20 (br s, 1H), 2.04-1.99 (m, 1H), 1.95-1.67 (m, 5H), 1.53-1.33 (m, 4H), 0.88 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 199.9, 154.9, 136.6, 132.0, 127.7, 125.9, 110.5, 98.5, 87.5, 79.9, 74.0, 73.7, 54.7, 49.4, 47.1, 43.4, 39.4, 39.0, 34.0, 32.8, 29.7, 27.3, 26.3, 22.8, 12.6; HRMS (ESI): calcd for $C_{30}H_{27}O_8Co_2$ ($[M-H]^-$): 633.0364, found: 633.0394.

9: red oil; IR (neat): 2018 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.20 (d, J = 8.7 Hz, 1H), 6.70 (d, J = 8.7 Hz, 1H), 5.93 (s, 1H), 4.24 (d, J = 15.0 Hz, 1H), 4.13 (d, J = 15.0 Hz, 1H), 3.80 (s, 3H), 3.01 (d, J = 16.8 Hz, 1H), 2.88-2.79 (m, 1H), 2.60 (br s, 1H), 2.35 (br s, 2H), 2.24 (br s, 1H), 2.06-1.67 (m, 6H), 1.53-1.29 (m, 4H), 0.87 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 199.8, 154.9, 135.7, 132.9, 126.6, 124.8, 107.7, 96.0, 87.5, 79.9, 74.0, 73.7, 54.7, 49.5, 47.0, 43.8, 39.0, 38.7, 32.7, 29.8, 27.2, 27.1, 26.6, 22.8, 12.6; HRMS (ESI): calcd for $C_{30}H_{27}O_8Co_2$ ($[M-H]^-$): 633.0364, found: 633.0388.

A 1 : 1 mixture of **S4** and **S5**: red oil; IR (neat): 2019 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.18 (d, J = 8.7 Hz, 0.5H), 7.07 (s, 0.5H), 6.70 (d, J = 8.7 Hz, 0.5H), 6.55 (s, 0.5H), 6.00 (s, 1.5H), 5.93 (s, 0.5H), 4.86 (d, J = 13.0 Hz, 1H), 4.72 (d, J = 13.0 Hz, 1H), 4.24 (d, J = 14.7 Hz, 0.5H), 4.13 (d, J = 14.7 Hz, 0.5H), 4.07 (s, 1H), 3.80 (s, 1.5H), 3.79 (s, 1.5H), 3.02-2.98 (m, 0.5H), 2.88-2.82 (m, 1.5H), 2.63 (s, 1H), 2.33-2.24 (m, 3H), 2.21-1.99 (m, 3H), 1.88-1.74 (m, 4H), 1.53-1.33 (m, 4H), 0.93 (s, 1.5H), 0.92 (s, 1.5H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 199.9, 154.87, 154.86, 136.6, 135.7, 133.0. 132.1, 127.7, 126.6, 125.8, 124.8, 110.5, 107.7, 98.5, 96.0, 93.3, 85.70, 85.67, 84.9, 84.8, 76.1, 73.7, 70.8, 65.8, 54.75, 54.71, 49.48, 49.42, 47.8, 47.7, 43.8, 43.4, 39.2, 38.5, 36.7, 34.0, 29.7, 27.3, 27.2, 26.7, 26.4, 22.9, 12.8; HRMS (FAB): calcd for $C_{36}H_{30}O_{11}Co_4$ ($[M-3CO]^+$): 873.9116, found: 873.9118.

Functionalization of benzyl (3,4-dimethoxyphenethyl)(methyl)carbamate (10)



10 **10a** (70%) **10b** (5%)

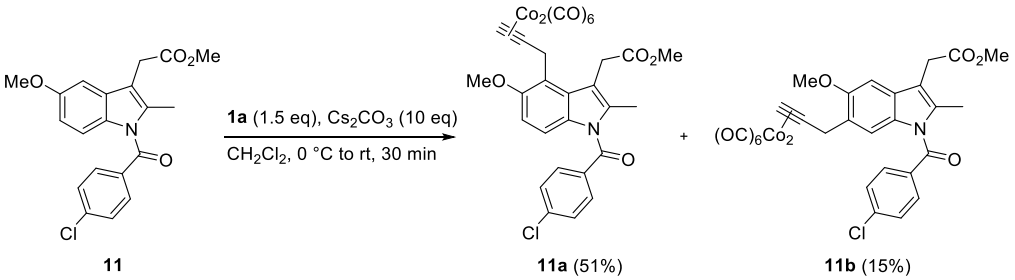
The procedure A was followed with a reaction time of 30 min. The crude product was purified by silica gel column chromatography (AcOEt : hexane = 1 : 8 to 1 : 2) to provide **10a** (45.5 mg, 0.0697 mmol, 70%) and **10b** (3.09 mg, 4.73 μmol, 5%).

10a (a mixture of two rotamers): red oil; IR (neat): 2018 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.35-7.30 (m, 5H), 6.72 (s, 0.5H), 6.67 (s, 1H), 6.52 (s, 0.5H), 6.07 (s, 0.5H), 5.95 (s, 0.5H), 5.13 (s, 1H), 5.10 (s, 1H), 4.13 (s, 1H), 3.97 (s, 1H), 3.86 (s, 3H), 3.82 (s, 1.5H), 3.74 (s,

1.5H), 3.45 (br s, 2H), 2.93-2.84 (m, 5H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 199.8, 156.3, 148.5, 147.9, 137.1, 136.9, 131.2, 131.0, 128.8, 128.7, 128.2, 128.0, 113.7, 113.1, 97.4, 97.2, 73.6, 67.5, 67.2, 56.2, 56.0, 51.2, 50.8, 37.1, 36.8, 35.3, 34.8, 31.4, 30.9; HRMS (EI): calcd for $C_{22}H_{25}NO_4Co_2$ ([M-6CO]$^+$): 485.0448, found: 485.0462.

10b (a mixture of two rotamers): red oil; IR (neat): 2019 cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$): δ 7.38-7.32 (m, 5H), 6.89 (d, *J* = 8.2 Hz, 0.5H), 6.79-6.73 (m, 1.5H), 5.98 (s, 0.5H), 5.88 (s, 0.5H), 5.12 (s, 1H), 5.11 (s, 1H), 4.23 (s, 1H), 4.06 (s, 1H), 3.85 (s, 2H), 3.82 (s, 4H), 3.44 (t, *J* = 7.6 Hz, 2H), 2.93 (s, 3H), 2.90-2.84 (m, 2H); ^{13}C-NMR (150 MHz, $CDCl_3$): δ 199.7, 156.0, 151.4, 147.4, 137.0, 136.8, 132.8, 132.5, 129.7, 129.6, 128.5, 128.0, 127.9, 127.8, 125.0, 111.5, 111.4, 95.9, 95.6, 73.8, 67.2, 67.0, 60.3, 55.8, 51.2, 50.6, 35.0, 34.5, 31.4, 30.9, 30.6; HRMS (ESI) $C_{28}H_{25}Co_2O_{10}NNa$ ([M+Na]$^+$) calcd for 676.0035, found: 676.0017.

Functionalization of indometacin methyl ester (11)[3]



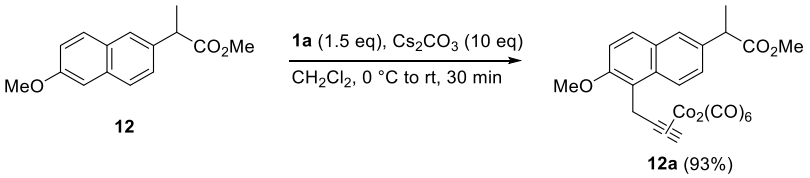
11 **11a** (51%) **11b** (15%)

The procedure A was followed with a reaction time of 30 min. The crude product was purified by silica gel column chromatography (AcOEt : hexane = 1 : 25) to provide **11a** (35.6 mg, 0.0511 mmol, 51%) and **11b** (10.2 mg, 0.0146 mmol, 15%).

11a: red oil; IR (neat): 2020 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 7.8 Hz, 2H), 7.45 (d, *J* = 7.8 Hz, 2H), 6.90 (d, *J* = 9.0 H, 1H), 6.64 (d, *J* = 9.0 Hz, 1H), 5.91 (s, 1H), 4.55 (s, 2H), 3.90 (s, 2H), 3.83 (s, 3H), 3.70 (s, 3H), 2.37 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 199.9, 171.7, 168.3, 152.9, 139.5, 137.2, 133.9, 131.7, 131.3, 129.1, 128.2, 119.4, 113.3, 111.6, 106.9, 96.7, 73.2, 55.6, 52.2, 31.3, 29.5, 13.2; HRMS (ESI): calcd for $C_{29}H_{21}NO_{10}ClCo_2$ ([M+H]$^+$): 695.9513, found: 695.9503.

11b: red oil; IR (neat): 2019 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 8.3 Hz, 2H), 7.49 (d, *J* = 8.3 Hz, 2H), 6.91 (s, 1H), 6.90 (s, 1H), 5.89 (s, 1H), 4.03 (s, 2H), 3.88 (s, 3H), 3.68 (s, 3H), 3.67 (s, 2H), 2.33 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 199.7, 171.3, 168.4, 153.8, 139.3, 135.2, 131.1, 134.1, 130.3, 129.5, 129.1, 125.1, 116.0, 112.6, 99.1, 97.9, 73.7, 55.1, 52.1, 34.6, 30.3, 13.4; HRMS (ESI): calcd for $C_{29}H_{20}NO_{10}ClCo_2Na$ ([M+Na]$^+$): 717.9332, found: 717.9320.

Functionalization of naproxen methyl ester (12)[4]

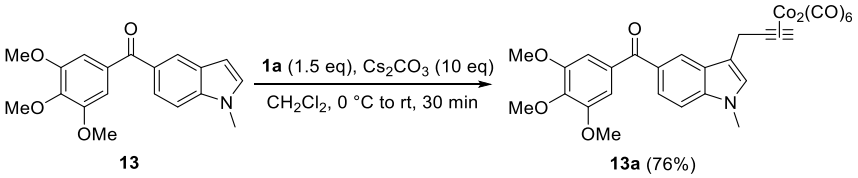


12 **12a** (93%)

The procedure A was followed with a reaction time of 30 min. The crude product was purified by silica gel column chromatography (AcOEt : hexane = 1 : 12) to provide **12a** (52.6 mg, 0.0925 mmol, 93%).

12a: red oil; IR (neat): 2019 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.90 (d, *J* = 8.9 Hz, 1H), 7.75 (d, *J* = 9.9 Hz, 1H), 7.68 (s, 1H), 7.48 (d, *J* = 8.9 Hz, 1H), 7.24 (d, *J* = 9.9 Hz, 1H), 5.91 (s, 1H), 4.61 (s, 2H), 3.96 (s, 3H), 3.87 (q, *J* = 7.1 Hz, 1H), 3.68 (s, 3H), 1.59 (d, *J* = 7.1 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 199.7, 175.1, 154.0, 135.3, 131.8, 129.1, 128.8, 126.8, 126.4, 123.7, 121.1, 112.7, 96.2, 73.5, 55.6, 52.0, 45.2, 29.0, 18.5; HRMS (EI): calcd for $C_{19}H_{18}O_4Co_2$ ($[M-5CO]^+$): 427.9869, found: 427.9864.

Functionalization of compound 13[5]

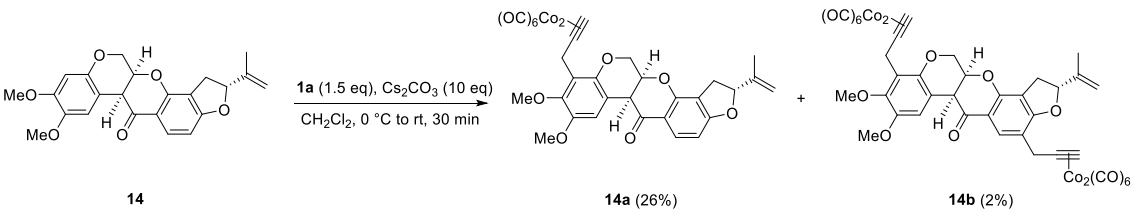


13 **13a** (76%)

The procedure A was followed with a reaction time of 30 min. The crude product was purified by silica gel column chromatography (AcOEt : hexane = 1 : 2) to provide **13a** (49.2 mg, 0.0758 mmol, 76%).

13a: red oil; IR (neat): 2018 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.18 (s, 1H), 7.76 (d, *J* = 8.7 Hz, 1H), 7.35 (d, *J* = 8.7 Hz, 1H), 7.08 (s, 2H), 7.06 (s, 1H), 6.04 (s, 1H), 4.29 (s, 2H), 3.94 (s, 3H), 3.89 (s, 6H), 3.82 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 199.6, 196.4, 152.8, 141.4, 139.2, 134.2, 129.1, 128.6, 126.9, 124.3, 122.7, 116.0, 108.9, 107.6, 97.8, 73.5, 60.9, 56.3, 32.9, 29.9; HRMS (ESI): calcd for $C_{28}H_{22}NO_{10}Co_2$ ($[M+H]^+$): 649.9902, found: 649.9902.

Functionalization of rotenone (14)



14 **14a** (26%) **14b** (2%)

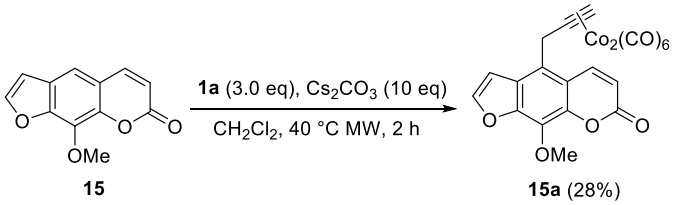
The procedure A was followed with a reaction time of 30 min. The crude product was

purified by HPLC (AcOEt : hexane = 3 : 7, 9 mL/min) to provide **14a** (18.9 mg, 0.0261 mmol, 26%) and **14b** (2.11 mg, 2.02 μmol, 2%).

14a (retention time: 10.8 min): red oil; IR (neat): 2017 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.83 (d, *J* = 8.4 Hz, 1H), 6.78 (s, 1H), 6.51 (d, *J* = 8.4 Hz, 1H), 6.00 (s, 1H), 5.28 (dd, *J* = 9.9 Hz, 8.0 Hz, 1H), 5.09 (s, 1H), 4.95-4.93 (m, 2H), 4.66 (dd, *J* = 11.9 Hz, 2.9 Hz, 1H), 4.17 (d, *J* = 11.9 Hz, 1H), 4.14 (s, 2H), 3.85 (d, *J* = 3.9 Hz, 1H), 3.83 (s, 3H), 3.74 (s, 3H), 3.32 (dd, *J* = 15.7 Hz, 9.9 Hz, 1H), 3.01 (dd, *J* = 15.7 Hz, 8.0 Hz, 1H), 1.78 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$,): δ 199.9, 188.8, 167.3, 158.0, 147.7, 147.2, 145.1, 143.0, 130.0, 122.3, 113.4, 112.8, 112.6, 110.8, 109.0, 104.8, 96.6, 87.8, 73.6, 72.1, 65.9, 60.5, 56.4, 45.0, 31.3, 27.6, 17.1; HRMS (ESI): calcd for $C_{32}H_{25}O_{12}Co_2$ ($[M+H]^+$): 719.0005, found: 718.9995.

14b (retention time: 8.8 min): red oil; IR (neat): 2018 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.73 (s, 1H), 6.73 (s, 1H), 6.03 (s, 1H), 5.99 (s, 1H), 5.29 (t, *J* = 9.2 Hz, 1H), 5.11 (s, 1H), 4.98 (s, 1H), 4.91-4.89 (m, 1H), 4.64 (dd, *J* = 11.8 Hz, 3.1 Hz, 1H), 4.17 (d, *J* = 12.1 Hz, 1H), 4.14 (s, 2H), 4.07 (d, *J* = 15.5 Hz, 1H), 3.98 (d, *J* = 15.5 Hz, 1H), 3.83 (s, 4H), 3.72 (s, 3H), 3.32 (dd, *J* = 15.9 Hz, 9.7 Hz, 1H), 3.04 (dd, *J* = 15.8 Hz, 8.4 Hz, 1H), 1.81 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 199.8, 188.8, 165.3, 157.1, 147.7, 147.1, 145.1, 142.8, 129.8, 122.3, 117.5, 113.3, 113.03, 112.98, 110.8, 109.0, 96.7, 96.2, 88.1, 73.67, 73.63, 72.2, 65.9, 60.6, 56.3, 45.1, 33.3, 31.6, 27.6, 17.3; HRMS (ESI): calcd for $C_{41}H_{27}O_{18}Co_4$ ($[M+H]^+$): 1042.8520, found: 1042.8508.

Functionalization of xanthotoxin (15)

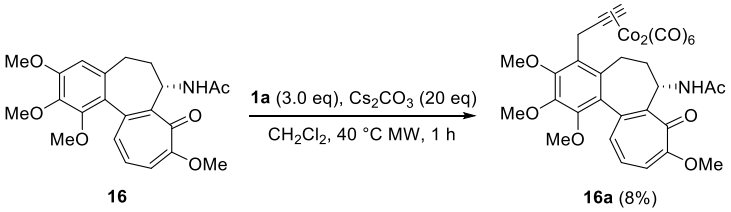


15 **15a** (28%)

The procedure B was followed with a reaction time of 2 h. The crude product was purified by silica gel column chromatography (AcOEt : hexane = 1 : 4) to provide 1**5a** (15.1 mg, 0.0280 mmol, 28%) along with recovered **15** (14.5 mg, 0.0669 mmol, 67%)

15a: red oil; IR (neat): 2021 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.03 (d, *J* = 9.8 Hz, 1H), 7.74 (d, *J* = 2.0 Hz, 1H), 6.91 (d, *J* = 2.0 Hz, 1H), 6.47 (d, *J* = 9.8 Hz, 1H), 5.95 (s, 1H), 4.50 (s, 2H), 4.24 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 199.1, 160.0, 147.3, 146.7, 143.9, 140.3, 132.3, 125.9, 123.5, 114.7, 114.1, 105.3, 94.2, 73.0, 61.5, 33.1; HRMS (ESI): calcd for $C_{21}H_{11}O_{10}Co_2$ ($[M+H]^+$): 540.9011, found: 540.8994.

Functionalization of colchicine (16)

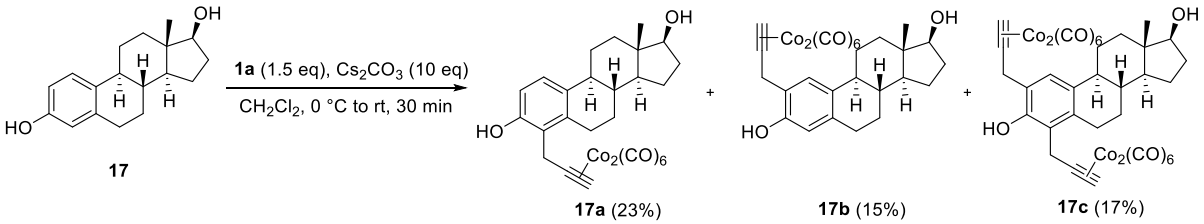


16 **16a** (8%)

On 0.05 mmol scale, the procedure B was followed, employing 20 equiv. of Cs_2CO_3 instead of 10 equiv. with a reaction time of 1 h. The crude product was purified by silica gel column chromatography (MeOH : $CHCl_3$ = 1 : 40) to provide **16a** (2.83 mg, 3.91 μmol, 8%) and recovered **16** (15.7 mg, 0.0392 mmol, 79%).

16a: red oil; IR (neat): 2022 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.56 (br s, 1H), 7.54 (s, 1H), 7.21 (d, *J* = 10.7, 1H), 6.85 (d, *J* = 10.7 Hz, 1H), 5.93 (s, 1H), 4.66-4.60 (m, 1H), 4.32 (d, *J* = 13.4 Hz, 1H), 4.00 (s, 6H), 3.92 (d, *J* = 13.4 Hz, 1H), 3.91 (s, 3H), 3.61 (s, 3H), 2.90-2.88 (m, 1H), 2.27-2.25 (m, 2H), 2.00 (s, 3H), 1.90-1.87 (m, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 199.7, 179.6, 170.1, 164.2, 152.1, 151.6, 150.5, 145.5, 136.7, 135.6, 132.1, 130.2, 129.4, 126.6, 112.7, 96.2, 96.1, 73.4, 61.4, 60.9, 60.7, 56.4, 52.5, 35.9, 30.3, 25.5, 22.9; HRMS (ESI): calcd for $C_{31}H_{27}NO_{12}Co_2Na$ ($[M+Na]^+$): 746.0089, found: 746.0067.

Funtionalizaation of estradiol (17)



17 **17a** (23%) **17b** (15%) **17c** (17%)

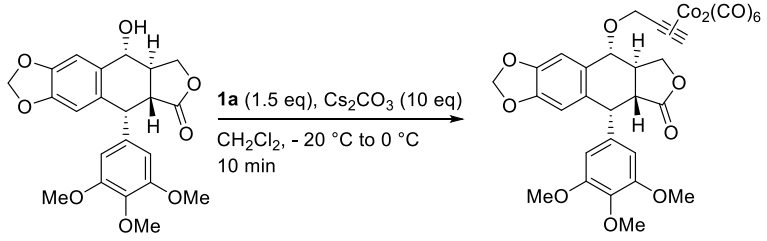
The procedure A was followed with a reaction time of 30 min. The crude product was purified by silica gel column chromatography (AcOEt : hexane = 1 : 8) to provide **17a** (15.3 mg, 0.0166 mmol, 17%), **17b** (8.88 mg, 0.0149 mmol, 15%), **17c** (13.6 mg, 0.0227 mmol, 23%) and recovered **17** (8.90 mg, 0.0327 mmol, 33%). In this case, starting material **17** was dissolved in 5 ml of CH_2Cl_2 (0.02 M) and added.

17a: red oil; IR (neat): 2017 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.02 (s, 1H), 6.04 (s, 1H), 5.98 (s, 1H), 4.80 (s, 1H), 4.18 (s, 2H), 4.13 (d, *J* = 16.1 Hz, 1H), 4.06 (d, *J* = 16.1 Hz, 1H), 3.73 (br d, *J* = 5.9 Hz, 1H), 2.94 (br d, *J* = 16.1 Hz, 1H), 2.81 (dd, *J* = 15.9 Hz, 10.5 Hz, 1H), 2.28 (br d, *J* = 11.2 Hz, 1H), 2.15 (br s, 2H), 1.95 (br d, *J* = 10.7 Hz , 2H), 1.70 (br s, 1H), 1.49-1.19 (m, 10H), 0.76 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 199.5, 149.2, 134.7, 133.6, 126.3, 125.2, 123.8, 95.6, 94.1, 81.9, 73.6, 72.9, 50.0, 44.1, 43.2, 38.1, 36.7, 35.3, 30.6, 27.2, 26.4, 23.1, 11.0; HRMS (ESI): calcd for $C_{36}H_{27}O_{14}Co_4$ ($[M-H]^-$): 918.8723, found: 918.8710.

17b: red oil; IR (neat): 2017 cm^{-1}; ^{1}H-NMR (400 MHz, CD_3COCD_3): δ 8.15 (s, 1H), 7.11 (s, 1H), 6.57 (s, 1H), 6.40 (s, 1H), 4.17 (d, *J* = 15.0 Hz, 1H), 4.10 (d, *J* = 15.0 Hz, 1H), 3.65 (br s, 1H), 3.58 (br s, 1H), 2.30 (br s, 1H), 2.12-1.95 (m, 3H), 1.83 (br s, 1H), 1.64 (br s, 1H), 1.46-1.19 (m, 10H), 0.76 (s, 3H); HRMS (ESI): calcd for $C_{27}H_{25}O_8Co_2$ ($[M-H]^-$): 595.0208, found: 595.0211.

17c: red oil; IR (neat): 2017 cm^{-1}; ^{1}H-NMR (400 MHz, CD_3COCD_3): δ 8.25 (br s, 1H), 7.04 (d, *J* = 8.2 Hz, 1H), 6.69 (d, *J* = 8.2 Hz, 1H), 6.37 (s, 1H), 4.28 (d, *J* = 14.7 Hz, 1H), 4.22 (d, *J* = 14.7 Hz, 1H), 3.66 (br s, 1H), 3.57 (br s, 1H), 3.03 (br s. 1H), 2.25 (brs, 1H), 2.13 (br s, 1H), 1.95 (br s, 4H), 1.48-1.19 (m, 8H), 0.75 (s, 3H); HRMS (ESI): calcd for $C_{27}H_{25}O_8Co_2$ ($[M-H]^-$): 595.0208, found: 595.0224.

Functionalization of podophyllotoxin (18)

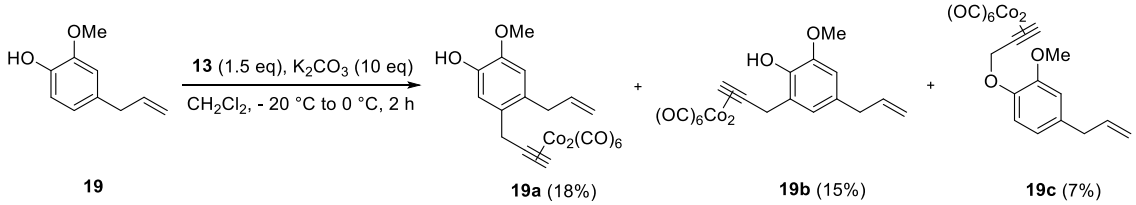


18 **18a** (28%)

The procedure A was followed with a reaction time of 10 min. The crude product was purified by silica gel column chromatography (AcOEt : hexane = 1 : 8) to provide **18a** (20.4 mg, 0.0276 mmol, 28%).

18a: red oil; IR (neat): 2029 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.07 (s, 1H), 6.52 (s, 1H), 6.37 (s, 2H), 6.08 (s, 1H), 5.98 (d, *J* = 1.0 Hz, 1H), 5.96 (d, *J* = 1.0 Hz, 1H), 4.82 (d, *J* = 10.7 Hz, 1H), 4.77 (d, *J* = 12.1 Hz, 1H), 4.69 (d, *J* = 12.1 Hz, 1H), 4.62-4.58 (m, 2H), 4.16 (t, *J* = 9.7 Hz, 1H), 3.81 (s, 3H), 3.72 (s, 6H), 3.04-2.95 (m, 1H), 2.87 (dd, *J* = 14.2 Hz, 4.6 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$,): δ 199.3, 173.9, 152.6, 147.9, 147.7, 137.0, 135.3, 131.8, 130.3, 109.7, 107.9, 106.8, 101.5, 90.3, 78.0, 71.4, 71.2, 68.7, 60.7, 55.9, 45.5, 43.9, 37.8; HRMS (ESI): calcd for $C_{31}H_{25}O_{14}Co_2$ ($[M+H]^+$): 738.9903, found: 738.9888.

Functionalization of eugenol (19)



19 **19a** (18%) **19b** (15%) **19c** (7%)

On 0.200 mmol scale, the procedure A was followed, employing K_2CO_3 instead of Cs_2CO_3 as a base, with a reaction time of 2 h. The crude product was purified by silica gel column

chromatography (AcOEt : hexane = 1 : 20 to 1 : 8) to provide a mixture of **19a** (18.4 mg, 0.0369 mmol, 15%) and **19b** (7.23 mg, 14.5 μmol, 7%) and a single product of **19a** (15.1 mg, 0.0303 mmol, 18%). The mixture of **19b** and **19c** was separated by HPLC (AcOEt : hexane = 1 : 19, 9.4 mL/min).

19a: red oil; IR (neat): 2020 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.81 (s, 1H), 6.65 (s, 1H), 6.04 (s, 1H), 5.97 (ddt, *J* = 17.0 Hz, 10.3 Hz, 6.4 Hz, 1H), 5.46 (s, 1H), 5.11 (dt, *J* = 10.3 Hz, 1.4 Hz, 1H), 5.04 (dt, *J* = 17.0 Hz, 1.4 Hz, 1H), 4.04 (s, 2H), 3.85 (s, 3H), 3.43 (dd, *J* = 6.4 Hz, 1.4 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 199.6, 145.7, 144.1, 137.2, 131.6, 128.8, 116.1, 115.9, 112.2, 97.1, 73.5, 56.0, 36.82, 36.78; HRMS (ESI): calcd for $C_{19}H_{14}O_8Co_2Na$ ($[M+Na]^+$): 510.9245, found: 510.9238.

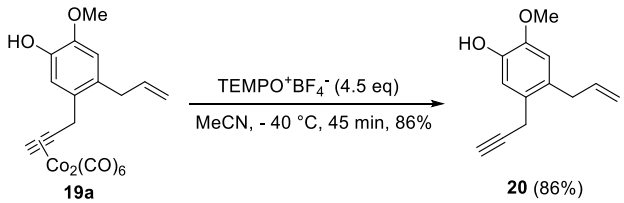
19b (retention time: 19.0 min): red oil; IR (neat): 2020 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.61 (s, 1H), 6.60 (s, 1H), 6.03 (s, 1H), 5.92 (ddt, *J* = 16.8 Hz, 10.0 Hz, 6.5Hz, 1H), 5.60 (s, 1H), 5.09-5.04 (m 2H), 4.10 (s, 2H), 3.86 (s, 3H), 3.30 (d, *J* = 6.5 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 199.7, 146.4, 141.9, 137.7, 131.3, 125.9, 122.7, 115.5, 109.9, 97.3, 73.7, 56.1, 39.9, 33.6; HRMS (EI): calcd for $C_{18}H_{14}O_7Co_2$ ($[M-CO]^+$): 459.9404, found: 459.9400.

19c (retention time: 20.7 min): red oil; IR (neat): 2023 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.88 (d, *J* = 9.0 Hz, 1H), 6.73 (s, 1H), 6.72 (d, *J* = 9.0 Hz, 1H), 6.03 (s, 1H), 6.01-5.91 (m, 1H), 5.25 (s, 2H), 5.10-5.06 (m, 2H), 3.81 (s, 3H), 3.34 (d, *J* = 6.8 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$,): δ 199.2, 150.2, 145.9, 137.6, 134.1, 120.3, 115.7, 115.1, 112.9, 89.6, 72.4, 69.7, 55.7, 39.9; HRMS (EI): calcd for $C_{12}H_{14}O_2Co_2$ ($[M-6CO]^+$): 319.9658, found: 319.9637.

6. Decomplexation of dicobalt hexacarbonyl complexes

Standard procedure: To a solution of cobalt complex in MeCN (0.01 M) was added $TEMPO^+BF_4^-$ (0.5 equiv. × 8 or 9) every 5 min at - 40 °C. After completion of the reaction, the reaction was quenched with sat. $NaHCO_3$ (2 mL) and extracted with AcOEt (4 mL × 3). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by silica gel column chromatography.

Decomplexation of compound 19a

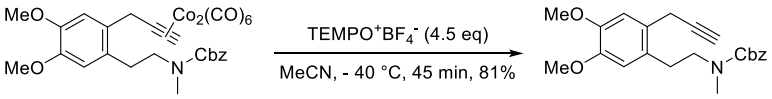


On 11.7 mg (0.0234 mmol) scale, the standard procedure was followed with $TEMPO^+BF_4^-$

(total 25.23 mg, 0.104 mmol) and a reaction time of 45 min. The crude product was purified by silica gel column chromatography (AcOEt : hexane = 1 : 4) to provide **20** (4.05 mg, 0.0200 mmol, 86%).

20: colorless oil; IR (neat): 3294, 205w cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.06 (s, 1H), 6.66 (s, 1H), 5.93 (ddt, *J* = 16.9 Hz, 10.2 Hz, 6.3 Hz, 1H), 5.46 (s, 1H), 5.06 (dd, *J* = 10.2 Hz, 1.4 Hz, 1H), 4.99 (dd, *J* = 16.9 Hz, 1.4 Hz, 1H), 3.87 (s, 3H), 3.46 (d, *J* = 2.4 Hz, 2H), 3.35 (d, *J* = 6.3 Hz, 2H), 2.15 (t, *J* = 2.4 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 145.4, 144.1, 136.6, 128.8, 127.2, 115.8, 115.1, 112.3, 82.1, 70.4, 56.0, 36.8, 21.7; HRMS (EI): calcd for $C_{13}H_{14}O_2$ (M^+): 202.0994, found: 202.0986.

Decomplexation of compound 10a



10a **21**

On 44.6 mg (0.0683 mmol) scale, the standard procedure was followed with $TEMPO^+BF_4^-$ (total 74.5 mg, 0.306 mmol) and a reaction time of 45 min. The crude product was purified by silica gel column chromatography (AcOEt : hexane = 1 : 1) to provide **21** (20.4 mg, 0.0555 mmol, 81%).

21: colorless oil; IR (neat): 3286 cm^{-1}; ^{1}H-NMR (400 MHz, CD_3SOCD_3): δ 7.36-7.30 (m, 5H), 6.97 (s, 1H), 6.72 (s, 1H), 5.06 (s, 2H), 3.74 (s, 1H), 3.70 (s, 3H), 3.49 (d, *J* = 2.5 Hz, 2H), 3.42 (t, *J* = 7.5 Hz, 2H), 2.86 (s, 3H), 2.78 (t, *J* = 7.5 Hz, 2H), 2.78 (t, *J* = 2.5 Hz, 1H); ^{13}C-NMR (100 MHz, CD_3SOCD_3): δ 154.9, 147.7, 147.3, 136.6, 128.8, 127.8, 127.1, 126.9, 126.6, 114.5, 113.8, 82.2, 71.7, 65.7, 55.7, 48.8, 40.1, 33.8, 29.6, 20.7; HRMS (EI): calcd for $C_{22}H_{25}NO_4$ (M^+): 367.1784, found: 367.1790.

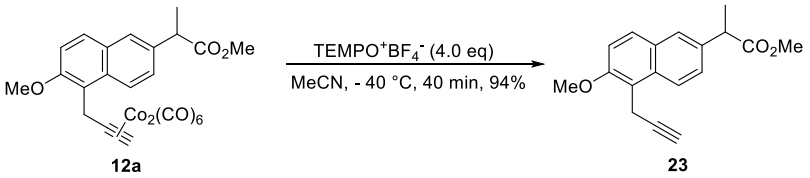
Decomplexation of compound 11b

11b **22**

On 10.4 mg (0.0149 mmol) scale, the standard procedure was followed with $TEMPO^+BF_4^-$ (total 15.9 mg, 0.0656 mmol) and a reaction time of 40 min. The crude product was purified by silica gel column chromatography (AcOEt : hexane = 1 : 12) to provide **22** (4.42 mg, 0.0108 mmol, 72%).

22: colorless oil; IR (neat): 3301 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 8.7 Hz, 2H), 7.48 (d, *J* = 8.7 Hz, 2H), 7.01 (s, 1H), 6.89 (s, 1H), 3.87 (s, 3H), 3.70 (s, 3H), 3.68 (s, 2H), 3.49 (d, *J* = 2.6 Hz, 2H), 2.46 (s, 3H), 1.97 (t, *J* = 2.6 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 171.4, 168.4, 153.4, 139.0, 135.5, 134.0, 131.1, 130.2, 129.14, 129.08, 120.7. 114.7, 112.5, 98.7, 81.5, 70.6, 55.7, 52.1, 30.2, 19.7, 13.3; HRMS (ESI): calcd for $C_{23}H_{21}NO_4Cl$ ($[M+H]^+$): 410.1154, found: 410.1148.

Decomplexation of compound 12a

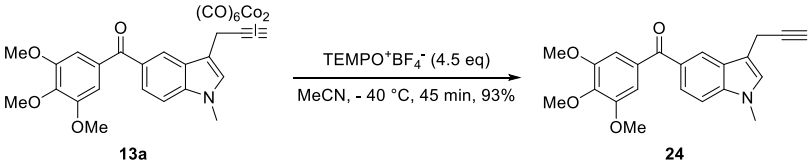


12a **23**

On 40.1 mg (0.0706 mmol) scale, the standard procedure was followed with $TEMPO^+BF_4^-$ (total 62.2 mg, 0.285 mmol) and a reaction time of 40 min. The crude product was purified by silica gel column chromatography (AcOEt : hexane = 1 : 20) to provide **23** (18.2 mg, 0.0643 mmol, 91%).

23: colorless oil; IR (neat): 3290 cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$): δ 8.02 (d, *J* = 8.9 Hz, 1H), 7.75 (d, *J* = 7.9 Hz, 1H), 7.69 (s, 1H), 7.50 (d, *J* = 8.9 Hz, 1H), 7.26 (d, *J* = 7.9 Hz, 1H), 3.97 (d, *J* = 2.3 Hz, 1H), 3.97 (s, 3H), 3.87 (q, *J* = 7.0 Hz, 1H), 3.67 (s, 3H), 1.97 (t, *J* = 2.3 Hz, 1H), 1.58 (d, *J* = 7.0 Hz, 3H); ^{13}C-NMR (150 MHz, $CDCl_3$): δ 175.0, 154.0, 135.6, 131.8, 129.3, 128.8, 126.7, 123.8, 117.5, 113.9, 82.8, 67.9, 56.8, 52.0, 45.2, 18.5, 14.4; HRMS (ESI): calcd for $C_{18}H_{19}O_3$ ($[M+H]^+$): 283.1329, found: 283.1324.

Decomplexation of compound 13a



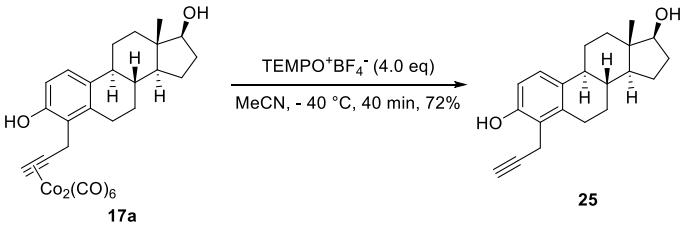
13a **24**

On 49.2 mg (0.0758 mmol) scale, the standard procedure was followed with $TEMPO^+BF_4^-$ (total 84.1 mg, 0.346 mmol) and a reaction time of 45 min. The crude product was purified by silica gel column chromatography (AcOEt : hexane = 1 : 2) to provide **24** (25.6 mg, 0.0704 mmol, 93%).

24: white amorphous; IR (neat): 3285 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.16 (d, *J* = 1.4 Hz, 1H), 7.80 (dd, *J* = 8.7 Hz, 1.4 Hz, 1H), 7.37 (d, *J* = 8.7 Hz, 1H), 7.13 (s, 1H), 7.10 (s, 2H), 3.95 (s, 3H), 3.88 (s, 6H), 3.82 (s, 3H), 3.70 (d, *J* = 2.6 Hz, 2H), 2.13 (t, 2.6 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 196.2, 152.8, 141.4, 139.4, 134.1, 129.0, 128.4, 126.3, 124.2, 122.9, 111.5, 109.1, 107.7, 82.0, 69.3, 61.0, 56.3, 32.9, 15.1; HRMS (EI): calcd for

$C_{22}H_{21}NO_4$ (M^+): 363.1471, found 363.1485.

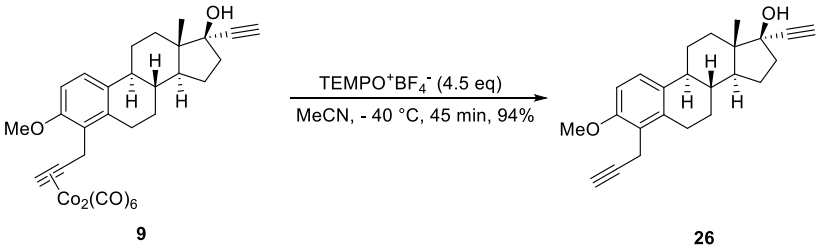
Decomplexation of compound 17a



On 19.0 mg (0.0318 mmol) scale, the standard procedure was followed with $TEMPO^+BF_4^-$ (total 31.9 mg, 0.131 mmol) and a reaction time of 45 min. The crude product was purified by silica gel column chromatography (AcOEt : hexane = 1 : 4 to 1 : 2) to provide **25** (7.13 mg, 0.0230 mmol, 72%).

25: colorless oil; IR (neat): 3305, 2115 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.12 (d, *J* = 8.3 Hz, 1H), 6.67 (d, *J* = 8.3 Hz, 1H), 5.23 (br s, 1H), 3.74 (t, *J* = 8.3 Hz, 1H), 3.55 (d, *J* = 2.4 Hz, 1H), 2.99-2.93 (m, 1H), 2.85-2.81 (m, 1H), 2.33-2.27 (m, 1H), 2.23-2.10 (m, 2H), 2.02 (t, *J* = 2.4 Hz, 1H), 2.00-1.92 (m, 2H), 1.75-1.68 (m, 1H), 1.54-1.14 (m, 7H), 0.77 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 151.3, 136.2, 133.5, 125.1, 120.8, 113.3, 81.9, 81.8, 68.4, 50.0, 44.2, 43.2, 38.0, 36.7, 30.6, 27.3, 26.9, 26.6, 23.1, 15.2, 11.0; HRMS (ESI): calcd for $C_{21}H_{25}O_2$ ($[M-H]^-$): 309.1849, found: 309.1863.

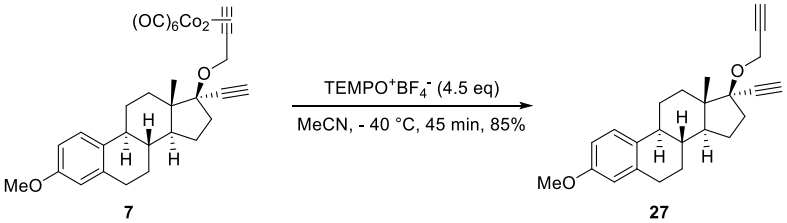
Decomplexation of compound 9



On 0.208 mmol scale, the standard procedure was followed with $TEMPO^+BF_4^-$ (total 22. 7 mg, 0.093 mmol) and a reaction time of 45 min. The crude product was purified by silica gel column chromatography (AcOEt : hexane = 1 : 8 to 1 : 4) to provide **26** (6.83 mg, 0.0196 mmol, 94%).

26: colorless oil; IR (neat): 3301 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.22 (d, *J* = 8.5 Hz, 1H), 6.76 (d, *J* = 8.5 Hz, 1H), 3.84 (s, 3H), 3.55 (s, 2H), 3.02 (dd, *J* = 17.4 Hz, 4.8 Hz, 1H), 2.89-2.80 (m, 1H), 2.61 (s, 1H), 2.39-2.23 (m, 3H), 2.04-1.66 (m, 8H), 1.56-1.33 (m, 5H), 0.88 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 154.8, 136.5, 133.2, 124.9, 122.9, 108.5, 87.6, 82.5, 79.9, 74.0, 67.0, 55.9, 49.5, 47.0, 43.8, 39.0, 38.6, 32.8, 27.3, 26.7, 26.6, 22.8, 14.9, 12.6; HRMS (ESI): calcd for $C_{24}H_{29}O_2$ ($[M+H]^+$): 349.2162, found: 349.2160.

Decomplexation of compound 7

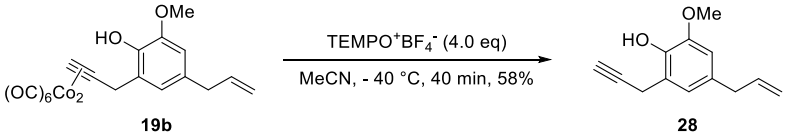


7 27

On 32.5 mg (0.0511 mmol) scale, the standard procedure was followed with $TEMPO^+BF_4^-$ (total 59.0 mg, 0.243 mmol) and a reaction time of 45 min. The crude product was purified by silica gel column chromatography (CH_2Cl_2) to provide **27** (15.1 mg, 0.0434 mmol, 85%).

27: colorless oil; IR (neat): 3288 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.20 (d, *J* = 8.4 Hz, 1H), 6.71 (dd, *J* = 8.4 Hz, 2.2 Hz, 1H), 6.63 (s, 1H), 4.34 (s, 2H), 3.77 (s, 3H), 2.87-2.84 (m, 2H), 2.67 (s, 1H), 2.43 (s, 1H), 2.35-2.25 (m, 3H), 2.22-2.09 (m, 1H), 2.02-1.94 (m, 1H), 1.88-1.71 (m, 4H), 1.54-1.30 (m, 4H), 0.92 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 157.4, 137.9, 132.5, 126.3, 113.8, 111.5, 86.1, 83.9, 80.8, 76.8, 73.5, 55.2, 53.9, 49.4, 47.7, 43.4, 39.2, 37.1, 33.9, 29.8, 27.2, 26.5, 22.8, 12.8; HRMS (ESI): calcd for $C_{24}H_{29}O_2$ ($[M+H]^+$): 349.2162, found: 349.2159.

Decomplexation of compound 19b

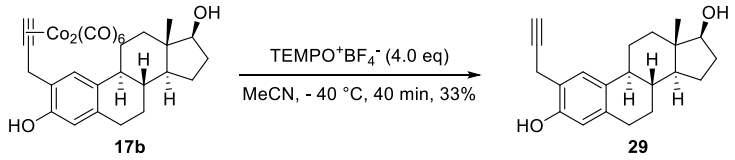


19b 28

On 13.1 mg (0.0263 mmol) scale, the standard procedure was followed with $TEMPO^+BF_4^-$ (total 25.3 mg, 0.104 mmol) and a reaction time of 40 min. The crude product was purified by silica gel column chromatography (CH_2Cl_2 : hexane = 1 : 4) to provide **28** (3.01 mg, 0.0149 mmol, 58%) and recovered **19b** (1.27 mg, 2.55 μmol, 10%).

28: colorless oil; IR (neat): 3307, 2120 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.89 (d, *J* = 3.0 Hz, 1H)), 6.61 (d, *J* = 3.0 Hz, 1H), 5.96 (ddt, *J* = 16.8 Hz, 10.0 Hz, 6.5 Hz, 1H), 5.62 (s, 1H), 5.11-5.05 (m, 2H), 3.87 (s, 3H), 3.58 (d, *J* = 2.8 Hz, 2H), 3.33 (d, *J* = 6.5 Hz, 2H), 2.15 (t, *J* = 2.8 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 146.1, 141.3, 137.8, 131.4, 121.7, 121.1, 115.6, 109.7, 81.9, 69.9, 56.1, 40.0, 18.8; HRMS (ESI): calcd for $C_{13}H_{15}O_2$ ($[M+H]^+$): 203.1067, found: 203.1068.

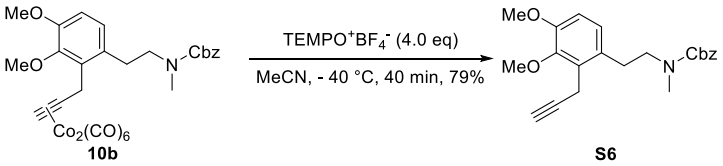
Decomplexation of compound 17b



On 15.43 mg (0.0260 mmol) scale, the standard procedure was followed with $TEMPO^+BF_4^-$ (total 30.5 mg, 0.125 mmol) and a reaction time of 45 min. The crude product was purified by silica gel column chromatography (AcOEt : hexane = 1 : 8 to 1 : 4) to provide **29** (2.68 mg, 8.63 µmol, 33%) and recovered **17b** (4.03 mg, 6.76 µmol, 26%).

29: colorless oil; IR (neat): 3306 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.22 (s, 1H), 6.54 (s, 1H), 5.12 (br s, 1H), 3.73 (t, *J* = 8.5 Hz, 1H), 3.54 (d, *J* = 2.8 Hz, 2H), 2.82-2.78 (m, 2H), 2.35-2.31 (m, 1H), 2.22 (t, *J* = 2.8 Hz, 1H), 2.17-2.07 (m, 2H), 1.98-1.93 (m, 1H), 1.88-1.84 (m, 1H), 1.73-1.66 (m, 1H), 1.52-1.15 (m, 8H), 0.78 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 151.3, 137.0, 133.0, 126.5, 119.5, 115.9, 81.9, 81.6, 70.9, 50.0, 44.0, 43.3, 38.8, 36.7, 30.6, 29.7, 29.2, 27.2, 26.4, 23.1, 19.8, 11.0; HRMS (ESI): calcd for $C_{21}H_{25}O_2$ ($[M-H]^-$): 309.1849, found: 309.1860.

Decomplexation of compound 10b



On 8.73 mg (0.0133 mmol) scale, the standard procedure was followed with TEMPO (13.0 mg, 0.0535 mmol) and a reaction time of 40 min. The crude product was purified by silica gel column chromatography (AcOEt : hexane = 1 : 4 to 1 : 1) to provide **S6** (3.86 mg, 0.0105 mmol, 79%).

S6: colorless oil; IR (neat): 3289 cm^{-1}; ^{1}H-NMR (400 MHz, CD_3SOCD_3): δ 7.36-7.30 (m, 5H), 7.36 (d, *J* = 8.6 Hz, 1H), 7.31 (d, *J* = 8.6 Hz, 1H), 5.07 (s, 2H), 3.79 (s, 3H), 3.77 (s, 3H), 3.51 (d, *J* = 2.7 Hz, 2H), 3.44 (t, *J* = 7.8 Hz, 2H), 2.86 (s, 3H), 2.84 (t, *J* = 7.8 Hz, 2H), 2.60 (t, *J* = 2.7 Hz, 1H); ^{13}C-NMR (100 MHz, CD_3SOCD_3): δ 154.9. 150.6, 146.6, 136.7, 129.6, 128.7, 127.8, 127.1, 126.9, 124.4, 111.8, 82.6, 69.7, 65.7, 59.7, 55.5, 49.1, 33.8, 29.8, 14.6; HRMS (ESI) $C_{22}H_{26}O_4N$ ($[M+H]^+$) calcd for 368.1856, found 368.1852.

7. References

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3. G. Fronza, A. Mele, E. Redenti and P. Ventura, *J. Org. Chem.*, **1996**, *61*, 909-914.
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8. ^{1}H-NMR Comparison of aromatic bioactive small molecules and their dicobalt hexacarbonyl complexes

Arrows indicate protons substituted by the propargyl dicobalt hexacarbonyl group.

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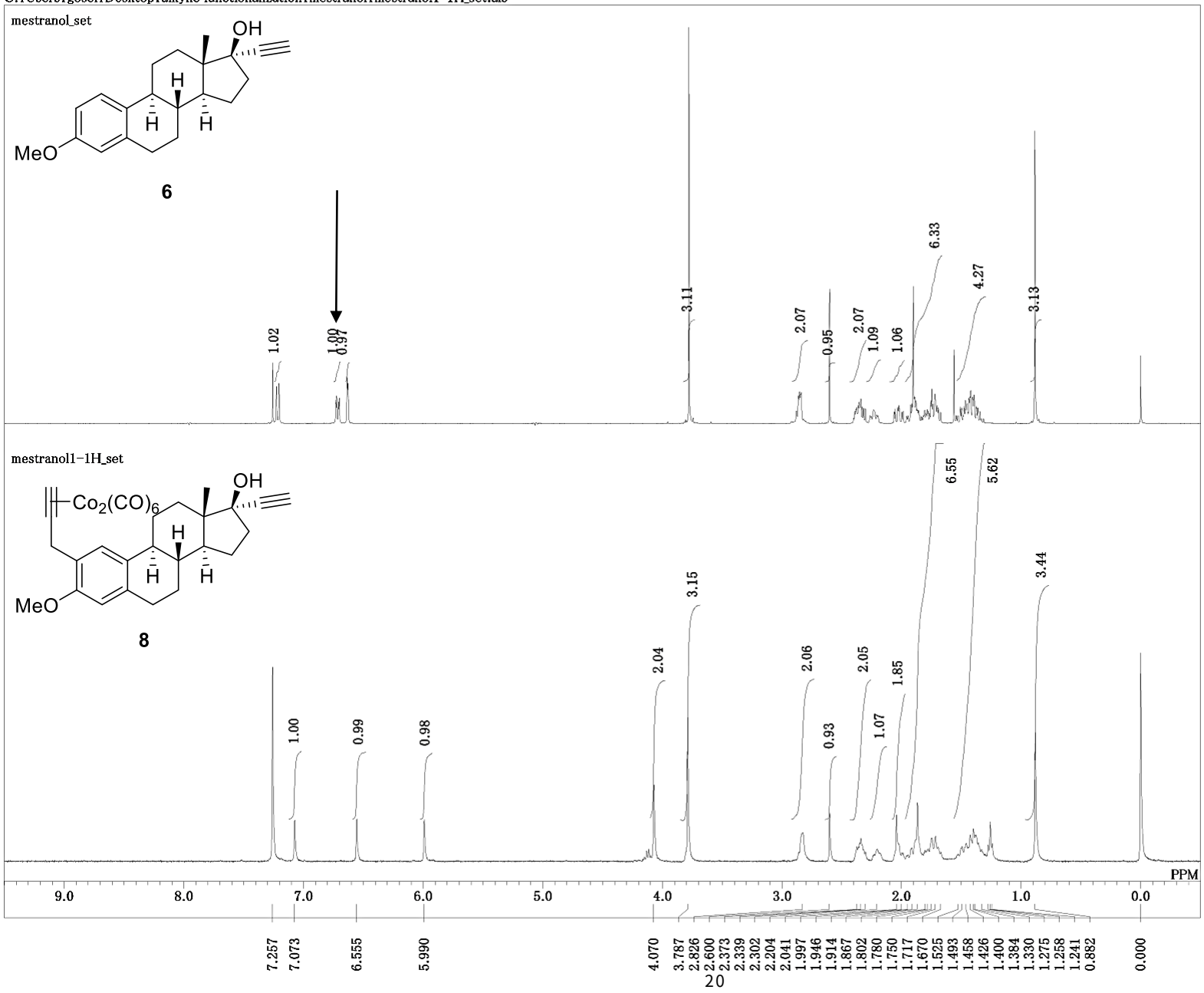

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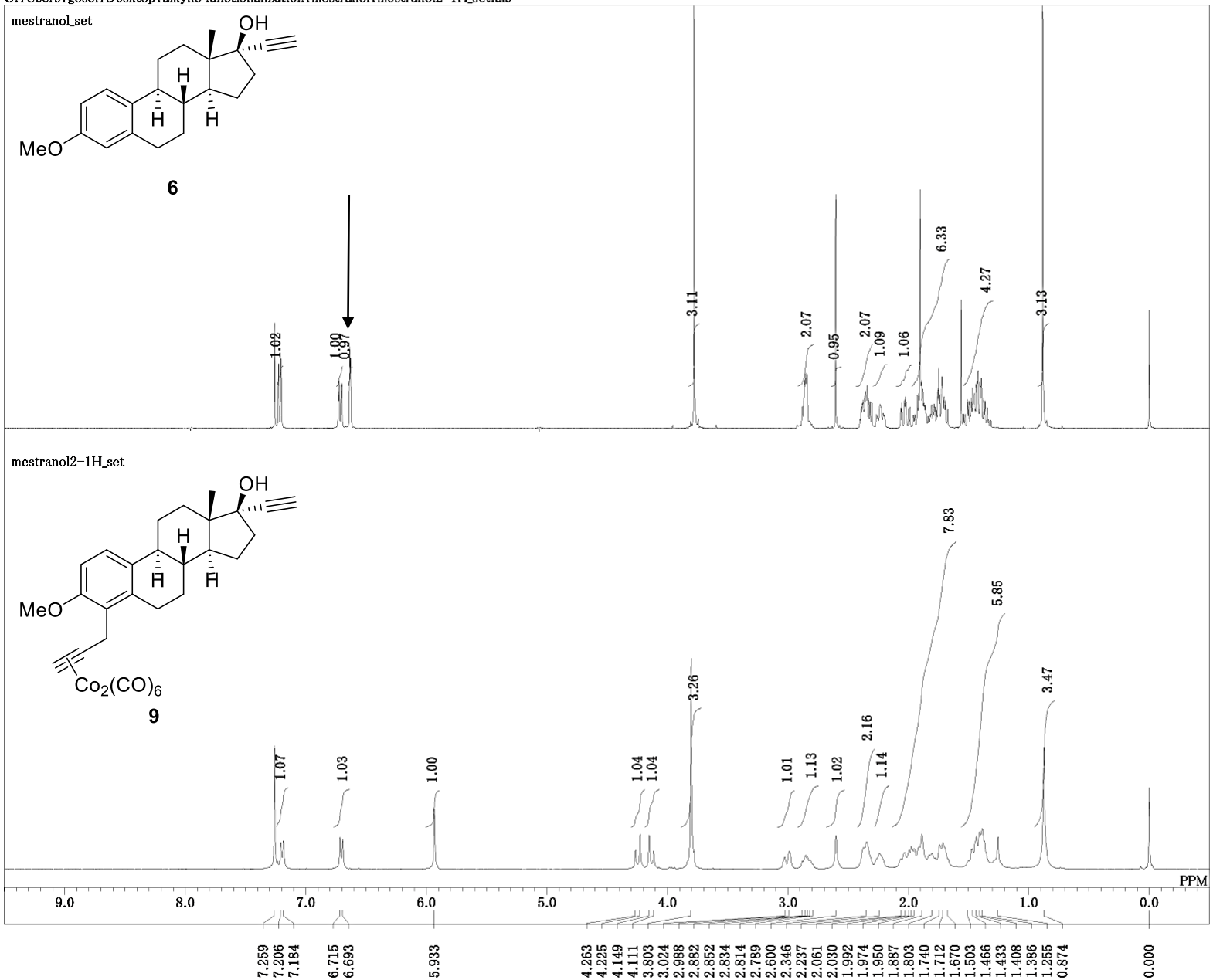

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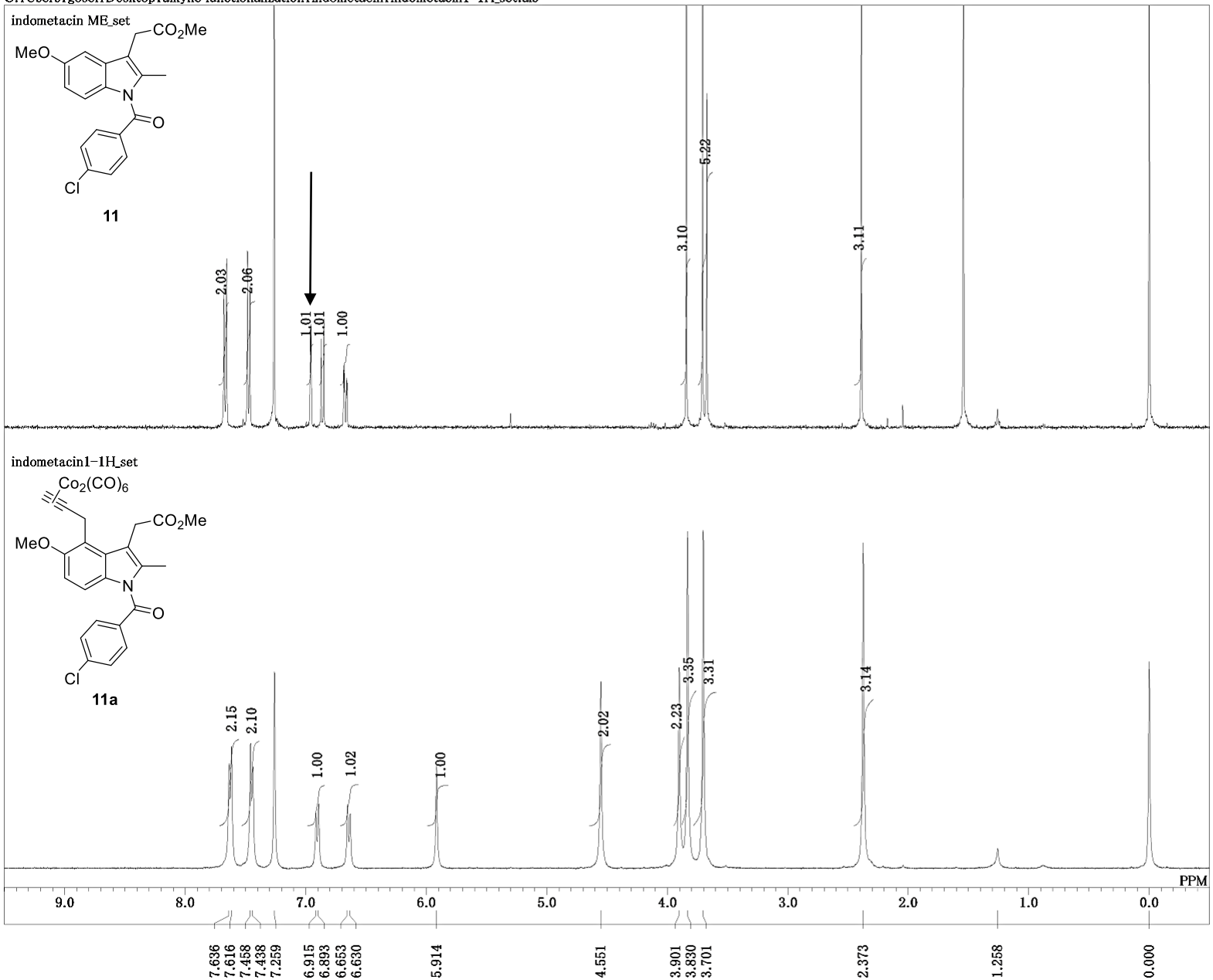

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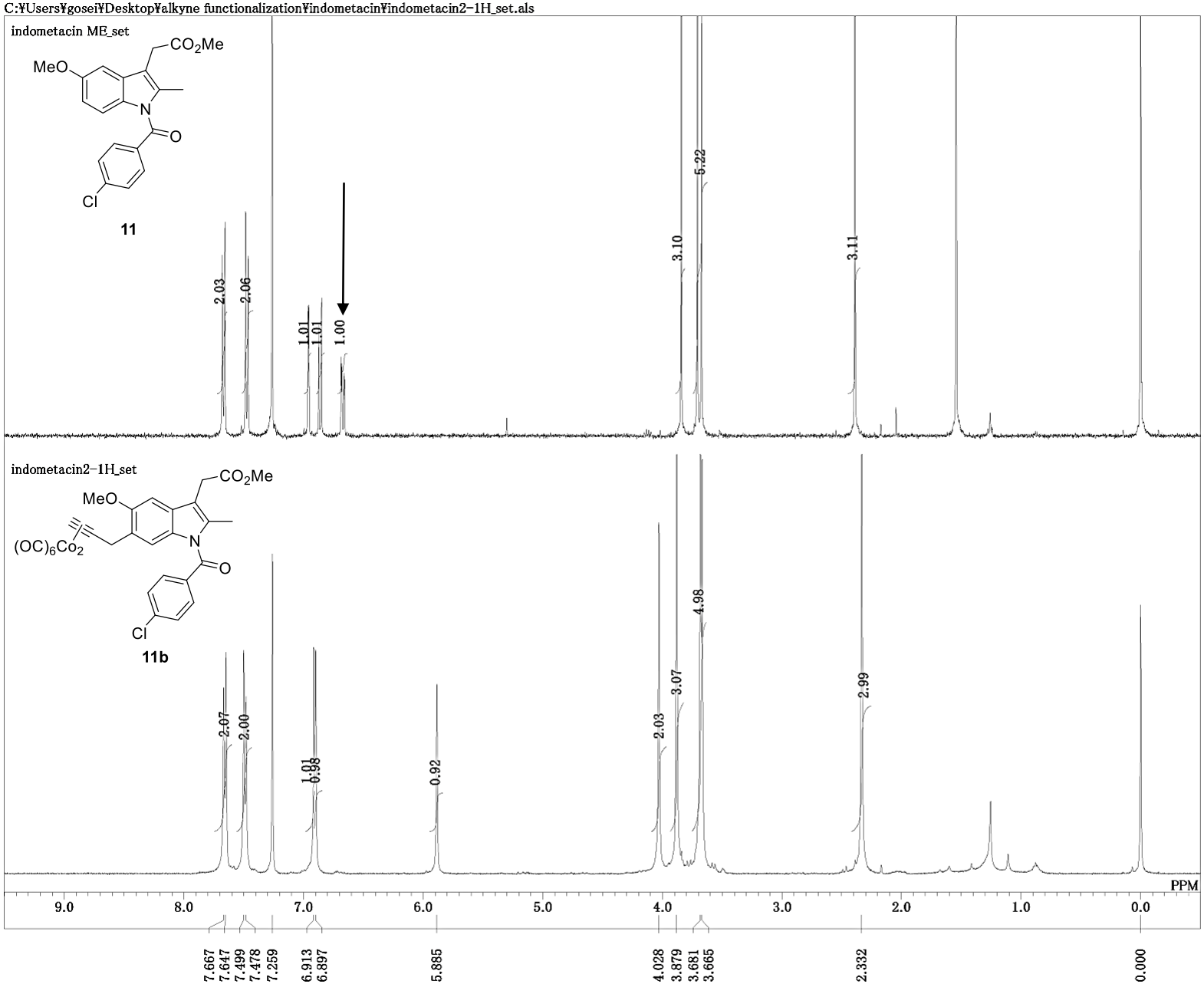

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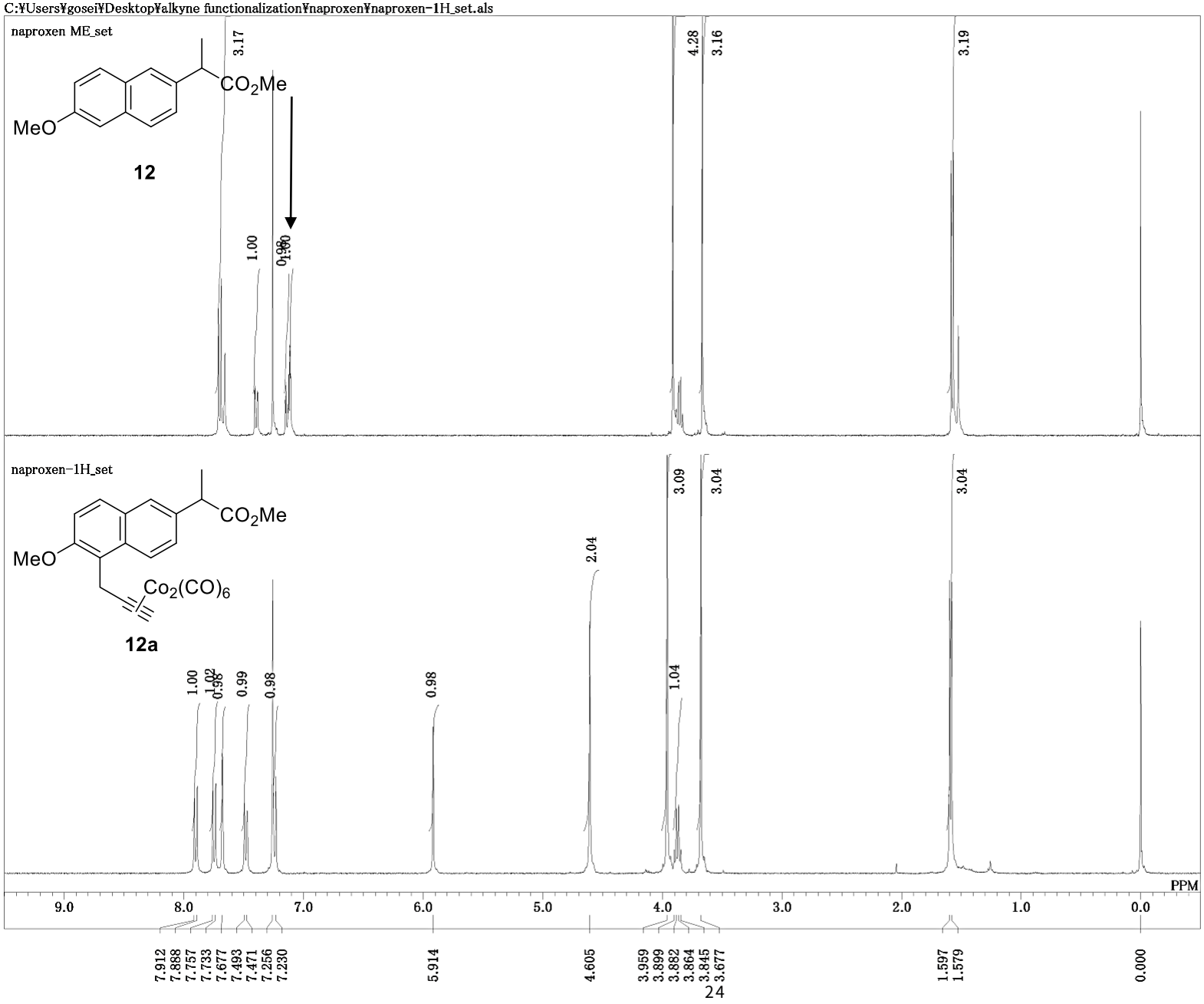

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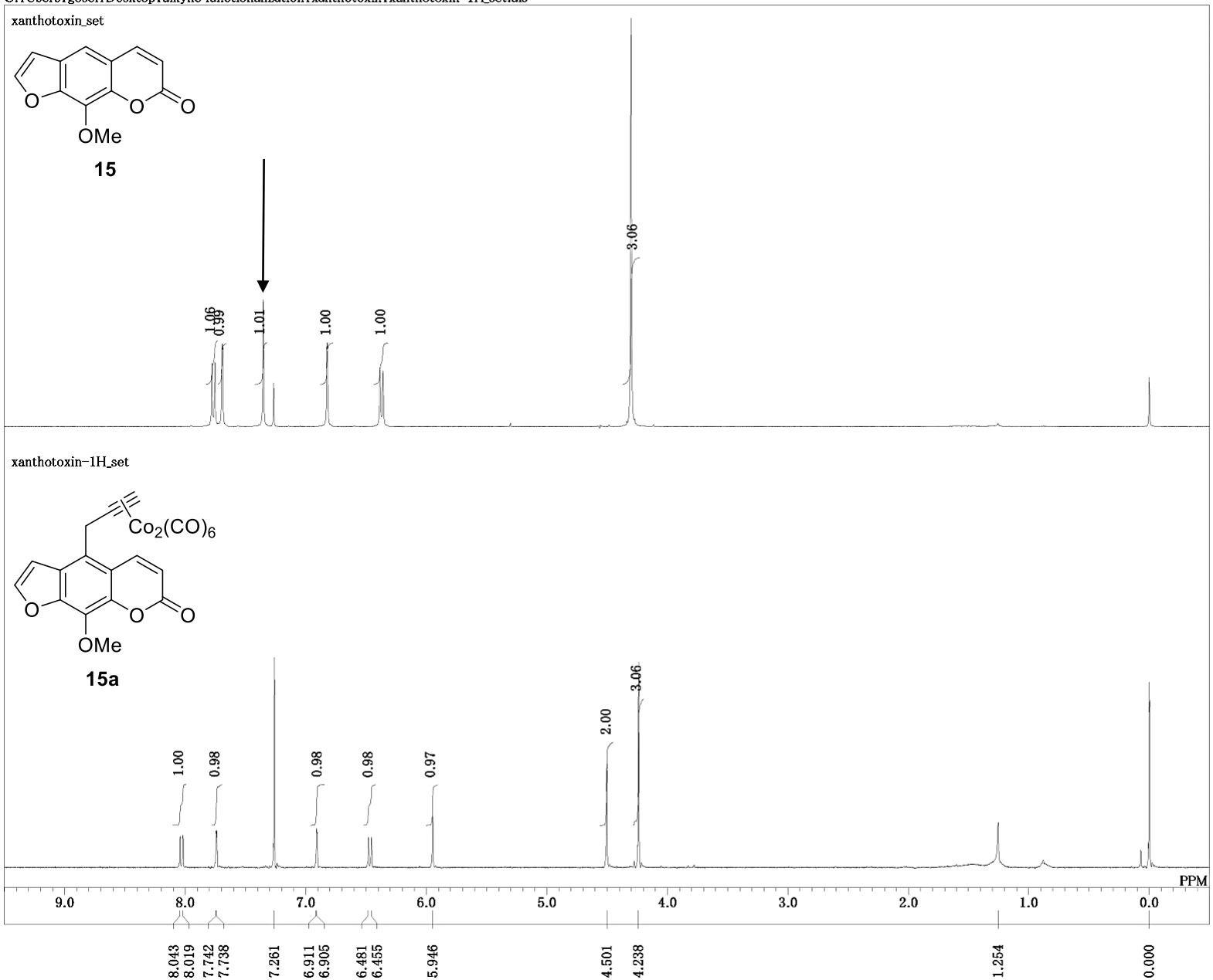

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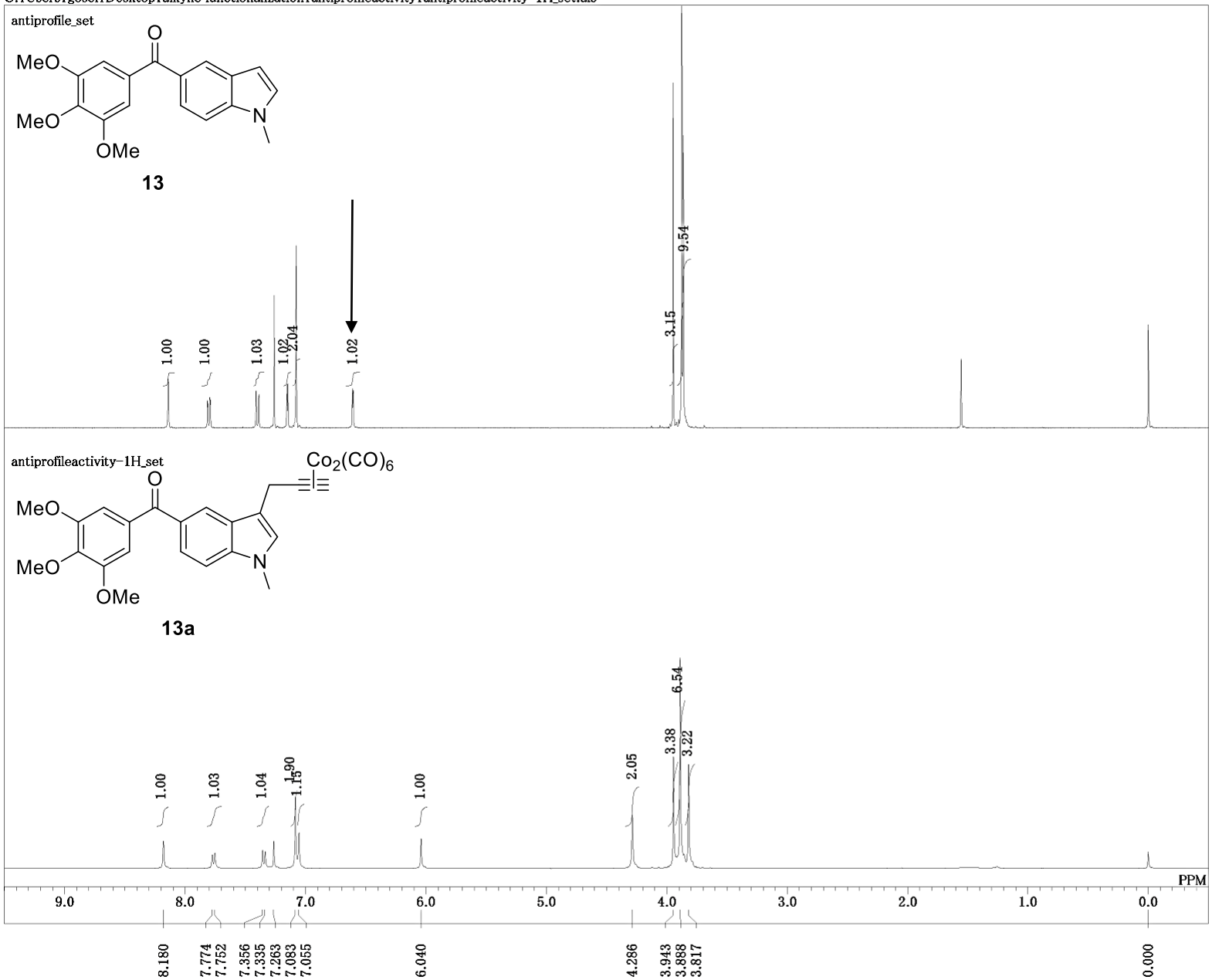

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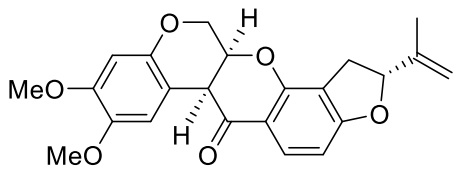
OBFRQ	395.75 MHz
OBSET	124.00 KHz
OBFIN	10277.00 Hz
POINT	16384
FREQU	7912.96 Hz
SCANS	15
ACQTM	2.0705 sec
PD	4.9290 sec
PW1	5.50 usec
IRNUC	1H
CTEMP	22.0 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	1.72 Hz
RGAIN	18

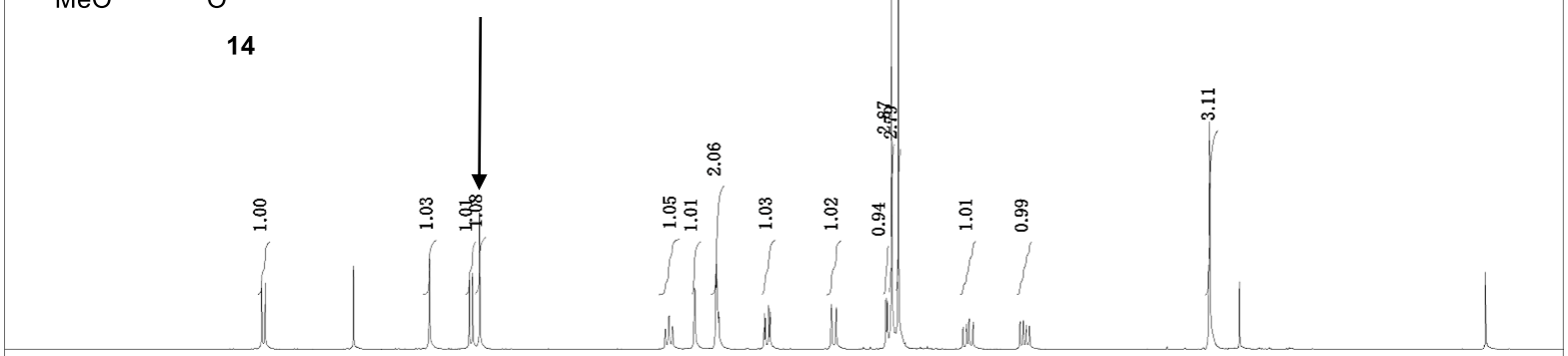
C:¥Users¥gosei¥Desktop¥alkyne functionalization¥rotenone¥rotrenone1-1H_set.als

rotenone_set

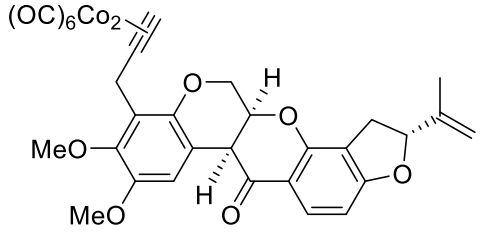


14

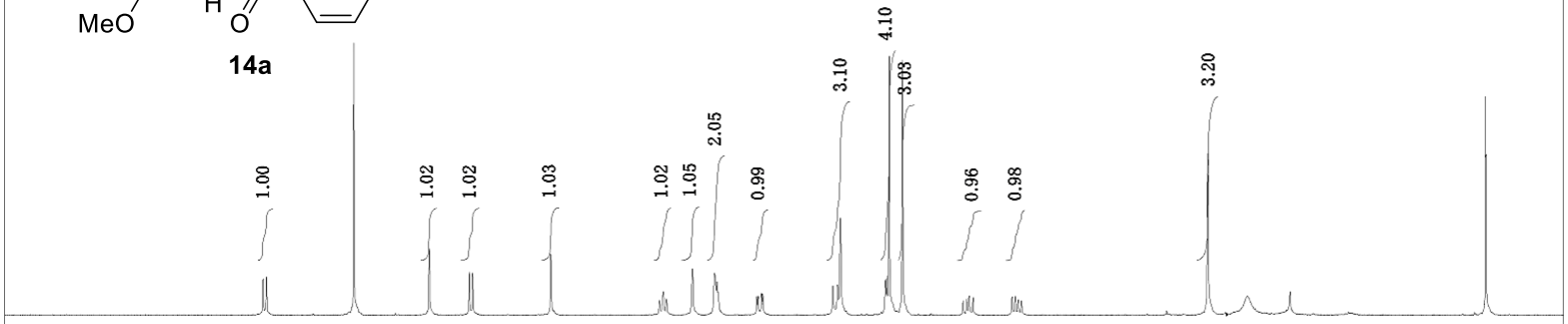
DFILE	rotrenone1-1H_set.als
COMNT	auto
DATIM	Thu Mar 10 20:55:45 2016
OBNUC	1H
EXMOD	NON
OBFRQ	395.75 MHz
OBSET	124.00 KHz
OBFIN	10277.00 Hz
POINT	16384
FREQU	7912.96 Hz
SCANS	32
ACQTM	2.0705 sec
PD	4.9290 sec
PW1	5.50 usec
IRNUC	1H
CTEMP	23.0 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	21

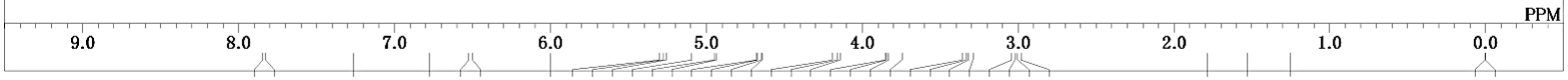


rotrenone1-1H_set



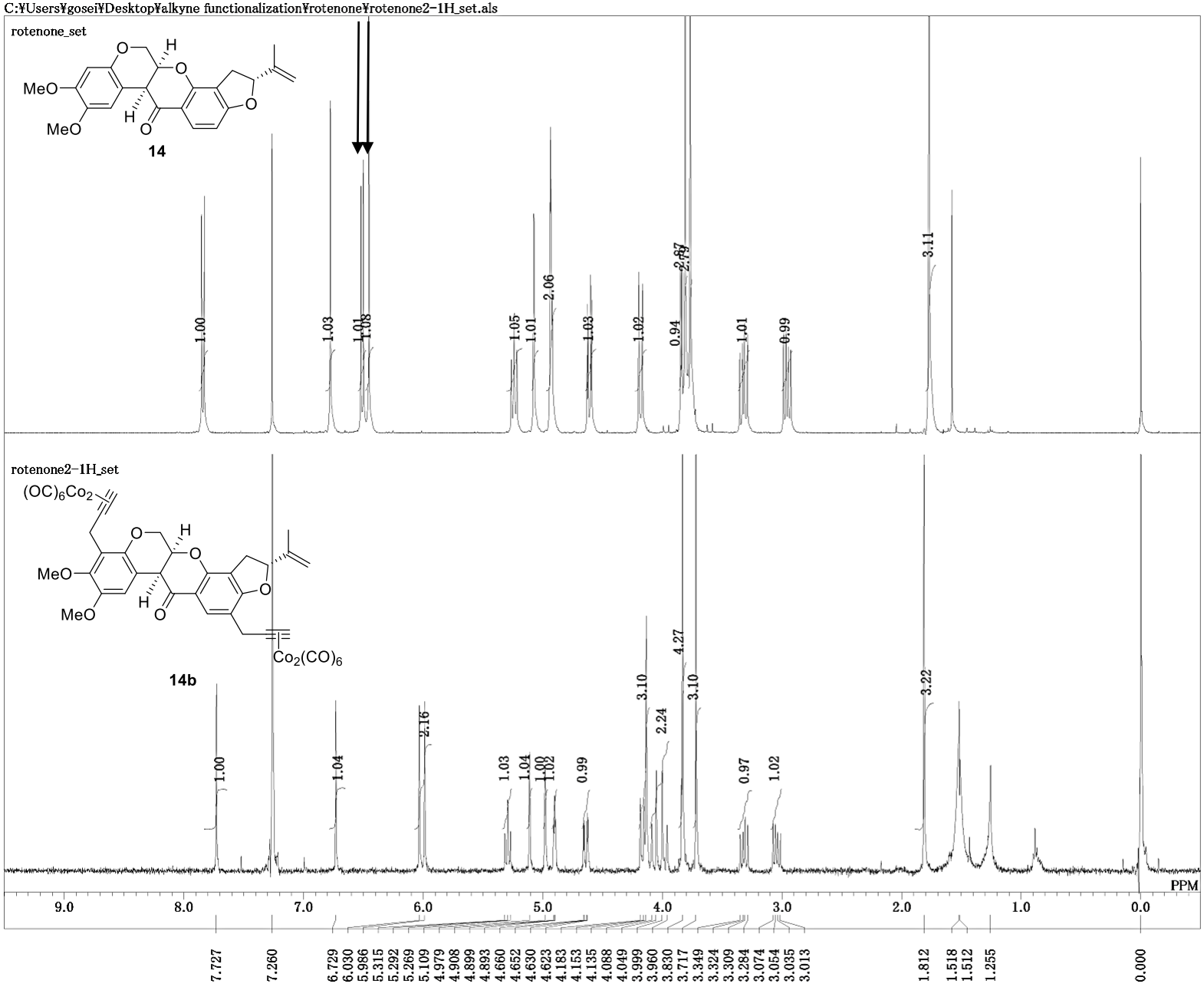
14a





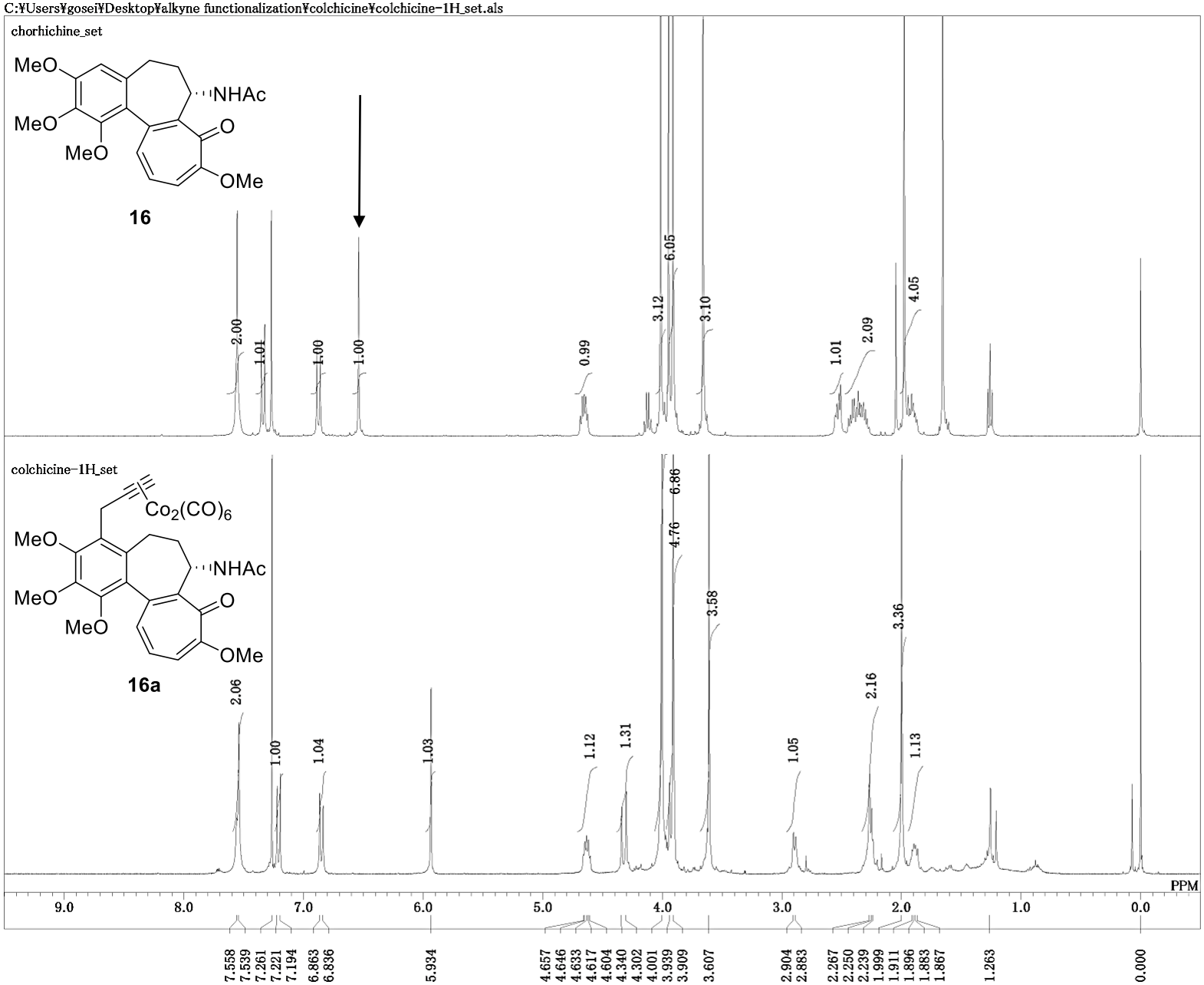
7.843 7.823 7.261 6.776 6.520 6.498 5.997 5.300 5.276 5.254 5.089 4.947 4.932 4.675 4.668 4.644 4.637 4.187 4.158 4.139 3.850 3.840 3.825 3.742 3.353 3.328 3.313 3.288 3.038 3.017 2.997 2.978 1.782 1.526 1.254 0.000 -0.002

C:¥Users¥gosei¥Desktop¥alkyne functionalization¥rotenone¥rotenone2-1H_set.als



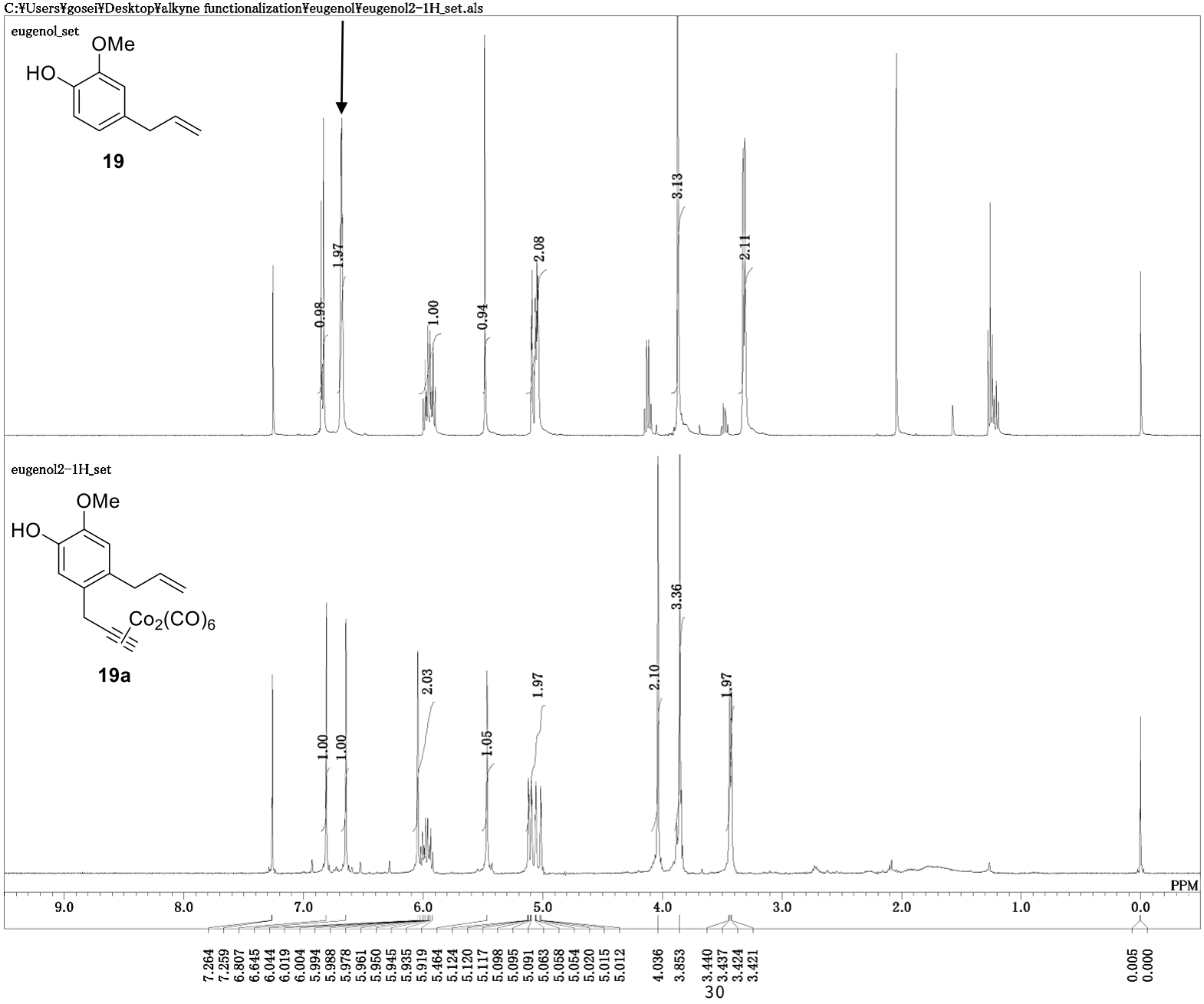
DFILE	rotenone2-1H_set.als
COMNT	auto
DATIM	Thu Mar 17 22:02:15 2016
OBNUC	1H
EXMOD	NON
OBFRQ	395.75 MHz
OBSET	124.00 KHz
OBFIN	10277.00 Hz
POINT	16384
FREQU	7912.96 Hz
SCANS	20
ACQTM	2.0705 sec
PD	4.9290 sec
PW1	5.50 usec
IRNUC	1H
CTEMP	24.7 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	24

C:¥Users¥gosei¥Desktop¥alkyne functionalization¥colchicine¥colchicine-1H_set.als



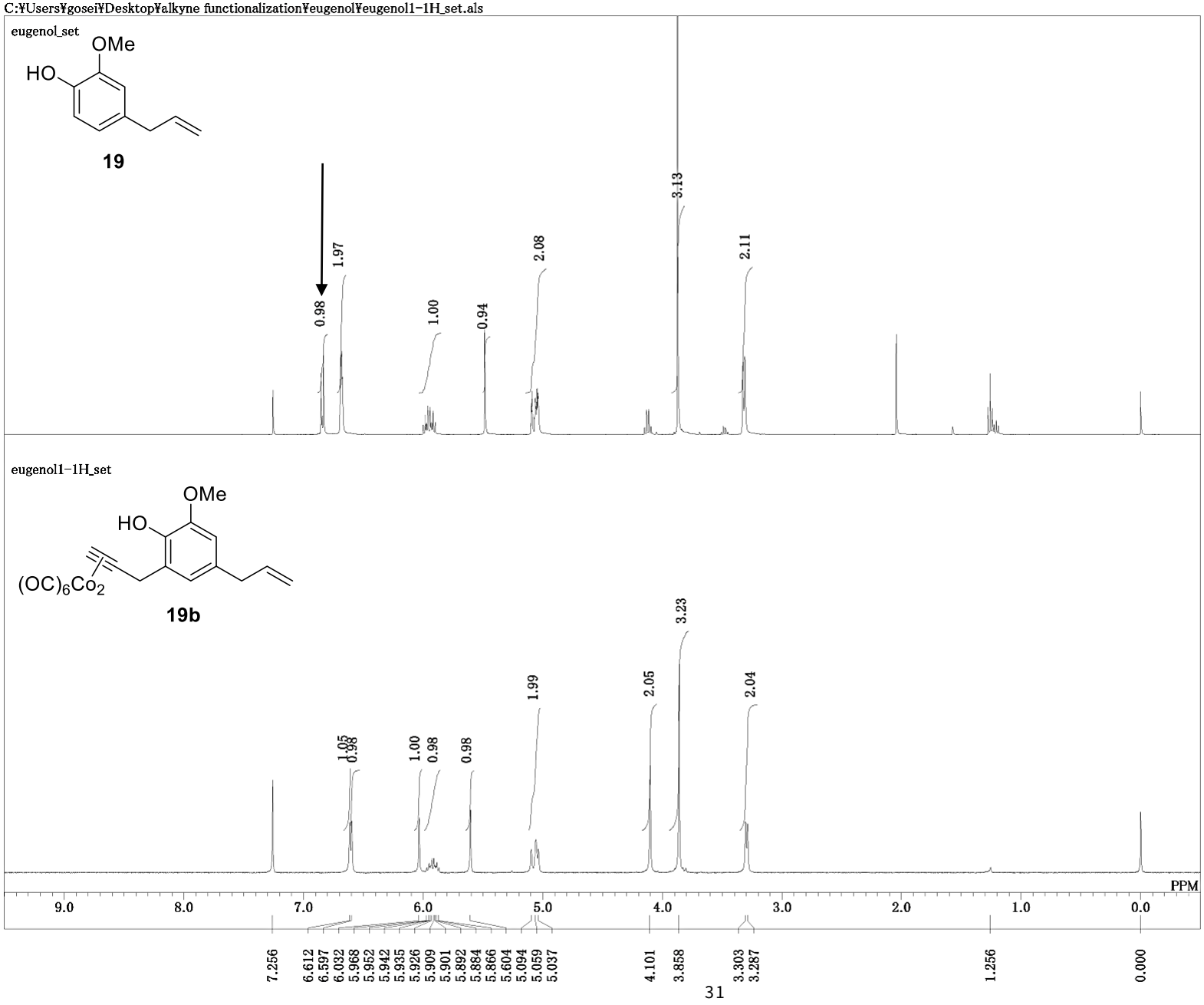
DFILE	colchicine-1H_set.als
COMNT	auto
DATIM	Sat Jun 04 18:07:36 2016
OBNUC	1H
EXMOD	NON
OBFRQ	399.65 MHz
OBSET	124.00 KHz
OBFIN	10500.00 Hz
POINT	16384
FREQU	7992.01 Hz
SCANS	64
ACQTM	2.0500 sec
PD	4.9500 sec
PW1	6.20 usec
IRNUC	1H
CTEMP	27.5 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	19

C:¥Users¥gosei¥Desktop¥alkyne functionalization¥eugenol¥eugenol2-1H_set.als



DFILE	eugenol2-1H_set.als
COMNT	auto
DATIM	Tue Jul 12 19:10:48 2016
OBNUC	1H
EXMOD	NON
OBFRQ	395.75 MHz
OBSET	124.00 KHz
OBFIN	10277.00 Hz
POINT	16384
FREQU	7912.96 Hz
SCANS	32
ACQTM	2.0705 sec
PD	4.9290 sec
PW1	5.50 usec
IRNUC	1H
CTEMP	26.5 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.00 Hz
RGAIN	19

C:¥Users¥gosei¥Desktop¥alkyne functionalization¥eugenol¥eugenol1-1H_set.als

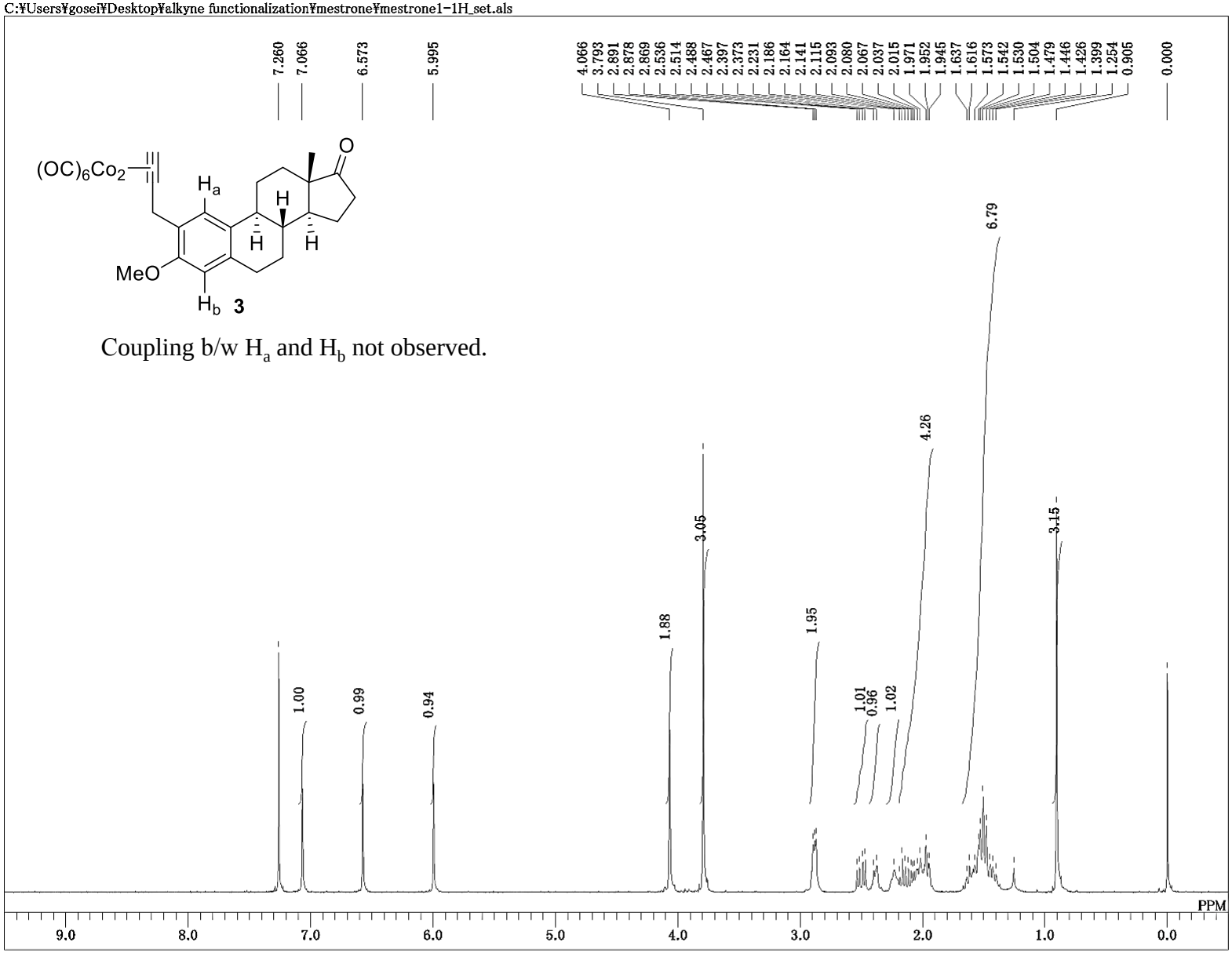


DFILE eugenol1-1H_set.als
COMNT auto
DATIM Sat Feb 20 01:08:52 2016
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 16384
FREQU 7992.01 Hz
SCANS 16
ACQTM 2.0500 sec
PD 4.9500 sec
PW1 6.20 usec
IRNUC 1H
CTEMP 25.0 c
SLVNT CDCL3
EXREF 0.00 ppm
BF -0.08 Hz
RGAIN 20

9. NMR Spectra

auto

C:¥Users¥gosei¥Desktop¥alkyne functionalization¥mestrone¥mestrone1-1H_set.als

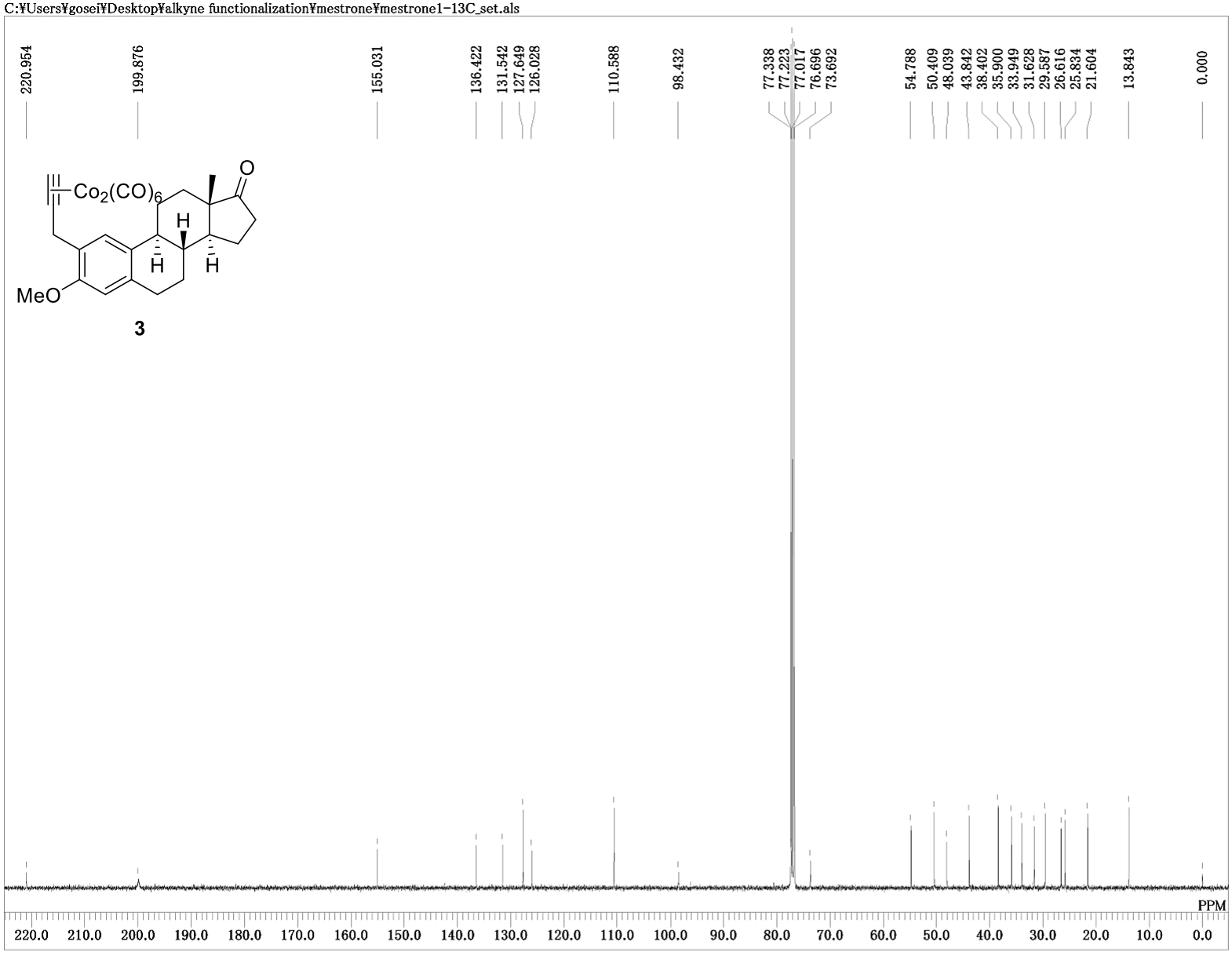


Coupling b/w H_a and H_b not observed.

DFILE	mestrone1-1H_set.als
COMNT	auto
DATIM	Sun Feb 07 23:46:16 2016
OBNUC	1H
EXMOD	NON
OBFRQ	395.75 MHz
OBSET	124.00 KHz
OBFIN	10277.00 Hz
POINT	16384
FREQU	7912.96 Hz
SCANS	32
ACQTM	2.0705 sec
PD	4.9290 sec
PW1	5.50 usec
IRNUC	1H
CTEMP	22.8 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	-0.08 Hz
RGAIN	20

auto

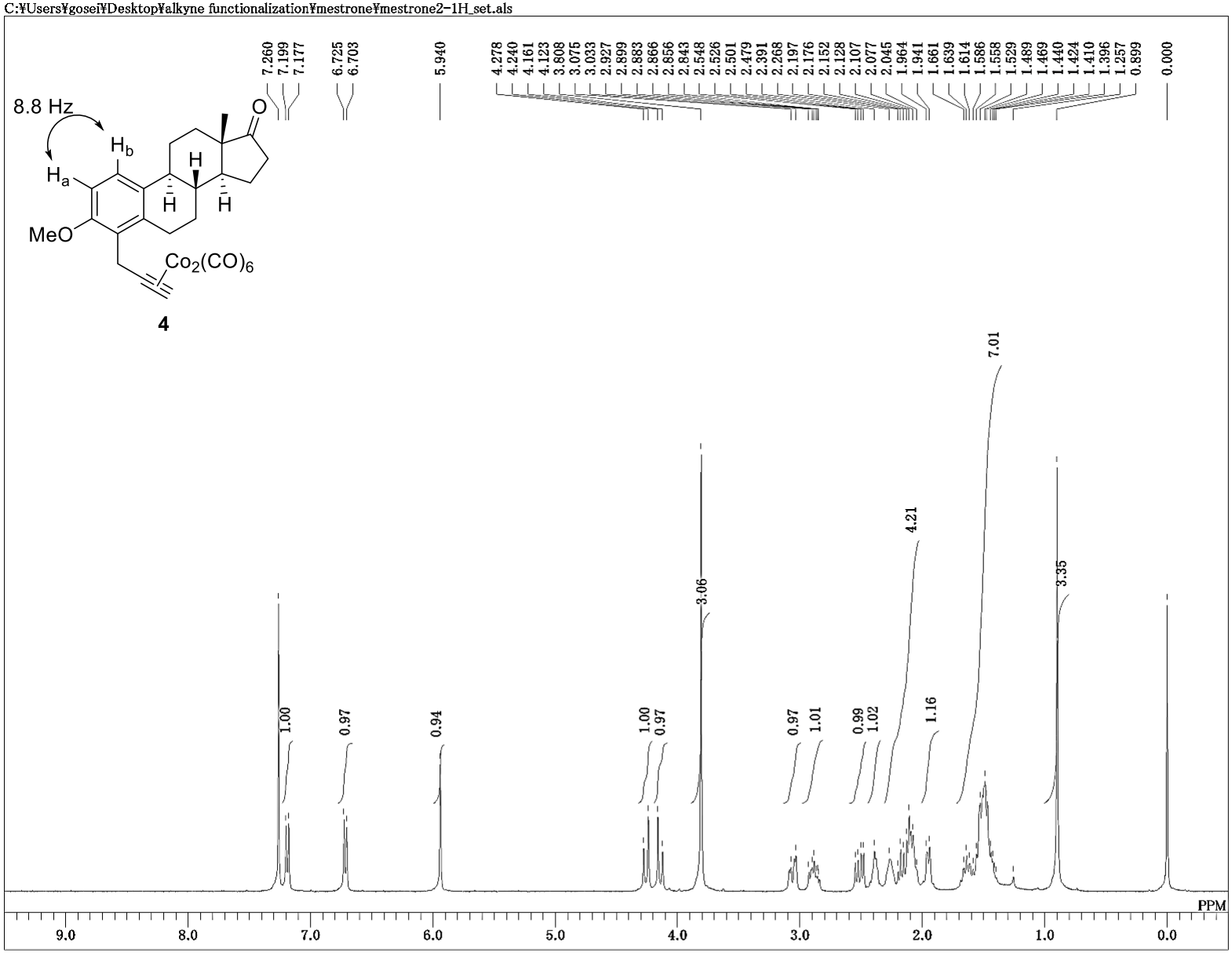
C:¥Users¥gosei¥Desktop¥alkyne functionalization¥mestrone¥mestrone1-13C_set.als



DFILE	mestrone1-13C_set.als
COMNT	auto
DATIM	Mon Feb 08 07:53:08 2016
OBNUC	13C
EXMOD	BCM
OBFRQ	99.45 MHz
OBSET	94.00 KHz
OBFIN	10309.00 Hz
POINT	32768
FREQU	26845.64 Hz
SCANS	9718
ACQTM	1.2206 sec
PD	1.7790 sec
PW1	6.50 usec
IRNUC	1H
CTEMP	22.0 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.52 Hz
RGAIN	22

auto

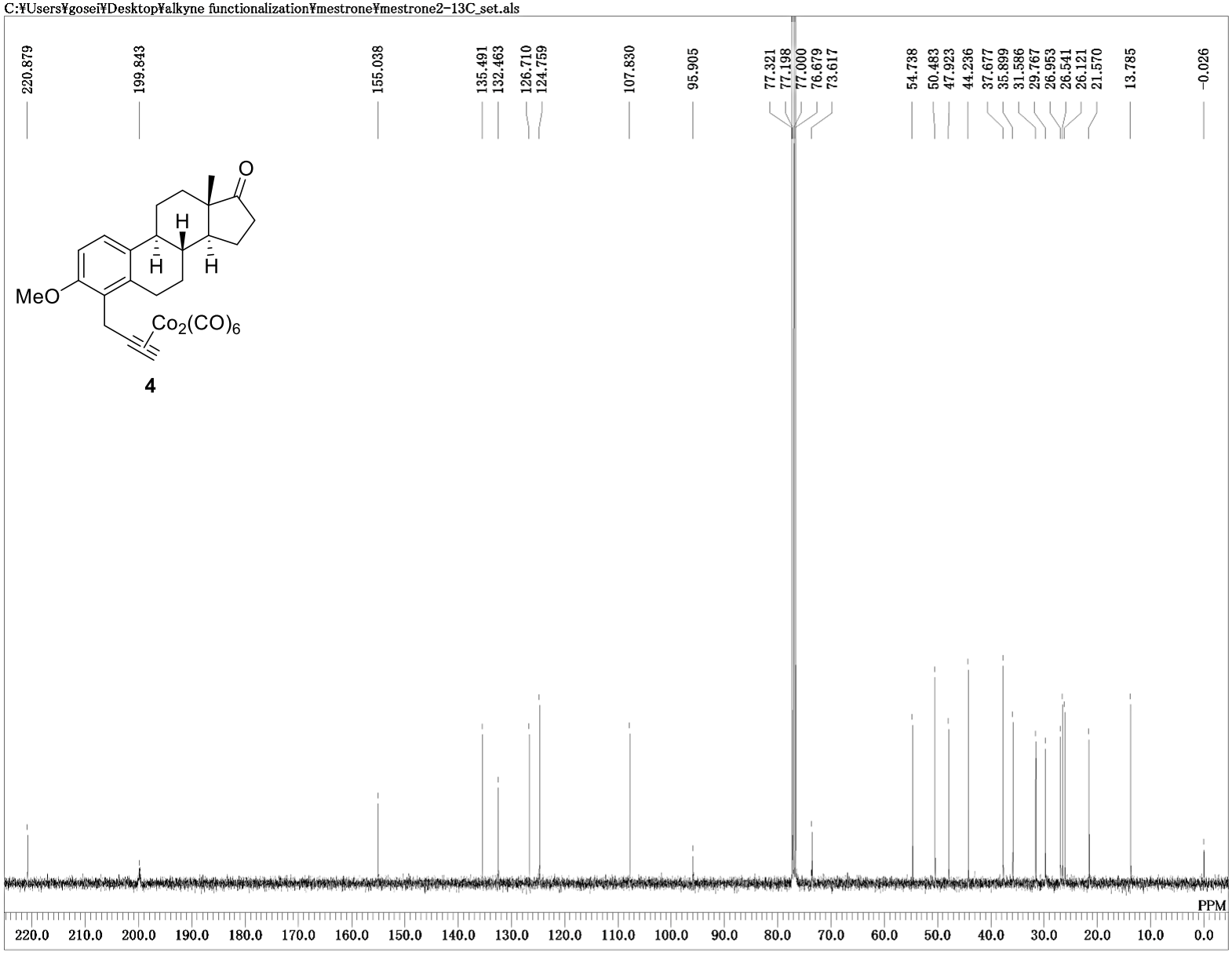
C:¥Users¥gosei¥Desktop¥alkyne functionalization¥mestrone¥mestrone2-1H_set.als



DFILE	mestrone2-1H_set.als
COMNT	auto
DATIM	Wed Nov 18 12:24:01 2015
OBNUC	1H
EXMOD	NON
OBFRQ	399.65 MHz
OBSET	124.00 KHz
OBFIN	10500.00 Hz
POINT	16384
FREQU	7992.01 Hz
SCANS	32
ACQTM	2.0500 sec
PD	4.9500 sec
PW1	6.20 usec
IRNUC	1H
CTEMP	22.6 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	18

auto

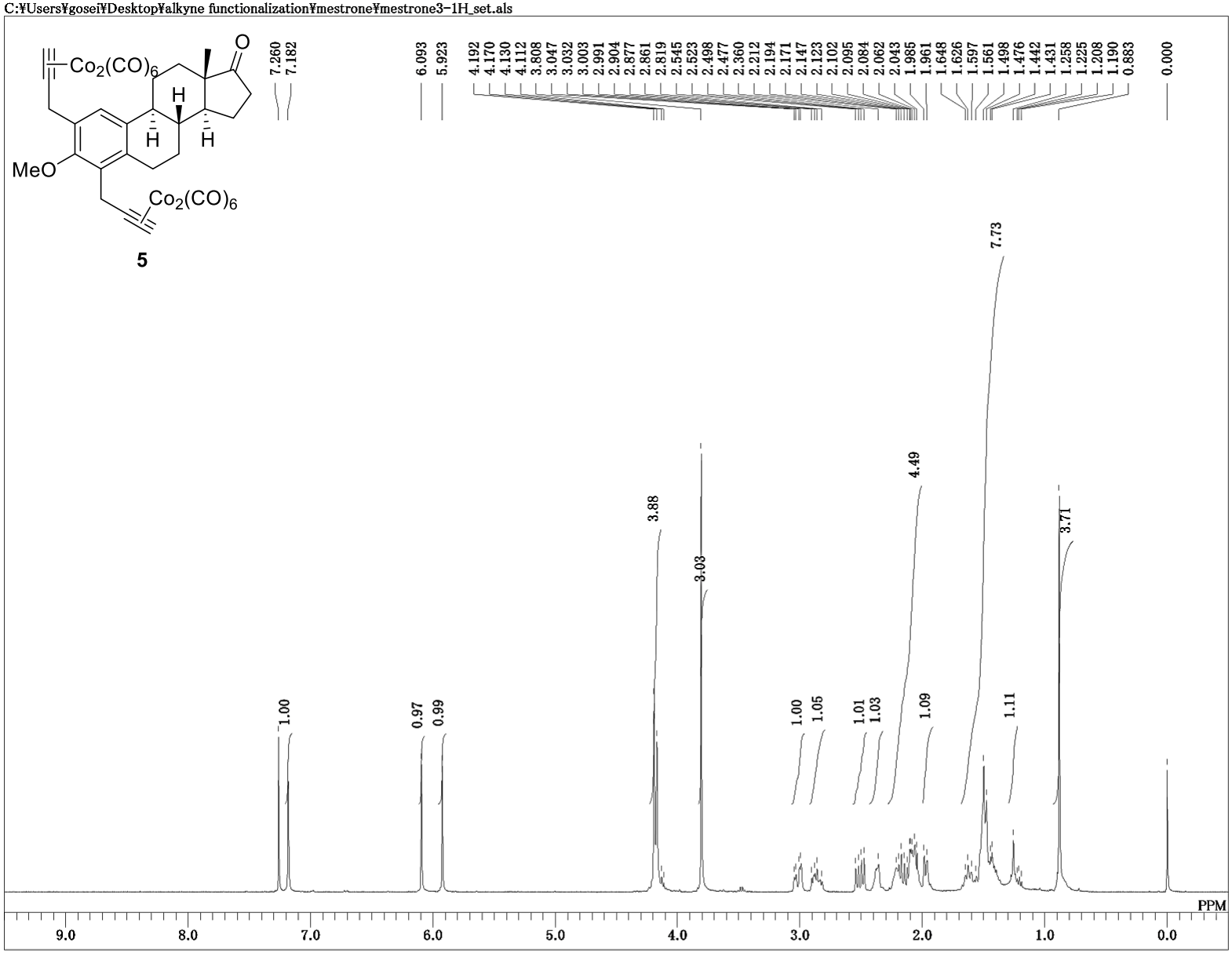
C:¥Users¥gosei¥Desktop¥alkyne functionalization¥mestrone¥mestrone2-13C_set.als



DFILE	mestrone2-13C_set.als
COMNT	auto
DATIM	Wed Nov 18 09:10:28 2015
OBNUC	13C
EXMOD	BCM
OBFRQ	99.45 MHz
OBSET	94.00 KHz
OBFIN	10309.00 Hz
POINT	32768
FREQU	26845.64 Hz
SCANS	9529
ACQTM	1.2206 sec
PD	1.7790 sec
PW1	6.10 usec
IRNUC	1H
CTEMP	25.6 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	-0.08 Hz
RGAIN	23

auto

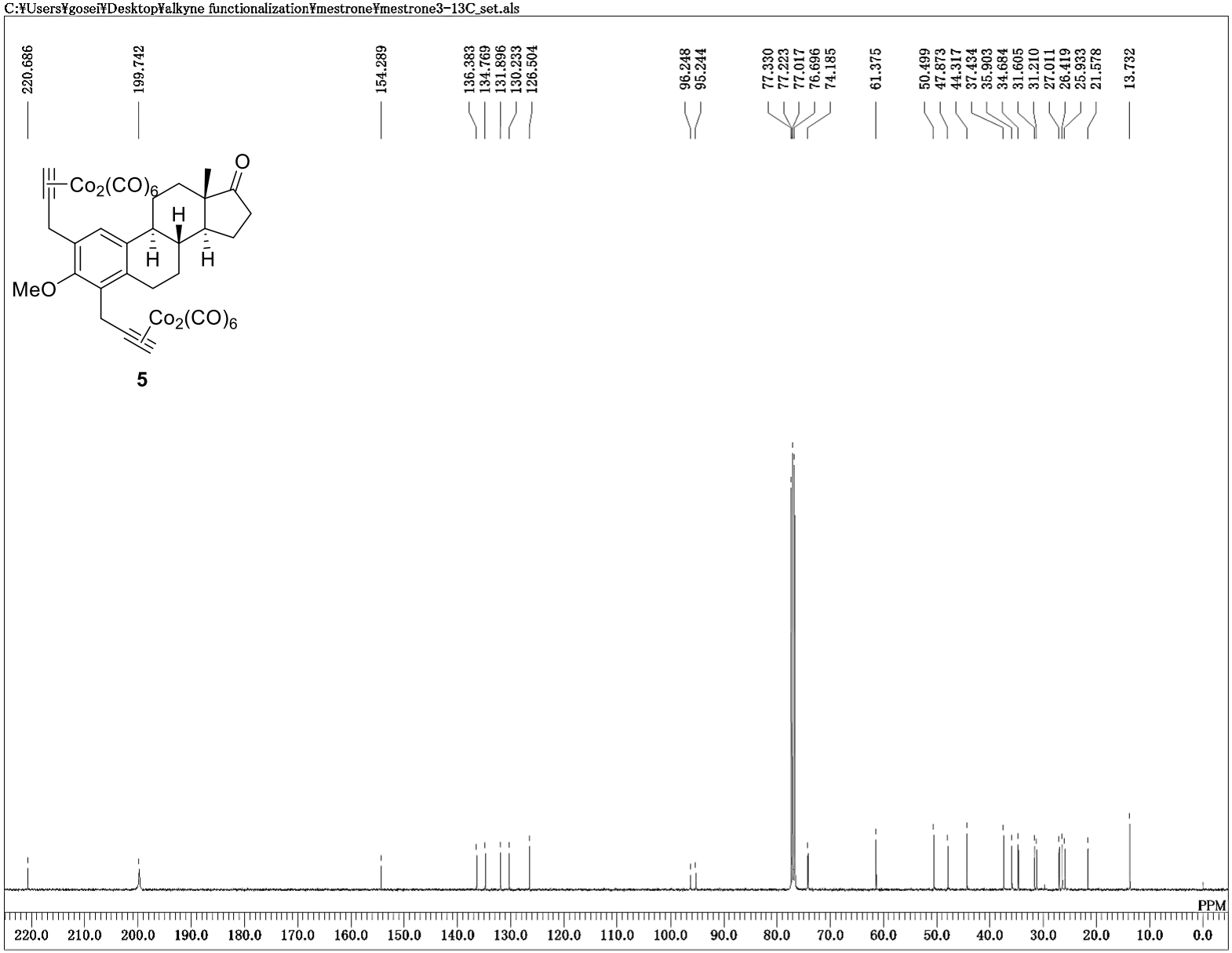
C:¥Users¥gosei¥Desktop¥alkyne functionalization¥mestrone¥mestrone3-1H_set.als



DFILE mestrone3-1H_set.als
COMNT auto
DATIM Tue May 10 20:07:09 2016
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 16384
FREQU 7992.01 Hz
SCANS 32
ACQTM 2.0500 sec
PD 4.9500 sec
PW1 6.20 usec
IRNUC 1H
CTEMP 24.1 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.02 Hz
RGAIN 16

auto

C:¥Users¥gosei¥Desktop¥alkyne functionalization¥mestrone¥mestrone3-13C_set.als

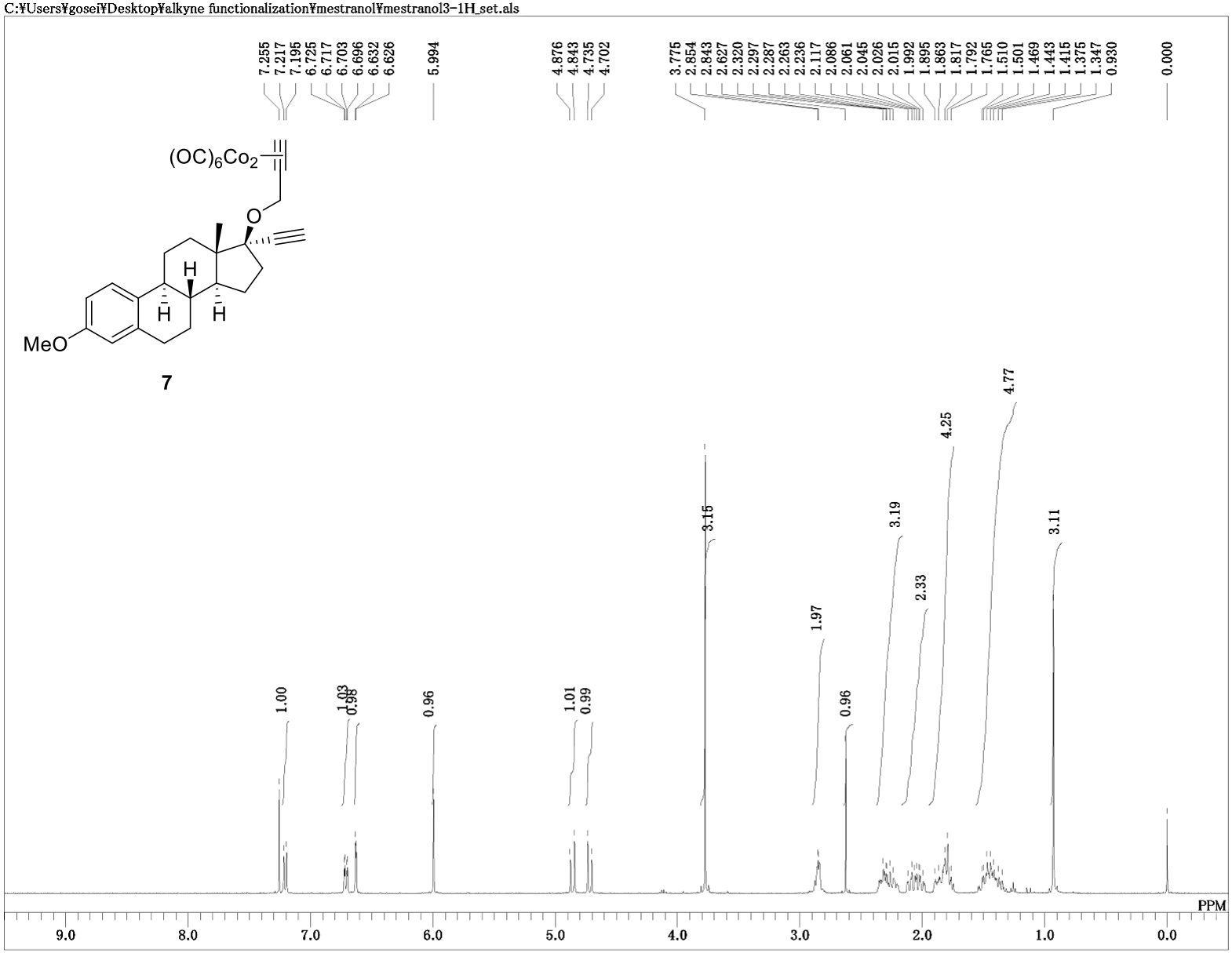


5

DFILE	mestrone3-13C_set.als
COMNT	auto
DATIM	Wed May 11 09:07:41 2016
OBNUC	13C
EXMOD	BCM
OBFRQ	100.40 MHz
OBSET	125.00 KHz
OBFIN	10500.00 Hz
POINT	32768
FREQU	27118.64 Hz
SCANS	11304
ACQTM	1.2083 sec
PD	1.7920 sec
PW1	6.20 usec
IRNUC	1H
CTEMP	23.7 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	1.02 Hz
RGAIN	22

auto

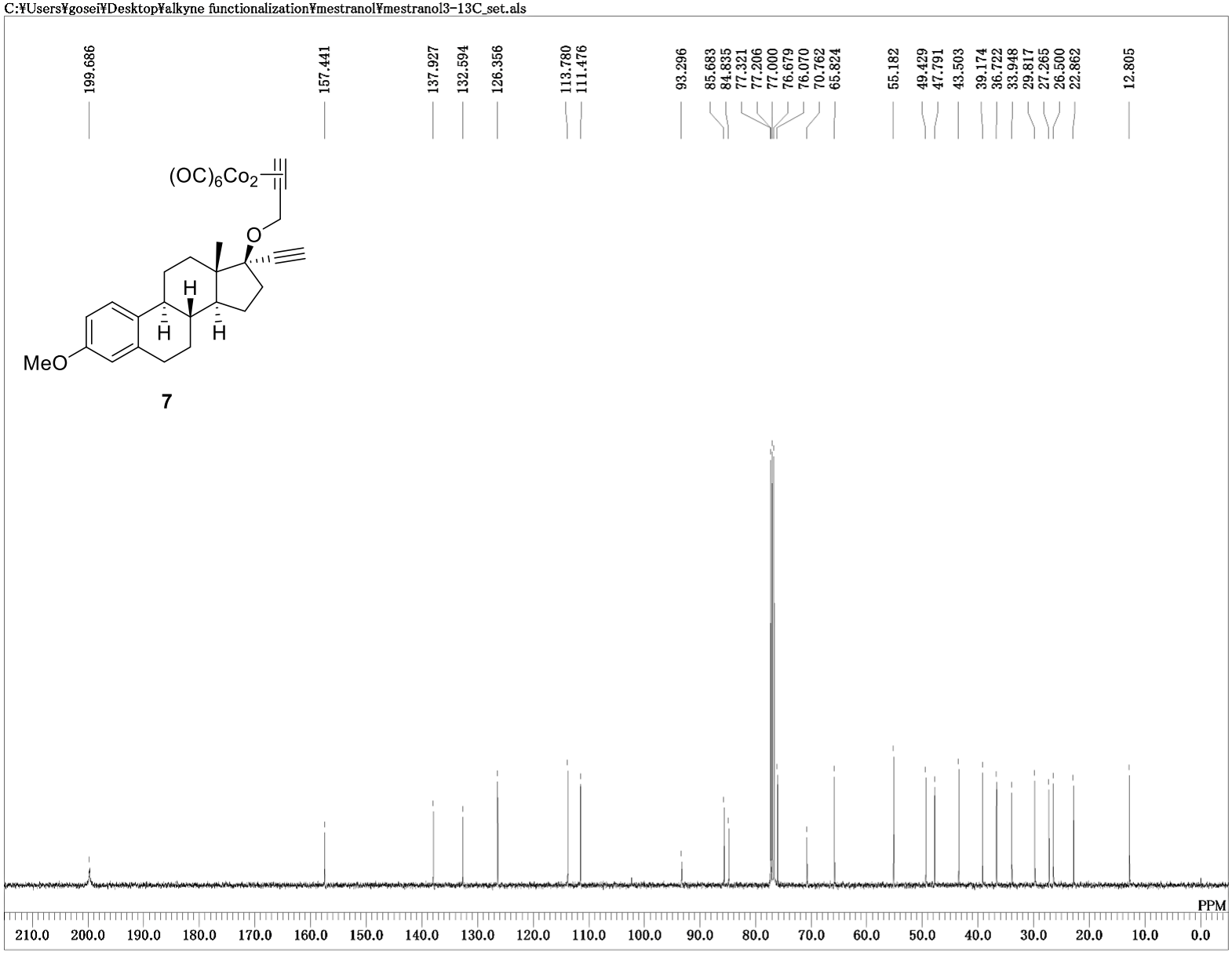
C:¥Users¥gosei¥Desktop¥alkyne functionalization¥mestranol¥mestranol3-1H_set.als



DFILE	mestranol3-1H_set.als
COMNT	auto
DATIM	Thu Jan 21 10:01:07 2016
OBNUC	1H
EXMOD	NON
OBFRQ	395.75 MHz
OBSET	124.00 KHz
OBFIN	10277.00 Hz
POINT	16384
FREQU	7912.96 Hz
SCANS	18
ACQTM	2.0705 sec
PD	4.9290 sec
PW1	5.50 usec
IRNUC	1H
CTEMP	23.0 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	-0.08 Hz
RGAIN	16

auto

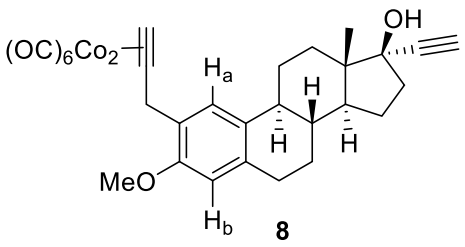
C:¥Users¥gosei¥Desktop¥alkyne functionalization¥mestranol¥mestranol3-13C_set.als



DFILE	mestranol3-13C_set.als
COMNT	auto
DATIM	Thu Mar 24 15:21:18 2016
OBNUC	13C
EXMOD	BCM
OBFRQ	99.45 MHz
OBSET	94.00 KHz
OBFIN	10309.00 Hz
POINT	32768
FREQU	26845.64 Hz
SCANS	745
ACQTM	1.2206 sec
PD	1.7790 sec
PW1	6.50 usec
IRNUC	1H
CTEMP	23.7 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.02 Hz
RGAIN	23

auto

C:¥Users¥gosei¥Desktop¥alkyne functionalization¥mestranol¥mestranol1-1H.als



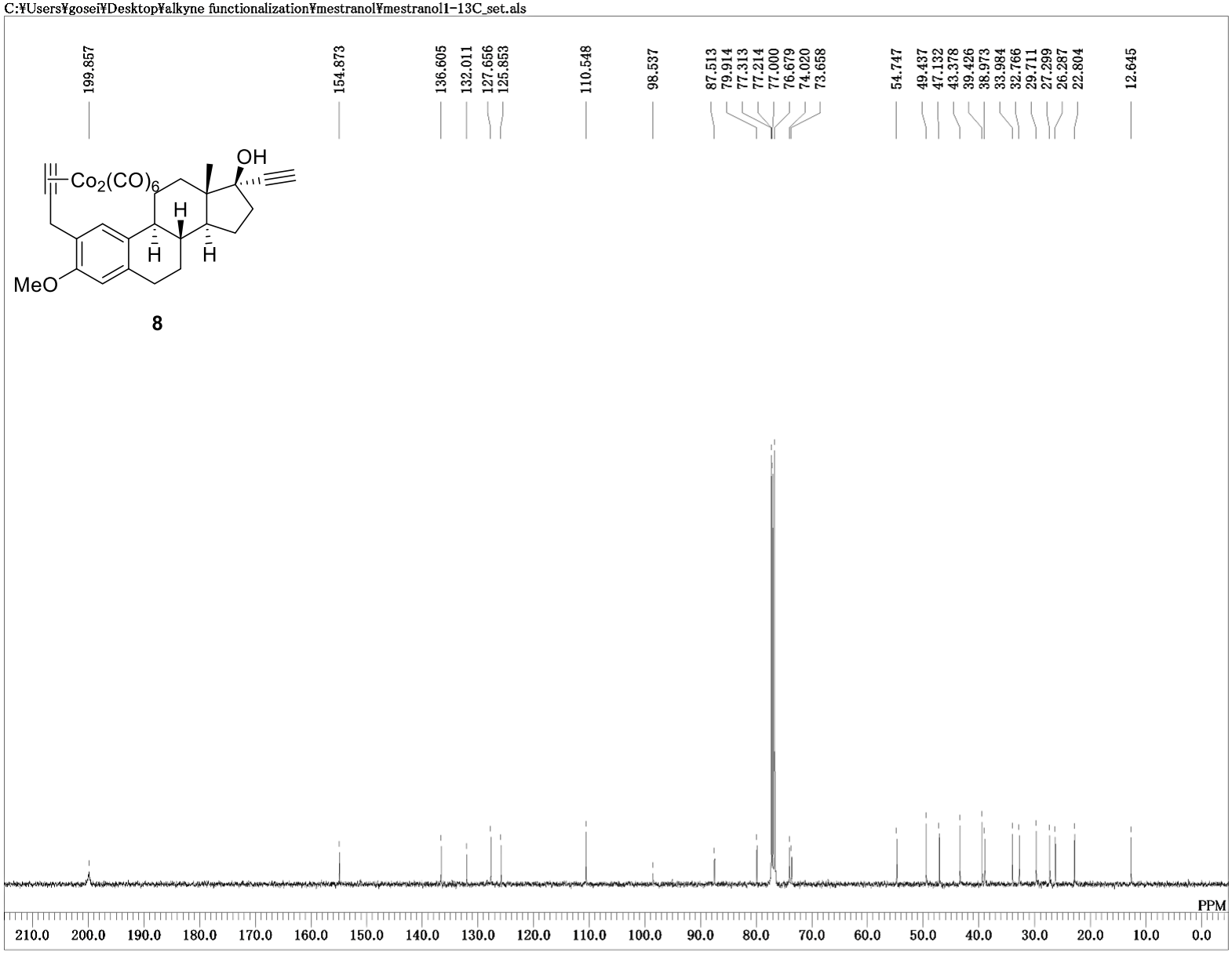
8

Coupling b/w H_a and H_b not observed.

DFILE	mestranol1-1H.als
COMNT	auto
DATIM	Thu May 14 09:58:10 2015
OBNUC	1H
EXMOD	NON
OBFRQ	399.65 MHz
OBSET	124.00 KHz
OBFIN	10500.00 Hz
POINT	16384
FREQU	7992.01 Hz
SCANS	16
ACQTM	2.0500 sec
PD	4.9500 sec
PW1	6.20 usec
IRNUC	1H
CTEMP	27.0 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	22

auto

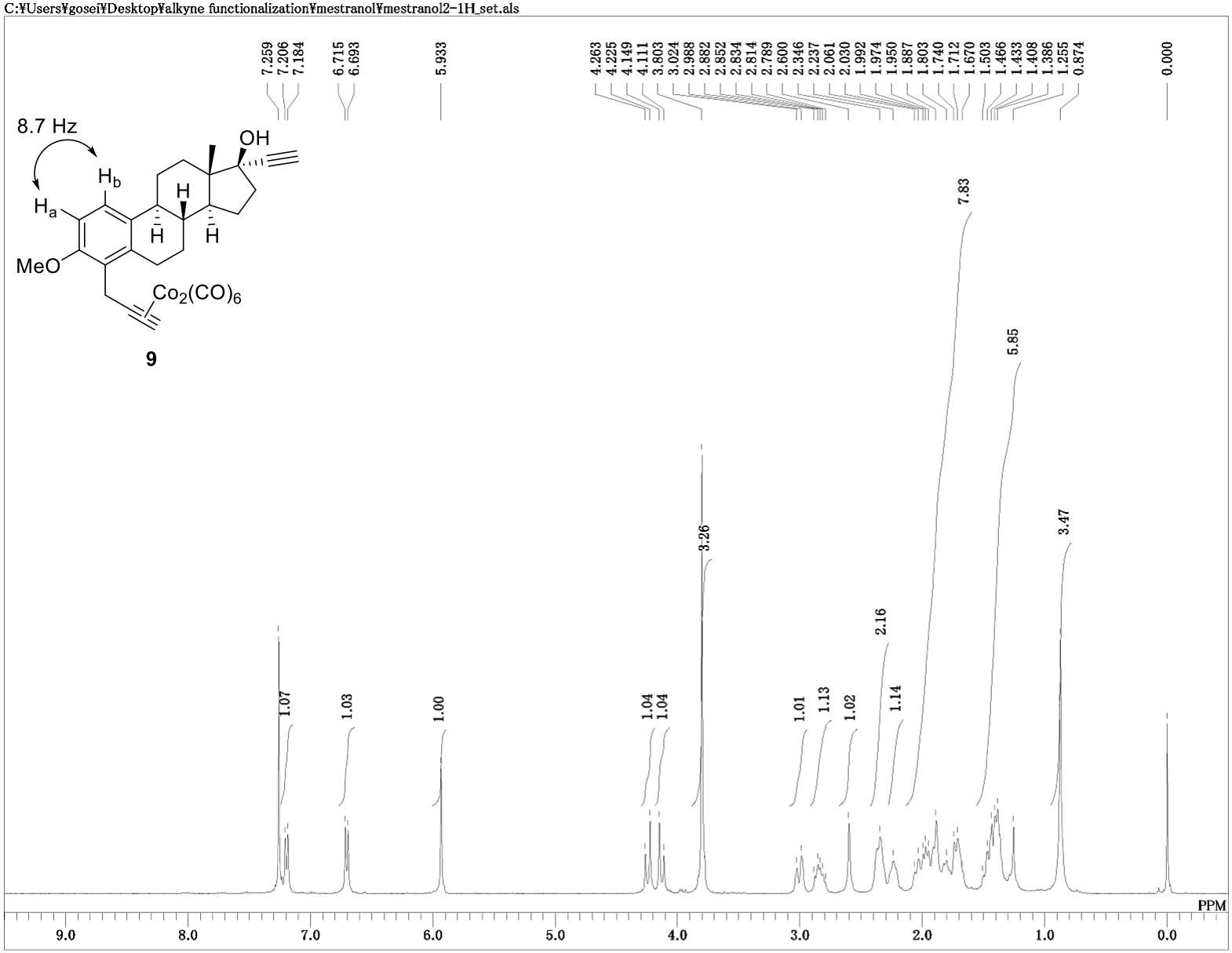
C:¥Users¥gosei¥Desktop¥alkyne functionalization¥mestranol¥mestranol1-13C_set.als



DFILE	mestranol1-13C_set.als
COMNT	auto
DATIM	Mon Jan 11 16:05:09 2016
OBNUC	13C
EXMOD	BCM
OBFRQ	100.40 MHz
OBSET	125.00 KHz
OBFIN	10500.00 Hz
POINT	32768
FREQU	27118.64 Hz
SCANS	1379
ACQTM	1.2083 sec
PD	1.7920 sec
PW1	6.20 usec
IRNUC	1H
CTEMP	22.7 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.52 Hz
RGAIN	22

auto

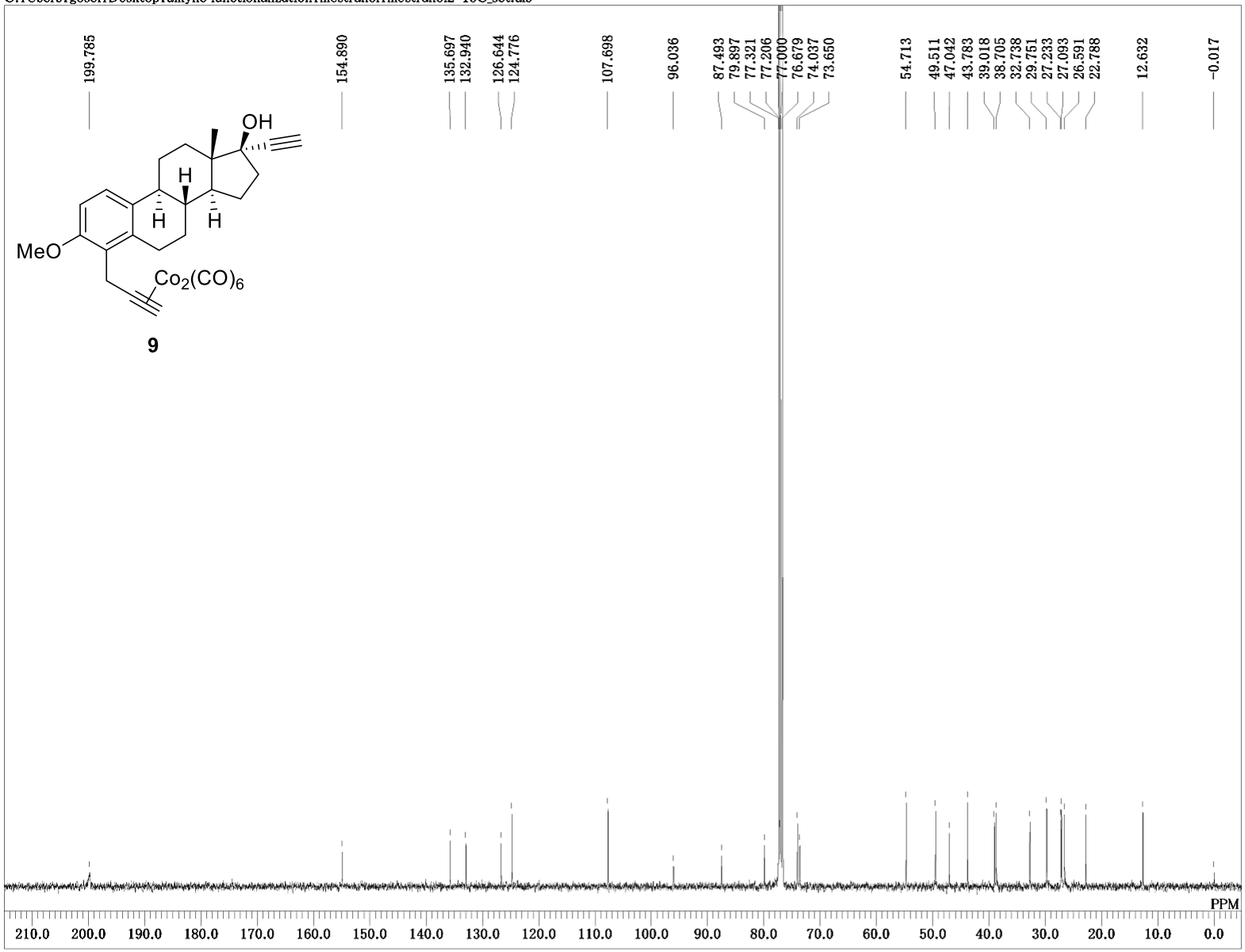
C:¥Users¥gosei¥Desktop¥alkyne functionalization¥mestranol¥mestranol2-1H_set.als



DFILE	mestranol2-1H_set.als
COMNT	auto
DATIM	Sun Feb 07 18:39:28 2016
OBNUC	1H
EXMOD	NON
OBFRQ	395.75 MHz
OBSET	124.00 KHz
OBFIN	10277.00 Hz
POINT	16384
FREQU	7912.96 Hz
SCANS	32
ACQTM	2.0705 sec
PD	4.9290 sec
PW1	5.50 usec
IRNUC	1H
CTEMP	21.6 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	1.22 Hz
RGAIN	17

auto

C:¥Users¥gosei¥Desktop¥alkyne functionalization¥mestranol¥mestranol2-13C_set.als

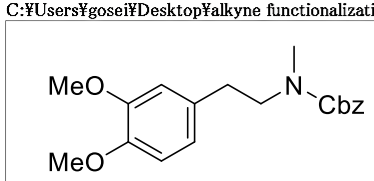


9

DFILE	mestranol2-13C_set.als
COMNT	auto
DATIM	Sun Feb 07 18:34:36 2016
OBNUC	13C
EXMOD	BCM
OBFRQ	99.45 MHz
OBSET	94.00 KHz
OBFIN	10309.00 Hz
POINT	32768
FREQU	26845.64 Hz
SCANS	2758
ACQTM	1.2206 sec
PD	1.7790 sec
PW1	6.50 usec
IRNUC	1H
CTEMP	23.1 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.52 Hz
RGAIN	22

auto

C:¥Users¥gosei¥Desktop¥alkyne functionalization¥N-CBZ-methyl homoveratorylamine¥N-Cbz,MeHVA-1H_set.als

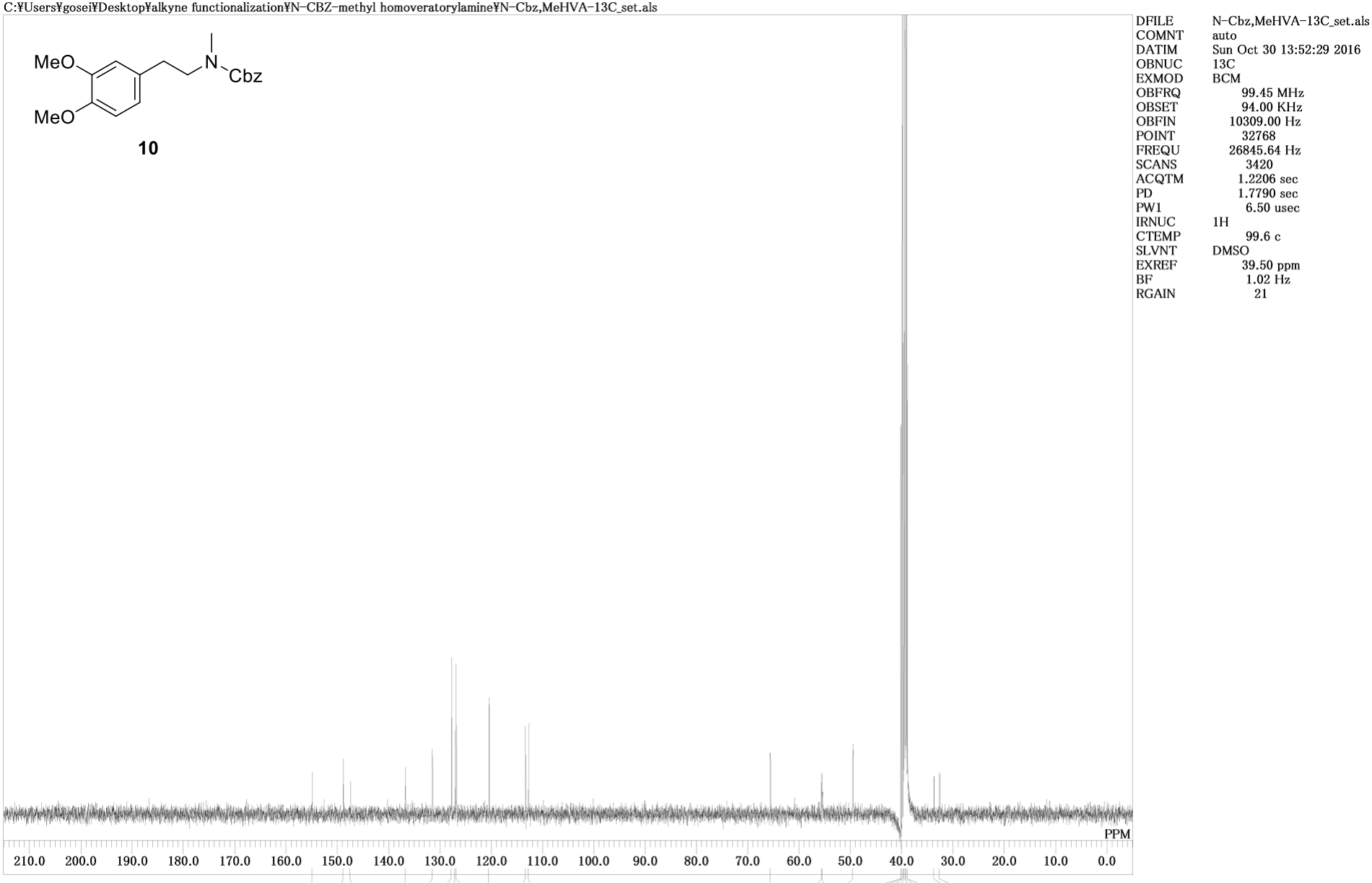


10

DFILE	N-Cbz,MeHVA-1H_set.als
COMNT	auto
DATIM	Sun Oct 30 13:57:01 2016
OBNUC	1H
EXMOD	NON
OBFRQ	395.75 MHz
OBSET	124.00 KHz
OBFIN	10277.00 Hz
POINT	16384
FREQU	7912.96 Hz
SCANS	32
ACQTM	2.0705 sec
PD	4.9290 sec
PW1	5.50 usec
IRNUC	1H
CTEMP	99.6 c
SLVNT	DMSO
EXREF	2.49 ppm
BF	0.02 Hz
RGAIN	9

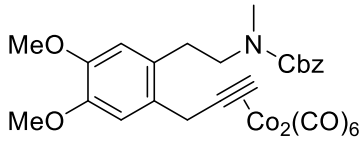
auto

C:¥Users¥gosei¥Desktop¥alkyne functionalization¥N-CBZ-methyl homoveratorylamine¥N-Cbz,MeHVA-13C_set.als



auto

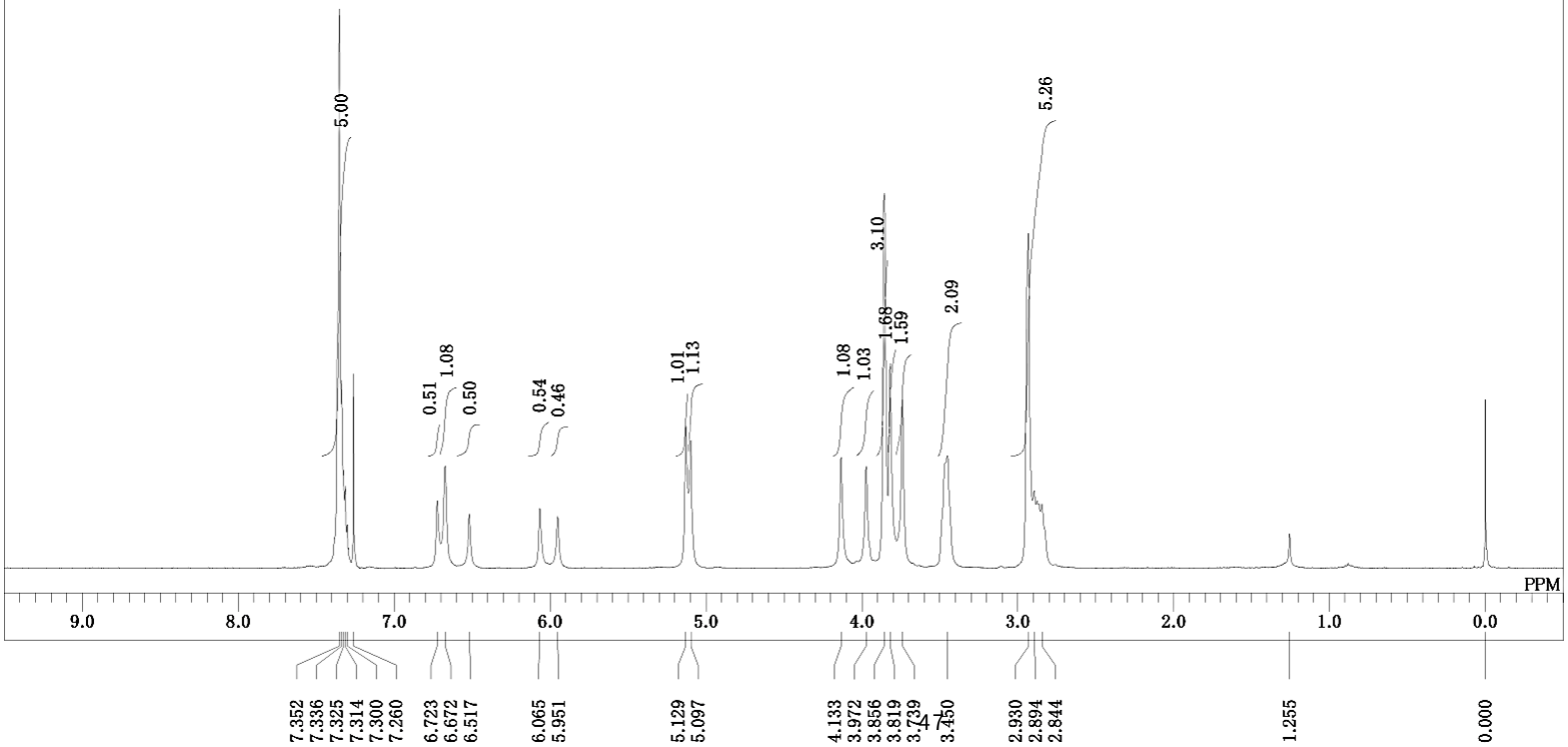
C:¥Users¥gosei¥Desktop¥alkyne functionalization¥N-CBZ-methyl homoveratorilamine¥N-Cbz,MeHVA1-1H_set.als



10a

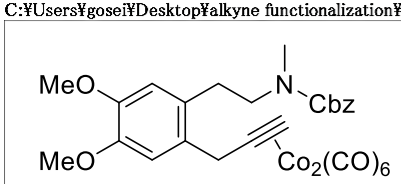
Structure determined after decomplexation.

DFILE	N-Cbz,MeHVA1-1H_set.als
COMNT	auto
DATIM	Thu Apr 14 09:04:13 2016
OBNUC	1H
EXMOD	NON
OBFRQ	395.75 MHz
OBSET	124.00 KHz
OBFIN	10277.00 Hz
POINT	16384
FREQU	7912.96 Hz
SCANS	32
ACQTM	2.0705 sec
PD	4.9290 sec
PW1	5.50 usec
IRNUC	1H
CTEMP	24.2 c
SLVNT	CD2CL
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	15



auto

C:¥Users¥gosei¥Desktop¥alkyne functionalization¥N-CBZ-methyl homoveratorilamine¥N-Cbz,MeHVA1-13C_set.als

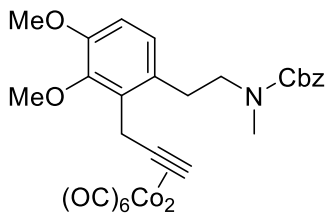


10a

DFILE	N-Cbz,MeHVA1-13C_set.als
COMNT	auto
DATIM	Thu Apr 14 08:59:28 2016
OBNUC	13C
EXMOD	BCM
OBFRQ	99.45 MHz
OBSET	94.00 KHz
OBFIN	10309.00 Hz
POINT	32768
FREQU	26845.64 Hz
SCANS	10491
ACQTM	1.2206 sec
PD	1.7790 sec
PW1	6.50 usec
IRNUC	1H
CTEMP	25.5 c
SLVNT	CD2CL
EXREF	77.20 ppm
BF	1.02 Hz
RGAIN	23

single_pulse

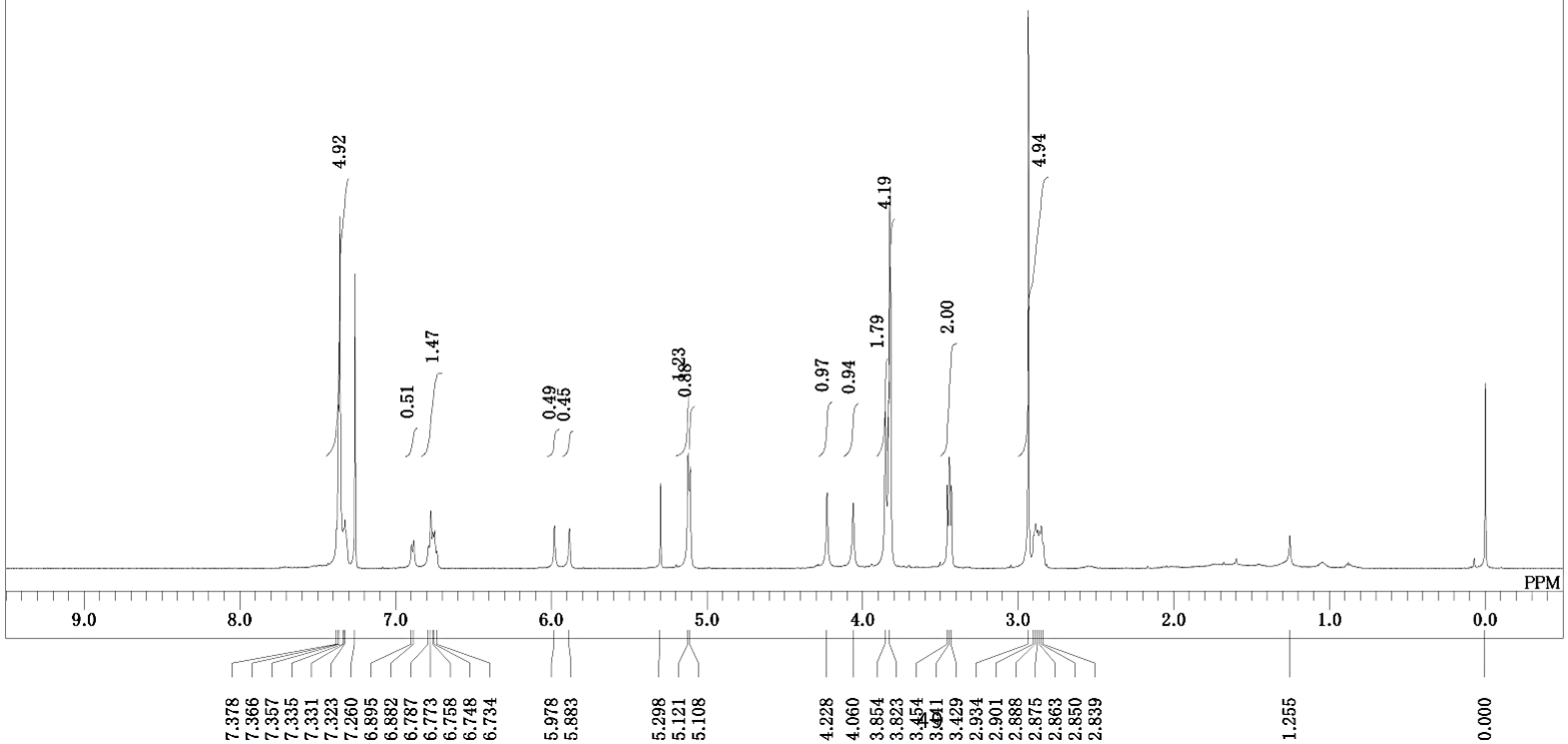
C:¥Users¥gosei¥Desktop¥alkyne functionalization¥N-CBZ-methyl homoveratorylamine¥N-Cbz,MeHVA2-1H_set.als



10b

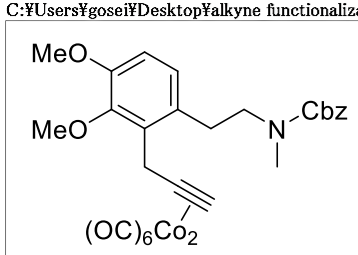
Structure determined after decomplexation.

DFILE	N-Cbz,MeHVA2-1H_set.als
COMNT	single_pulse
DATIM	2016-11-08 09:10:16
OBNUC	1H
EXMOD	single_pulse.ex2
OBFRQ	600.17 MHz
OBSET	5.30 KHz
OBFIN	5.47 Hz
POINT	13107
FREQU	9008.87 Hz
SCANS	32
ACQTM	1.4549 sec
PD	5.0000 sec
PW1	7.15 usec
IRNUC	1H
CTEMP	25.1 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	40



single pulse decoupled gated NOE

C:¥Users¥gosei¥Desktop¥alkyne functionalization¥N-CBZ-methyl homoveratorylamine¥N-Cbz,MeHVA2-13C_set.als

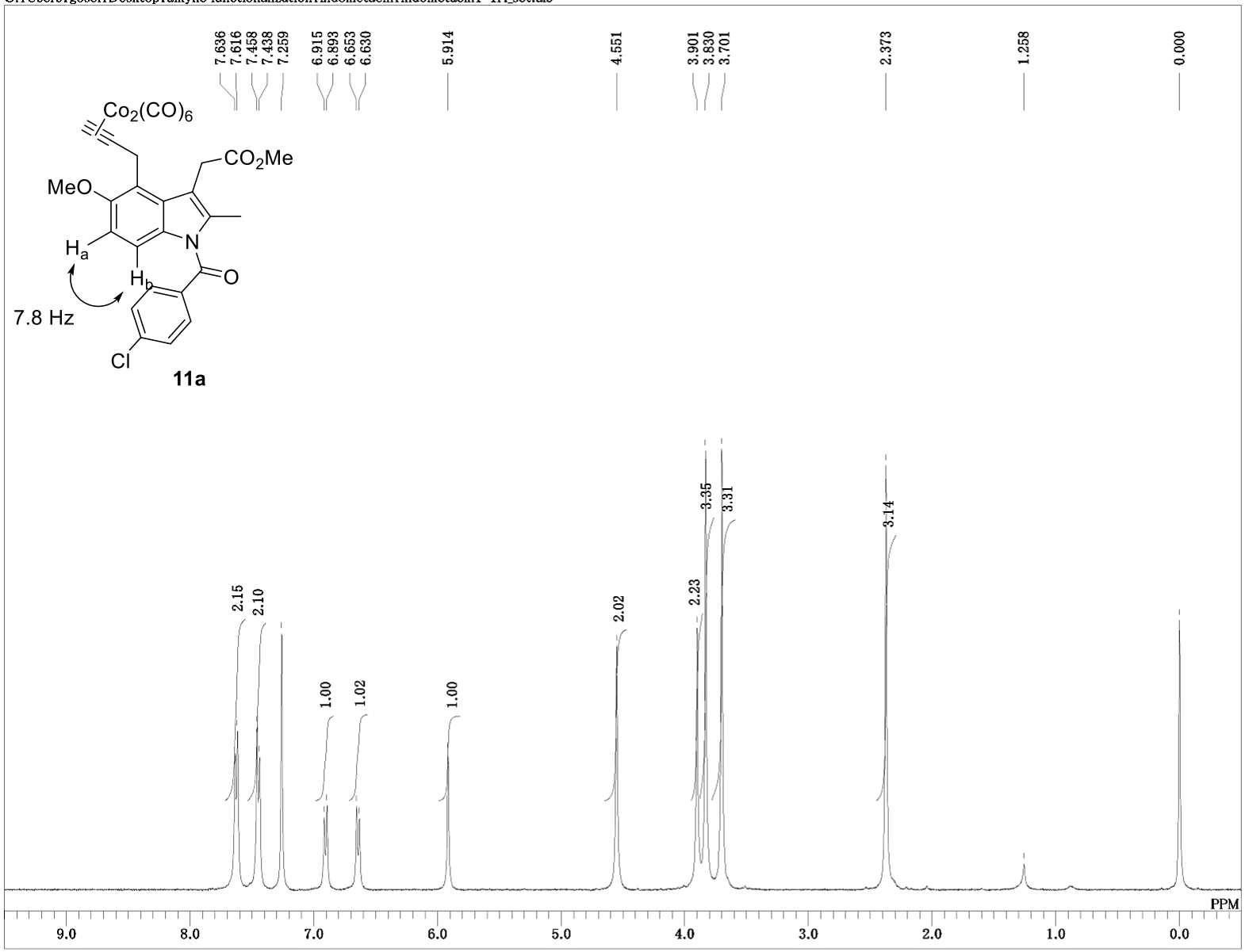


10b

DFILE	N-Cbz,MeHVA2-13C_set.als
COMNT	single pulse decoupled gated
DATIM	2016-11-02 07:47:06
OBNUC	13C
EXMOD	single_pulse_dec
OBFRQ	150.92 MHz
OBSET	8.52 KHz
OBFIN	1.74 Hz
POINT	26214
FREQU	37878.21 Hz
SCANS	13854
ACQTM	0.6921 sec
PD	2.0000 sec
PW1	4.90 usec
IRNUC	1H
CTEMP	26.2 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.62 Hz
RGAIN	38

auto

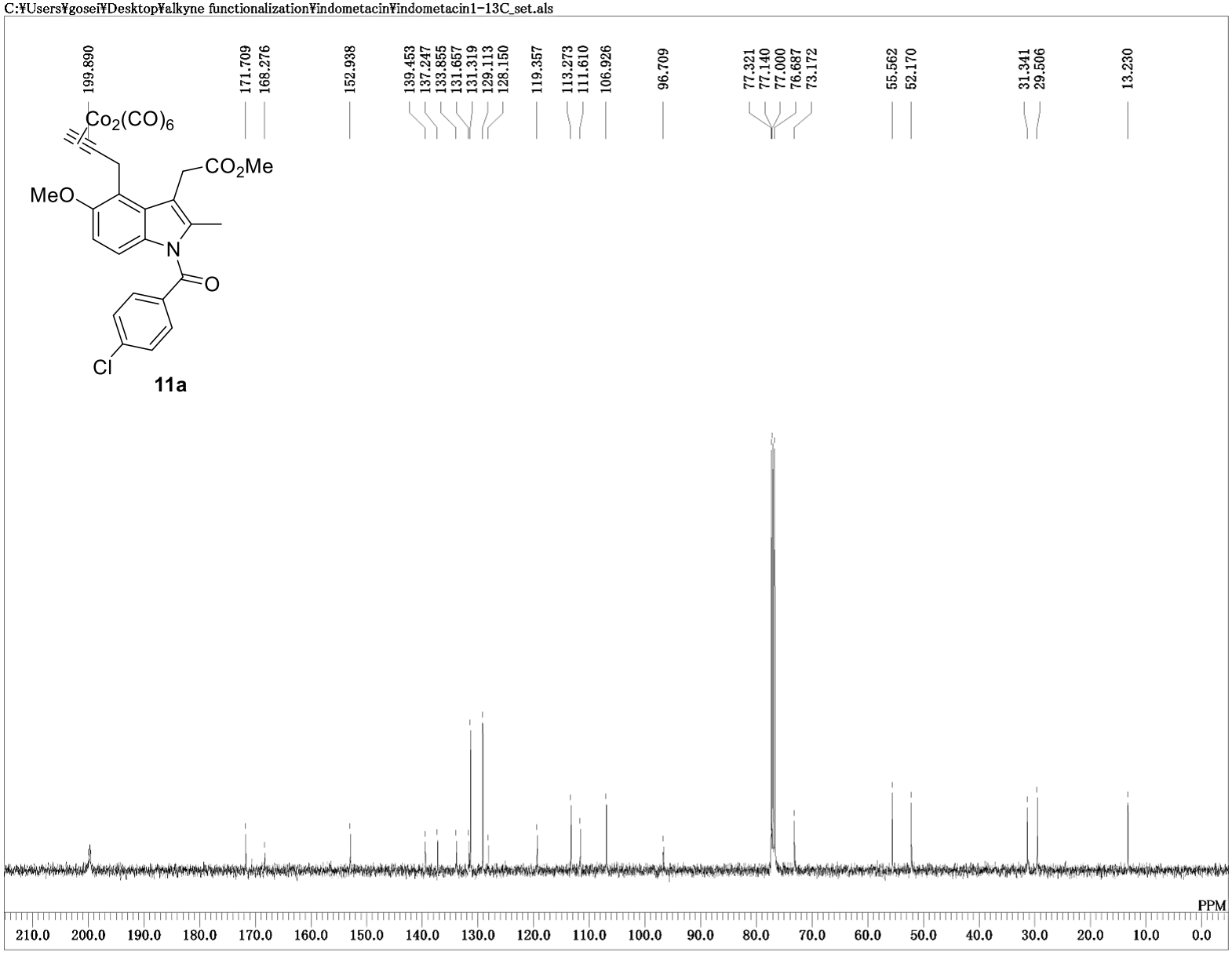
C:¥Users¥gosei¥Desktop¥alkyne functionalization¥indometacin¥indometacin1-1H_set.als



DFILE	indometacin1-1H_set.als
COMNT	auto
DATIM	Wed Mar 16 13:20:44 2016
OBNUC	1H
EXMOD	NON
OBFRQ	399.65 MHz
OBSET	124.00 KHz
OBFIN	10500.00 Hz
POINT	16384
FREQU	7992.01 Hz
SCANS	32
ACQTM	2.0500 sec
PD	4.9500 sec
PW1	6.20 usec
IRNUC	1H
CTEMP	25.1 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	20

auto

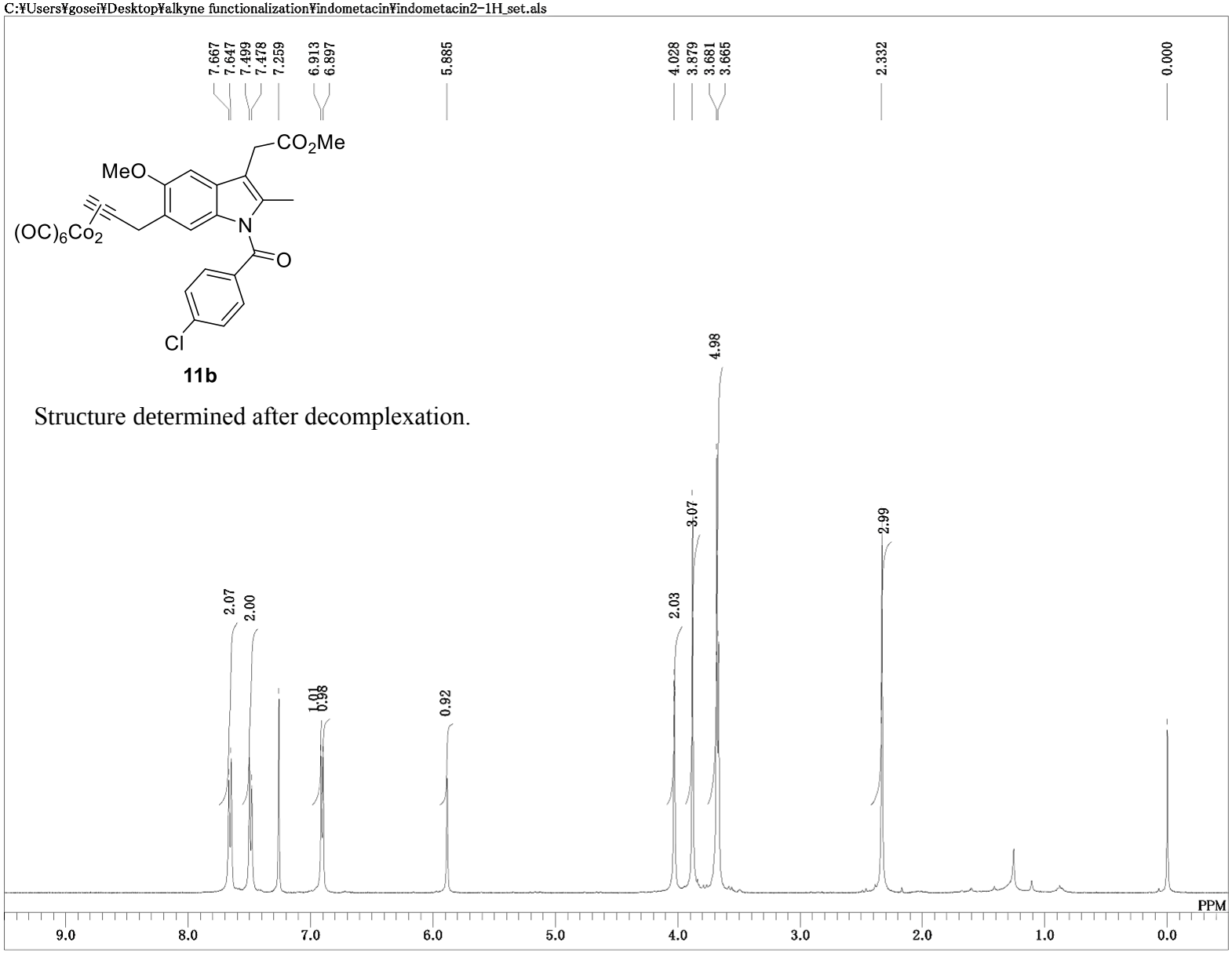
C:¥Users¥gosei¥Desktop¥alkyne functionalization¥indometacin¥indometacin1-13C_set.als



DFILE	indometacin1-13C_set.als
COMNT	auto
DATIM	Tue Mar 15 21:37:27 2016
OBNUC	13C
EXMOD	BCM
OBFRQ	100.40 MHz
OBSET	125.00 KHz
OBFIN	10500.00 Hz
POINT	32768
FREQU	27118.64 Hz
SCANS	733
ACQTM	1.2083 sec
PD	1.7920 sec
PW1	6.20 usec
IRNUC	1H
CTEMP	24.6 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.02 Hz
RGAIN	22

auto

C:¥Users¥gosei¥Desktop¥alkyne functionalization¥indometacin¥indometacin2-1H_set.als

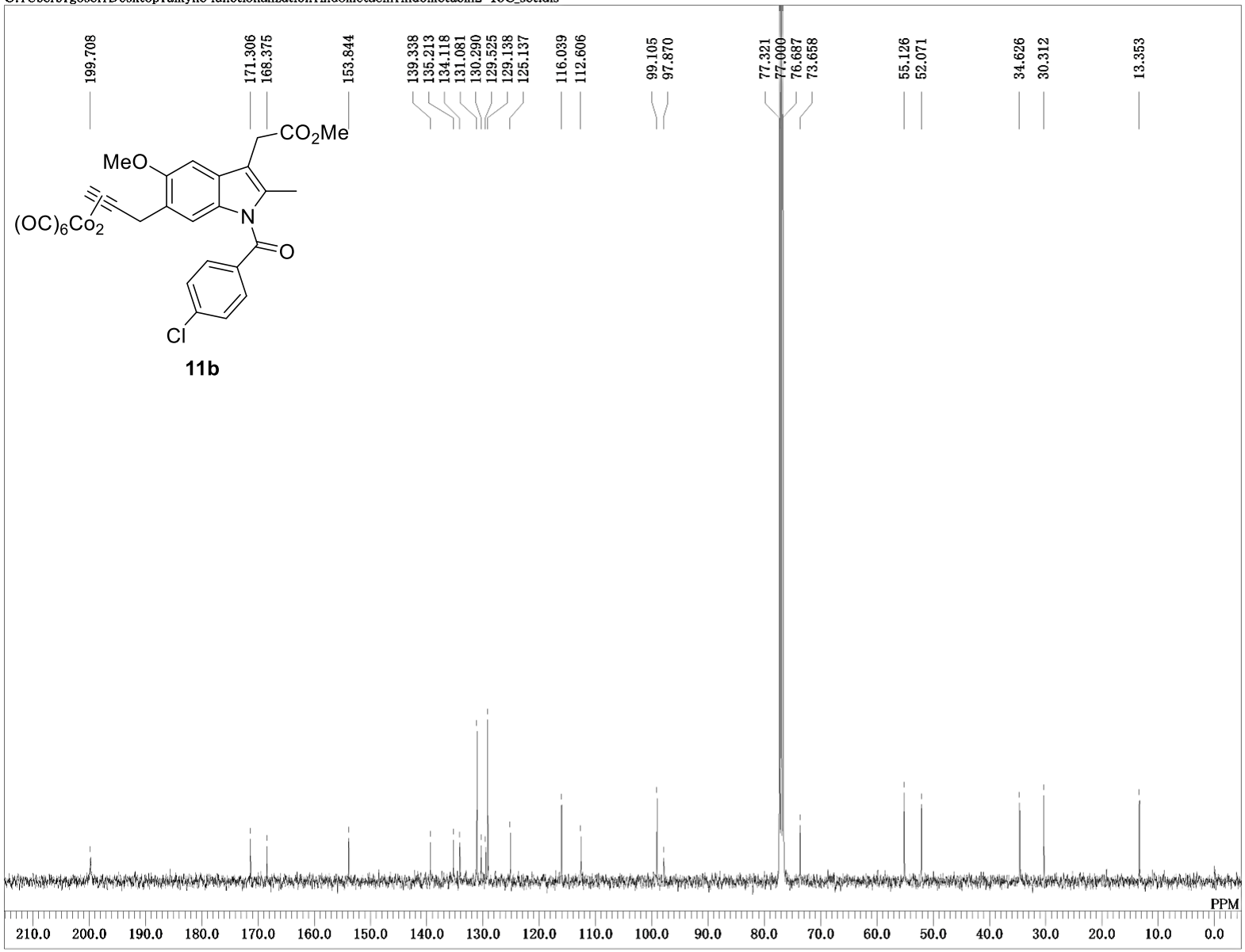


Structure determined after decomplexation.

DFILE	indometacin2-1H_set.als
COMNT	auto
DATIM	Tue Mar 15 20:03:41 2016
OBNUC	1H
EXMOD	NON
OBFRQ	399.65 MHz
OBSET	124.00 KHz
OBFIN	10500.00 Hz
POINT	16384
FREQU	7992.01 Hz
SCANS	32
ACQTM	2.0500 sec
PD	4.9500 sec
PW1	6.20 usec
IRNUC	1H
CTEMP	23.5 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	19

auto

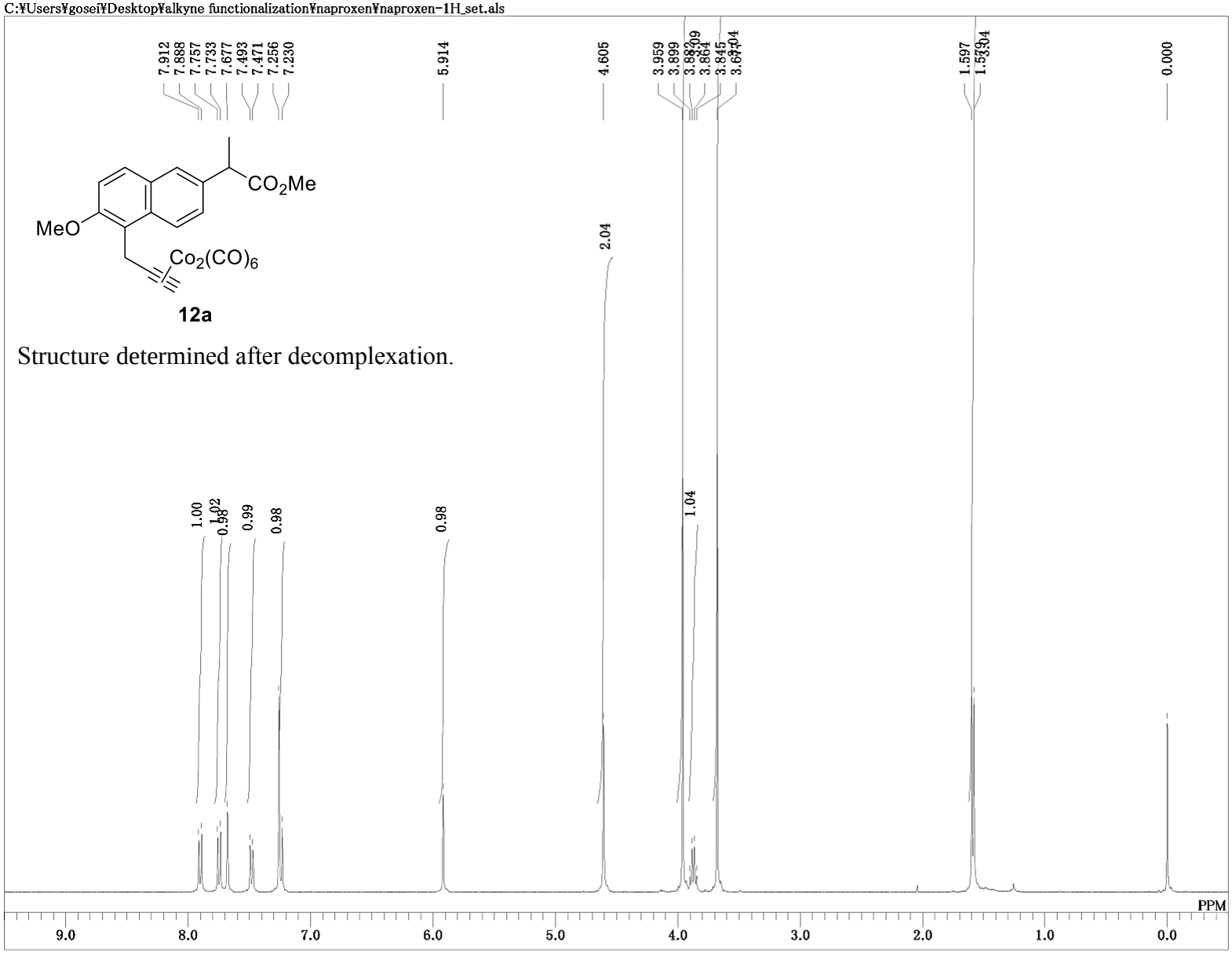
C:¥Users¥gosei¥Desktop¥alkyne functionalization¥indometacin¥indometacin2-13C_set.als



DFILE	indometacin2-13C_set.als
COMNT	auto
DATIM	Tue Mar 15 12:53:43 2016
OBNUC	13C
EXMOD	BCM
OBFRQ	100.40 MHz
OBSET	125.00 KHz
OBFIN	10500.00 Hz
POINT	32768
FREQU	27118.64 Hz
SCANS	717
ACQTM	1.2083 sec
PD	1.7920 sec
PW1	6.20 usec
IRNUC	1H
CTEMP	24.4 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	2.12 Hz
RGAIN	22

auto

C:¥Users¥gosei¥Desktop¥alkyne functionalization¥naproxen¥naproxen-1H_set.als



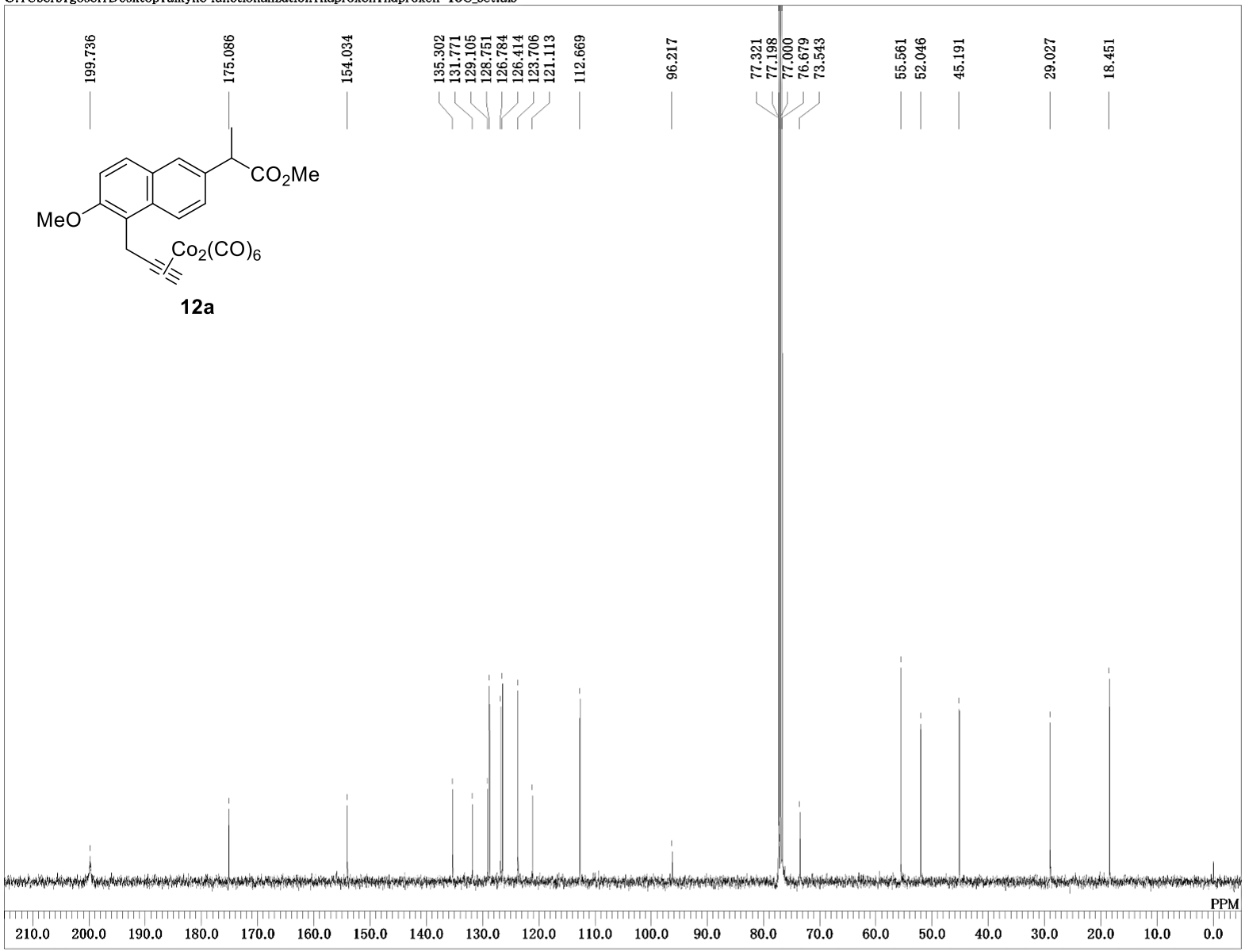
DFILE naproxen-1H_set.als
COMNT auto
DATIM Tue Jan 05 19:54:48 2016
OBNUC 1H
EXMOD NON
OBFRQ 395.75 MHz
OBSET 124.00 KHz
OBFIN 10277.00 Hz
POINT 16384
FREQU 7912.96 Hz
SCANS 16
ACQTM 2.0705 sec
PD 4.9290 sec
PW1 5.50 usec
IRNUC 1H
CTEMP 23.6 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 21

12a

Structure determined after decomplexation.

auto

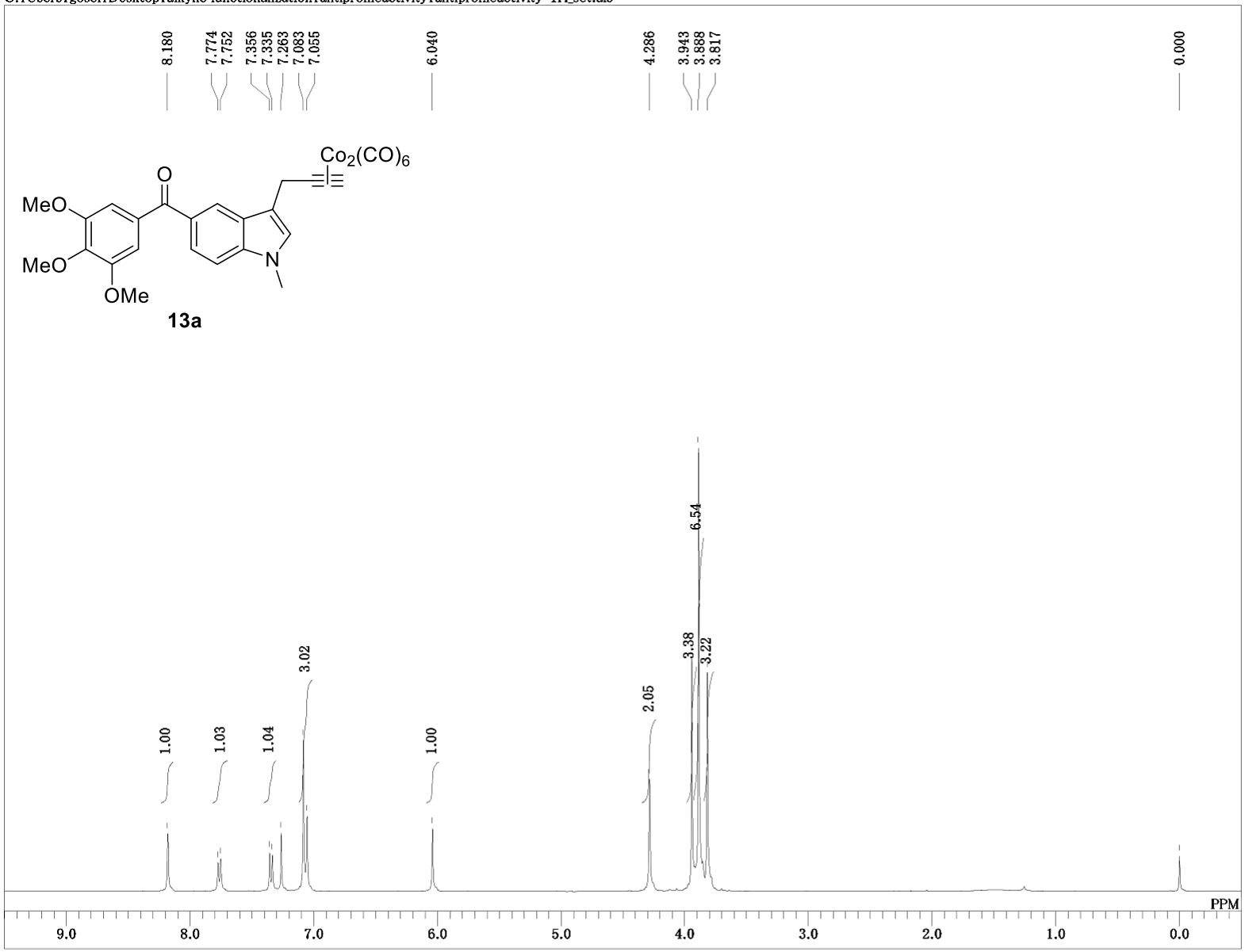
C:¥Users¥gosei¥Desktop¥alkyne functionalization¥naproxen¥naproxen-13C_set.als



DFILE	naproxen-13C_set.als
COMNT	auto
DATIM	Fri Mar 25 16:46:10 2016
OBNUC	13C
EXMOD	BCM
OBFRQ	99.45 MHz
OBSET	94.00 KHz
OBFIN	10309.00 Hz
POINT	32768
FREQU	26845.64 Hz
SCANS	1400
ACQTM	1.2206 sec
PD	1.7790 sec
PW1	6.50 usec
IRNUC	1H
CTEMP	22.8 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.22 Hz
RGAIN	22

auto

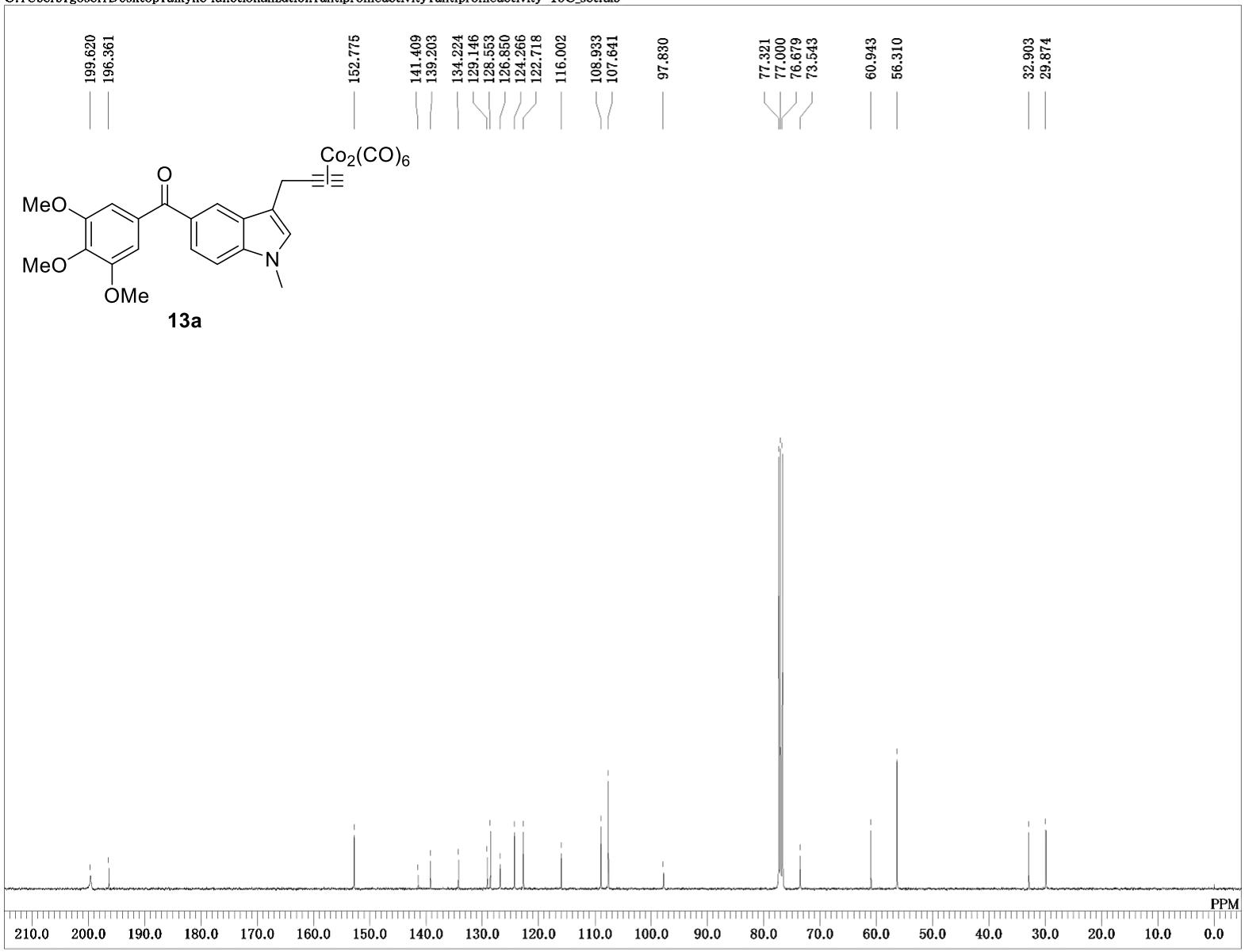
C:¥Users¥gosei¥Desktop¥alkyne functionalization¥antiprofileactivity¥antiprofileactivity-1H_set.als



DFILE	antiprofileactivity-1H_set.als
COMNT	auto
DATIM	Wed Feb 17 19:49:05 2016
OBNUC	1H
EXMOD	NON
OBFRQ	395.75 MHz
OBSET	124.00 KHz
OBFIN	10277.00 Hz
POINT	16384
FREQU	7912.96 Hz
SCANS	15
ACQTM	2.0705 sec
PD	4.9290 sec
PW1	5.50 usec
IRNUC	1H
CTEMP	22.0 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	1.72 Hz
RGAIN	18

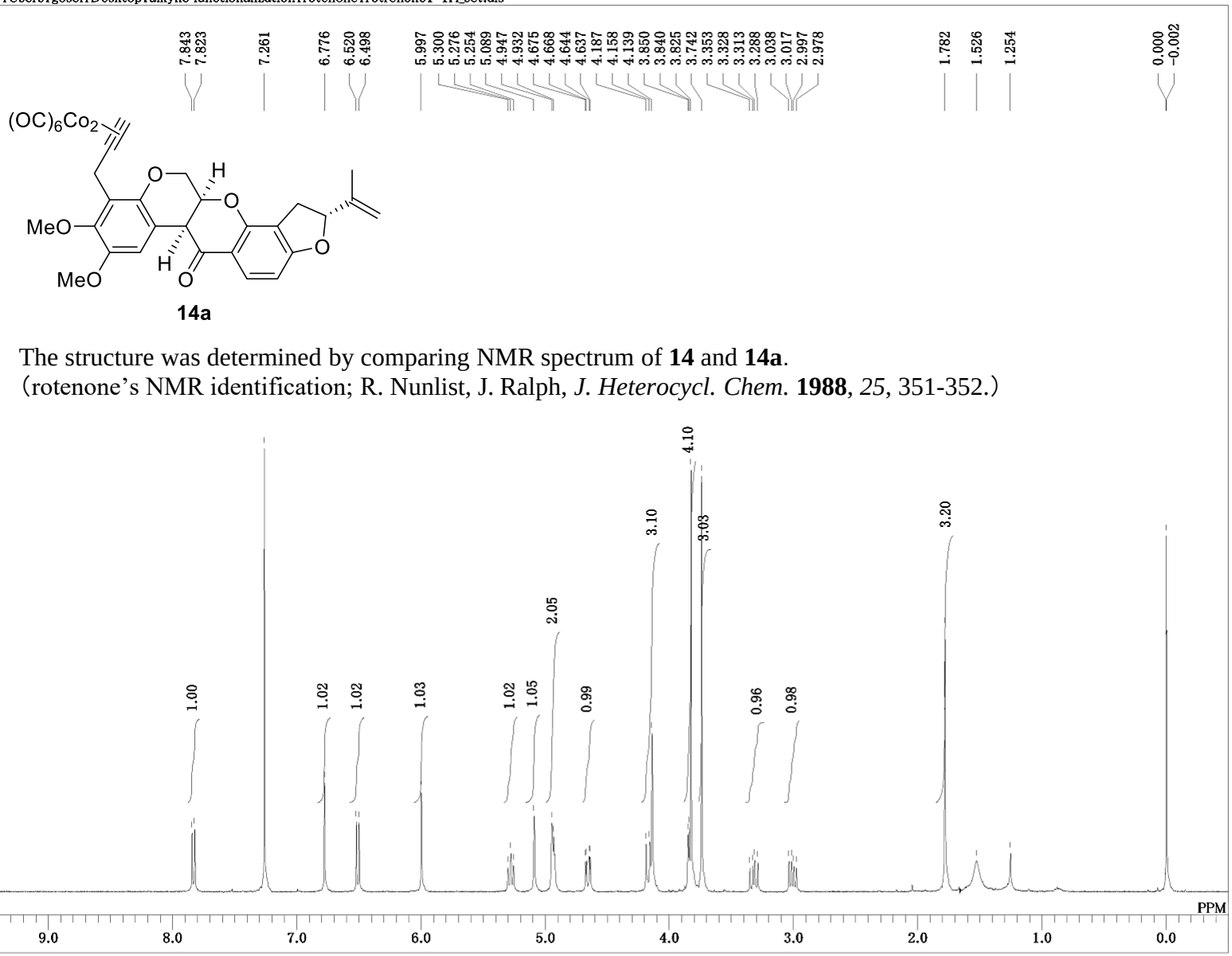
auto

C:¥Users¥gosei¥Desktop¥alkyne functionalization¥antiprofileactivity¥antiprofileactivity-13C_set.als



DFILE	antiprofileactivity-13C_set.al
COMNT	auto
DATIM	Thu Feb 18 07:39:10 2016
OBNUC	13C
EXMOD	BCM
OBFRQ	99.45 MHz
OBSET	94.00 KHz
OBFIN	10309.00 Hz
POINT	32768
FREQU	26845.64 Hz
SCANS	8000
ACQTM	1.2206 sec
PD	1.7790 sec
PW1	6.50 usec
IRNUC	1H
CTEMP	22.1 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.72 Hz
RGAIN	22

auto
C:¥Users¥gosei¥Desktop¥alkyne functionalization¥rotenone¥rotrenone1-1H_set.als



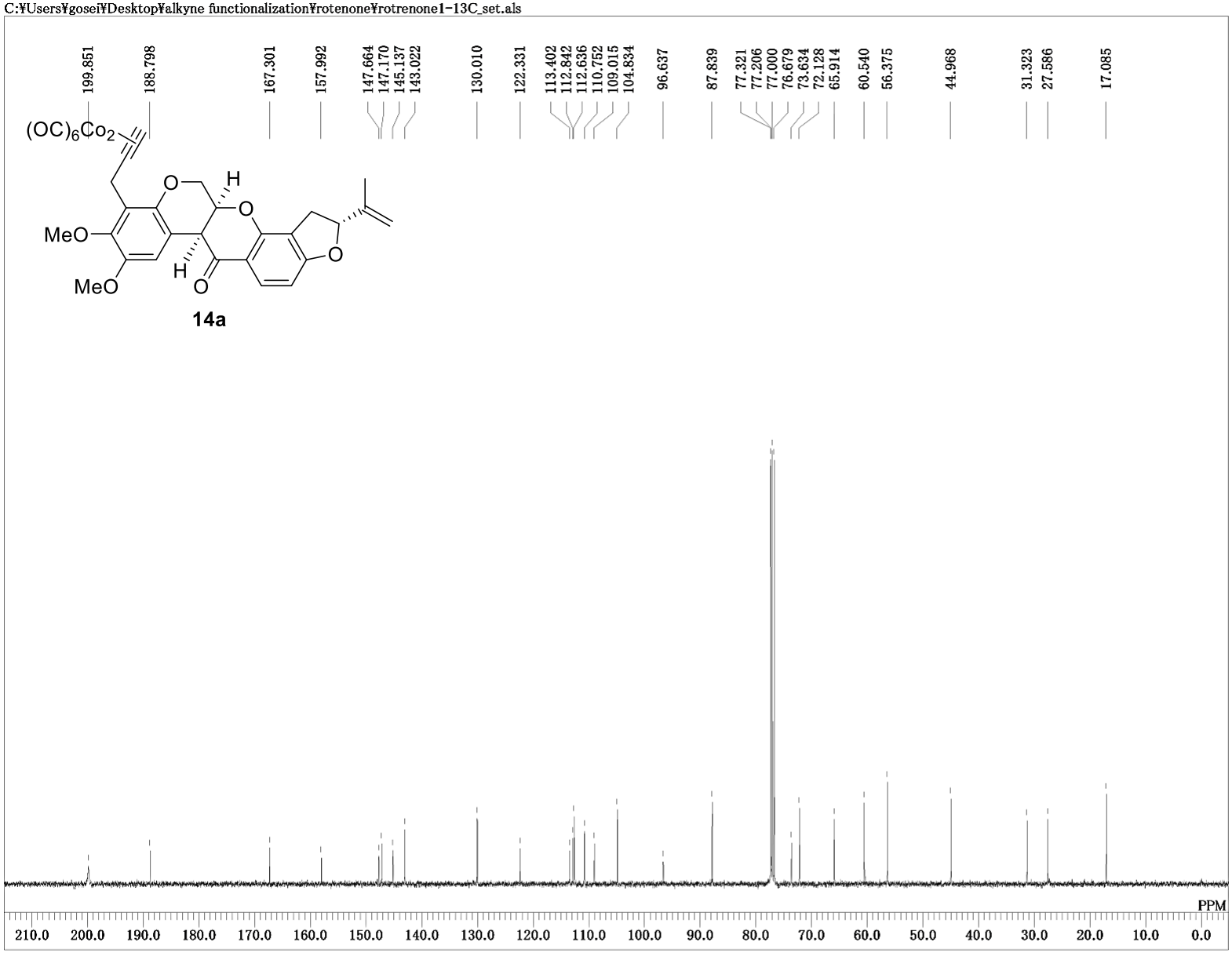
14a

DFILE rotrenone1-1H_set.als
COMNT auto
DATIM Thu Mar 10 20:55:45 2016
OBNUC 1H
EXMOD NON
OBFRQ 395.75 MHz
OBSET 124.00 KHz
OBFIN 10277.00 Hz
POINT 16384
FREQU 7912.96 Hz
SCANS 32
ACQTM 2.0705 sec
PD 4.9290 sec
PW1 5.50 usec
IRNUC 1H
CTEMP 23.0 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 21

The structure was determined by comparing NMR spectrum of **14** and **14a**.
（rotenone's NMR identification; R. Nunlist, J. Ralph, *J. Heterocycl. Chem.* **1988**, *25*, 351-352.）

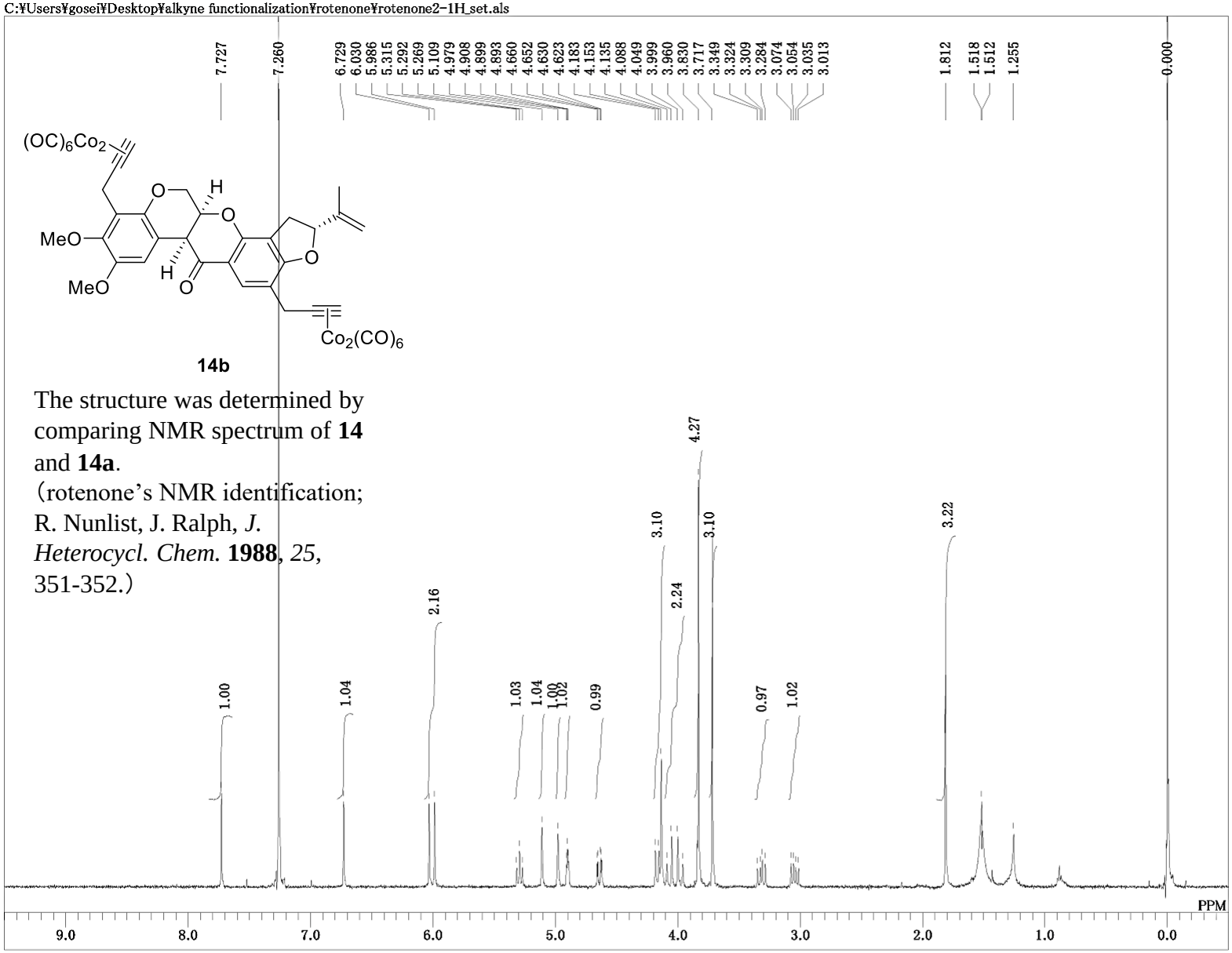
auto

C:¥Users¥gosei¥Desktop¥alkyne functionalization¥rotenone¥rotrenone1-13C_set.als



DFILE	rotrenone1-13C_set.als
COMNT	auto
DATIM	Tue Apr 19 19:30:20 2016
OBNUC	13C
EXMOD	BCM
OBFRQ	99.45 MHz
OBSET	94.00 KHz
OBFIN	10309.00 Hz
POINT	32768
FREQU	26845.64 Hz
SCANS	988
ACQTM	1.2206 sec
PD	1.7790 sec
PW1	6.50 usec
IRNUC	1H
CTEMP	25.7 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.02 Hz
RGAIN	23

auto
C:¥Users¥gosei¥Desktop¥alkyne functionalization¥rotenone¥rotenone2-1H_set.als

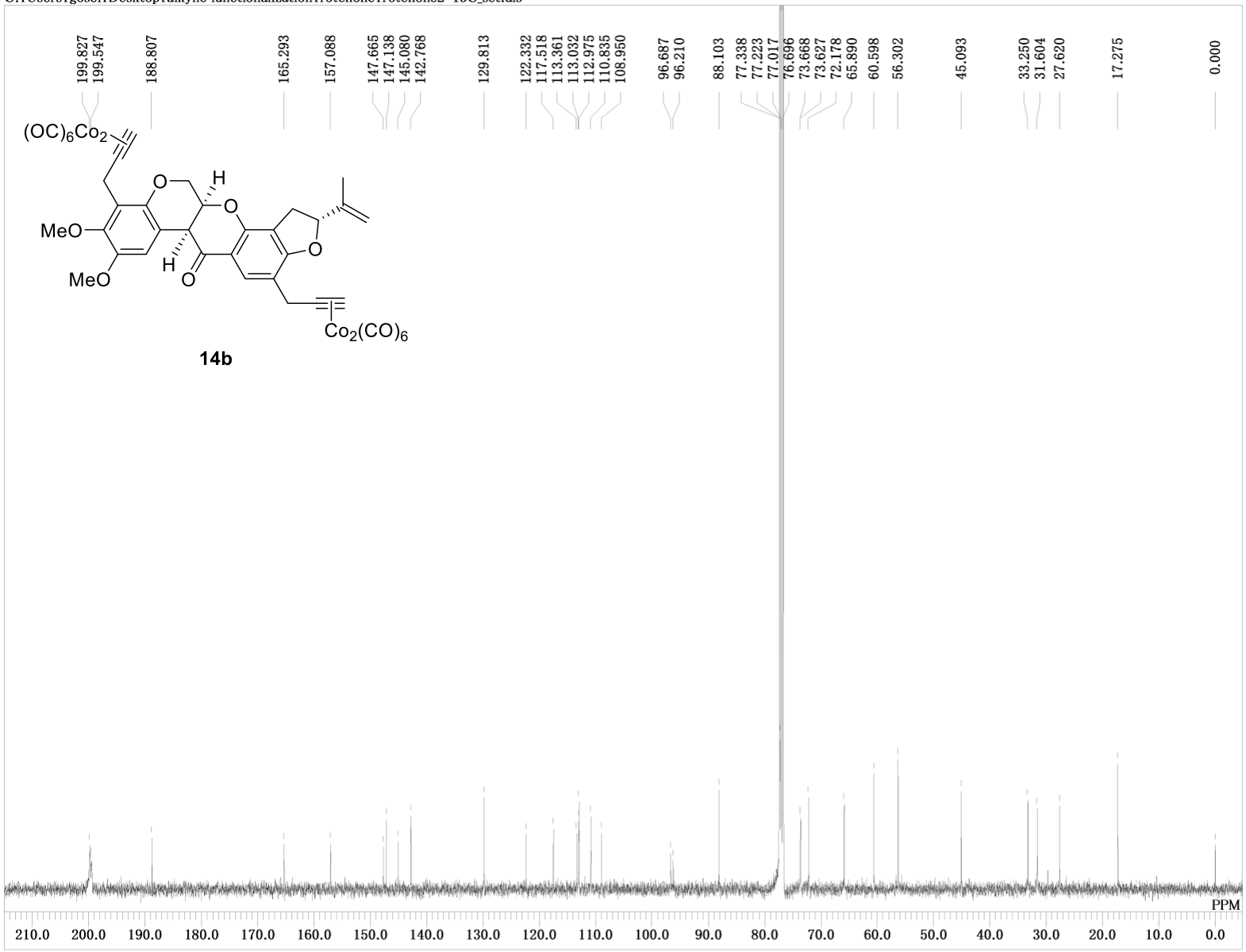


DFILE rotenone2-1H_set.als
COMNT auto
DATIM Thu Mar 17 22:02:15 2016
OBNUC 1H
EXMOD NON
OBFRQ 395.75 MHz
OBSET 124.00 KHz
OBFIN 10277.00 Hz
POINT 16384
FREQU 7912.96 Hz
SCANS 20
ACQTM 2.0705 sec
PD 4.9290 sec
PW1 5.50 usec
IRNUC 1H
CTEMP 24.7 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 24

The structure was determined by comparing NMR spectrum of **14** and **14a**.
（rotenone's NMR identification; R. Nunlist, J. Ralph, *J. Heterocycl. Chem.* **1988**, *25*, 351-352.）

auto

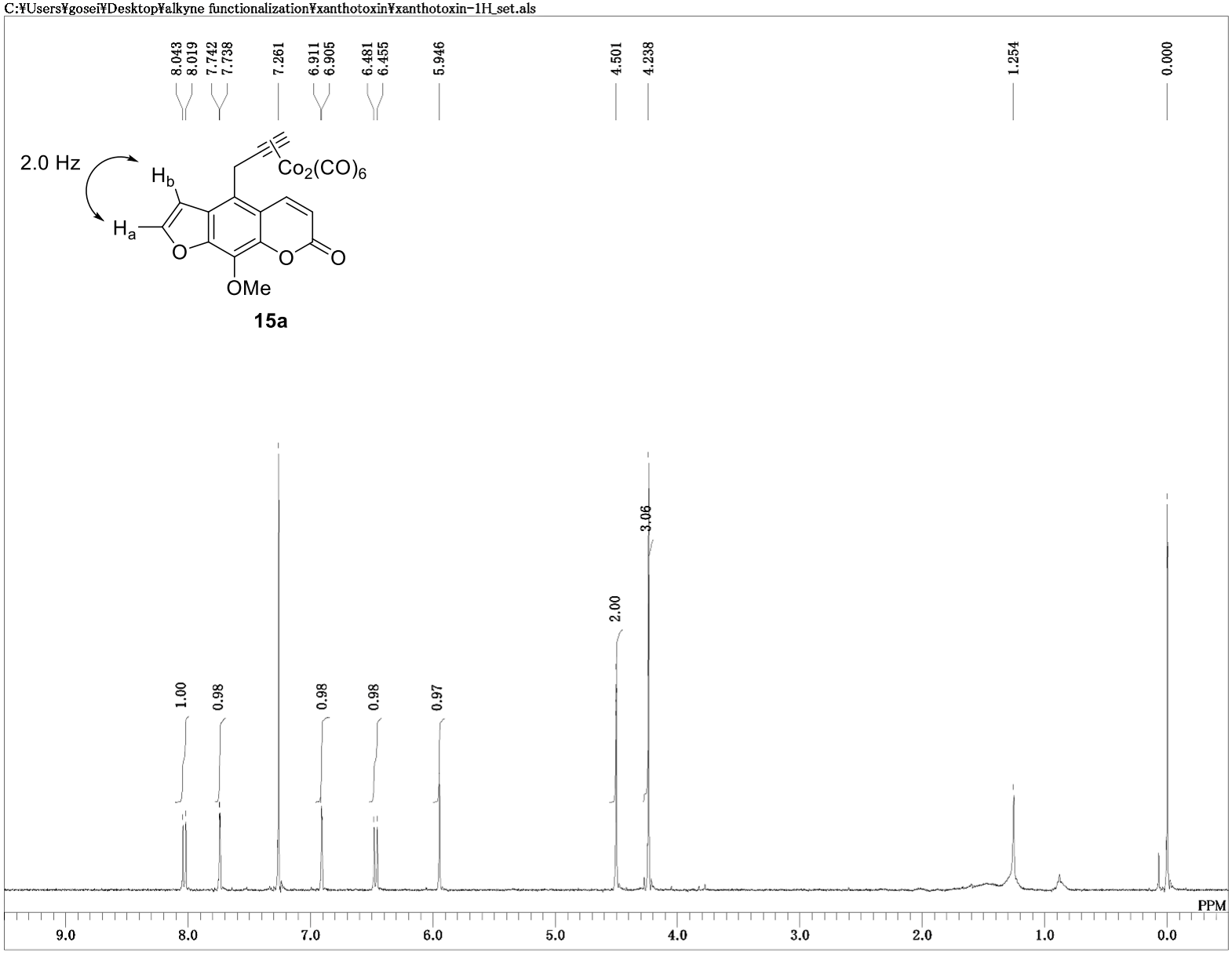
C:¥Users¥gosei¥Desktop¥alkyne functionalization¥rotenone¥rotenone2-13C_set.als



DFILE	rotenone2-13C_set.als
COMNT	auto
DATIM	Wed Apr 20 09:10:10 2016
OBNUC	13C
EXMOD	BCM
OBFRQ	99.45 MHz
OBSET	94.00 KHz
OBFIN	10309.00 Hz
POINT	32768
FREQU	26845.64 Hz
SCANS	10956
ACQTM	1.2206 sec
PD	1.7790 sec
PW1	6.50 usec
IRNUC	1H
CTEMP	27.2 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	1.02 Hz
RGAIN	23

auto

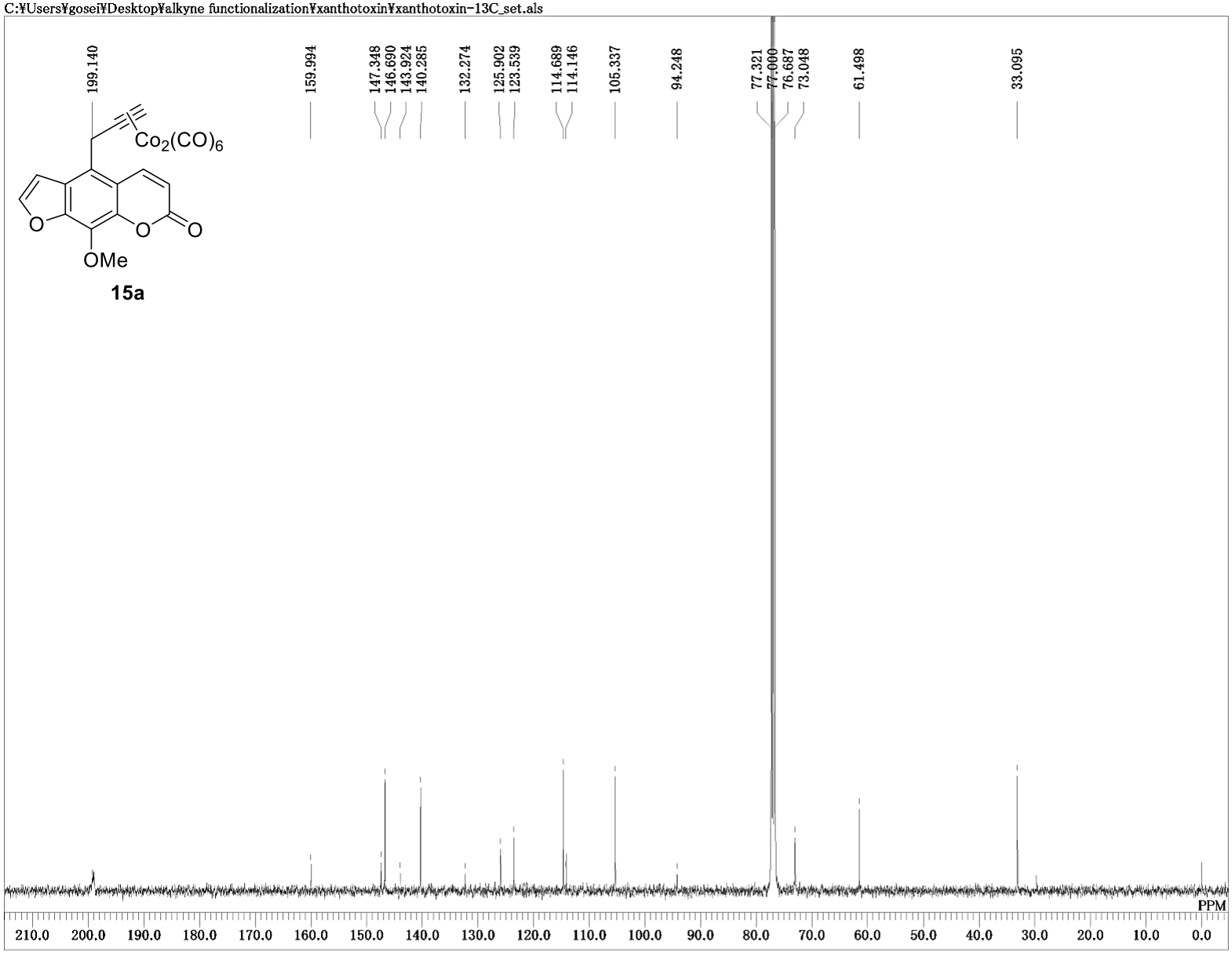
C:¥Users¥gosei¥Desktop¥alkyne functionalization¥xanthotoxin¥xanthotoxin-1H_set.als



DFILE	xanthotoxin-1H_set.als
COMNT	auto
DATIM	Wed Feb 10 21:02:09 2016
OBNUC	1H
EXMOD	NON
OBFRQ	395.75 MHz
OBSET	124.00 KHz
OBFIN	10277.00 Hz
POINT	16384
FREQU	7912.96 Hz
SCANS	9
ACQTM	2.0705 sec
PD	4.9290 sec
PW1	5.50 usec
IRNUC	1H
CTEMP	23.1 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	23

auto

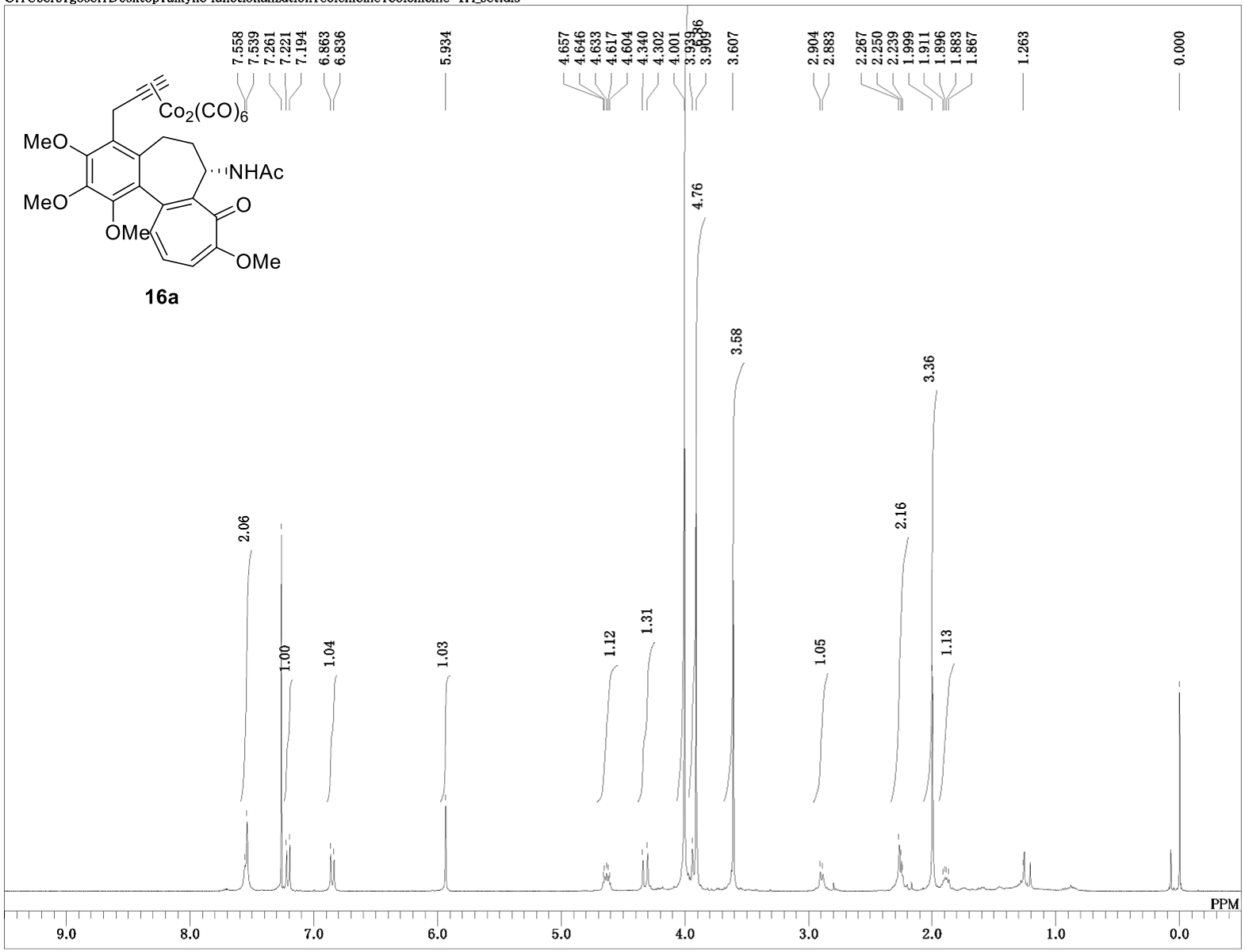
C:¥Users¥gosei¥Desktop¥alkyne functionalization¥xanthotoxin¥xanthotoxin-13C_set.als



DFILE	xanthotoxin-13C_set.als
COMNT	auto
DATIM	Mon Feb 08 07:22:12 2016
OBNUC	13C
EXMOD	BCM
OBFRQ	100.40 MHz
OBSET	125.00 KHz
OBFIN	10500.00 Hz
POINT	32768
FREQU	27118.64 Hz
SCANS	10000
ACQTM	1.2083 sec
PD	1.7920 sec
PW1	6.20 usec
IRNUC	1H
CTEMP	19.3 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.72 Hz
RGAIN	22

auto

C:¥Users¥gosei¥Desktop¥alkyne functionalization¥colchicine¥colchicine-1H_set.als

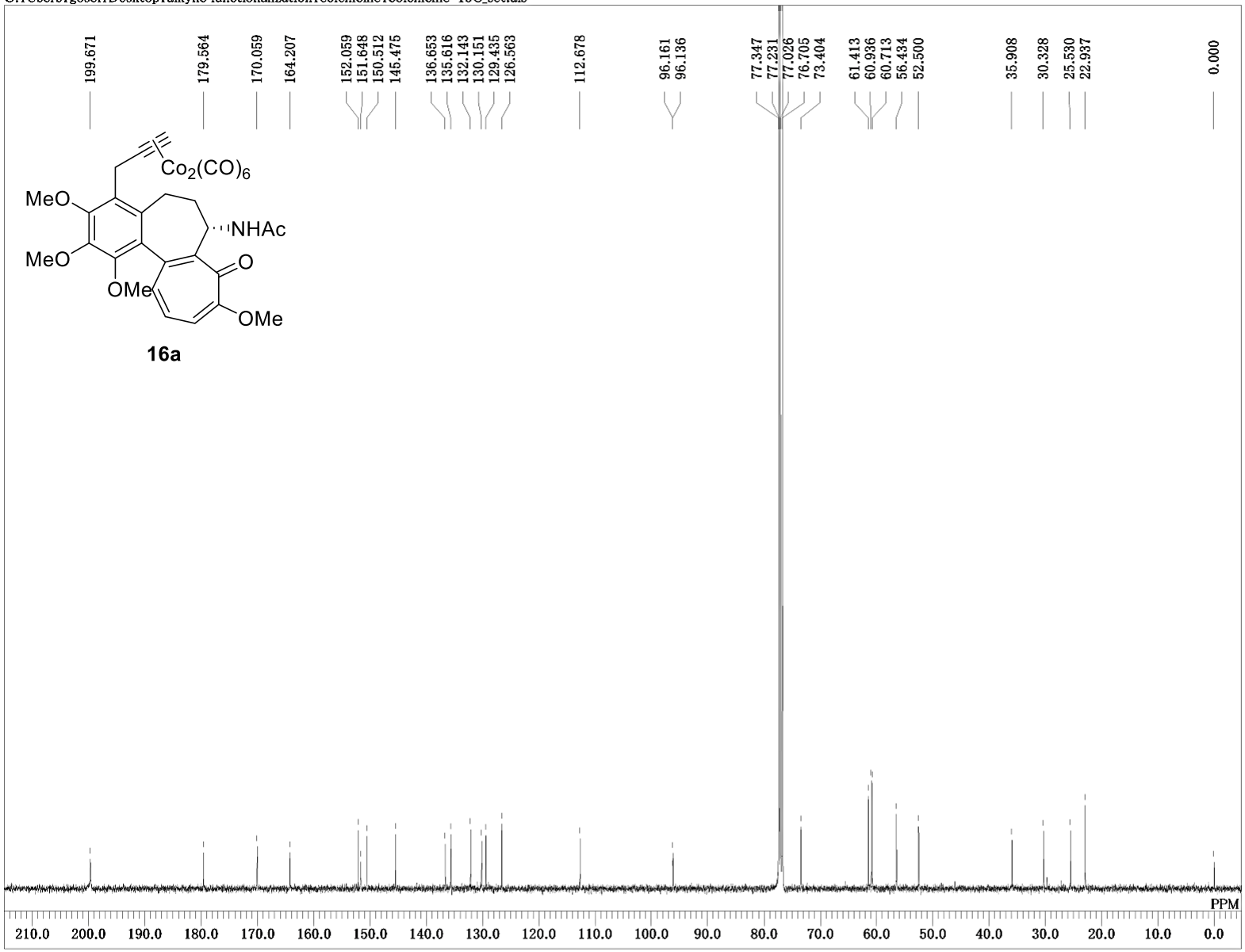


16a

DFILE	colchicine-1H_set.als
COMNT	auto
DATIM	Sat Jun 04 18:07:36 2016
OBNUC	1H
EXMOD	NON
OBFRQ	399.65 MHz
OBSET	124.00 KHz
OBFIN	10500.00 Hz
POINT	16384
FREQU	7992.01 Hz
SCANS	64
ACQTM	2.0500 sec
PD	4.9500 sec
PW1	6.20 usec
IRNUC	1H
CTEMP	27.5 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	19

auto

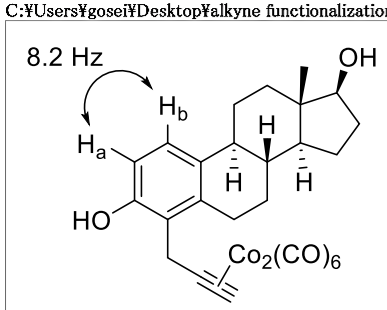
C:¥Users¥gosei¥Desktop¥alkyne functionalization¥colchicine¥colchicine-13C_set.als



DFILE	colchicine-13C_set.als
COMNT	auto
DATIM	Sat Jun 04 09:32:27 2016
OBNUC	13C
EXMOD	BCM
OBFRQ	99.45 MHz
OBSET	94.00 KHz
OBFIN	10309.00 Hz
POINT	32768
FREQU	26845.64 Hz
SCANS	11226
ACQTM	1.2206 sec
PD	1.7790 sec
PW1	6.50 usec
IRNUC	1H
CTEMP	24.1 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.82 Hz
RGAIN	23

auto

C:¥Users¥gosei¥Desktop¥alkyne functionalization¥estradiol¥estradiol2-1H_set.als

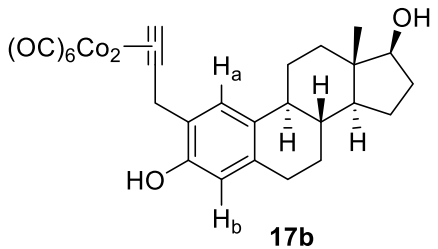


17a

DFILE	estradiol2-1H_set.als
COMNT	auto
DATIM	Mon Jun 22 13:54:18 2015
OBNUC	1H
EXMOD	NON
OBFRQ	395.75 MHz
OBSET	124.00 KHz
OBFIN	10277.00 Hz
POINT	16384
FREQU	7912.96 Hz
SCANS	16
ACQTM	2.0705 sec
PD	4.9290 sec
PW1	5.50 usec
IRNUC	1H
CTEMP	23.7 c
SLVNT	ACETN
EXREF	2.04 ppm
BF	0.12 Hz
RGAIN	16

auto

C:¥Users¥gosei¥Desktop¥alkyne functionalization¥estradiol¥estradiol1-1H_set.als



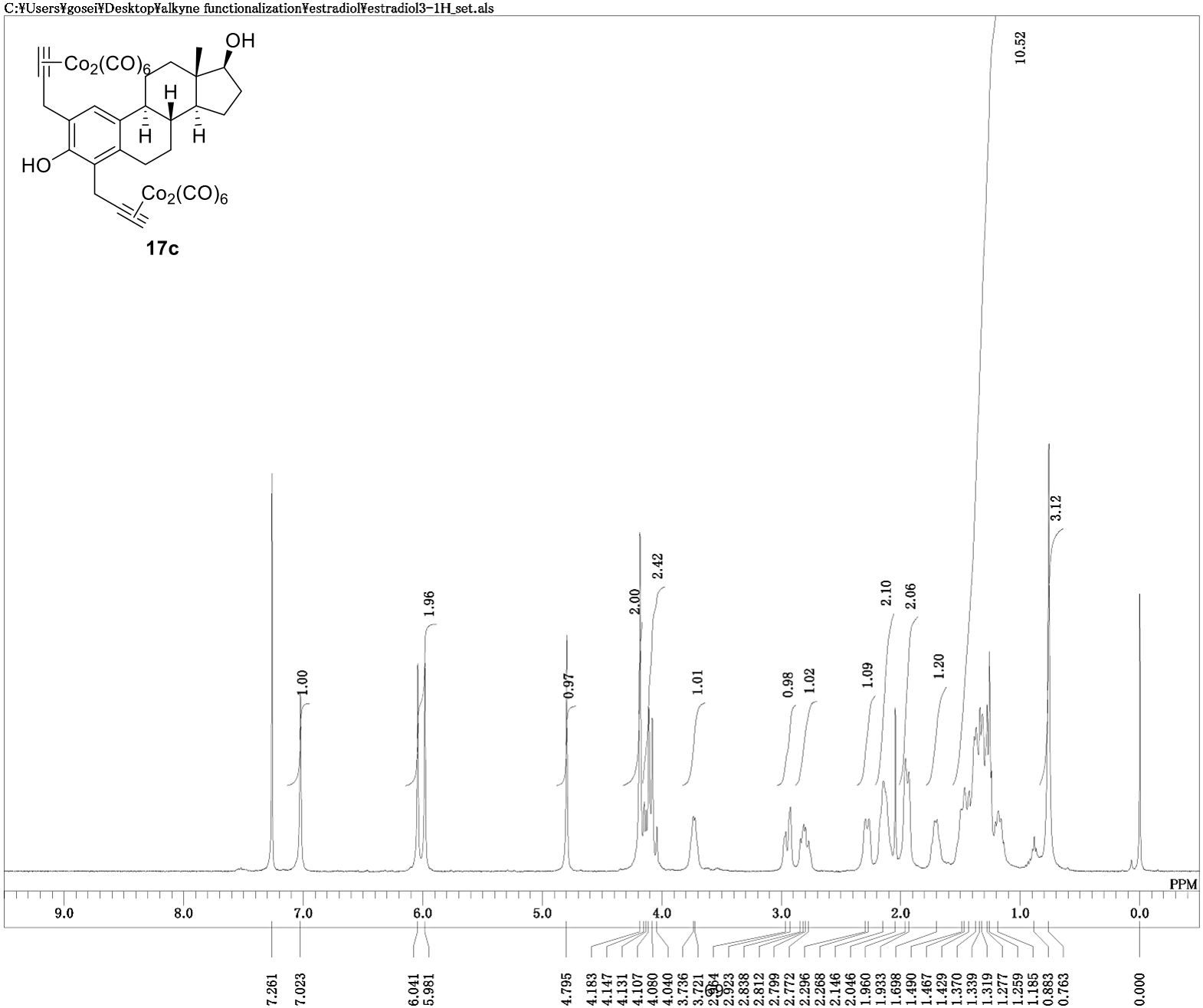
17b

Coupling b/w H_a and H_b not observed.

DFILE	estradiol1-1H_set.als
COMNT	auto
DATIM	Mon Jun 22 13:47:35 2015
OBNUC	1H
EXMOD	NON
OBFRQ	395.75 MHz
OBSET	124.00 KHz
OBFIN	10277.00 Hz
POINT	16384
FREQU	7912.96 Hz
SCANS	16
ACQTM	2.0705 sec
PD	4.9290 sec
PW1	5.50 usec
IRNUC	1H
CTEMP	23.8 c
SLVNT	ACETN
EXREF	2.04 ppm
BF	0.12 Hz
RGAIN	17

auto

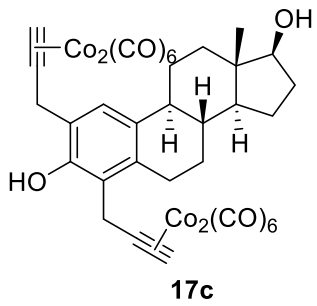
C:¥Users¥gosei¥Desktop¥alkyne functionalization¥estradiol¥estradiol3-1H_set.als



DFILE	estradiol3-1H_set.als
COMNT	auto
DATIM	Sun Oct 16 15:19:19 2016
OBNUC	1H
EXMOD	NON
OBFRQ	399.65 MHz
OBSET	124.00 KHz
OBFIN	10500.00 Hz
POINT	16384
FREQU	7992.01 Hz
SCANS	32
ACQTM	2.0500 sec
PD	4.9500 sec
PW1	6.30 usec
IRNUC	1H
CTEMP	21.5 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.42 Hz
RGAIN	18

auto

C:¥Users¥gosei¥Desktop¥alkyne functionalization¥estradiol¥estradiol3-13C_set.als

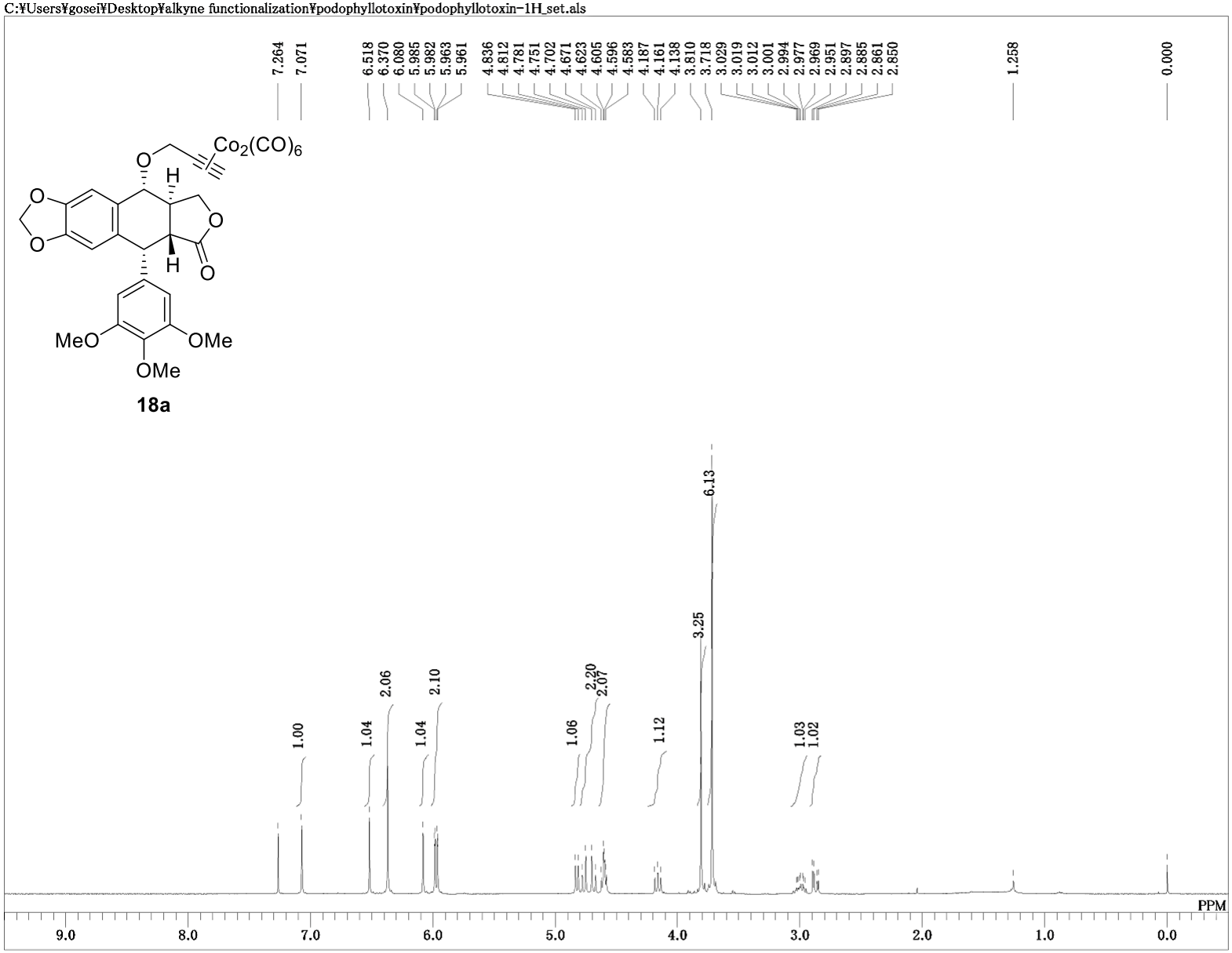


17c

DFILE	estradiol3-13C_set.als
COMNT	auto
DATIM	Sun Oct 16 17:51:54 2016
OBNUC	13C
EXMOD	BCM
OBFRQ	100.40 MHz
OBSET	125.00 KHz
OBFIN	10500.00 Hz
POINT	32768
FREQU	27118.64 Hz
SCANS	3037
ACQTM	1.2083 sec
PD	1.7920 sec
PW1	6.30 usec
IRNUC	1H
CTEMP	22.1 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.02 Hz
RGAIN	25

auto

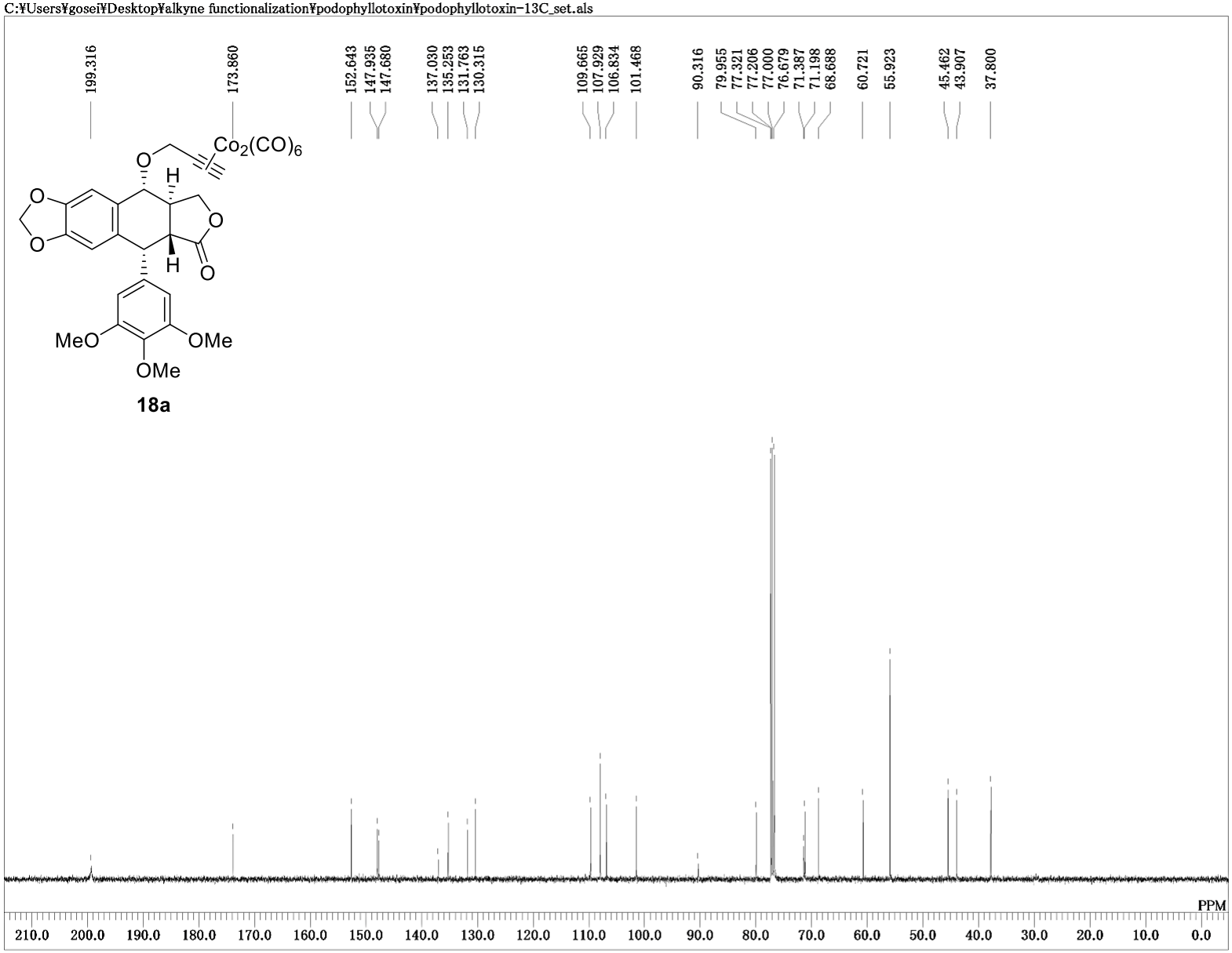
C:¥Users¥gosei¥Desktop¥alkyne functionalization¥podophyllotoxin¥podophyllotoxin-1H_set.als



DFILE	podophyllotoxin-1H_set.als
COMNT	auto
DATIM	Thu Jun 23 19:12:29 2016
OBNUC	1H
EXMOD	NON
OBFRQ	395.75 MHz
OBSET	124.00 KHz
OBFIN	10277.00 Hz
POINT	16384
FREQU	7912.96 Hz
SCANS	64
ACQTM	2.0705 sec
PD	4.9290 sec
PW1	5.50 usec
IRNUC	1H
CTEMP	23.3 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	16

auto

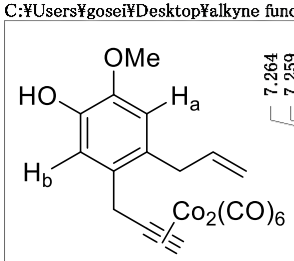
C:¥Users¥gosei¥Desktop¥alkyne functionalization¥podophyllotoxin¥podophyllotoxin-13C_set.als



DFILE	podophyllotoxin-13C_set.als
COMNT	auto
DATIM	Thu Jun 23 19:04:09 2016
OBNUC	13C
EXMOD	BCM
OBFRQ	99.45 MHz
OBSET	94.00 KHz
OBFIN	10309.00 Hz
POINT	32768
FREQU	26845.64 Hz
SCANS	1162
ACQTM	1.2206 sec
PD	1.7790 sec
PW1	6.50 usec
IRNUC	1H
CTEMP	24.9 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.52 Hz
RGAIN	24

auto

C:¥Users¥gosei¥Desktop¥alkyne functionalization¥eugenol¥eugenol2-1H_set.als



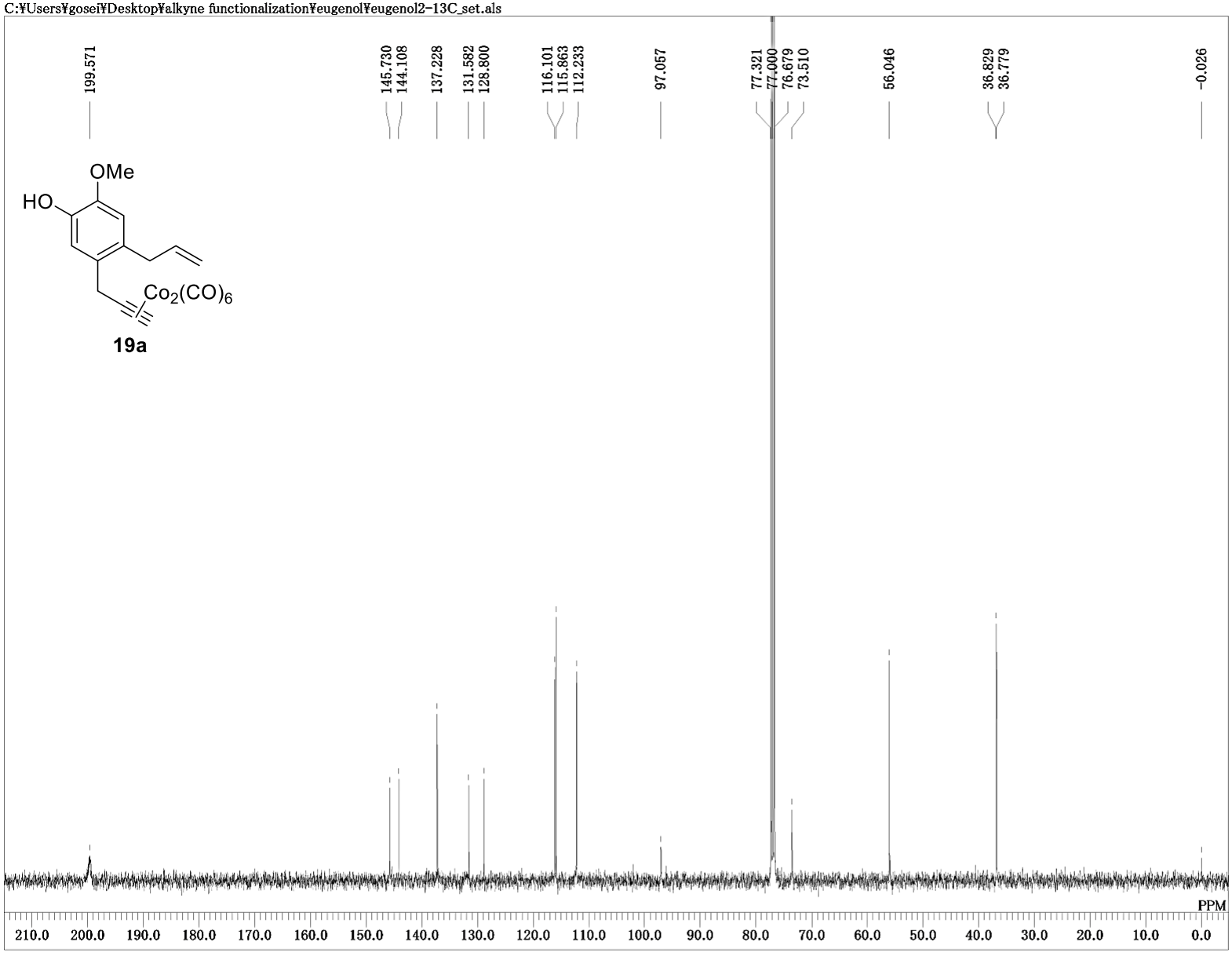
19a

Coupling b/w H_a and H_b not observed.

DFILE	eugenol2-1H_set.als
COMNT	auto
DATIM	Tue Jul 12 19:10:48 2016
OBNUC	1H
EXMOD	NON
OBFRQ	395.75 MHz
OBSET	124.00 KHz
OBFIN	10277.00 Hz
POINT	16384
FREQU	7912.96 Hz
SCANS	32
ACQTM	2.0705 sec
PD	4.9290 sec
PW1	5.50 usec
IRNUC	1H
CTEMP	26.5 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.00 Hz
RGAIN	19

auto

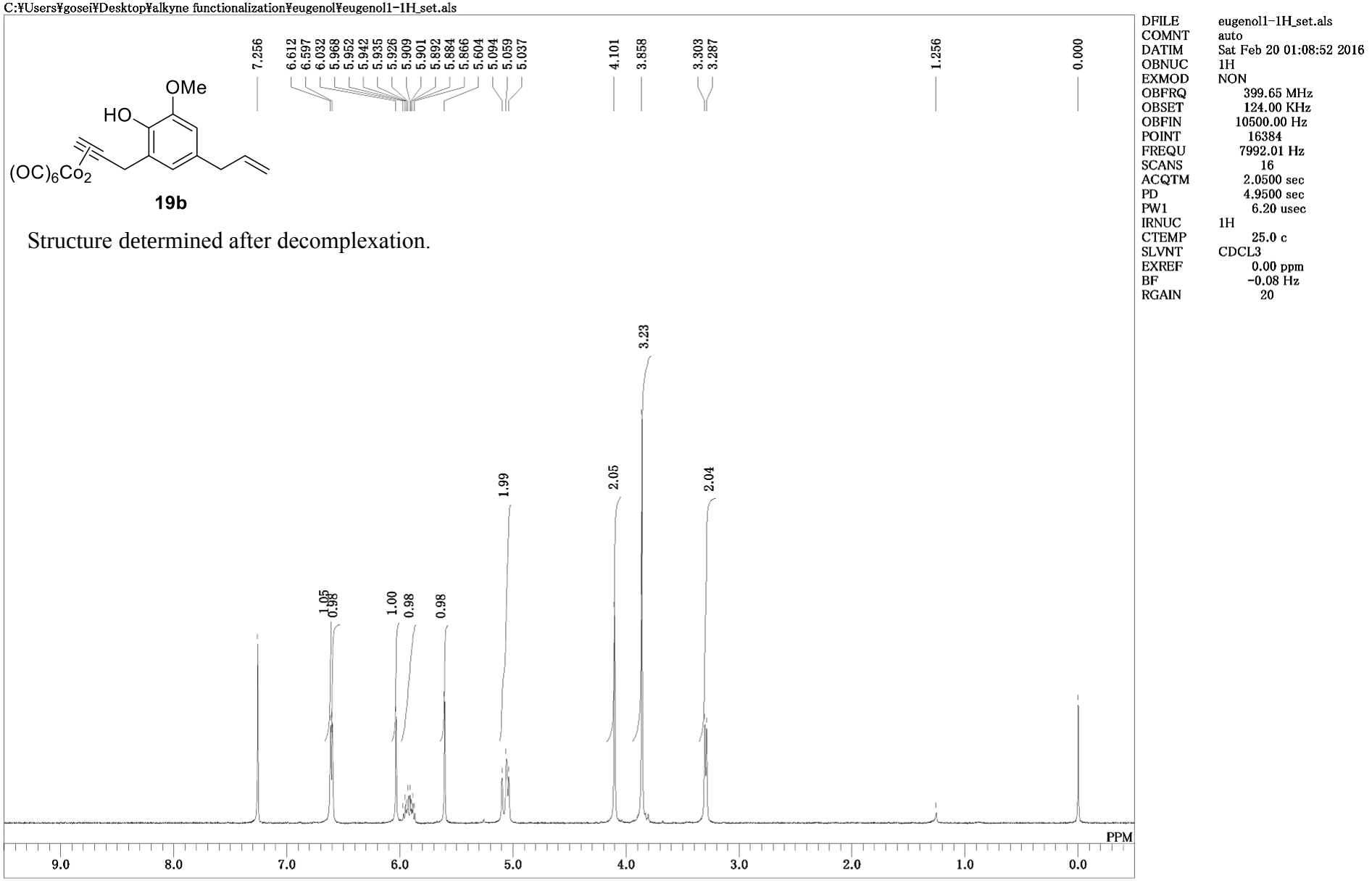
C:¥Users¥gosei¥Desktop¥alkyne functionalization¥eugenol¥eugenol2-13C_set.als



DFILE	eugenol2-13C_set.als
COMNT	auto
DATIM	Tue Jul 12 19:06:01 2016
OBNUC	13C
EXMOD	BCM
OBFRQ	99.45 MHz
OBSET	94.00 KHz
OBFIN	10309.00 Hz
POINT	32768
FREQU	26845.64 Hz
SCANS	1525
ACQTM	1.2206 sec
PD	1.7790 sec
PW1	6.50 usec
IRNUC	1H
CTEMP	27.9 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.02 Hz
RGAIN	23

auto

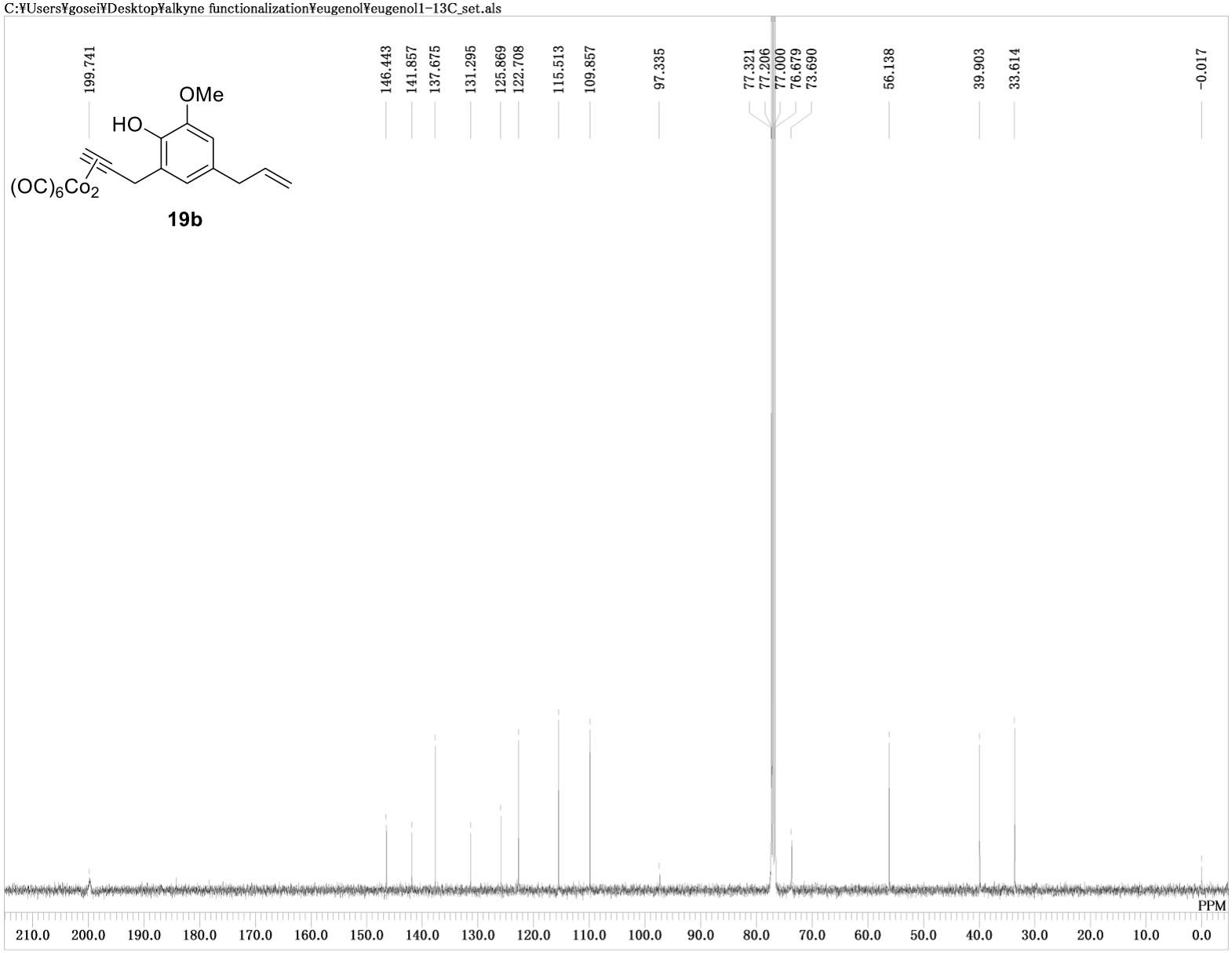
C:¥Users¥gosei¥Desktop¥alkyne functionalization¥eugenol¥eugenol1-1H_set.als



Structure determined after decomplexation.

auto

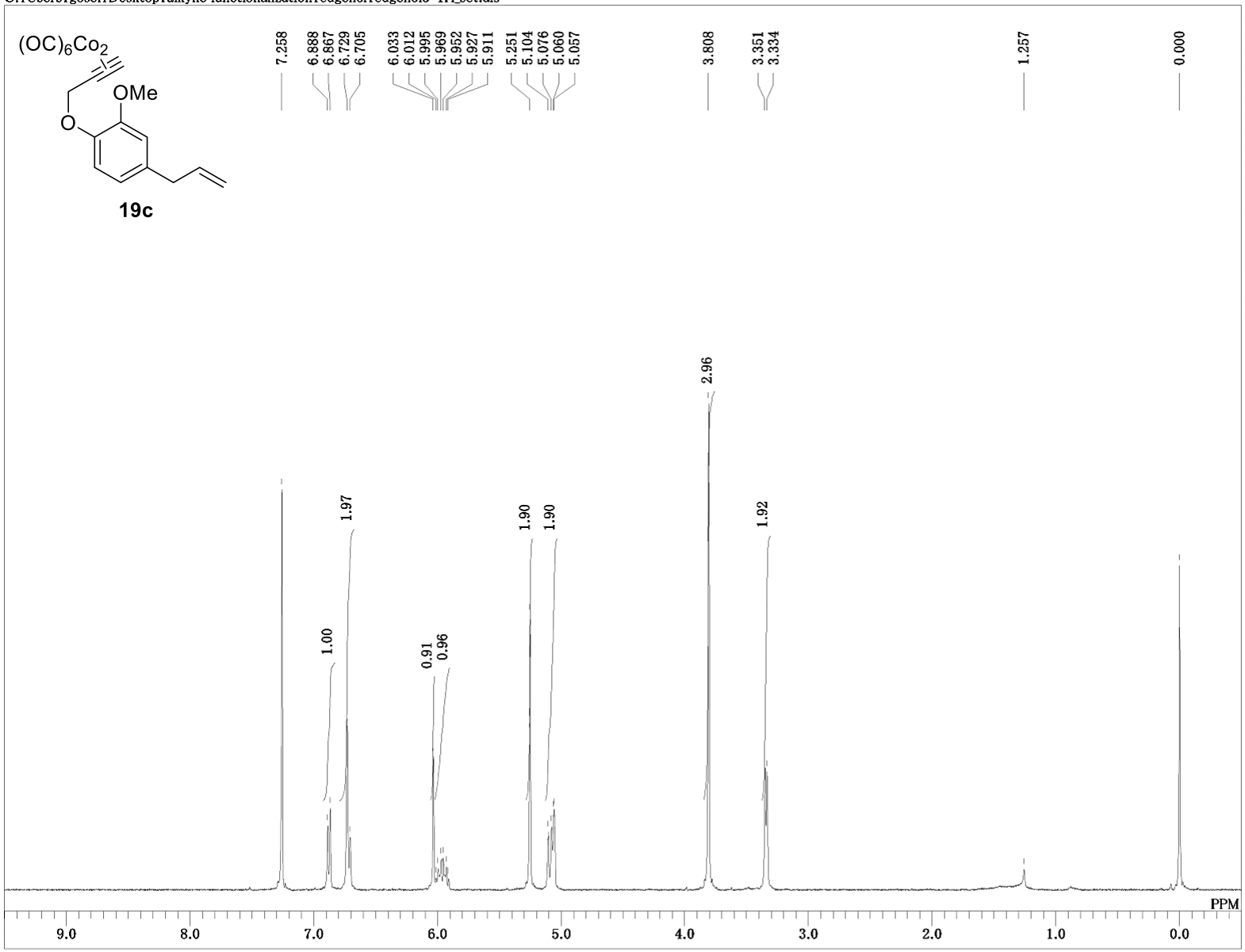
C:¥Users¥gosei¥Desktop¥alkyne functionalization¥eugenol¥eugenol1-13C_set.als



DFILE	eugenol1-13C_set.als
COMNT	auto
DATIM	Sat Feb 20 08:49:35 2016
OBNUC	13C
EXMOD	BCM
OBFRQ	100.40 MHz
OBSET	125.00 KHz
OBFIN	10500.00 Hz
POINT	32768
FREQU	27118.64 Hz
SCANS	7075
ACQTM	1.2083 sec
PD	1.7920 sec
PW1	6.20 usec
IRNUC	1H
CTEMP	24.9 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.72 Hz
RGAIN	22

auto

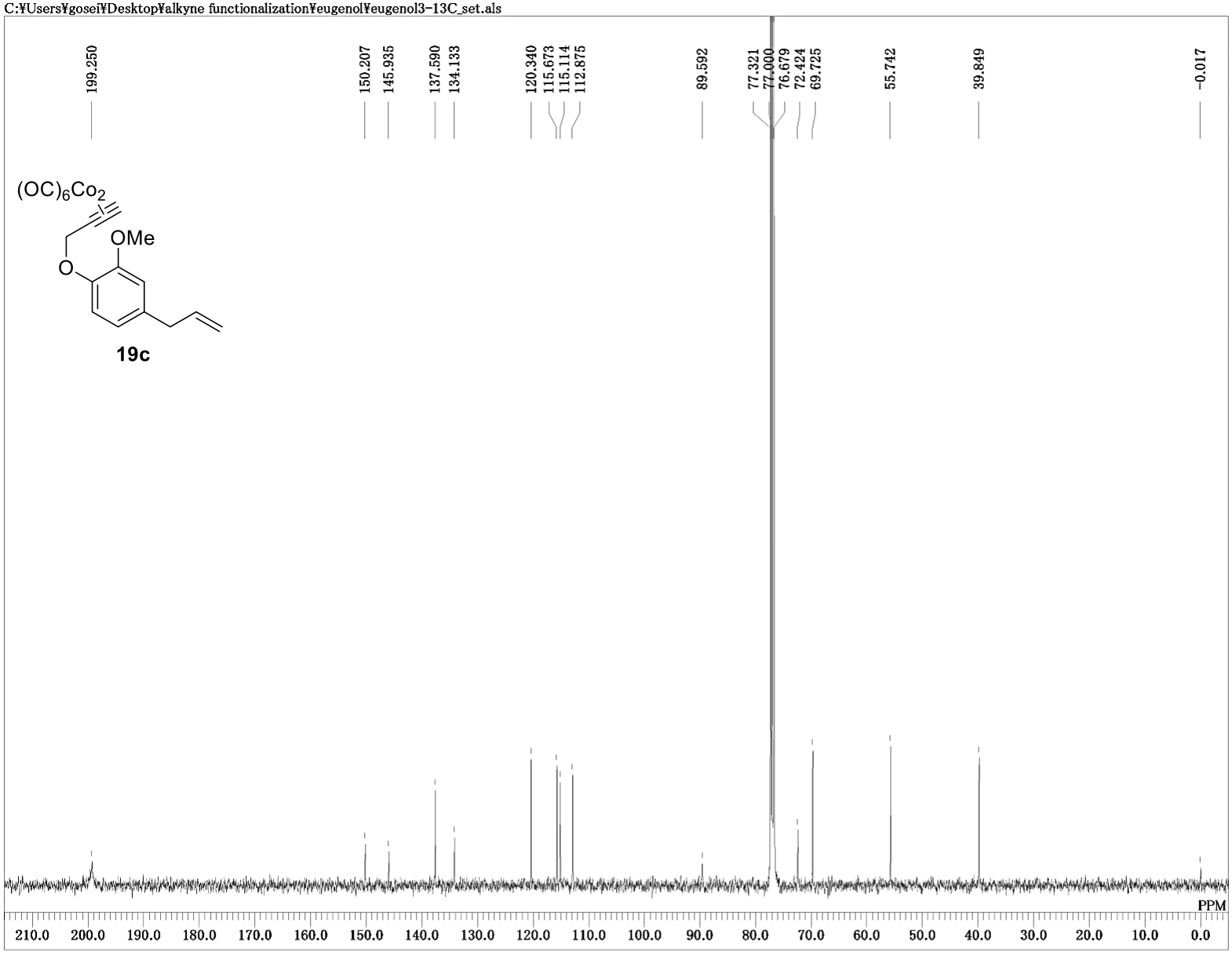
C:¥Users¥gosei¥Desktop¥alkyne functionalization¥eugenol¥eugenol3-1H_set.als



DFILE	eugenol3-1H_set.als
COMNT	auto
DATIM	Sat Apr 25 17:37:33 2015
OBNUC	1H
EXMOD	NON
OBFRQ	395.75 MHz
OBSET	124.00 KHz
OBFIN	10277.00 Hz
POINT	16384
FREQU	7912.96 Hz
SCANS	21
ACQTM	2.0705 sec
PD	4.9290 sec
PW1	5.50 usec
IRNUC	1H
CTEMP	27.4 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	23

auto

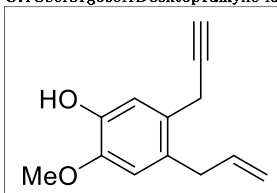
C:¥Users¥gosei¥Desktop¥alkyne functionalization¥eugenol¥eugenol3-13C_set.als



DFILE	eugenol3-13C_set.als
COMNT	auto
DATIM	Sat Apr 25 21:36:50 2015
OBNUC	13C
EXMOD	BCM
OBFRQ	99.45 MHz
OBSET	94.00 KHz
OBFIN	10309.00 Hz
POINT	32768
FREQU	26845.64 Hz
SCANS	1990
ACQTM	1.2206 sec
PD	1.7790 sec
PW1	6.50 usec
IRNUC	1H
CTEMP	27.7 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	2.52 Hz
RGAIN	23

auto

C:¥Users¥gosei¥Desktop¥alkyne functionalization¥eugenol¥dec-eugenol1-1H_set.als

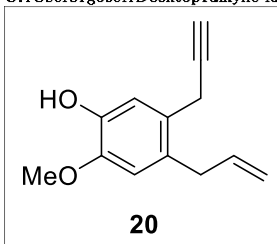


20

DFILE	dec-eugenol1-1H_set.als
COMNT	auto
DATIM	Wed Apr 29 15:41:20 2015
OBNUC	1H
EXMOD	NON
OBFRQ	395.75 MHz
OBSET	124.00 KHz
OBFIN	10277.00 Hz
POINT	16384
FREQU	7912.96 Hz
SCANS	16
ACQTM	2.0705 sec
PD	4.9290 sec
PW1	5.50 usec
IRNUC	1H
CTEMP	24.1 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	20

auto

C:¥Users¥gosei¥Desktop¥alkyne functionalization¥eugenol¥dec-eugenol1-13C_set.als

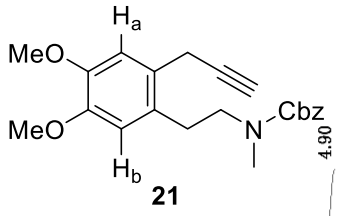


20

DFILE	dec-eugenol1-13C_set.als
COMNT	auto
DATIM	Wed Apr 29 17:26:18 2015
OBNUC	13C
EXMOD	BCM
OBFRQ	99.45 MHz
OBSET	94.00 KHz
OBFIN	10309.00 Hz
POINT	32768
FREQU	26845.64 Hz
SCANS	2082
ACQTM	1.2206 sec
PD	1.7790 sec
PW1	6.50 usec
IRNUC	1H
CTEMP	24.2 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.02 Hz
RGAIN	22

auto

C:¥Users¥gosei¥Desktop¥alkyne functionalization¥N-CBZ-methyl homoveratorilamine¥dec-N-Cbz,MeHVA1-1H_set.als



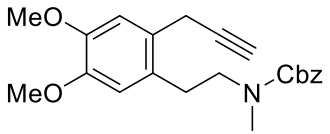
21

Coupling b/w H_a and H_b not observed.

DFILE	dec-N-Cbz,MeHVA1-1H_set
COMNT	auto
DATIM	Sun Jun 26 19:17:49 2016
OBNUC	1H
EXMOD	NON
OBFRQ	395.75 MHz
OBSET	124.00 KHz
OBFIN	10277.00 Hz
POINT	16384
FREQU	7912.96 Hz
SCANS	32
ACQTM	2.0705 sec
PD	4.9290 sec
PW1	5.50 usec
IRNUC	1H
CTEMP	99.5 c
SLVNT	DMSO
EXREF	2.49 ppm
BF	0.12 Hz
RGAIN	15

auto

C:¥Users¥gosei¥Desktop¥alkyne functionalization¥N-CBZ-methyl homoveratorilamine¥dec-N-Cbz,MeHVA1-13C_set.als

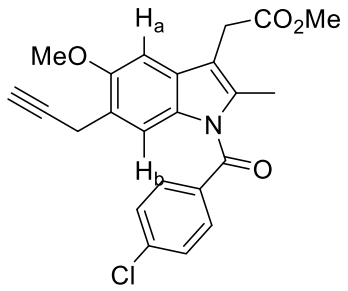


21

DFILE	dec-N-Cbz,MeHVA1-13C_s
COMNT	auto
DATIM	Sun Jun 26 19:09:55 2016
OBNUC	13C
EXMOD	BCM
OBFRQ	99.45 MHz
OBSET	94.00 KHz
OBFIN	10309.00 Hz
POINT	32768
FREQU	26845.64 Hz
SCANS	2502
ACQTM	1.2206 sec
PD	1.7790 sec
PW1	6.50 usec
IRNUC	1H
CTEMP	99.6 c
SLVNT	DMSO
EXREF	39.50 ppm
BF	0.42 Hz
RGAIN	22

auto

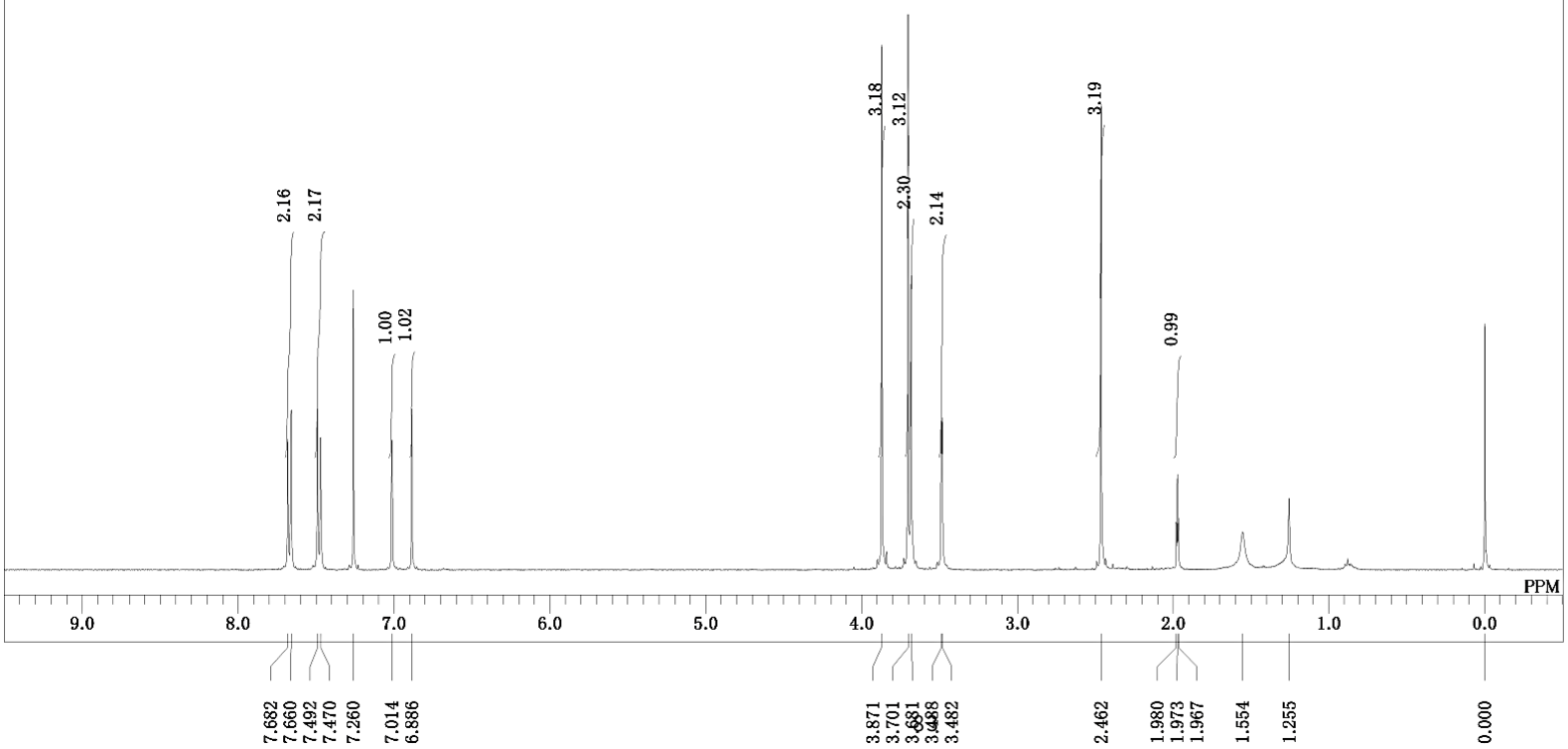
C:¥Users¥gosei¥Desktop¥alkyne functionalization¥indometacin¥dec-indometacin-1H_set.als



22

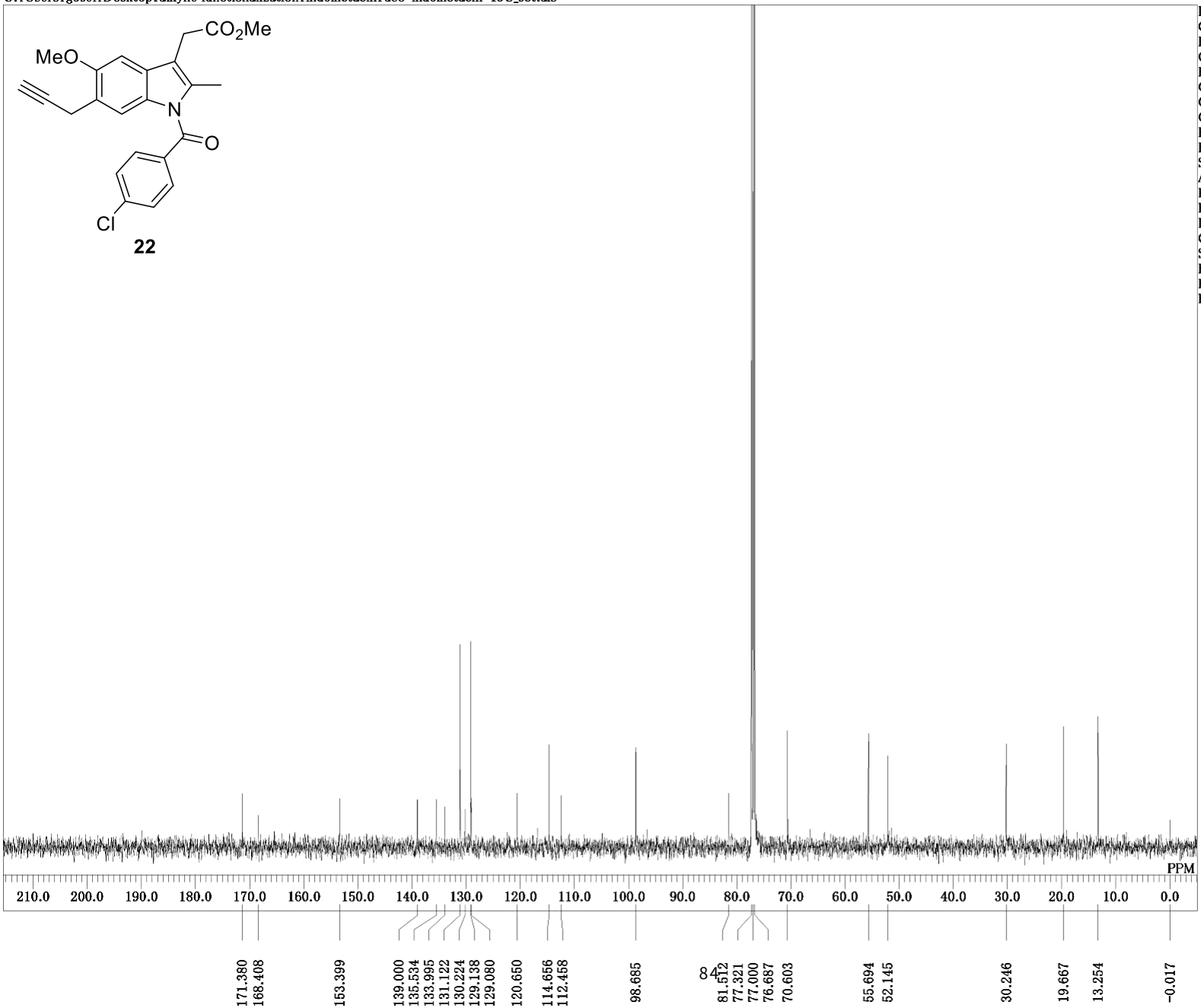
Coupling b/w H_a and H_b not observed.

DFILE	dec-indometacin-1H_set.als
COMNT	auto
DATIM	Mon Apr 04 23:17:53 2016
OBNUC	1H
EXMOD	NON
OBFRQ	395.75 MHz
OBSET	124.00 KHz
OBFIN	10277.00 Hz
POINT	16384
FREQU	7912.96 Hz
SCANS	32
ACQTM	2.0705 sec
PD	4.9290 sec
PW1	5.50 usec
IRNUC	1H
CTEMP	24.3 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	21



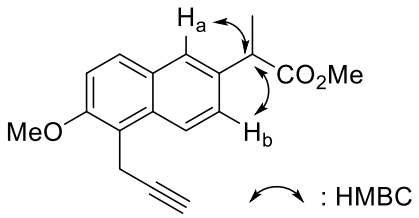
auto

C:¥Users¥gosei¥Desktop¥alkyne functionalization¥indometacin¥dec-indometacin-13C_set.als



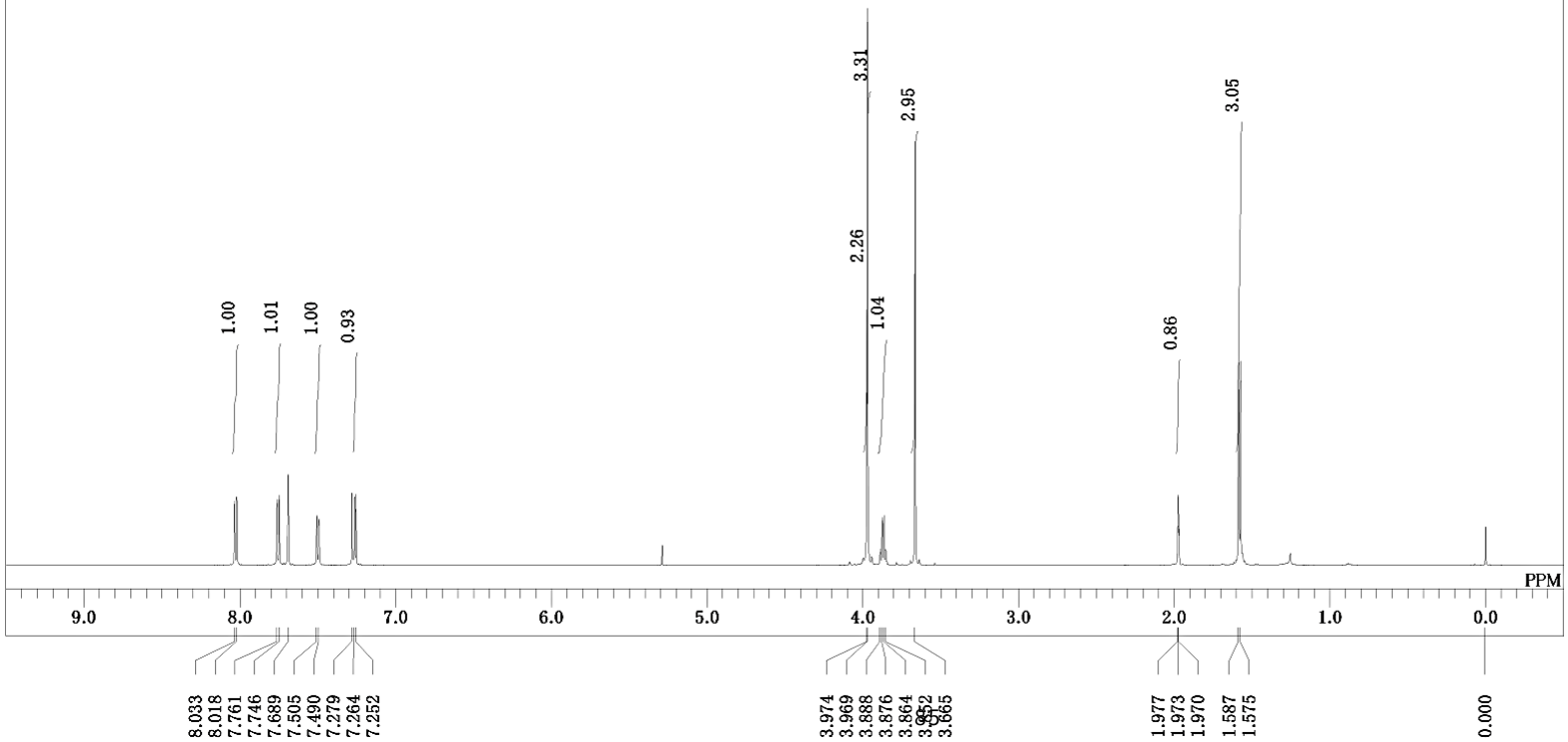
single_pulse

C:¥Users¥gosei¥Desktop¥alkyne functionalization¥naproxen¥dec-naproxen-1H_set.als



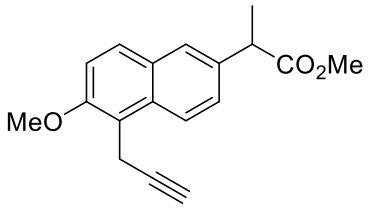
23

DFILE	dec-naproxen-1H_set.als
COMNT	single_pulse
DATIM	2016-01-12 10:10:07
OBNUC	1H
EXMOD	proton.jxp
OBFRQ	597.17 MHz
OBSET	4.42 KHz
OBFIN	8.78 Hz
POINT	13107
FREQU	8960.57 Hz
SCANS	32
ACQTM	1.4628 sec
PD	5.0000 sec
PW1	3.47 usec
IRNUC	1H
CTEMP	24.0 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.02 Hz
RGAIN	36



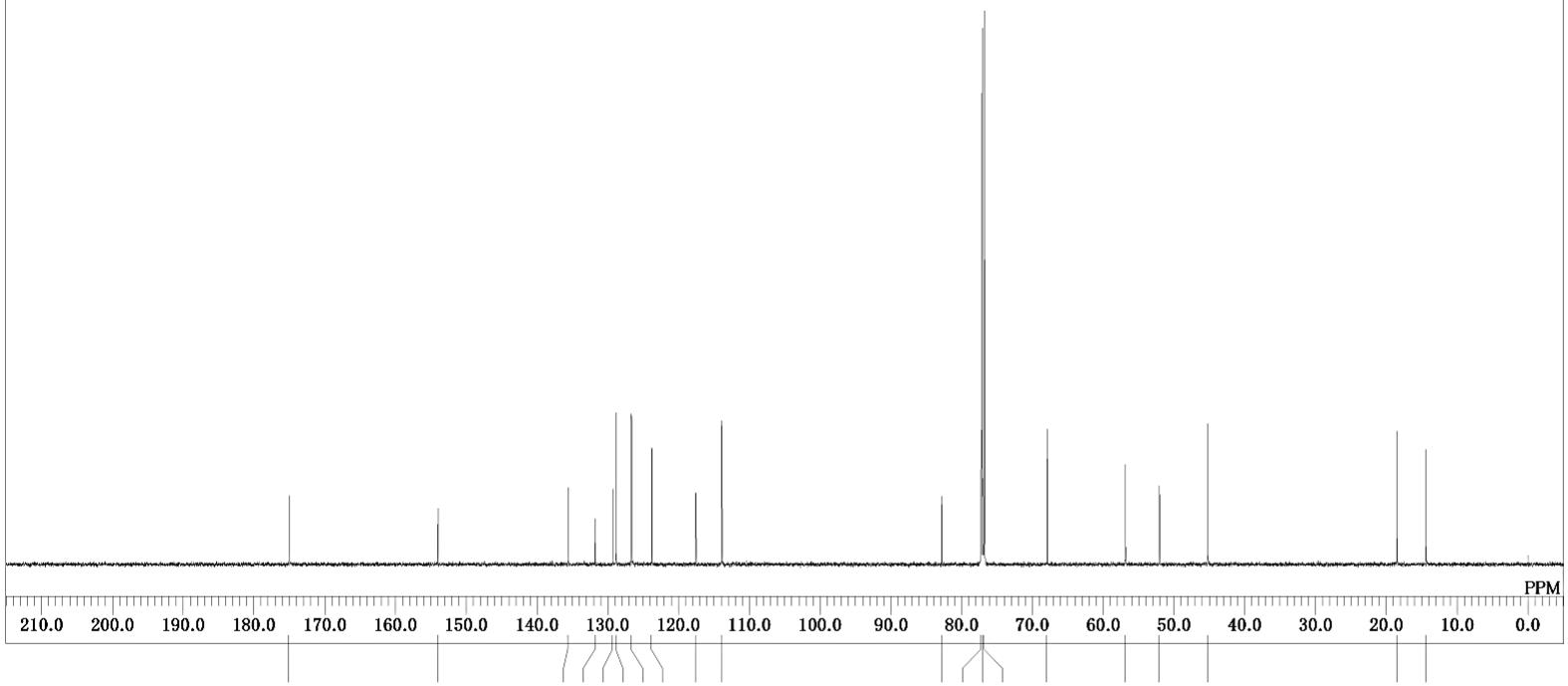
single pulse decoupled gated NOE

C:¥Users¥gosei¥Desktop¥alkyne functionalization¥naproxen¥dec-naproxen-13C_set.als



23

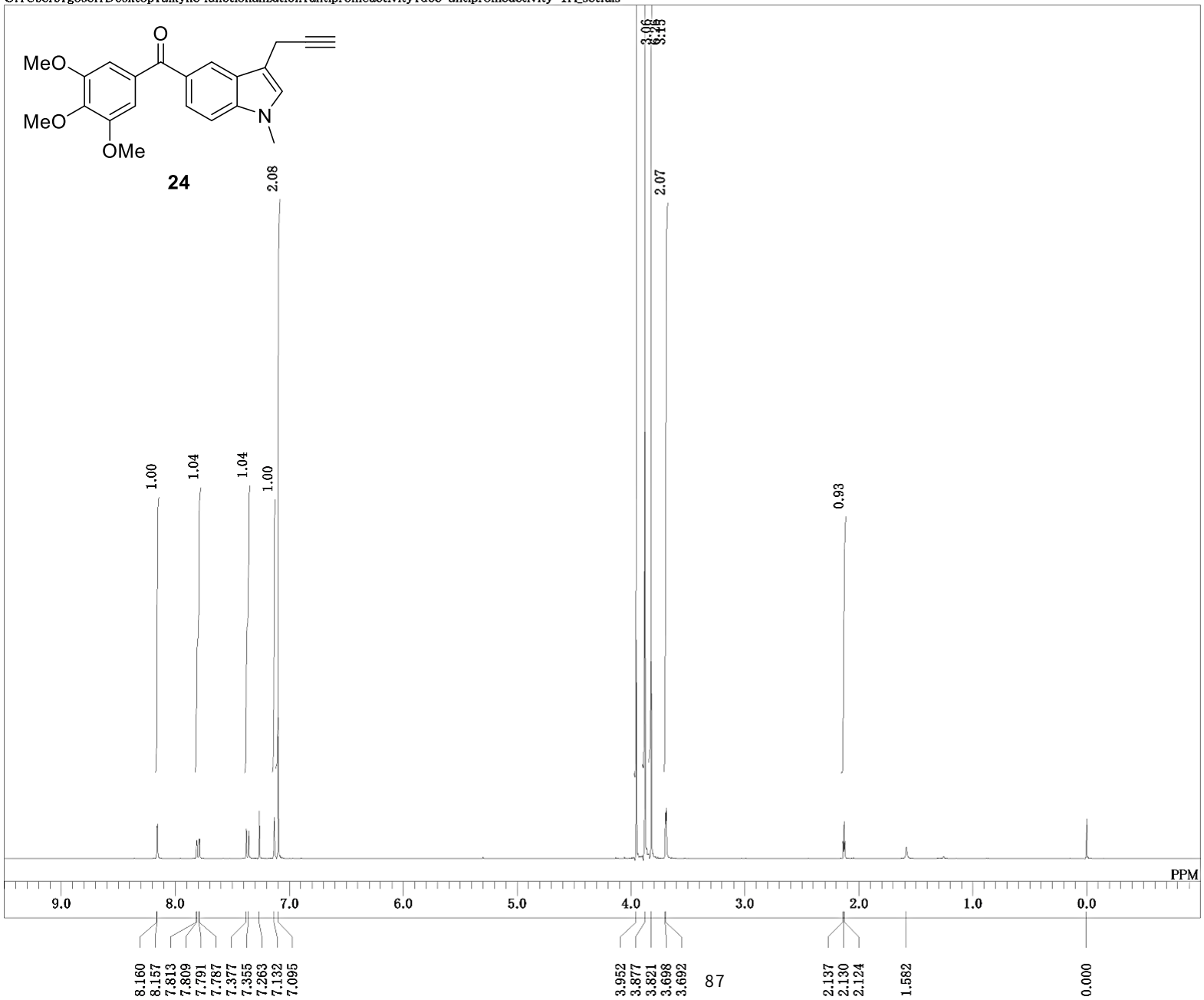
DFILE	dec-naproxen-13C_set.als
COMNT	single pulse decoupled gated
DATIM	2016-01-12 10:21:25
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	150.17 MHz
OBSET	3.87 KHz
OBFIN	9.09 Hz
POINT	26214
FREQU	37593.98 Hz
SCANS	1024
ACQTM	0.6973 sec
PD	2.0000 sec
PW1	3.97 usec
IRNUC	1H
CTEMP	24.2 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.02 Hz
RGAIN	50



175.028
153.978
135.593
131.754
129.280
128.822
126.654
123.798
117.543
113.885
82.816
77.210
77.000
76.790
67.936
56.848
52.044
45.225
18.502
14.367

auto

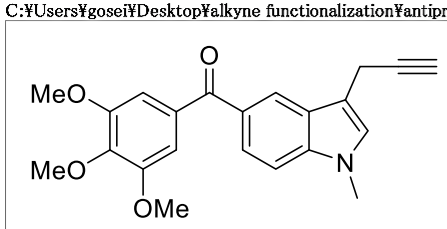
C:¥Users¥gosei¥Desktop¥alkyne functionalization¥antiprofileactivity¥dec-antiprofileactivity-1H_set.als



DFILE	dec-antiprofileactivity-1H_se
COMNT	auto
DATIM	Wed Mar 02 12:05:36 2016
OBNUC	1H
EXMOD	NON
OBFRQ	395.75 MHz
OBSET	124.00 KHz
OBFIN	10277.00 Hz
POINT	16384
FREQU	7912.96 Hz
SCANS	32
ACQTM	2.0705 sec
PD	4.9290 sec
PW1	5.50 usec
IRNUC	1H
CTEMP	23.1 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	16

auto

C:¥Users¥gosei¥Desktop¥alkyne functionalization¥antiprofileactivity¥dec-antiprofileactivity-13C_set.als

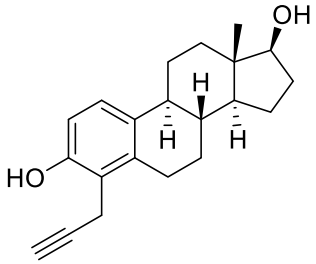


24

DFILE	dec-antiprofileactivity-13C_s
COMNT	auto
DATIM	Wed Mar 02 12:36:04 2016
OBNUC	13C
EXMOD	BCM
OBFRQ	99.45 MHz
OBSET	94.00 KHz
OBFIN	10309.00 Hz
POINT	32768
FREQU	26845.64 Hz
SCANS	594
ACQTM	1.2206 sec
PD	1.7790 sec
PW1	6.50 usec
IRNUC	1H
CTEMP	24.3 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.72 Hz
RGAIN	22

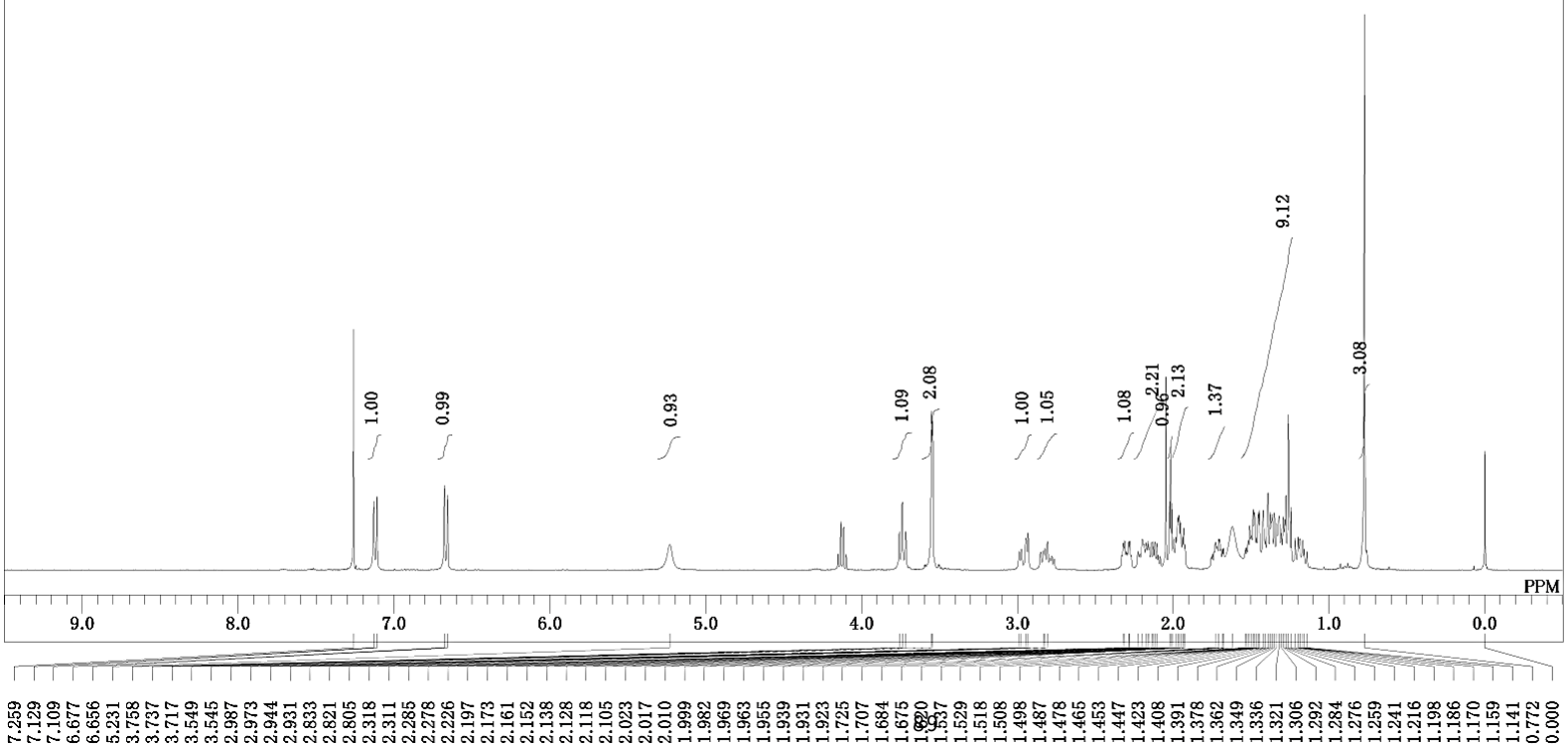
auto

C:¥Users¥gosei¥Desktop¥alkyne functionalization¥estradiol¥dec-estradiol2-1H_set.als



25

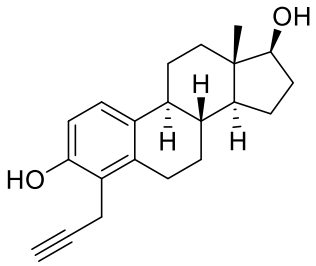
DFILE	dec-estradiol2-1H_set.als
COMNT	auto
DATIM	Fri Jul 15 18:03:07 2016
OBNUC	1H
EXMOD	NON
OBFRQ	399.65 MHz
OBSET	124.00 KHz
OBFIN	10500.00 Hz
POINT	16384
FREQU	7992.01 Hz
SCANS	32
ACQTM	2.0500 sec
PD	4.9500 sec
PW1	6.20 usec
IRNUC	1H
CTEMP	24.9 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	15



7.259 7.129 7.109 6.677 6.656 5.231 3.758 3.737 3.717 3.549 3.545 2.987 2.973 2.944 2.931 2.833 2.821 2.805 2.318 2.311 2.285 2.278 2.226 2.197 2.173 2.161 2.152 2.138 2.128 2.118 2.105 2.023 2.017 2.010 1.999 1.982 1.969 1.963 1.955 1.939 1.931 1.923 1.725 1.707 1.684 1.675 1.620 1.537 1.529 1.518 1.508 1.498 1.487 1.478 1.465 1.453 1.447 1.423 1.408 1.391 1.378 1.362 1.349 1.336 1.321 1.306 1.292 1.284 1.276 1.259 1.241 1.216 1.198 1.186 1.170 1.159 1.141 0.772 0.000

auto

C:¥Users¥gosei¥Desktop¥alkyne functionalization¥estradiol¥dec-estradiol2-13_set.als

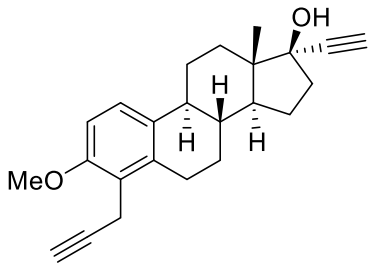


25

DFILE	dec-estradiol2-13_set.als
COMNT	auto
DATIM	Fri Jul 15 18:39:40 2016
OBNUC	13C
EXMOD	BCM
OBFRQ	100.40 MHz
OBSET	125.00 KHz
OBFIN	10500.00 Hz
POINT	32768
FREQU	27118.64 Hz
SCANS	707
ACQTM	1.2083 sec
PD	1.7920 sec
PW1	6.20 usec
IRNUC	1H
CTEMP	25.8 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.82 Hz
RGAIN	22

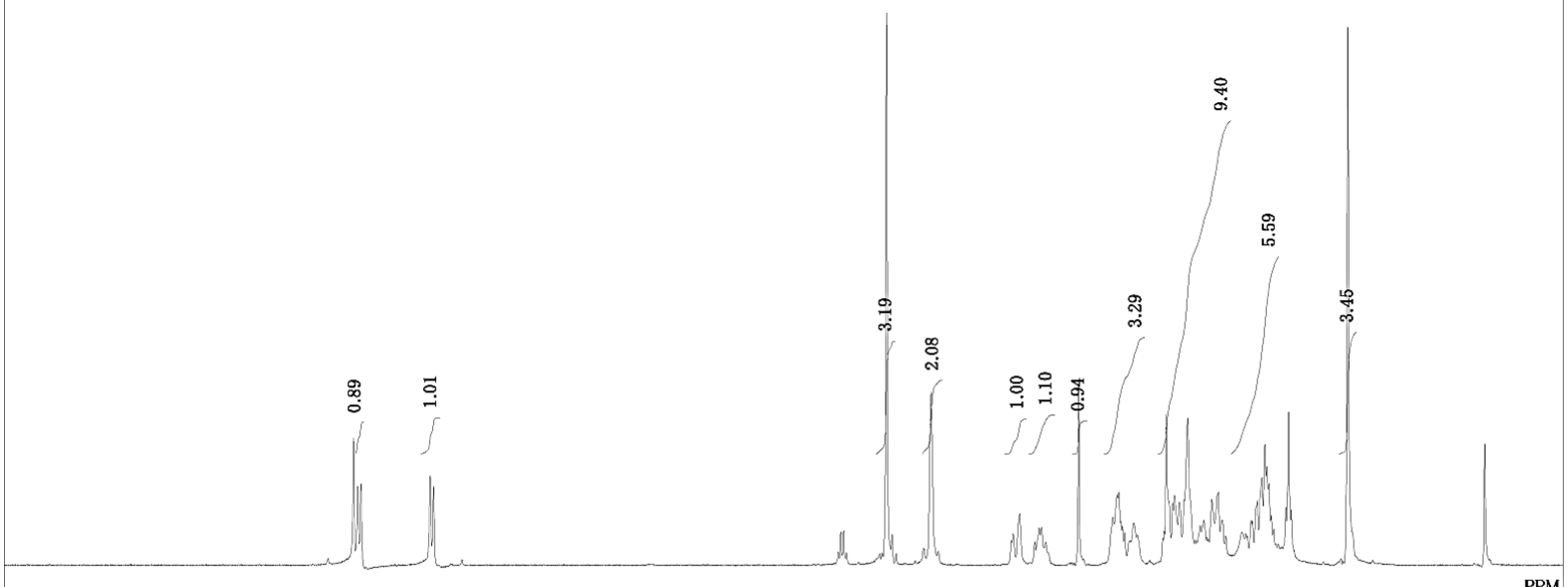
auto

C:¥Users¥gosei¥Desktop¥alkyne functionalization¥mestranol¥dec-mestranol1-1H_set.als



26

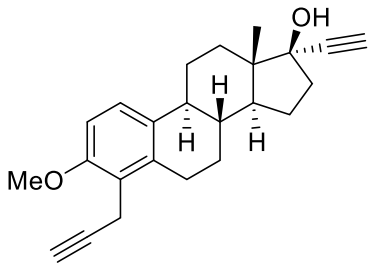
DFILE	dec-mestranol1-1H_set.als
COMNT	auto
DATIM	Fri May 15 11:40:46 2015
OBNUC	1H
EXMOD	NON
OBFRQ	395.75 MHz
OBSET	124.00 KHz
OBFIN	10277.00 Hz
POINT	16384
FREQU	7912.96 Hz
SCANS	8
ACQTM	2.0705 sec
PD	4.9290 sec
PW1	5.50 usec
IRNUC	1H
CTEMP	25.8 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	16



7.258 7.232 7.211 6.768 6.746 4.131 4.114 3.838 3.803 3.777 3.601 3.554 3.026 2.884 2.845 2.606 2.348 2.312 2.252 2.043 2.002 1.991 1.961 1.907 1.804 1.752 1.710 1.688 1.662 1.558 1.501 1.459 1.430 1.410 1.398 1.276 1.258 1.241 0.878 0.000

auto

C:¥Users¥gosei¥Desktop¥alkyne functionalization¥mestranol¥dec-mestranol1-13C_set.als

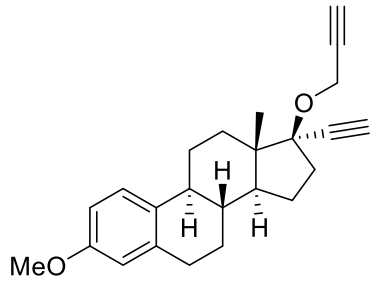


26

DFILE	dec-mestranol1-13C_set.als
COMNT	auto
DATIM	Fri May 15 16:40:46 2015
OBNUC	13C
EXMOD	BCM
OBFRQ	99.45 MHz
OBSET	94.00 KHz
OBFIN	10309.00 Hz
POINT	32768
FREQU	26845.64 Hz
SCANS	660
ACQTM	1.2206 sec
PD	1.7790 sec
PW1	6.50 usec
IRNUC	1H
CTEMP	25.6 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.02 Hz
RGAIN	22

auto

C:¥Users¥gosei¥Desktop¥alkyne functionalization¥mestranol¥dec-mestranol2-1H_set.als

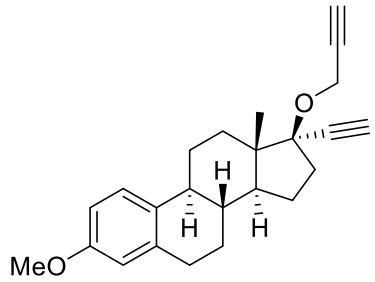


27

DFILE	dec-mestranol2-1H_set.als
COMNT	auto
DATIM	Thu Jan 21 18:55:31 2016
OBNUC	1H
EXMOD	NON
OBFRQ	399.65 MHz
OBSET	124.00 KHz
OBFIN	10500.00 Hz
POINT	16384
FREQU	7992.01 Hz
SCANS	24
ACQTM	2.0500 sec
PD	4.9500 sec
PW1	6.20 usec
IRNUC	1H
CTEMP	21.7 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	13

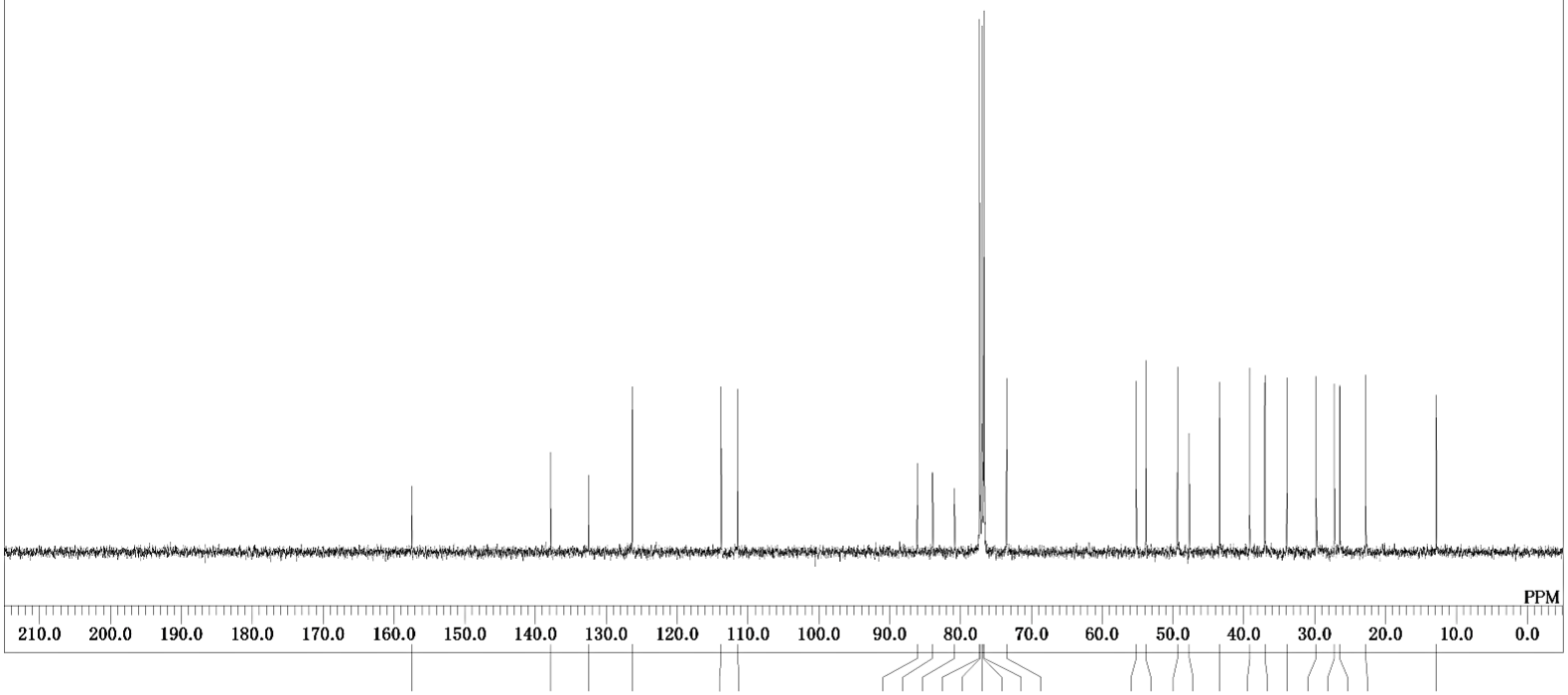
auto

C:¥Users¥gosei¥Desktop¥alkyne functionalization¥mestranol¥dec-mestranol2-13C_set.als



27

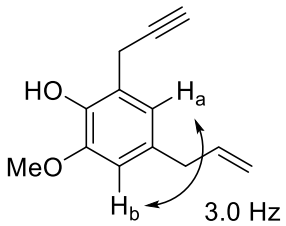
DFILE	dec-mestranol2-13C_set.als
COMNT	auto
DATIM	Thu Jan 21 18:51:27 2016
OBNUC	13C
EXMOD	BCM
OBFRQ	100.40 MHz
OBSET	125.00 KHz
OBFIN	10500.00 Hz
POINT	32768
FREQU	27118.64 Hz
SCANS	801
ACQTM	1.2083 sec
PD	1.7920 sec
PW1	6.20 usec
IRNUC	1H
CTEMP	22.8 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.12 Hz
RGAIN	22



157.442
137.889
132.480
126.330
113.767
111.479
86.089
83.932
80.880
77.313
77.198
77.000
76.778
76.679
73.509
55.175
53.850
49.371
47.683
43.444
39.154
37.063
33.918
29.794
27.209
26.468
22.788
12.818

auto

C:¥Users¥gosei¥個人ファイル_NMR¥岡村¥alkyne functionalization¥eugenol¥脱保護¥160714_TO-eugenol-1H_再処理.als

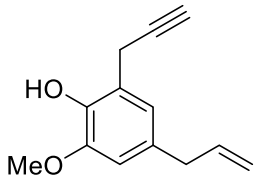


28

DFILE	160714_TO-eugenol-1H_再処
COMNT	auto
DATIM	Thu Jul 14 09:04:12 2016
OBNUC	1H
EXMOD	NON
OBFRQ	399.65 MHz
OBSET	124.00 KHz
OBFIN	10500.00 Hz
POINT	16384
FREQU	7992.01 Hz
SCANS	64
ACQTM	2.0500 sec
PD	4.9500 sec
PW1	6.20 usec
IRNUC	1H
CTEMP	24.8 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	-0.38 Hz
RGAIN	19

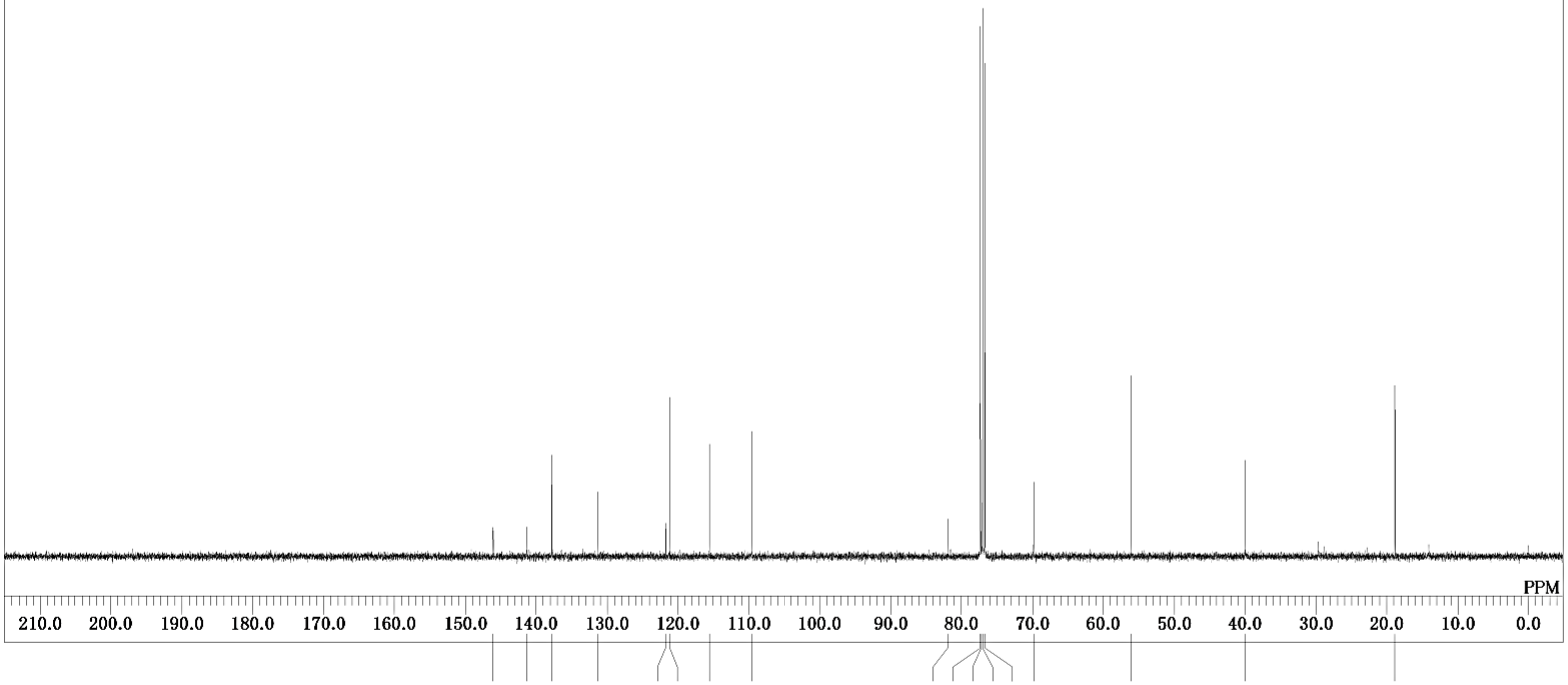
auto

C:¥Users¥gosei¥Desktop¥alkyne functionalization¥eugenol¥dec-eugenol2-13C_set.als



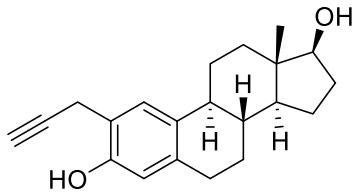
28

DFILE	dec-eugenol2-13C_set.als
COMNT	auto
DATIM	Thu Jul 14 03:17:36 2016
OBNUC	13C
EXMOD	BCM
OBFRQ	100.40 MHz
OBSET	125.00 KHz
OBFIN	10500.00 Hz
POINT	32768
FREQU	27118.64 Hz
SCANS	2944
ACQTM	1.2083 sec
PD	1.7920 sec
PW1	6.20 usec
IRNUC	1H
CTEMP	26.0 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.12 Hz
RGAIN	25



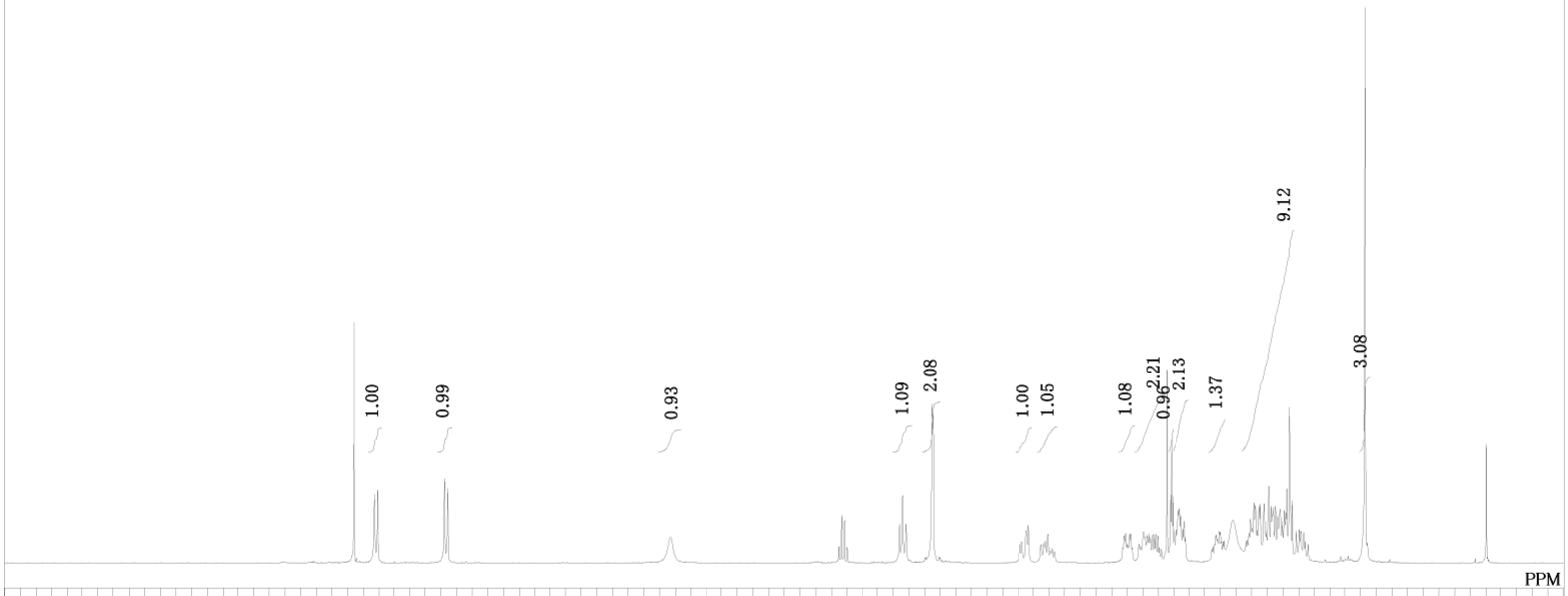
auto

C:¥Users¥gosei¥Desktop¥alkyne functionalization¥estradiol¥dec-estradiol2-1H_set.als



29

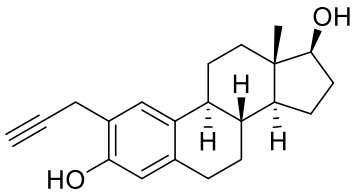
DFILE	dec-estradiol2-1H_set.als
COMNT	auto
DATIM	Fri Jul 15 18:03:07 2016
OBNUC	1H
EXMOD	NON
OBFRQ	399.65 MHz
OBSET	124.00 KHz
OBFIN	10500.00 Hz
POINT	16384
FREQU	7992.01 Hz
SCANS	32
ACQTM	2.0500 sec
PD	4.9500 sec
PW1	6.20 usec
IRNUC	1H
CTEMP	24.9 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.12 Hz
RGAIN	15



7.259 7.129 7.109 6.677 6.656 5.231 3.758 3.737 3.717 3.549 3.545 2.987 2.973 2.944 2.931 2.833 2.821 2.805 2.318 2.311 2.285 2.278 2.226 2.197 2.173 2.161 2.152 2.138 2.128 2.118 2.105 2.023 2.017 2.010 1.999 1.982 1.969 1.963 1.955 1.939 1.931 1.923 1.725 1.707 1.684 1.675 1.620 1.537 1.529 1.518 1.508 1.498 1.487 1.478 1.465 1.453 1.447 1.423 1.408 1.391 1.378 1.362 1.349 1.336 1.321 1.306 1.292 1.284 1.276 1.259 1.241 1.216 1.198 1.186 1.170 1.159 1.141 0.772 0.000

auto

C:¥Users¥gosei¥Desktop¥alkyne functionalization¥estradiol¥dec-estradiol2-13_set.als

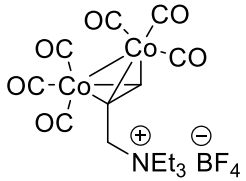


29

DFILE	dec-estradiol2-13_set.als
COMNT	auto
DATIM	Fri Jul 15 18:39:40 2016
OBNUC	13C
EXMOD	BCM
OBFRQ	100.40 MHz
OBSET	125.00 KHz
OBFIN	10500.00 Hz
POINT	32768
FREQU	27118.64 Hz
SCANS	707
ACQTM	1.2083 sec
PD	1.7920 sec
PW1	6.20 usec
IRNUC	1H
CTEMP	25.8 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	0.82 Hz
RGAIN	22

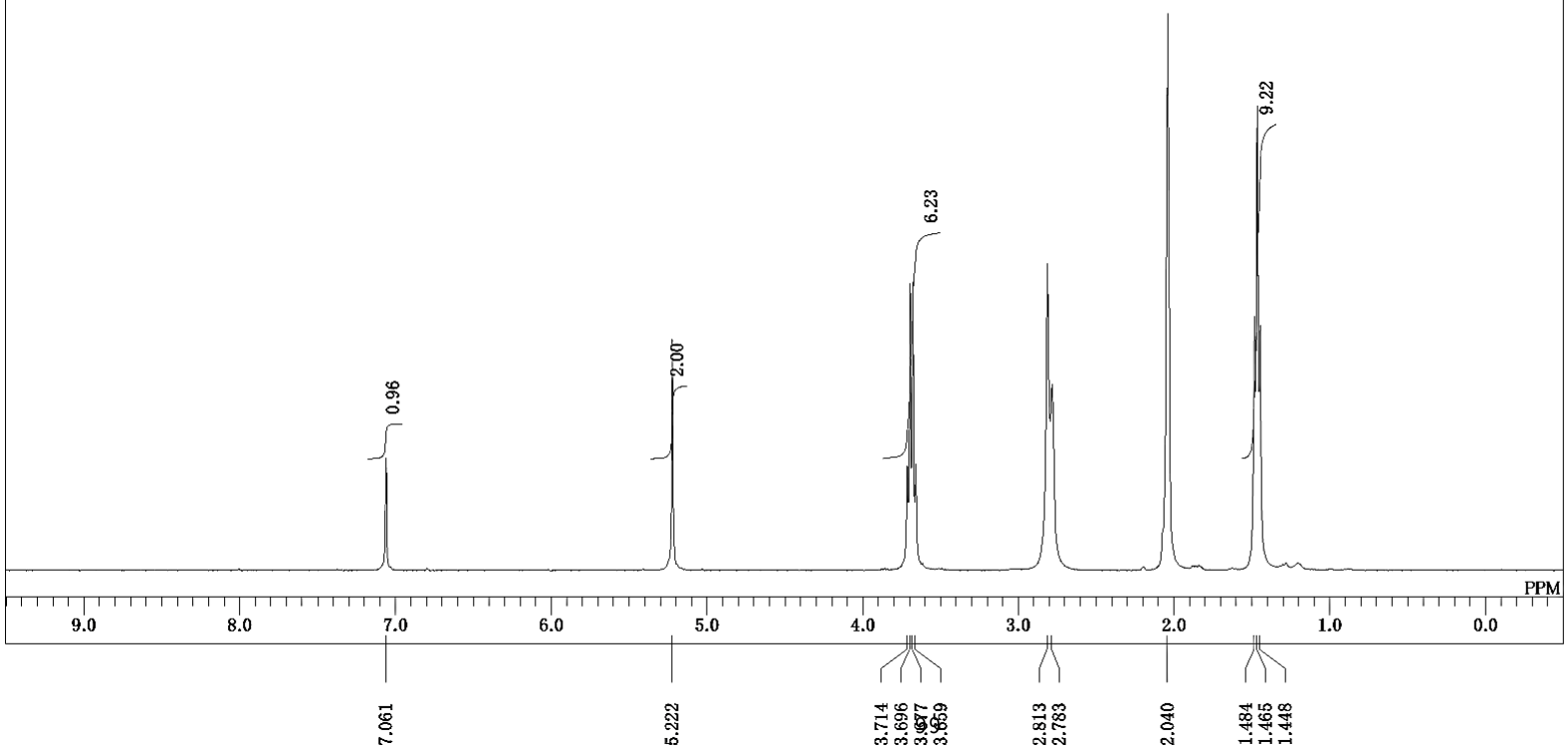
auto

C:¥Users¥gosei¥Desktop¥alkyne functionalization¥Et3N complex¥Et3Ncomplex−1H_set.als

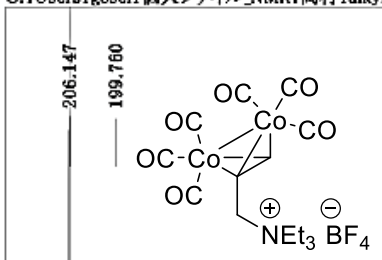


S2

DFILE	Et3Ncomplex−1H_set.als
COMNT	auto
DATIM	Sat Nov 19 21:23:46 2016
OBNUC	1H
EXMOD	NON
OBFRQ	395.75 MHz
OBSET	124.00 KHz
OBFIN	10277.00 Hz
POINT	16384
FREQU	7912.96 Hz
SCANS	32
ACQTM	2.0705 sec
PD	4.9290 sec
PW1	5.50 usec
IRNUC	1H
CTEMP	23.0 c
SLVNT	ACETN
EXREF	2.04 ppm
BF	0.42 Hz
RGAIN	20



C:¥Users¥gosci¥個人ファイル_NMR¥岡村¥alkyne functionalization¥Et3N complex¥161119_Et3Ncomplex-13C_set.als



S2

206.147 199.760 77.197 75.732 60.630 53.577 30.384 30.195 29.998 29.800 29.611 29.413 29.224 8.147

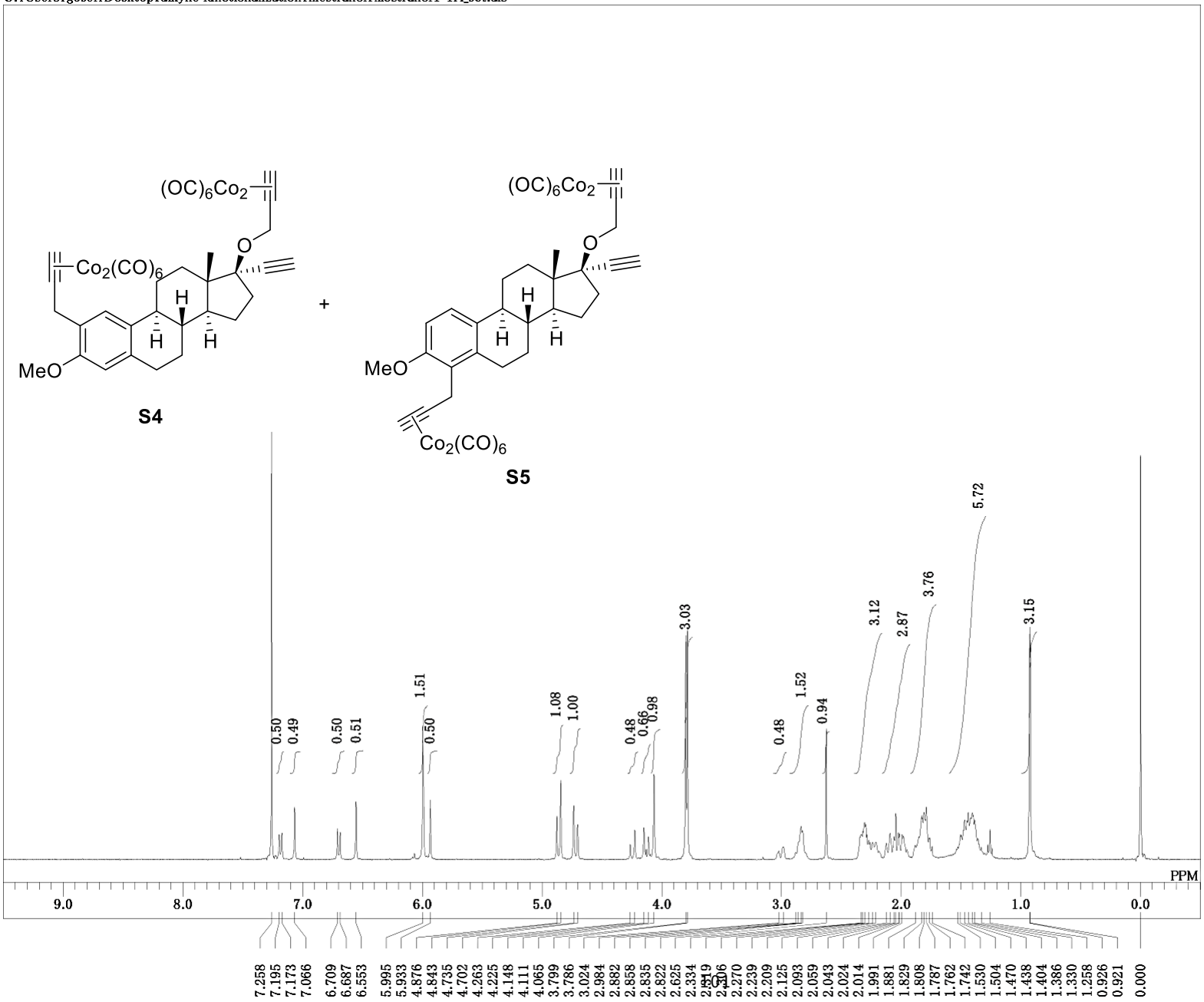
DFILE	161119_Et3Ncomplex-13C_sc
COMNT	auto
DATIM	Sun Nov 20 09:58:49 2016
OBNUC	13C
EXMOD	BCM
OBFRQ	99.45 MHz
OBSET	94.00 KHz
OBFIN	10309.00 Hz
POINT	32768
FREQU	26845.64 Hz
SCANS	14608
ACQTM	1.2206 sec
PD	1.7790 sec
PW1	6.50 usec
IRNUC	1H
CTEMP	24.2 c
SLVNT	ACETN
EXREF	29.80 ppm
BF	1.22 Hz
RGAIN	21

PPM

210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0

auto

C:¥Users¥gosei¥Desktop¥alkyne functionalization¥mestranol¥mestranol4-1H_set.als

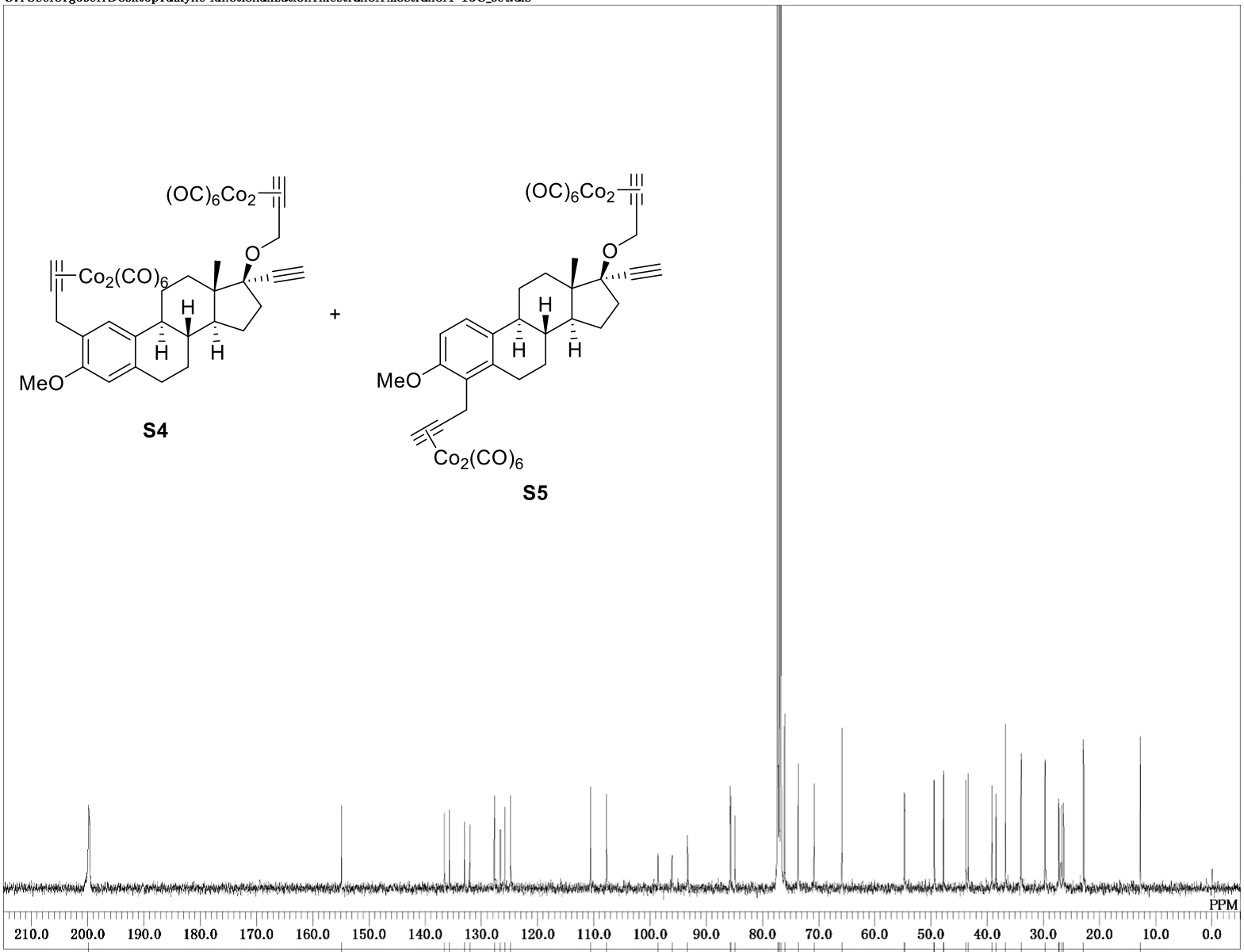


DFILE	mestranol4-1H_set.als
COMNT	auto
DATIM	Wed May 20 17:53:02 2015
OBNUC	1H
EXMOD	NON
OBFRQ	395.75 MHz
OBSET	124.00 KHz
OBFIN	10277.00 Hz
POINT	16384
FREQU	7912.96 Hz
SCANS	16
ACQTM	2.0705 sec
PD	4.9290 sec
PW1	5.50 usec
IRNUC	1H
CTEMP	25.3 c
SLVNT	CDCL3
EXREF	0.00 ppm
BF	0.42 Hz
RGAIN	20

7.258 7.195 7.173 7.066 6.709 6.687 6.553 5.995 5.933 4.876 4.843 4.735 4.702 4.263 4.225 4.148 4.111 4.065 3.799 3.786 3.024 2.984 2.882 2.858 2.835 2.822 2.625 2.334 2.319 2.306 2.270 2.239 2.209 2.125 2.093 2.059 2.043 2.024 2.014 1.991 1.881 1.829 1.808 1.787 1.762 1.742 1.530 1.504 1.470 1.438 1.404 1.386 1.330 1.258 0.926 0.921 0.000

auto

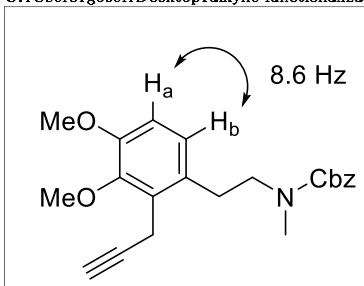
C:¥Users¥gosei¥Desktop¥alkyne functionalization¥mestranol¥mestranol4−13C_set.als



DFILE	mestranol4−13C_set.als
COMNT	auto
DATIM	Sat Oct 29 08:53:04 2016
OBNUC	13C
EXMOD	BCM
OBFRQ	99.45 MHz
OBSET	94.00 KHz
OBFIN	10309.00 Hz
POINT	32768
FREQU	26845.64 Hz
SCANS	10645
ACQTM	1.2206 sec
PD	1.7790 sec
PW1	6.50 usec
IRNUC	1H
CTEMP	23.5 c
SLVNT	CDCL3
EXREF	77.00 ppm
BF	1.02 Hz
RGAIN	23

auto

C:¥Users¥gosei¥Desktop¥alkyne functionalization¥N-CBZ-methyl homoveratrylamine¥dec-N-Cbz,MeHVA2-1H_set.als

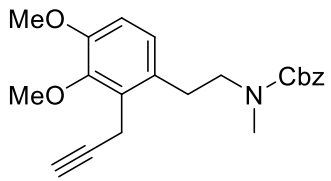


S6

DFILE	dec-N-Cbz,MeHVA2-1H_set
COMNT	auto
DATIM	Sun Jul 10 21:09:17 2016
OBNUC	1H
EXMOD	NON
OBFRQ	395.75 MHz
OBSET	124.00 KHz
OBFIN	10277.00 Hz
POINT	16384
FREQU	7912.96 Hz
SCANS	32
ACQTM	2.0705 sec
PD	4.9290 sec
PW1	5.50 usec
IRNUC	1H
CTEMP	99.6 c
SLVNT	DMSO
EXREF	2.49 ppm
BF	0.12 Hz
RGAIN	21

auto

C:¥Users¥gosei¥Desktop¥alkyne functionalization¥N-CBZ-methyl homoveratorilamine¥dec-N-Cbz,MeHVA2-13C_set.als



S6

DFILE	dec-N-Cbz,MeHVA2-13C_s
COMNT	auto
DATIM	Mon Jul 11 08:57:22 2016
OBNUC	13C
EXMOD	BCM
OBFRQ	99.45 MHz
OBSET	94.00 KHz
OBFIN	10309.00 Hz
POINT	32768
FREQU	26845.64 Hz
SCANS	14142
ACQTM	1.2206 sec
PD	1.7790 sec
PW1	6.50 usec
IRNUC	1H
CTEMP	99.6 c
SLVNT	DMSO
EXREF	39.50 ppm
BF	1.02 Hz
RGAIN	23