Supporting Information

Indium- and Zinc-catalyzed enantioselective amide propargylation of aldehydes with stannylated allenyl amides

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The following data are included in this material:

General methods:

All solvents and reagents were of reagent grade quality, and used without further purification unless otherwise stated. Chloroform, acetonitrile, toluene, and dichloromethane were dried over MS 4 Å or MS 3 Å prior to use, respectively. Tetrahydrofuran was dried over Na wire under a nitrogen atmosphere. The ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra operating at the frequencies of 300 and 75 MHz, respectively, on a JEOL JNM-AL300 spectrometer were recorded in chloroform–*d* ($CDCl_3$) unless otherwise noted. Chemical shifts are reported in parts per million (ppm) relative to TMS and the solvent used as internal standards, and the coupling constants are reported in hertz (Hz). Reactions were monitored by thin layer chromatography (TLC) using Merck TLC silica gel $60F_{254}$, visualized by irradiation with UV light and/or by treatment with phosphomolybdic acid or *p*-anisaldehyde stain followed by heating. Column chromatography was performed using silica gel 60N (spherical neutral) from Kanto Chemical Co. and eluting with the indicated solvent system. Fourier transform infrared (FTIR) spectra were recorded on a JASCO FT/IR-550 spectrometer. Elemental analyses were performed by JSL Model JM 10 instruments. Alkynylamide **3a** was prepared according to the literature procedure.[1]

Screening of metal additives on the reaction of benzaldehyde with 1a:

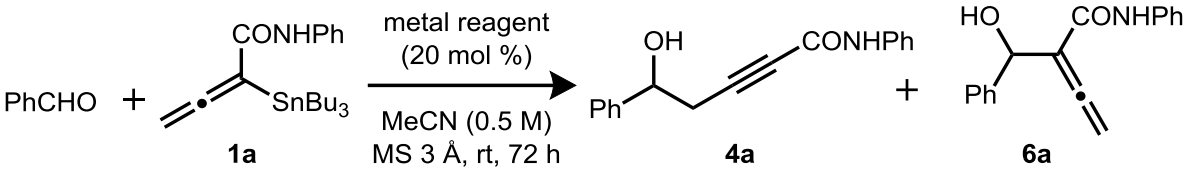


Table S1. Screening of metal additives on the reaction of benzaldehyde with **1a**[a]

Entry	Metal reagent	**4a** (%)	**6a** (%)
1	$Sc(OTf)_3$	0	37
2	$Yb(OTf)_3$	0	32
3	$Zn(OTf)_2$	49	13
4	$In(OTf)_3$	61	13
5	$ZnCl_2$	52	18
6	$InCl_3$	41	25

[a] All reactions were carried out with benzaldehyde (1.0 equiv.) and **1a** (1.2 equiv.) in dry MeCN in the presence of metal reagent (20 mol %) at rt.

^{1}H NMR spectra of the sample prepared from 1a and $ZnCl_2$:

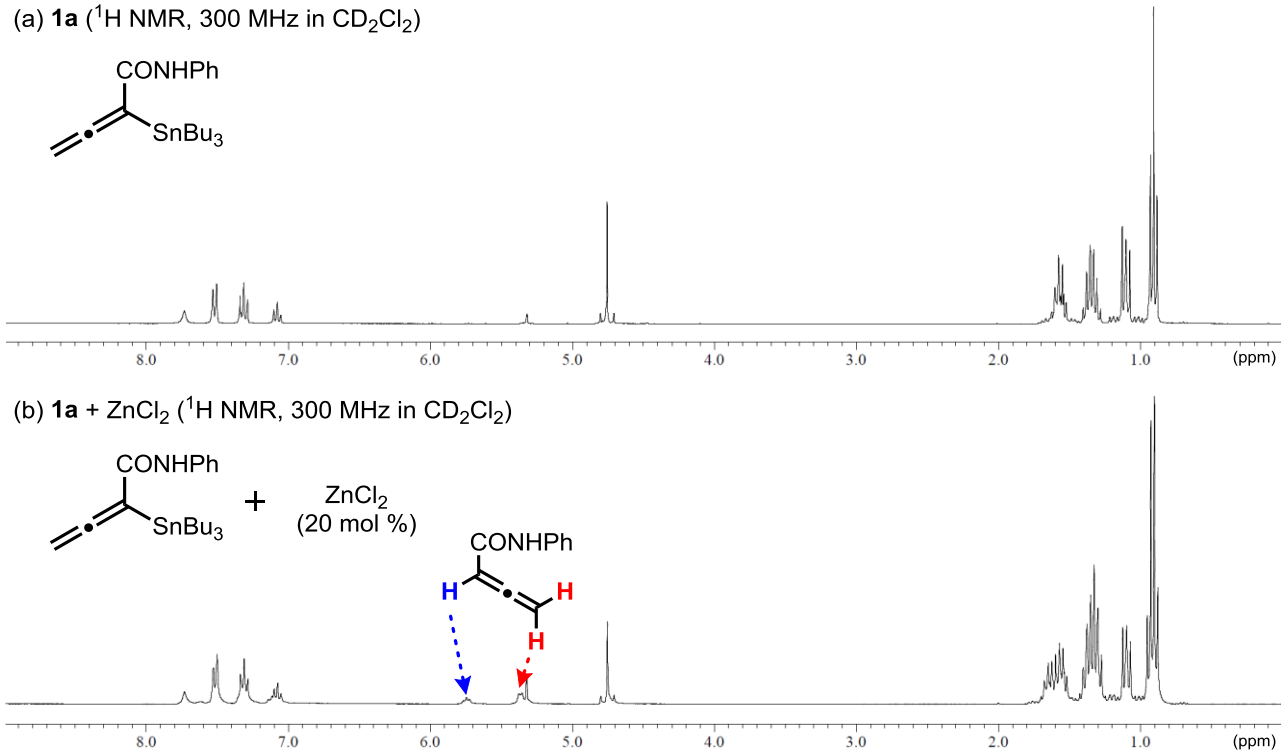


Figure S1. ^{1}H NMR spectra (300 MHz, CD_2Cl_2) of (a) **1a**, (b) **1a** with $ZnCl_2$ (1/0.2, stirred for 30 min at rt).

Transition state for the amide propargylation:

On the basis of our previous works on the amide allylation of carbonyl compounds,[2] transition state for the amide propargylation was hypothesized as Figure S2. Indium(III) ion would coordinates to two oxygen atoms of the BINOL ligand, one oxygen atom of the aldehyde, and one oxygen atom of the propargylating reagent to form a highly ordered structure with a well-defined chiral environment supported by C=O···H−N−C=O hydrogen-bond interactions between the catalyst-bound substrate and the reagent. The nucleophilic attack of another reagent molecule at the *Re*-face should be prevented owing to the steric repulsion from the naphthyl group of the chiral ligand and the *Si*-face attack is preferred.

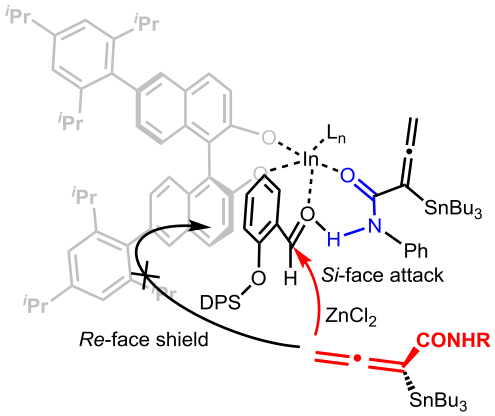


Figure S2. Possible transition state for the reaction of aryl aldehydes with **1**. ($ZnCl_2$ is involved in the transition state but its role is not understood.)

Experimental procedures and characterization data:

Synthesis and characterization of 1a

To a solution of **3a** (500 mg, 3.14 mmol) in THF (16 mL) was added LDA (2.0 M solution in THF, 4.7 mL, 9.4 mmmol, 3.0 equiv.) under a nitrogen atmosphere at -78 ºC. After stirring at the same temperature for 30 min, tributyltin chloride (2.5 mL, 9.4 mmol, 3.0 equiv.) was added to the solution. The reaction mixture was stirred at -78°C for an additional 1 hour. The reaction was quenched by addition of saturated aqueous $NaHCO_3$ (5 mL), and the resulting solution was extracted with EtOAc (30×3 mL). The combined organic extracts were washed with brine (10 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo to provide a crude material. This material was purified by column chromatography (10% w/w K_2CO_3–silica gel, hexane/EtOAc = 25/1) to give **1a** (633 mg, 1.41 mmol, 45%) as a white solid. R_f = 0.82 (silica gel, hexane/EtOAc = 2/1); m.p. 45-46 °C; IR (KBr) 3279 (N–H), 1917 (C=C=C), 1627 (C=O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.68 (brs, 1H, N*H*), 7.51 (dd, *J* = 1.2, 8.7 Hz, 2H, Ar*H*), 7.31 (m, 2H, Ar*H*), 7.07 (m, 1H, Ar*H*), 4.74 (t, *J* = 14.1 Hz, 2H, CH_2), 1.68–0.98 (m, 18H, CH_2), 0.89 (t, *J* = 7.8 Hz, 9H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 208.0 (*C*), 165.1 (*C*), 138.3 (*C*), 128.9 (*C*H), 123.8 (*C*H), 119.2 (*C*H), 96.2 (*C*), 70.3 (*C*H_2), 28.9 (*C*H_2), 27.2 (*C*H_2), 13.7 (*C*H_3), 11.1 (*C*H_2). Anal. Calcd for $C_{22}H_{35}NOSn$: C, 58.95; H, 7.87; N, 3.12. Found: C, 58.71; H, 7.65; N, 3.27.

General procedure for the synthesis of 1b–d

All the experiments for the synthesis of **1b–d** were carried out as described in the following typical procedure. The synthesis of **1b** from tetrolic acid (2-butynoic acid) was exemplified as follows.

Synthesis and characterization of 1b

According to the synthetic procedure of **3a**,[1] *N*,*N'*-dicyclohexylcarbodiimide (812 mg, 3.93 mmol, 1.1 equiv.), *p*-chloroaniline (911 mg, 7.14 mmol, 2.0 equiv.), and *N*,*N*-dimethyl-4-aminopyridine (43.6 mg, 0.357 mmol, 0.1 equiv.) were added to a solution of tetrolic acid (302 mg, 3.59 mmol) in dichloromethane (3.6 mL) at 0 ºC under a nitrogen atmosphere. After stirring at room temperature for 4 hours, the reaction mixture was filtered with Celite. The reaction was quenched by addition of 3% hydrochloric acid (20 mL) to the filtrate, and the resulting solution was extracted with dichloromethane (30×3 mL). The combined organic extracts were washed with brine (20 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo to provide a crude material. This material was purified by column chromatography (silica gel, hexane/EtOAc = 4/1 to 2/1) to give **3b** (564 mg, 2.91 mmol, 81%) as a white solid. R_f = 0.27 (silica gel, hexane/EtOAc = 2/1); m.p. 136–137 °C; IR (KBr) 3276 (N–H), 2239 (C≡C), 1646 (C=O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.01 (brs, 1H, N*H*), 7.50 (d, *J* = 9.0 Hz, 1H, Ar*H*), 7.26 (d, *J* = 9.0 Hz, 1H, Ar*H*), 1.95 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.2 (*C*), 136.0 (*C*), 129.6 (*C*), 128.9 (*C*H), 121.1 (*C*H), 85.0 (*C*), 75.1 (*C*), 3.7 (*C*H_3). Anal. Calcd for $C_{10}H_8ClNO$: C, 62.03; H, 4.16; N, 7.23. Found: C, 61.70; H, 4.53; N, 7.45.

According to the synthetic procedure of **1a**, **1b** was synthesized from **3b** (300 mg, 1.55 mmol). After addition of tributyltin chloride, the reaction mixture was warmed to 0 °C over 1 hour. The crude product was purified by column chromatography (10% w/w K_2CO_3–silica gel, hexane/EtOAc = 25/1) to give **1b** (169 mg, 0.350 mmol, 23%) as a white solid. R_f = 0.81 (silica gel, hexane/EtOAc =

2/1); m.p. 49–50 °C; IR (KBr) 3267 (N–H), 1917 (C=C=C), 1626 (C=O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.69 (brs, 1H, N*H*), 7.47 (d, *J* = 9.0 Hz, 2H, Ar*H*), 7.25 (d, *J* = 9.0 Hz, 2H, Ar*H*), 4.74 (t, *J* = 13.8 Hz, 2H, CH_2), 1.66–0.98 (m, 18H, CH_2), 0.89 (t, *J* = 7.2 Hz, 9H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 208.2 (*C*), 165.2 (*C*), 136.9 (*C*), 128.9 (*C*H), 128.6 (*C*), 120.4 (*C*H), 96.0 (*C*), 70.5 (*C*H_2), 28.8 (*C*H_2), 27.1 (*C*H_2), 13.7 (*C*H_3), 11.1 (*C*H_2). Anal. Calcd for $C_{22}H_{34}ClNOSn$: C, 54.74; H, 7.10; N, 2.90. Found: C, 54.97; H, 7.13; N, 2.98.

Synthesis and characterization of 1c

According to the synthetic procedure of **3b**, **3c** was synthesized from *p*-anisidine (879 mg, 7.14 mmol) and tetrolic acid (301 mg, 3.58 mmol). The crude product was purified by column chromatography (silica gel, hexane/EtOAc = 4/1 to 2/1) to give **3c** (646 mg, 3.41 mmol, 95%) as a white solid. R_f = 0.21 (silica gel, hexane/EtOAc = 2/1); m.p. 100–101 °C; IR (KBr) 3275 (N–H), 2240 (C≡C), 1638 (C=O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.49 (brs, 1H, N*H*), 7.44 (d, *J* = 9.0 Hz, 2H, Ar*H*), 6.84 (d, *J* = 9.0 Hz, 2H, Ar*H*), 3.77 (s, 3H, OCH_3), 1.95 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 50 ºC) δ 156.8 (*C*), 151.1 (*C*), 130.7 (*C*), 128.9 (*C*), 121.8 (*C*H), 114.2 (*C*H), 84.0 (*C*), 75.5 (*C*), 55.4 (*C*H_3), 3.52 (*C*H_3). Anal. Calcd for $C_{11}H_{11}NO_2$: C, 69.83; H, 5.86; N, 7.40. Found: C, 69.85; H, 6.10; N, 7.71.

According to the synthetic procedure of **1a**, **1c** was synthesized from **3c** (300 mg, 1.59 mmol). After addition of tributyltin chloride, the reaction mixture was stirred at -78 °C for 1 hour. The crude product was purified by column chromatography (10% w/w K_2CO_3–silica gel, hexane/EtOAc = 25/1)

to give **1c** (396 mg, 0.828 mmol, 52%) as a white solid. R_f = 0.72 (silica gel, hexane/EtOAc = 2/1); m.p. 65–66 °C; IR (KBr) 3268 (N–H), 1955 (C=C=C), 1917 (C=C=C), 1622 (C=O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.58 (brs, 1H, N*H*), 7.41 (d, *J* = 9.0 Hz, 2H, Ar*H*), 6.84 (d, *J* = 9.0 Hz, 2H, Ar*H*), 4.71 (t, *J* = 14.1 Hz, 2H, CH_2), 3.78 (s, 3H, CH_3), 1.66–0.98 (m, 18H, CH_2), 0.89 (t, *J* = 7.2 Hz, 9H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.9 (*C*), 165.0 (*C*), 156.1 (*C*), 131.5 (*C*), 121.2 (*C*H), 114.1 (*C*H), 96.0 (*C*), 70.2 (*C*H_2), 55.5 (*C*H_3), 28.9 (*C*H_2), 27.2 (*C*H_2), 13.7 (*C*H_3), 11.1 (*C*H_2). Anal. Calcd for $C_{23}H_{37}NO_2Sn$: C, 57.76; H, 7.80; N, 2.93. Found: C, 57.65; H, 7.46; N, 3.09.

Synthesis and characterization of 1d

According to the synthetic procedure of **3b**, **3b** was synthesized from *p*-toluidine (770 mg, 7.14 mmol) and tetrolic acid (301 mg, 3.58 mmol). The crude product was purified by column chromatography (silica gel, hexane/EtOAc = 4/1 to 2/1) to give **3d** (488 mg, 2.82 mmol, 79%) as a white solid. R_f = 0.23 (silica gel, hexane/EtOAc = 2/1); m.p. 110–111 °C; IR (KBr) 3279 (N–H), 2237 (C≡C), 1637 (C=O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.85 (brs, 1H, N*H*), 7.41 (d, *J* = 8.4 Hz, 2H, Ar*H*), 7.10 (d, *J* = 8.4 Hz, 2H, Ar*H*), 2.30 (s, 3H, CH_3), 1.94 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.1 (*C*), 134.9 (*C*), 134.2 (*C*), 129.4 (*C*H), 119.9 (*C*H), 84.2 (*C*), 75.3 (*C*), 20.8 (*C*H_3), 3.6 (*C*H_3). Anal. Calcd for $C_{11}H_{11}NO$: C, 76.28; H, 6.40; N, 8.09. Found: C, 76.58; H, 6.59; N, 8.44.

According to the synthetic procedure of **1a**, **1d** was synthesized from **3d** (300 mg, 1.73 mmol). After addition of tributyltin chloride, the reaction mixture was stirred at -78 °C for 1 hour. The crude product was purified by column chromatography (10% w/w K_2CO_3–silica gel, hexane/EtOAc = 25/1)

to give **1d** (304 mg, 0.658 mmol, 38%) as a white solid. R_f = 0.83 (silica gel, hexane/EtOAc = 2/1); m.p. 70–71 °C; IR (KBr) 3266 (N–H), 1961 (C=C=C), 1918 (C=C=C), 1623 (C=O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.63 (brs, 1H, N*H*), 7.39 (d, *J* = 8.4 Hz, 1H, Ar*H*), 7.10 (d, *J* = 8.4 Hz, 1H, Ar*H*), 4.73 (d, *J* = 14.4 Hz, 1H, CH_2), 4.69 (d, *J* = 14.1 Hz, 1H, CH_2), 2.29 (s, 3H, CH_3), 1.66–0.98 (m, 18H, CH_2), 0.89 (t, *J* = 7.2 Hz, 9H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.8 (*C*), 164.9 (*C*), 135.7 (*C*), 133.1 (*C*), 129.3 (*C*H), 119.2 (*C*H), 96.1 (*C*), 70.1 (*C*H_2), 28.8 (*C*H_2), 27.1 (*C*H_2), 20.7 (*C*H_3), 13.6 (*C*H_3), 11.0 (*C*H_2). Anal. Calcd for $C_{23}H_{37}NOSn$: C, 59.76; H, 8.07; N, 3.03. Found: C, 59.74; H, 7.91; N, 3.13.

General procedure for amide propargylation of aldehydes

All the experiments for amide propargylation of aldehydes were carried out as described in the following typical procedure. The reaction of benzaldehyde with **1a** was exemplified as follows.

Synthesis and characterization of 4a

To a suspension of $InCl_3$ (9.4 mg, 0.042 mmol, 20 mol %) and MS 3 Å (318 mg, 1.5 g/mmol) in MeCN (0.43 mL) was added $ZnCl_2$ (5.7 mg, 0.042 mmol, 20 mol %) and 6,6'-(2,4,6-*i*-Pr_3-C_6H_4)$_2$-(*S*)-BINOL (36.6 mg, 0.0530 mmol, 25 mol %) at room temperature under an argon atmosphere. After stirring at the same temperature for 1 hour, benzaldehyde (22.5 mg, 0.212 mmol) was added to the solution. Then, the resulting mixture was stirred at room temperature for 30 minutes. After addition of **1a** (114 mg, 0.254 mmol, 1.2 equiv.), the reaction mixture was stirred at the

same temperature for an additional 18 h. The reaction was quenched by addition of saturated aqueous $NaHCO_3$ (5 mL), and the resulting mixture was extracted with dichloromethane (20 mL×3), washed with brine (5 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo to give a crude material. This material was purified by column chromatography (10% w/w K_2CO_3–silica gel, toluene/EtOAc = 10/1 to 4/1) to give **4a** (46.0 mg, 0.173 mmol, 82%, 94:6 er) as a white solid: R_f = 0.32 (silica gel, toluene/EtOAc = 2/1); m.p. 52–54 °C; $[\alpha]_D^{21}$ -27.5 (*c* 1.00, $CHCl_3$); IR (KBr) 3409 (O–H), 3280 (O–H), 2240 (C≡C), 1638 (C=O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.98 (brs, 1H, N*H*), 7.47–7.26 (m, 10H, Ar*H*), 7.12 (t, *J* = 6.3 Hz, Ar*H*), 4.95 (dd, *J* = 6.3, 9.6 Hz, 2H, C*H*), 3.57 (d, *J* = 3.6 Hz, 1H, O*H*), 2.90–2.68 (m, 2H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.5 (*C*), 142.1 (*C*), 137.3 (*C*), 128.9 (*C*H), 128.5 (*C*H), 128.0 (*C*H), 125.7 (*C*H), 124.8 (*C*H), 120.1 (*C*H), 85.7 (*C*), 77.7 (*C*), 71.8 (*C*H), 29.4 (*C*H_2). Anal. Calcd for $C_{17}H_{15}NO_2$: C, 76.96; H, 5.70; N, 5.28. Found: C, 77.17; H, 6.06; N, 5.66. The enantiomeric excess was determined by HPLC with a Daicel Chiralpak IC column (hexane/EtOH = 95/5), flow rate 0.5 mL/min, UV detection 254 nm, t_R (major) = 39.4 min, t_R (minor) = 45.0 min.

Synthesis and characterization of 4b

The reaction of decanal (30.0 mg, 0.192 mmol) with **1a** (1.2 eq., 103 mg, 0.230 mmol) was performed at room temperature for 18 h. The crude material was purified by column chromatography (10% w/w K_2CO_3–silica gel, hexane/EtOAc = 6/1 to 4/1 to 2/1) to give **4b** (39.9 mg, 0.126 mmol, 66%, 80:20 er) as a white solid: R_f = 0.23 (silica gel, hexane/EtOAc = 2/1); m.p. 51–53 °C; $[\alpha]_D^{24}$ -4.3 (*c* 0.750, $CHCl_3$); IR (KBr) 3292 (O–H), 2238 (C≡C), 1645 (C=O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.29

(brs, 1H, N*H*), 7.50 (d, *J* = 7.5 Hz, 2H, Ar*H*), 7.30 (t, *J* = 7.5 Hz, 2H, Ar*H*), 7.11 (t, *J* = 7.5 Hz, 1H, Ar*H*), 3.86 (brs, 1H, C*H*), 3.54 (brs, 1H, O*H*), 2.59 (dd, *J* = 17.1, 4.2 Hz, 1H, CH_2), 2.44 (dd, *J* = 17.1, 6.3 Hz, 1H, CH_2), 1.65–1.25 (m, 16H, CH_2), 0.88 (t, *J* = 6.6 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.1 (*C*), 137.3 (*C*), 129.0 (*C*H), 124.8 (*C*H), 119.9 (*C*H), 85.5 (*C*), 77.8 (*C*), 69.7 (*C*H), 36.5 (*C*H_2), 31.9 (*C*H_2), 29.6 (*C*H_2), 29.53 (*C*H_2), 29.46 (*C*H_2), 29.3 (*C*H_2), 27.6 (*C*H_2), 25.7 (*C*H_2), 22.7 (*C*H_2), 14.1 (*C*H_3). Anal. Calcd for $C_{20}H_{29}NO_2$: C, 76.15; H, 9.27; N, 4.44. Found: C, 76.48; H, 9.32; N, 4.70. The enantiomeric excess was determined by HPLC with a Daicel Chiralpak IC column (hexane/EtOH = 90/10), flow rate 0.5 mL/min, UV detection 254 nm, t_R (major) = 11.5 min, t_R (minor) = 14.5 min.

Synthesis and characterization of 4c

The reaction of pivalaldehyde (16.4 mg, 0.190 mmol) with **1a** (1.2 eq., 102 mg, 0.228 mmol) was performed at room temperature for 18 h. The crude material was purified by column chromatography (10% w/w K_2CO_3–silica gel, $CHCl_3$/EtOAc = 5/1) to give **4c** (34.6 mg, 0.141 mmol, 74%, 83:17 er) as a white solid: R_f = 0.25 (silica gel, hexane/EtOAc = 2/1); m.p. 49–51 °C; $[\alpha]_D^{20}$ -22.6 (*c* 0.250, $CHCl_3$); IR (KBr) 3266 (O–H), 2239 (C≡C), 1646 (C=O) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.32 (s, 1H, N*H*), 7.51 (d, *J* = 7.5 Hz, 2H, Ar*H*), 7.30 (d, *J* = 7.5 Hz, 3H, Ar*H*), 7.10 (t, *J* = 7.5 Hz, 1H, Ar*H*), 3.51 (d, *J* = 9.9 Hz, 1H, C*H*), 3.25 (brs, 1H, O*H*), 2.53 (dd, *J* = 1.8, 17.1 Hz, 1H, CH_2), 2.35 (dd, *J* = 9.9, 17.1 Hz, 1H, CH_2), 0.90 (s, 9H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ ^{13}C NMR (75 MHz, CD_3OD) δ 153.9 (*C*), 137.7 (*C*), 130.2 (*C*H), 125.9 (*C*H), 121.4 (*C*H), 89.1 (*C*), 79.0 (*C*H), 77.8 (*C*),

36.4 (*C*), 26.4 (*C*H_3), 23.7 (*C*H_2). Anal. Calcd for $C_{15}H_{19}NO_2$: C, 73.44; H, 7.81; N, 5.71. Found: C, 73.18; H, 7.84; N, 5.43. The enantiomeric excess was determined by HPLC with a Daicel Chiralpak IC column (hexane/EtOH = 95/5), flow rate 0.5 mL/min, UV detection 254 nm, t_R (major) = 22.9 min, t_R (minor) = 25.2 min.

Synthesis and characterization of 4d

The reaction of *p*-tolaldehyde (22.8 mg, 0.190 mmol) with **1a** (1.2 eq., 102 mg, 0.228 mmol) was performed at room temperature for 18 h. The crude material was purified by column chromatography (10% w/w K_2CO_3–silica gel, hexane/EtOAc = 6/1 to 2/1) to give **4d** (36.9 mg, 0.132 mmol, 70%, 87:13 er) as a white solid: R_f = 0.21 (silica gel, hexane/EtOAc = 2/1); m.p. 57–58 °C; $[\alpha]_D^{24}$ -19.1 (*c* 1.00, $CHCl_3$); IR (KBr) 3449 (O–H), 3276 (O–H), 2236 (C≡C), 1642 (C=O) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69 (brs, 1H, N*H*), 7.46 (d, *J* = 7.8 Hz, 2H, Ar*H*), 7.33–7.27 (m, 4H, Ar*H*), 7.19–7.09 (m, 3H, Ar*H*), 4.94 (brs, 1H, C*H*), 2.92 (d, *J* = 2.7 Hz, 1H, O*H*), 2.85–2.71 (m, 2H, CH_2), 2.35 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.2 (*C*), 139.2 (*C*), 137.9 (*C*), 137.3 (*C*), 129.2 (*C*H), 128.9 (*C*H), 125.6 (*C*H), 124.8 (*C*H), 120.0 (*C*H), 85.4 (*C*), 77.7 (*C*), 71.8 (*C*H), 29.4 (*C*H_2), 21.1 (*C*H_3). Anal. Calcd for $C_{18}H_{17}NO_2$: C, 77.40; H, 6.13; N, 5.01. Found: C, 77.00; H, 5.78; N, 5.07. The enantiomeric excess was determined by HPLC with a Daicel Chiralpak IC column (hexane/EtOH = 95/5), flow rate 0.5 mL/min, UV detection 254 nm, t_R (major) = 36.0 min, t_R (minor) = 39.4 min.

Synthesis and characterization of 4e

The reaction of *p*-anisaldehyde (28.0 mg, 0.206 mmol) with **1a** (1.2 eq., 111 mg, 0.247 mmol) was

performed at room temperature for 18 h. The crude material was purified by column chromatography (10% w/w K_2CO_3–silica gel, hexane/EtOAc = 6/1 to 4/1 to 1/1) to give **4e** (45.8 mg, 0.155 mmol, 75%, 90:10 er) as a white solid: R_f = 0.11 (silica gel, hexane/EtOAc = 2/1); m.p. 101–102 °C; $[\alpha]_D^{24}$ -18.3 (*c* 1.00, $CHCl_3$); IR (KBr) 3484 (O–H), 3263 (O–H), 2237 (C≡C), 1647 (C=O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.18 (brs, 1H, N*H*), 7.44 (d, *J* = 7.8 Hz, 2H, Ar*H*), 7.29–7.24 (m, 4H, Ar*H*), 7.09 (t, *J* = 7.5 Hz, 1H, Ar*H*), 6.85 (d, *J* = 8.7 Hz, 2H, Ar*H*), 4.88 (t, *J* = 6.0 Hz, 1H, C*H*), 3.81 (s, 3H, CH_3), 3.75 (brs, 1H, O*H*), 2.76 (dd, *J* = 7.2, 17.1 Hz, 1H, CH_2), 2.69 (dd, *J* = 4.8, 17.1 Hz, 1H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.3 (*C*), 151.2 (*C*), 137.3 (*C*), 134.3 (*C*), 129.0 (*C*H), 127.0 (*C*H), 124.8 (*C*H), 119.9 (*C*H), 113.9 (*C*H), 85.4 (*C*), 77.7 (*C*), 71.5 (*C*H), 55.2 (*C*H_3), 29.4 (*C*H_2). Anal. Calcd for $C_{18}H_{17}NO_3$: C, 73.20; H, 5.80; N, 4.74. Found: C, 72.80; H, 5.44; N, 4.67. The enantiomeric excess was determined by HPLC with a Daicel Chiralpak IC column (hexane/EtOH = 92/8), flow rate 0.5 mL/min, UV detection 254 nm, t_R (major) = 35.6 min, t_R (minor) = 38.8 min.

Synthesis and characterization of 4f

The reaction of *p*-chlorobenzaldehyde (28.1 mg, 0.200 mmol) with **1a** (1.2 eq., 108 mg, 0.240 mmol) was performed at room temperature for 18 h. The crude material was purified by column chromatography (10% w/w K_2CO_3–silica gel, hexane/EtOAc = 6/1 to 4/1 to 1/1) to give **4f** (43.4 mg, 0.145 mmol, 72%, 92:8 er) as a white solid: R_f = 0.16 (silica gel, hexane/EtOAc = 2/1); m.p. 103–104 °C; $[\alpha]_D^{24}$ -27.1 (*c* 1.00, $CHCl_3$); IR (KBr) 3247 (O–H), 3256 (O–H), 2241 (C≡C), 1639 (C=O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.87 (brs, 1H, N*H*), 7.44 (d, *J* = 7.8 Hz, 2H, Ar*H*), 7.32–7.27 (m, 6H, Ar*H*),

7.12 (t, *J* = 7.5 Hz, 1H, Ar*H*), 4.94 (m, 1H, C*H*), 3.66 (d, *J* = 3.6 Hz, 1H, O*H*), 2.74 (d, *J* = 6.0 Hz, 2H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.0 (*C*), 140.6 (*C*), 137.1 (*C*), 133.8 (*C*), 129.0 (*C*H), 128.7 (*C*H), 127.1 (*C*H), 125.0 (*C*H), 120.0 (*C*H), 84.9 (*C*), 77.9 (*C*), 71.2 (*C*H), 29.6 (*C*H_2). Anal. Calcd for $C_{17}H_{14}ClNO_2$: C, 68.12; H, 4.71; N, 4.67. Found: C, 67.76; H, 4.86; N, 4.59. The enantiomeric excess was determined by HPLC with a Daicel Chiralpak IC column (hexane/EtOH = 95/5), flow rate 0.5 mL/min, UV detection 254 nm, t_R (major) = 28.9 min, t_R (minor) = 32.1 min.

Synthesis and characterization of 4g

The reaction of *o*-tolaldehyde (25.0 mg, 0.208 mmol) with **1a** (1.2 eq., 112 mg, 0.250 mmol) was performed at room temperature for 18 h. The crude material was purified by column chromatography (10% w/w K_2CO_3–silica gel, hexane/EtOAc = 6/1 to 4/1 to 1/1) to give **4g** (45.3 mg, 0.162 mmol, 78%, 90:10 er) as a white solid: R_f = 0.22 (silica gel, hexane/EtOAc = 2/1); m.p. 117–119 °C; $[\alpha]_D^{27}$ -42.2 (*c* 0.500, $CHCl_3$); IR (KBr) 3250 (O–H), 2232 (C≡C), 1638 (C=O) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.18 (brs, 1H, N*H*), 7.52–7.42 (m, 3H, Ar*H*), 7.30–7.06 (m, 6H, Ar*H*), 5.16 (brs, 1H, C*H*), 3.76 (brs, 1H, O*H*), 2.70 (d, *J* = 6.0 Hz, 2H, CH_2), 2.30 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.3 (*C*), 140.1 (*C*), 137.2 (*C*), 134.4 (*C*), 130.5 (*C*H), 128.9 (*C*H), 127.8 (*C*H), 126.3 (*C*H), 125.0 (*C*H), 124.8 (*C*H), 120.0 (*C*H), 85.7 (*C*), 77.5 (*C*), 68.4 (*C*H), 28.3 (*C*H_2), 18.9 (*C*H_3). Anal. Calcd for $C_{18}H_{17}NO_2$: C, 77.40; H, 6.13; N, 5.01. Found: C, 77.31; H, 6.14; N, 4.88. The enantiomeric excess was determined by HPLC with a Daicel Chiralpak IC column (hexane/EtOH = 95/5), flow rate 0.5 mL/min, UV detection 254 nm, t_R (major) = 31.3 min, t_R (minor) = 34.1 min.

Synthesis and characterization of 4h

The reaction of *o*-anisaldehyde (13.2 mg, 0.0970 mmol) with **1a** (1.2 eq., 52.1 mg, 0.116 mmol) was performed at room temperature for 18 h. The crude material was purified by column chromatography (10% w/w K_2CO_3–silica gel, hexane/EtOAc = 6/1 to 4/1 to 1/1) to give **4h** (22.1 mg, 0.0748 mmol, 77%, 90:10 er) as a pale yellow oil: R_f = 0.21 (silica gel, hexane/EtOAc = 2/1); $[\alpha]_D^{21}$ -16.6 (*c* 0.250, $CHCl_3$); IR (NaCl) 3379 (O–H), 3276 (O–H), 2234 (C≡C), 1645 (C=O) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 (d, *J* = 9.0 Hz, 2H, Ar*H*), 7.41 (dd, *J* = 1.8, 7.5 Hz, 1H, Ar*H*), 7.35–7.25 (m, 3H, Ar*H*), 7.12 (t, *J* = 7.5 Hz, 1H, Ar*H*), 7.01 (t, *J* = 7.5 Hz, 1H, Ar*H*), 6.91 (d, *J* = 8.1 Hz, 1H, Ar*H*), 5.16 (m, 1H, C*H*), 3.88 (s, 3H, CH_3), 3.05 (d, *J* = 6.3 Hz, 1H, O*H*), 2.91 (dd, *J* = 5.1, 17.1 Hz, 1H, CH_3), 2.83 (dd, *J* = 9.3, 17.1 Hz, 1H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.1 (*C*), 151.2 (*C*), 137.5 (*C*), 130.0 (*C*), 129.0 (*C*H), 126.7 (*C*H), 124.7 (*C*H), 120.8 (*C*H), 119.9 (*C*H), 110.5 (*C*H), 85.7 (*C*), 77.6 (*C*), 68.6 (*C*H), 55.3 (*C*H_3), 27.7 (*C*H_2). Anal. Calcd for $C_{18}H_{17}NO_3$: C, 73.20; H, 5.80; N, 4.74. Found: C, 73.06; H, 5.86; N, 5.00. The enantiomeric excess was determined by HPLC with a Daicel Chiralpak IC column (hexane/EtOH = 95/5), flow rate 0.5 mL/min, UV detection 254 nm, t_R (major) = 42.3 min, t_R (minor) = 48.7 min.

Synthesis and characterization of 4i

The reaction of *o*-chlorobenzaldehyde (13.2 mg, 0.0970 mmol) with **1a** (1.2 eq., 52.1 mg, 0.116 mmol) was performed at room temperature for 18 h. The crude material was purified by column chromatography (10% w/w K_2CO_3–silica gel, hexane/EtOAc = 6/1 to 4/1 to 1/1) to give **4i** (22.4 mg,

0.0747 mmol, 77%, 81:19 er) as a white solid: R_f = 0.32 (silica gel, hexane/EtOAc = 2/1); m.p. 65–67 °C; $[\alpha]_D^{21}$ -40.8 (*c* 0.250, $CHCl_3$); IR (NaCl) 3379 (O–H), 3275 (O–H), 2236 (C≡C), 1645 (C=O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.89 (s, 1H, N*H*), 7.65 (dd, *J* = 1.5, 7.5 Hz, 1H, Ar*H*), 7.46 (d, *J* = 8.1 Hz, 2H, Ar*H*), 7.35–7.20 (m, 5H, Ar*H*), 7.11 (t, *J* = 7.5 Hz, 1H, Ar*H*), 5.38 (m, 1H, C*H*), 3.66 (d, *J* = 3.8 Hz, 1H, O*H*), 2.91 (dd, *J* = 3.9, 17.1 Hz, 1H, CH_3), 2.72 (dd, *J* = 7.5, 17.1 Hz, 1H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.3 (*C*), 139.5 (*C*), 137.2 (*C*), 131.4 (*C*), 129.4 (*C*H), 129.03 (*C*H), 128.96 (*C*H), 127.2 (*C*H), 127.0 (*C*H), 124.9 (*C*H), 120.0 (*C*H), 85.2 (*C*), 77.7 (*C*), 68.4 (*C*H), 27.9 (*C*H_2). Anal. Calcd for $C_{17}H_{14}ClNO_2$: C, 68.12; H, 4.71; N, 4.67. Found: C, 67.79; H, 4.82; N, 5.02. The enantiomeric excess was determined by HPLC with a Daicel Chiralpak IC column (hexane/EtOH = 98/2), flow rate 0.5 mL/min, UV detection 254 nm, t_R (major) = 77.6 min, t_R (minor) = 84.7 min.

Synthesis and characterization of 4j

The reaction of *o*-(*tert*-butyldimethylsilyloxy)benzaldehyde (47.3 mg, 0.200 mmol) with **1a** (1.2 eq., 107 mg, 0.240 mmol) was performed at room temperature for 18 h. The crude material was purified by column chromatography (10% w/w K_2CO_3–silica gel, hexane/EtOAc = 6/1 to 4/1 to 1/1) to give **4j** (72.0 mg, 0.182 mmol, 91%, 97:3 er) as a white solid: R_f = 0.23 (silica gel, hexane/EtOAc = 2/1); m.p. 103–104 °C; $[\alpha]_D^{21}$ -45.6 (*c* 0.500, $CHCl_3$); IR (KBr) 3387 (O–H), 2234 (C≡C), 1631 (C=O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.74 (brs, 1H, N*H*), 7.46–7.49 (m, 3H, Ar*H*), 7.30 (t, *J* = 7.5 Hz, 2H, Ar*H*), 7.22–7.08 (m, 2H, Ar*H*), 7.00 (t, *J* = 7.5 Hz, 1H, Ar*H*), 6.82 (d, *J* = 8.1 Hz, 1H, Ar*H*), 5.23

(m, 1H, C*H*), 3.88 (s, 3H, CH_3), 3.27 (d, *J* = 4.5 Hz, 1H, O*H*), 2.89 (dd, *J* = 4.5, 17.1 Hz, 1H, CH_3), 2.75 (dd, *J* = 7.5, 17.1 Hz, 1H, CH_3), 1.02 (s, 9H, CH_3), 0.28 (s, 9H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.1 (*C*), 151.0 (*C*), 137.4 (*C*), 132.3 (*C*), 129.0 (*C*H), 128.7 (*C*H), 126.6 (*C*H), 124.7 (*C*H), 121.3 (*C*H), 119.8 (*C*H), 118.1 (*C*H), 85.3 (*C*), 77.6 (*C*), 67.7 (*C*H), 27.9 (*C*H_2), 25.8 (*C*H_3), 18.2 (*C*), -4.0 (*C*H_3), -4.3 (*C*H_3). Anal. Calcd for $C_{23}H_{29}NO_3Si$: C, 69.84; H, 7.39; N, 3.54. Found: C, 69.56; H, 7.40; N, 3.66. The enantiomeric excess was determined by HPLC with a Daicel Chiralpak IC column (hexane/EtOH = 97/3), flow rate 0.5 mL/min, UV detection 254 nm, t_R (major) = 24.1 min, t_R (minor) = 27.0 min.

Synthesis and characterization of 4k

The reaction of *o*-[(triisopropylsilyl)oxy]benzaldehyde (55.7 mg, 0.200 mmol) with **1a** (1.2 eq., 108 mg, 0.240 mmol) was performed at room temperature for 18 h. The crude material was purified by column chromatography (10% w/w K_2CO_3–silica gel, hexane/EtOAc = 6/1 to 4/1 to 1/1) to give **4k** (79.6 mg, 0.182 mmol, 91%, 96:4 er) as a white solid: R_f = 0.27 (silica gel, hexane/EtOAc = 2/1); m.p. 146–147 °C; $[\alpha]_D^{25}$ -57.2 (*c* 1.00, $CHCl_3$); IR (KBr) 3367 (O–H), 3269 (O–H), 2240 (C≡C), 1644 (C=O) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (s, 1H, N*H*), 7.49–7.47 (m, 3H, Ar*H*), 7.30 (t, *J* = 7.5 Hz, 2H, Ar*H*), 7.20–7.08 (m, 2H, Ar*H*), 6.98 (t, *J* = 7.5 Hz, 1H, Ar*H*), 6.82 (d, *J* = 8.1 Hz, 1H, Ar*H*), 5.29 (t, *J* = 3.3 Hz, 1H, C*H*), 3.25 (s, 1H, O*H*), 2.92 (dd, *J* = 4.2, 17.1 Hz, 1H), 2.76 (dd, *J* = 7.8, 17.1 Hz, 1H), 1.40–1.26 (m, 3H, C*H*), 1.13 (d, *J* = 7.5 Hz, 9H, CH_3), 1.12 (d, *J* = 7.2 Hz, 9H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.5 (*C*), 150.9 (*C*), 137.3 (*C*), 131.8 (*C*), 129.0 (*C*H), 128.7 (*C*H), 126.5

(*C*H), 124.7 (*C*H), 121.0 (*C*H), 119.8 (*C*H), 117.8 (*C*H), 85.3 (*C*), 77.6 (*C*), 67.9 (*C*H), 27.8 (CH_2), 18.1 (CH_3), 13.0 (*C*H). Anal. Calcd for $C_{26}H_{35}NO_3Si$: C, 71.35; H, 8.06; N, 3.20. Found: C, 71.38; H, 7.75; N, 3.37. The enantiomeric excess was determined by HPLC with a Daicel Chiralpak IC column (hexane/EtOH = 97/3), flow rate 0.5 mL/min, UV detection 254 nm, t_R (major) = 24.3 min, t_R (minor) = 26.9 min.

Synthesis and characterization of 4l

The reaction of *o*-(*tert*-butyldiphenylsilyloxy)benzaldehyde (70.2 mg, 0.195 mmol) with **1a** (1.2 eq., 104 mg, 0.234 mmol) was performed at room temperature for 18 h. The crude material was purified by column chromatography (10% w/w K_2CO_3–silica gel, hexane/EtOAc = 8/1 to 4/1) to give **4l** (90.5 mg, 0.174 mmol, 89%, 98:2 er) as a white solid: R_f = 0.33 (silica gel, hexane/EtOAc = 2/1); m.p. 114–116 °C; $[\alpha]_D^{25}$ -44.1 (*c* 1.00, $CHCl_3$); IR (KBr) 3275 (O–H), 2236 (C≡C), 1739 (C=O), 1637 (C=O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.73–7.67 (m, 4H, Ar*H*), 7.61 (nrs, 1H, N*H*), 7.53–7.27 (m, 11H, Ar*H*), 7.11 (t, *J* = 7.5 Hz, 1H, Ar*H*), 6.95–6.84 (m, 2H, Ar*H*), 6.47 (dd, *J* = 1.2, 8.1 Hz, 1H, Ar*H*), 5.52 (m, 1H, C*H*), 3.13 (d, *J* = 4.8 Hz, 1H, O*H*), 3.05 (dd, *J* = 4.2, 17.1 Hz, 1H, CH_2), 2.88 (dd, *J* = 7.5, 17.1 Hz, 1H, CH_2), 1.12 (s, 9H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.8 (*C*), 151.1 (*C*), 137.3 (*C*), 135.3 (*C*H), 135.2 (*C*H), 132.1 (*C*), 131.9 (*C*), 131.8 (*C*), 130.12 (*C*H), 130.08 (*C*H), 128.9 (*C*H), 128.3 (*C*H), 128.0 (*C*H), 127.9 (*C*H), 126.3 (*C*H), 124.7 (*C*H), 121.3 (*C*H), 119.9 (*C*H), 118.9 (*C*H), 85.5 (*C*), 77.8 (*C*), 67.5 (*C*H), 28.2 (CH_2), 26.6 (CH_3), 19.4 (*C*). Anal. Calcd for $C_{33}H_{33}NO_3Si$: C, 76.27; H, 6.40; N, 2.70. Found: C, 76.28; H, 6.61; N, 2.86. The enantiomeric excess

was determined by HPLC with a Daicel Chiralpak IC column (hexane/EtOH = 98/2), flow rate 0.5 mL/min, UV detection 254 nm, t_R (major) = 40.5 min, t_R (minor) = 45.5 min.

Synthesis and characterization of 4m

The reaction of *m*-(*tert*-butyldiphenylsilyloxy)benzaldehyde (72.1 mg, 0.200 mmol) with **1a** (1.2 eq., 108 mg, 0.240 mmol) was performed at room temperature for 18 h. The crude material was purified by column chromatography (10% w/w K_2CO_3–silica gel, hexane/EtOAc = 6/1 to 4/1 to 1/1) to give **4m** (83.3 mg, 0.160 mmol, 80%, 91:9 er) as a yellow oil: R_f = 0.28 (silica gel, hexane/EtOAc = 2/1); $[\alpha]_D^{25}$ -12.4 (*c* 1.00, $CHCl_3$); IR (NaCl) 3375 (O–H), 3278 (O–H), 2233 (C≡C), 1648 (C=O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.70–7.65 (m, 5H, Ar*H*, N*H*), 7.45–7.29 (m, 10H, Ar*H*), 7.12–7.04 (m, 2H, Ar*H*), 6.88 (d, *J* = 7.8 Hz, 1H, Ar*H*), 6.75–6.69 (m, 2H, Ar*H*), 4.74 (brs, 1H, C*H*), 2.76 (d, *J* = 3.0 Hz, 1H, O*H*), 2.62–2.48 (m, 2H, CH_2), 1.10 (s, 9H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.6 (*C*), 150.8 (*C*), 143.5 (*C*), 137.2 (*C*), 135.5 (*C*H), 132.6 (*C*H), 130.0 (*C*H), 129.4 (*C*H), 129.0 (*C*H), 127.8 (*C*H), 124.8 (*C*H), 119.8 (*C*H), 119.6 (*C*H), 118.4 (*C*H), 117.0 (*C*H), 84.9 (*C*), 77.6 (*C*), 71.7 (*C*H), 29.3 (*C*H_2), 26.5 (*C*H_3), 19.4 (*C*). Anal. Calcd for $C_{33}H_{33}NO_3Si$: C, 76.27; H, 6.40; N, 2.70. Found: C, 76.55; H, 6.41; N, 2.95. The enantiomeric excess was determined by HPLC with a Daicel Chiralpak IC column (hexane/EtOH = 97/3), flow rate 0.5 mL/min, UV detection 254 nm, t_R (major) = 31.3 min, t_R (minor) = 38.7 min.

Synthesis and characterization of 4n

The reaction of *p*-(*tert*-butyldiphenylsilyloxy)benzaldehyde (72.1 mg, 0.200 mmol) with **1a** (1.2 eq.,

108 mg, 0.240 mmol) was performed at room temperature for 18 h. The crude material was purified by column chromatography (10% w/w K_2CO_3–silica gel, hexane/EtOAc = 6/1 to 4/1 to 1/1) to give **4n** (83.6 mg, 0.161 mmol, 80%, 92:8 er) as a white solid: R_f = 0.25 (silica gel, hexane/EtOAc = 2/1); m.p. 66–68 °C; $[\alpha]_D^{25}$ -7.2 (*c* 1.00, $CHCl_3$); IR (KBr) 3371 (O–H), 3277 (O–H), 2233 (C≡C), 1647 (C=O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.88 (brs, 1H, N*H*), 7.71–7.68 (m, 4H, Ar*H*), 7.44–7.06 (m, 13H, Ar*H*), 6.73 (d, *J* = 8.4 Hz, 2H, Ar*H*), 4.79 (brs, 1H, C*H*), 3.18 (brs, 1H, O*H*), 2.68–2.65 (m, 2H, CH_2), 1.09 (s, 9H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.5 (*C*), 151.0 (*C*), 137.3 (*C*), 135.4 (*C*H), 134.6 (*C*), 132.7 (*C*), 129.9 (*C*H), 129.0 (*C*H), 127.8 (*C*H), 126.7 (*C*H), 124.8 (*C*H), 119.9 (*C*H), 119.7 (*C*H), 85.2 (*C*), 77.6 (*C*), 71.6 (*C*H), 29.4 (*C*H_2), 26.4 (*C*H_3), 19.4 (*C*). Anal. Calcd for $C_{33}H_{33}NO_3Si$: C, 76.27; H, 6.40; N, 2.70. Found: C, 76.61; H, 6.43; N, 2.91. The enantiomeric excess was determined by HPLC with a Daicel Chiralpak IC column (hexane/EtOH = 97/3), flow rate 0.5 mL/min, UV detection 254 nm, t_R (major) = 48.5 min, t_R (minor) = 54.3 min.

Synthesis and characterization of 4o

The reaction of *o*-(*tert*-butyldiphenylsilyloxy)benzaldehyde (35.0 mg, 0.0970 mmol) with **1b** (1.2 eq., 56.0 mg, 0.116 mmol) was performed at room temperature for 18 h. The crude material was purified by column chromatography (10% w/w K_2CO_3–silica gel, hexane/EtOAc = 6/1 to 4/1 to 1/1) to give **4o** (46.6 mg, 0.0841 mmol, 87%, 95:5 er) as a white solid: R_f = 0.47 (silica gel, hexane/EtOAc = 2/1); m.p. 82–83 °C; $[\alpha]_D^{21}$ -31.2 (*c* 1.00, $CHCl_3$); IR (KBr) 3375 (O–H), 3278 (O–H), 2233 (C≡C), 1648 (C=O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.80 (brs, 1H), 7.71-7.67 (m, 4H), 7.51-7.33 (m, 9H),

7.26-7.23 (m, 2H), 6.94-6.84 (m, 2H), 6.47 (dd, *J* = 7.5, 1.5 Hz, 1H), 5.52 (brs, 1H), 3.25 (brs, 1H), 3.04 (dd, *J* = 4.2, 17.1 Hz, 1H), 2.89 (dd, *J* = 7.5, 17.1 Hz, 1H), 1.12 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.9 (*C*), 150.8 (*C*), 135.9 (*C*H), 135.31 (*C*H), 135.26 (*C*H), 132.0 (*C*), 131.8 (*C*), 130.2 (*C*H), 129.7 (*C*), 129.0 (*C*H), 128.5 (*C*H), 128.02 (*C*H), 127.98 (*C*H), 126.3 (*C*H), 121.4 (*C*H), 121.0 (*C*H), 119.1 (*C*H), 85.7 (*C*), 77.6 (*C*), 67.8 (*C*H), 28.1 (CH_2), 26.6 (CH_3), 19.4 (*C*). Anal. Calcd for $C_{33}H_{32}ClNO_3Si$: C, 71.53; H, 5.82; N, 2.53. Found: C, 71.82; H, 5.63; N, 2.46. The enantiomeric excess was determined by HPLC with a Daicel Chiralpak IC column (hexane/EtOH = 98/2), flow rate 0.5 mL/min, UV detection 254 nm, t_R (major) = 26.7 min, t_R (minor) = 29.9 min.

Synthesis and characterization of 4p

The reaction of *o*-(*tert*-butyldiphenylsilyloxy)benzaldehyde (35.0 mg, 0.0970 mmol) with **1c** (1.2 eq., 55.5 mg, 0.116 mmol) was performed at room temperature for 18 h. The crude material was purified by column chromatography (10% w/w K_2CO_3–silica gel, hexane/EtOAc = 6/1 to 4/1 to 1/1) to give **4p** (47.3 mg, 0.0860 mmol, 89%, 96:4 er) as a white solid: R_f = 0.29 (silica gel, hexane/EtOAc = 2/1); m.p. 153-154 °C; $[\alpha]_D^{21}$ -31.2 (*c* 1.00, $CHCl_3$); IR (KBr) 3371 (O–H), 3285 (O–H), 2241 (C≡C), 1638 (C=O) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72-7.68 (m, 4H, Ar*H*), 7.58-7.33 (m, 9H, Ar*H*), 6.95-6.81 (m, 4H, Ar*H*), 6.47 (d, *J* = 7.8 Hz, 1H, Ar*H*), 5.51 (brs, 1H, C*H*), 3.78 (s, 3H, CH_3), 3.15 (brs, 1H, O*H*), 3.04 (d, *J* = 4.5, 17.1 Hz, 1H, CH_2), 2.88 (d, *J* = 7.5, 17.1 Hz, 1H, CH_2), 1.12 (s, 9H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.7 (*C*), 151.9 (*C*), 150.9 (*C*), 135.5 (*C*), 135.42 (*C*H), 135.36 (*C*H), 135.2 (*C*H), 132.1 (*C*), 131.93 (*C*), 131.85 (*C*), 130.4 (*C*H), 130.1 (*C*H), 128.4 (*C*H), 128.0

(*C*H), 126.4 (*C*H), 121.7 (*C*H), 121.3 (*C*H), 119.0 (*C*H), 114.1 (*C*H), 85.0 (*C*), 77.9 (*C*), 67.8 (*C*H), 67.7 (*C*H), 55.5 (CH_3), 55.4 (CH_3), 28.2 (CH_2), 26.7 (CH_3), 26.5 (CH_3), 19.4 (*C*). Anal. Calcd for $C_{34}H_{35}NO_4Si$: C, 74.28; H, 6.42; N, 2.55. Found: C, 74.14; H, 6.39; N, 2.95. The enantiomeric excess was determined by HPLC with a Daicel Chiralpak IC column (hexane/EtOH = 98/2), flow rate 0.5 mL/min, UV detection 254 nm, t_R (major) = 100.8 min, t_R (minor) = 108.4 min.

Synthesis and characterization of 4q

The reaction of *o*-(*tert*-butyldiphenylsilyloxy)benzaldehyde (35.0 mg, 0.0970 mmol) with **1d** (1.2 eq., 53.6 mg, 0.116 mmol) was performed at room temperature for 18 h. The crude material was purified by column chromatography (10% w/w K_2CO_3–silica gel, hexane/EtOAc = 6/1 to 4/1 to 1/1) to give **4q** (45.1 mg, 0.0845 mmol, 87%, 97:3 er) as a white solid: R_f = 0.41 (silica gel, hexane/EtOAc = 2/1); m.p. 149-150 °C; $[\alpha]_D^{25}$ -37.4 (*c* 1.00, $CHCl_3$); IR (KBr) 3275 (O–H), 2236 (C≡C), 1627 (C=O) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72-7.67 (m, 4H, Ar*H*), 7.58 (brs, 1H, N*H*), 7.52-7.33 (m, 9H, Ar*H*), 7.10 (d, *J* = 8.4 Hz, 2H, Ar*H*), 6.95-6.84 (m, 2H, Ar*H*), 6.61 (d, *J* = 6.6 Hz, 1H, Ar*H*), 5.51 (brs, 1H, C*H*), 3.13 (brs, 1H, O*H*), 3.04 (d, *J* = 4.5, 17.1 Hz, 1H, CH_2), 2.87 (d, *J* = 7.5, 17.1 Hz, 1H, CH_2), 2.30 (s, 3H, CH_3), 1.12 (s, 9H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.9 (*C*), 150.7 (*C*), 135.32 (*C*H), 135.27 (*C*H), 134.8 (*C*), 134.5 (*C*), 132.1 (*C*), 132.1 (*C*), 131.9 (*C*), 130.2 (*C*H), 129.5 (*C*H), 128.4 (*C*H), 128.0 (*C*H), 126.4 (*C*H), 121.3 (*C*H), 119.9 (*C*H), 119.1 (*C*H), 84.9 (*C*), 77.8 (*C*), 67.7 (*C*H), 28.2 (CH_2), 26.6 (CH_3), 20.9 (CH_3) 19.4 (*C*). Anal. Calcd for $C_{34}H_{35}NO_3Si$: C, 76.51; H, 6.61; N, 2.62. Found: C, 76.31; H, 6.68; N, 2.96. The enantiomeric excess was determined by HPLC with a

Daicel Chiralpak IC column (hexane/EtOH = 98/2), flow rate 0.5 mL/min, UV detection 254 nm, t_R (major) = 58.2 min, t_R (minor) = 62.7 min.

Synthesis and characterization of 5a

To a solution of **4a** (85.1 mg, 0.321 mmol, 94:6 er) in MeOH (0.64 mL) was added 5% Rh-Al_2O_3 (21.2 mg,). The resulting suspension was stirred for 1 hour under a hydrogen atmosphere at room temperature. The catalyst was removed by filtration through a pad of Celite and washed with EtOAc. The solvent was removed in vacuo and the residue was roughly purified by column chromatography (silica gel, hexane/EtOAc = 3/1 to 0/1) to give a crude material (78.1 mg). To a solution of this material in dry dichloromethane (1.5 mL) was added *p*-toluenesulfonic acid (monohydrate, 59.2 mg, 0.290 mmol). After stirring at room temperature for 4 hours, the reaction was quenched by addition of saturated aqueous $NaHCO_3$ (5 mL). The resulting mixture was extracted with EtOAc (20 mL×3), and the combined organic extracts were washed with brine (5 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo to give a crude material. This material was purified by column chromatography (silica gel, hexane/EtOAc = 5/1 to 3/1) to give **5a** (44.5 mg, 0.253 mmol, 79%, 95:5 er) as a white solid: R_f = 0.52 (silica gel, hexane/EtOAc = 1/1); m.p. 59-61 °C; $[\alpha]_D^{21}$ -32.6 (*c* 1.00, $CHCl_3$); IR (KBr) 1719 (C=O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.41-7.29 (m, 5H, Ar*H*), 5.35 (dd, *J* = 3.0, 10.2 Hz, 1H, C*H*), 2.73-2.50 (m, 2H, CH_2), 2.16 (m, 1H, CH_2), 2.02-1.79 (m, 3H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.2 (*C*), 139.6 (*C*), 128.4 (*C*H), 128.1 (*C*H), 125.6 (*C*H), 81.5 (*C*H), 30.4 (*C*H_2), 29.3 (*C*H_2), 18.4 (*C*H_2). Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86; N, 0.00. Found: C, 74.58; H, 6.53; N, 0.00.

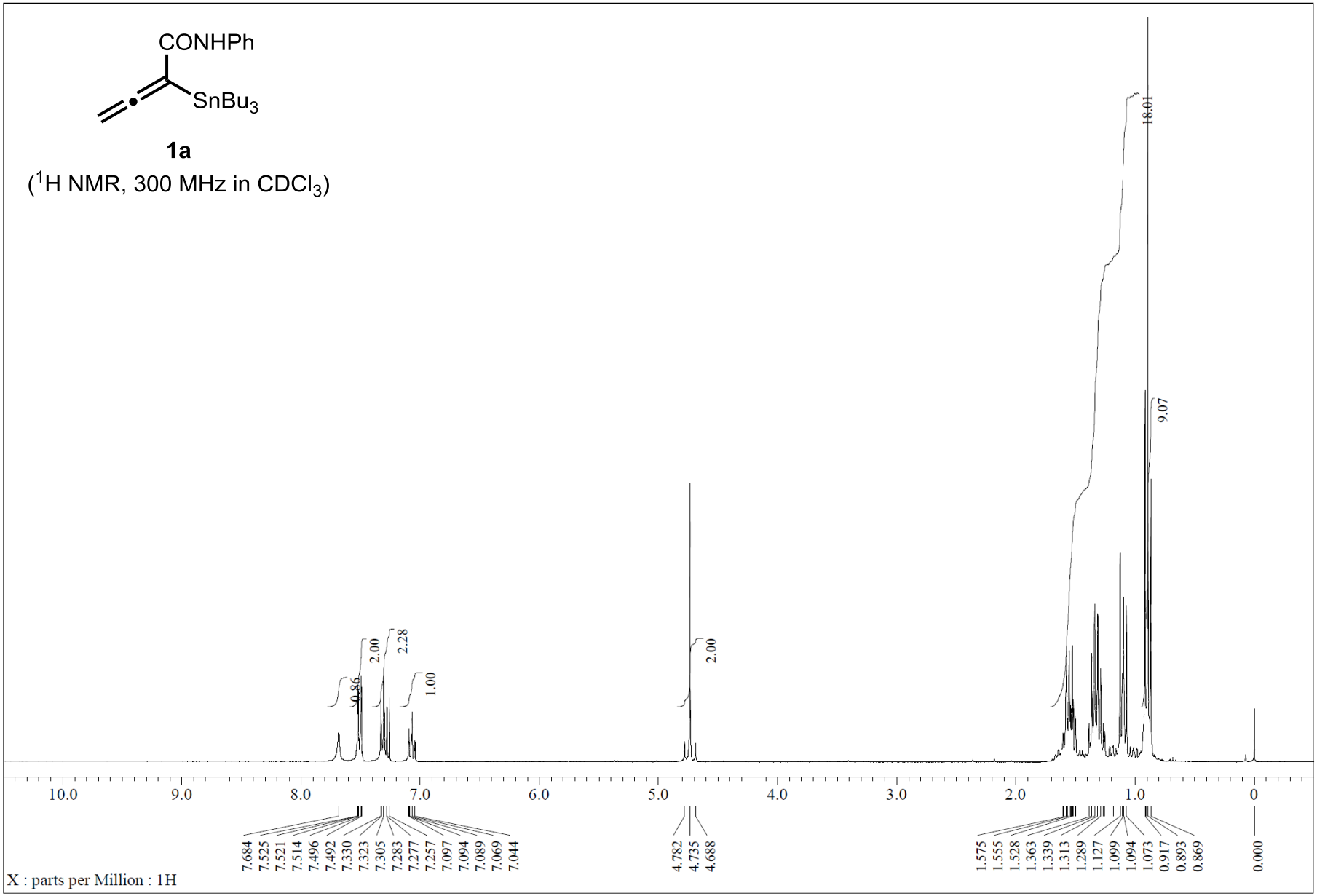
Synthesis and characterization of 7

To a solution of **4o** (20.0 mg, 0.0361 mmol, 95:5 er) in THF (0.18 mL) was added a solution of tetra-*n*-butylammonium fluoride (TBAF, 1.0 M in THF, 0.11 mL, 0.11 mmol) at 0 ºC. After stirring at the same temperature for 10 min, the reaction was quenched by addition of water (10 mL). The resulting mixture was extracted with EtOAc (20 mL×3), and the combined organic extracts were washed with brine (5 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo to give a crude material. This material was purified by column chromatography (silica gel, hexane/EtOAc = 2/1) to give **7** (9.8 mg, 0.0310 mmol, 86%, 93:7 er) as a white solid: R_f = 0.32 (silica gel, hexane/EtOAc = 1/1); m.p. 109-111 °C; $[\alpha]_D^{20}$ -34.5 (*c* 0.25, MeOH); IR (KBr) 3631 (O–H), 3457 (O–H), 2238 (C≡C), 1638 (C=O) cm^{-1}; ^1H NMR (300 MHz, CD_3OD) δ 7.56-7.51 (m, 2H, Ar*H*), 7.38 (dd, *J* = 1.5, 7.5 Hz, 1H, Ar*H*), 7.31-7.26 (m, 2H, CH, Ar*H*), 7.09 (dt, *J* = 1.5, 7.5 Hz, 1H, ArH), 6.84 (dt, *J* = 0.9, 7.5 Hz, 1H, Ar*H*), 6.76 (dd, *J* = 0.9, 8.1 Hz, 1H, Ar*H*), 5.21 (dd, *J* = 4.2, 7.5 Hz, 1H, C*H*), 2.90 (dd, *J* = 4.5, 17.1 Hz, 1H, CH_2), 2.72 (dd, *J* = 7.5, 17.1 Hz, 1H, CH_2); ^{13}C NMR (75 MHz, CD_3OD) δ 155.2 (*C*), 153.5 (*C*), 138.3 (*C*), 130.4 (*C*), 130.3 (*C*), 129.9 (*C*H), 129.5 (*C*H), 127.4 (*C*H), 122.4 (*C*H), 120.5 (*C*H), 116.0 (*C*H), 87.7 (*C*), 77.7 (*C*), 68.5 (*C*H), 28.5 (*C*H_2). Anal. Calcd for $C_{17}H_{16}ClNO_4$: C, 61.18; H, 4.83; N, 4.20. Found: C, 61.55; H, 5.21; N, 4.25. The enantiomeric excess was determined by HPLC with a Daicel Chiralpak IG column (hexane/EtOH = 80/20), flow rate 0.5 mL/min, UV detection 254 nm, t_R (major) = 21.7 min, t_R (minor) = 14.9 min.

References

[1] R. Karmakar, S. Y. Yun, J. Chen, Y. Xia, D. Lee, *Angew. Chmem. Int Ed*. **2015**, *54*, 6582–6586.

[2] (a) M. Takahashi, Y. Murata, F. Yagishita, M. Sakamoto, T. Sengoku, H. Yoda, *Chem. Eur. J.* **2014**, *20*, 11091–11100; (b) M. Takahashi, Y. Murata, M. Ishida, F. Yagishita, M. Sakamoto, T. Sengoku, H. Yoda, *Org. Biomol. Chem.* **2014**, *12*, 7686–7689.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8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
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7.525
7.521
7.514
7.496
7.492
7.330
7.323
7.305
7.283
7.277
7.257
7.097
7.094
7.089
7.069
7.044
4.782
4.735
4.688
1.575
1.555
1.528
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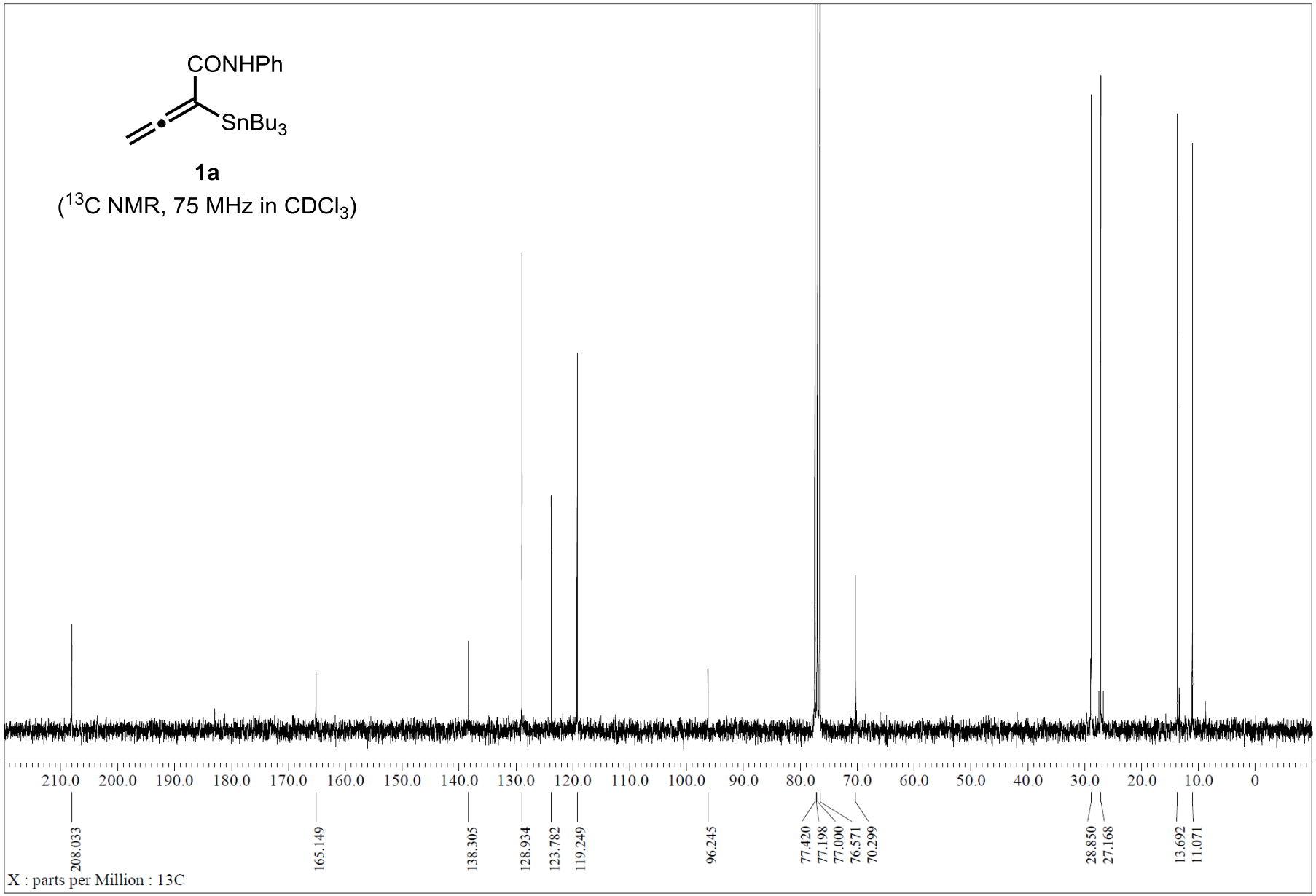
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165.149
138.305
128.934
123.782
119.249
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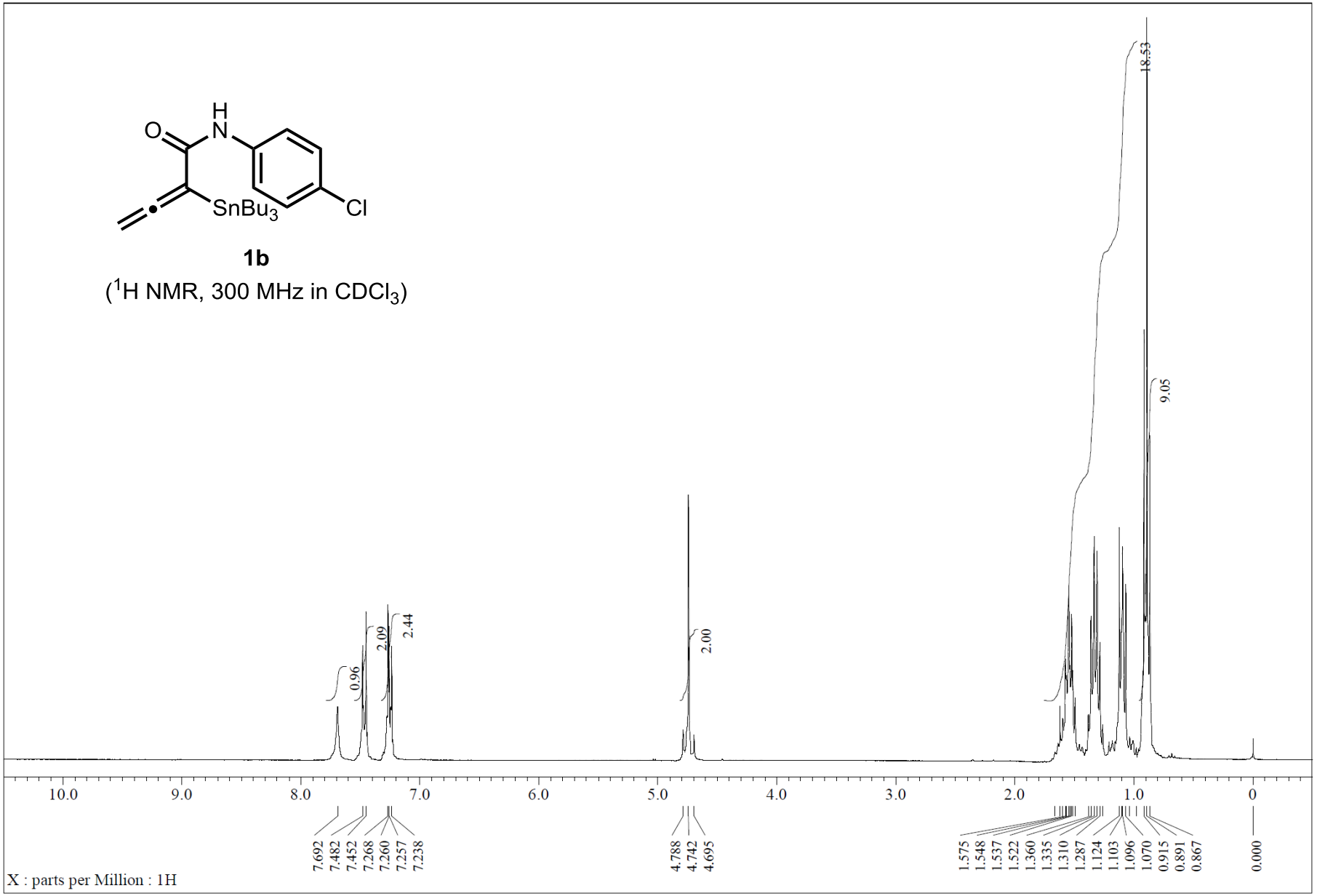
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7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.692
7.482
7.452
7.268
7.260
7.257
7.238
4.788
4.742
4.695
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1.522
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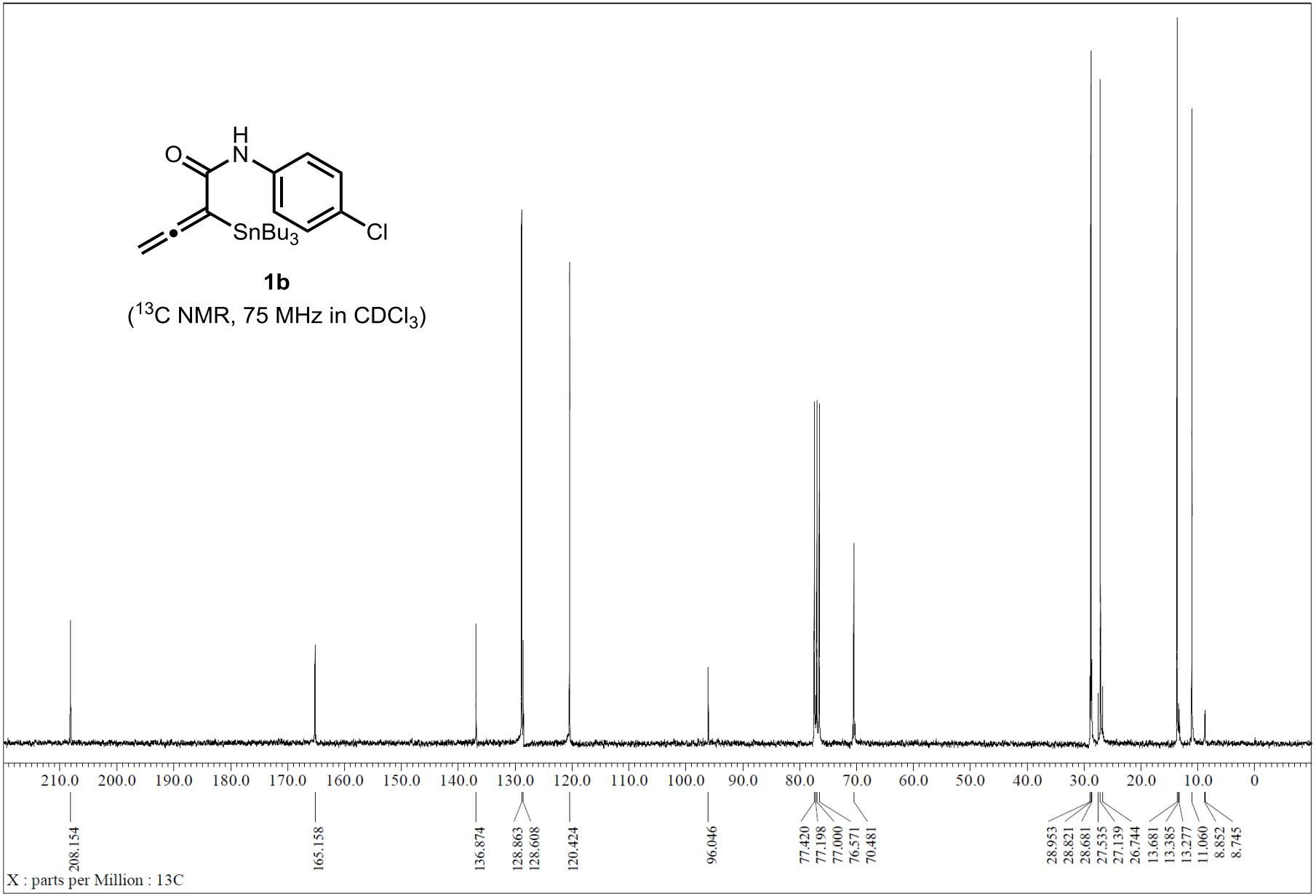
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N
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77.198
77.000
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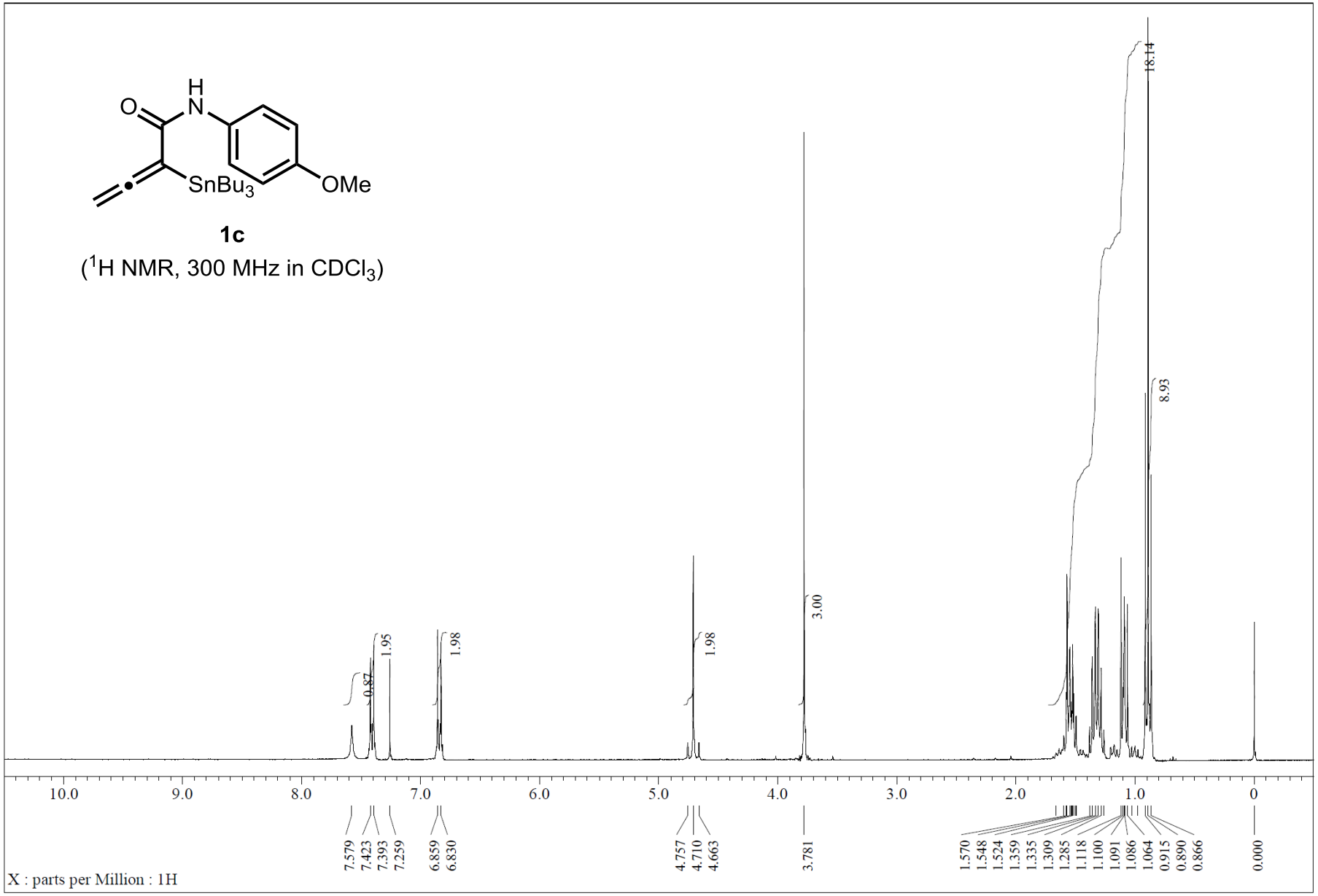
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7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
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7.393
7.259
6.859
6.830
4.757
4.710
4.663
3.781
1.570
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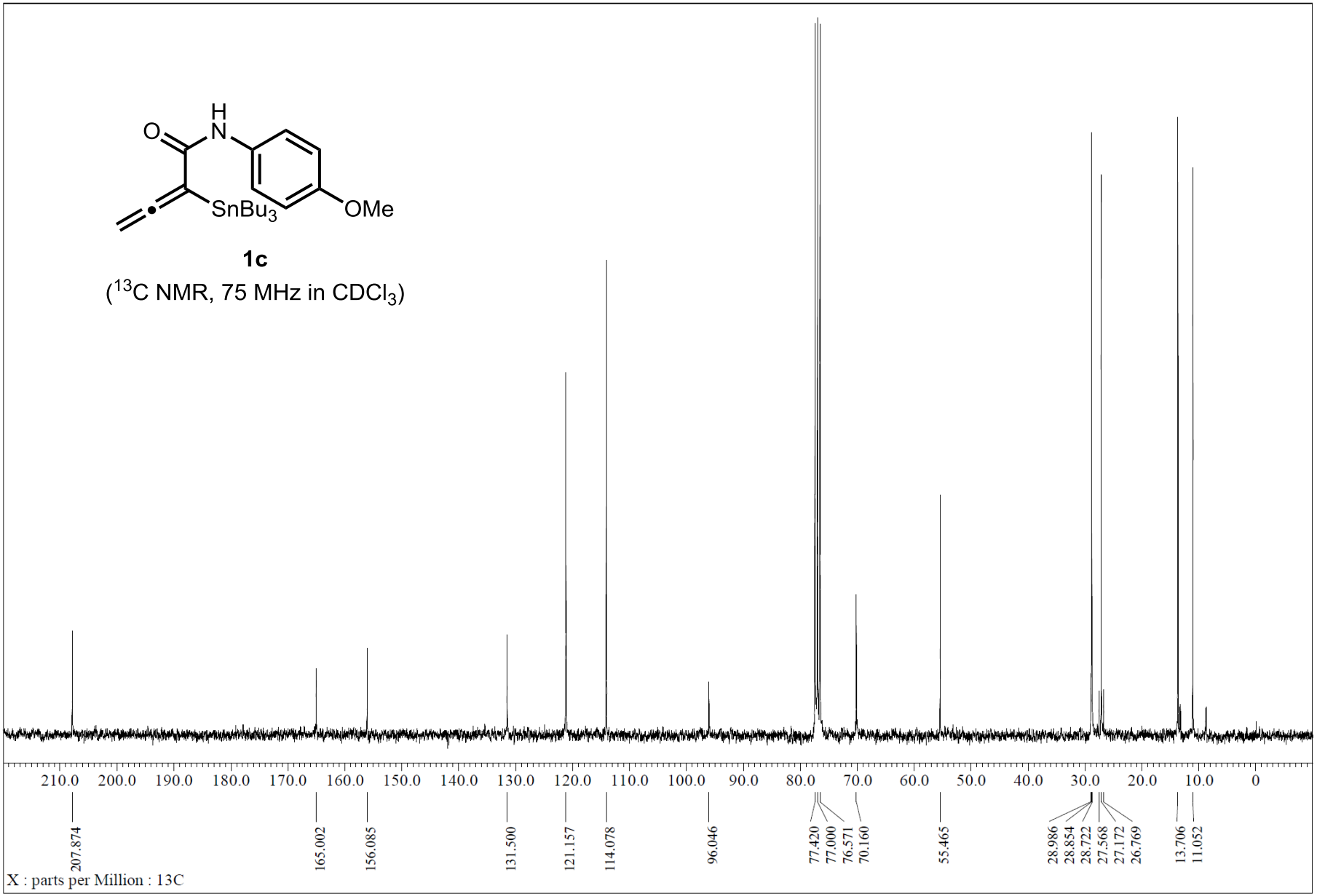
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N
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165.002
156.085
131.500
121.157
114.078
96.046
77.420
77.000
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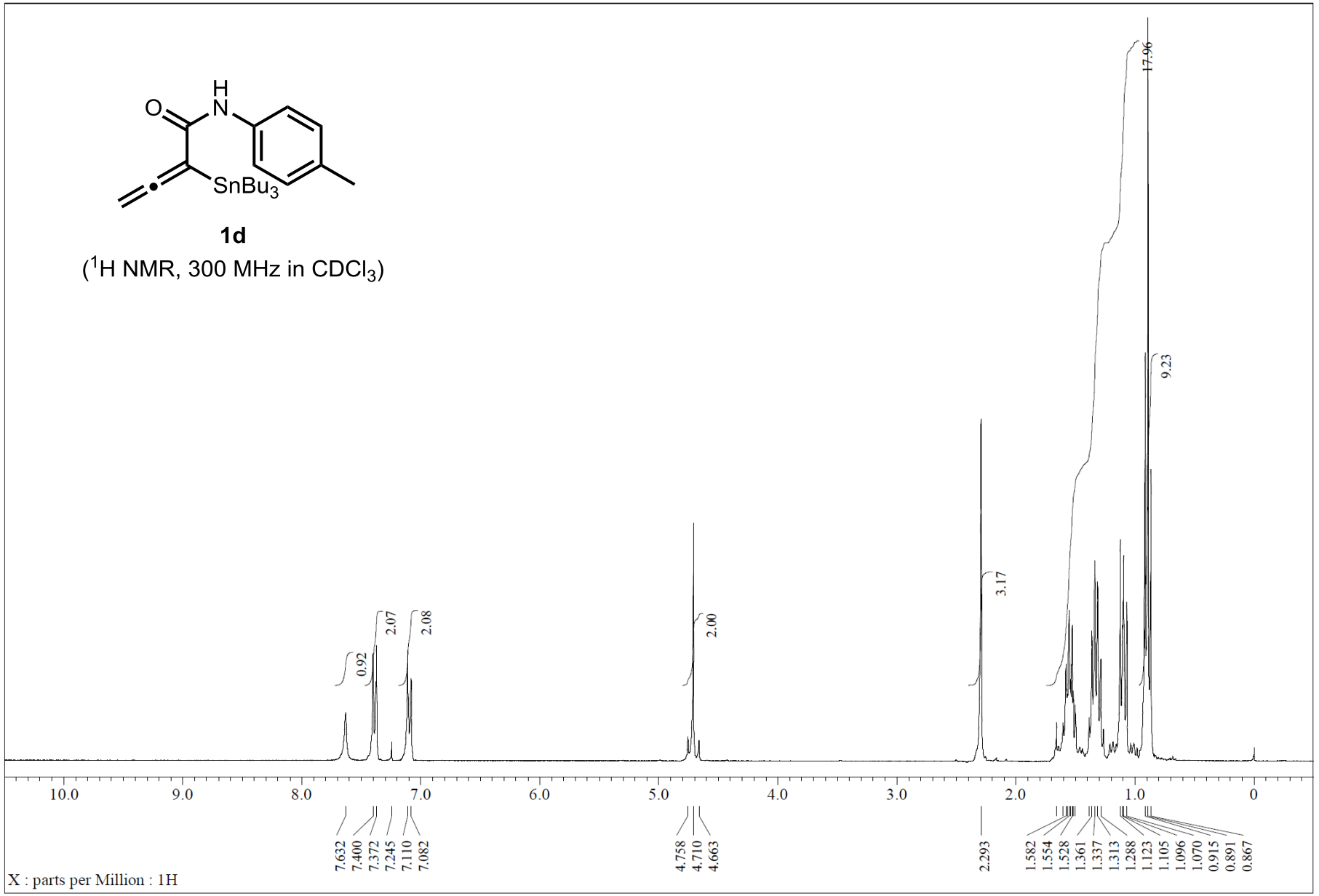
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8.0
7.0
6.0
5.0
4.0
3.0
2.0
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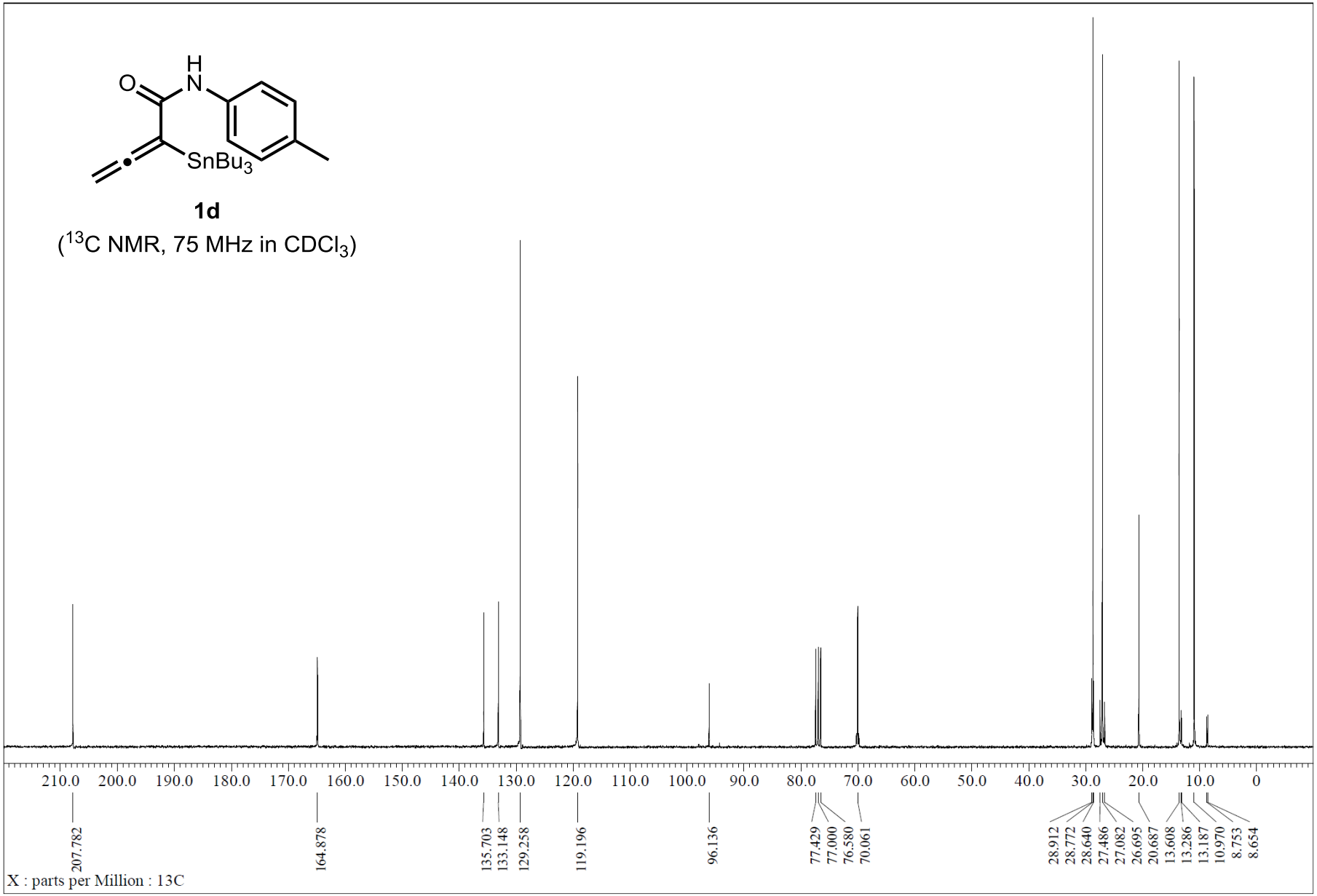
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135.703
133.148
129.258
119.196
96.136
77.429
77.000
76.580
70.061
28.912
28.772
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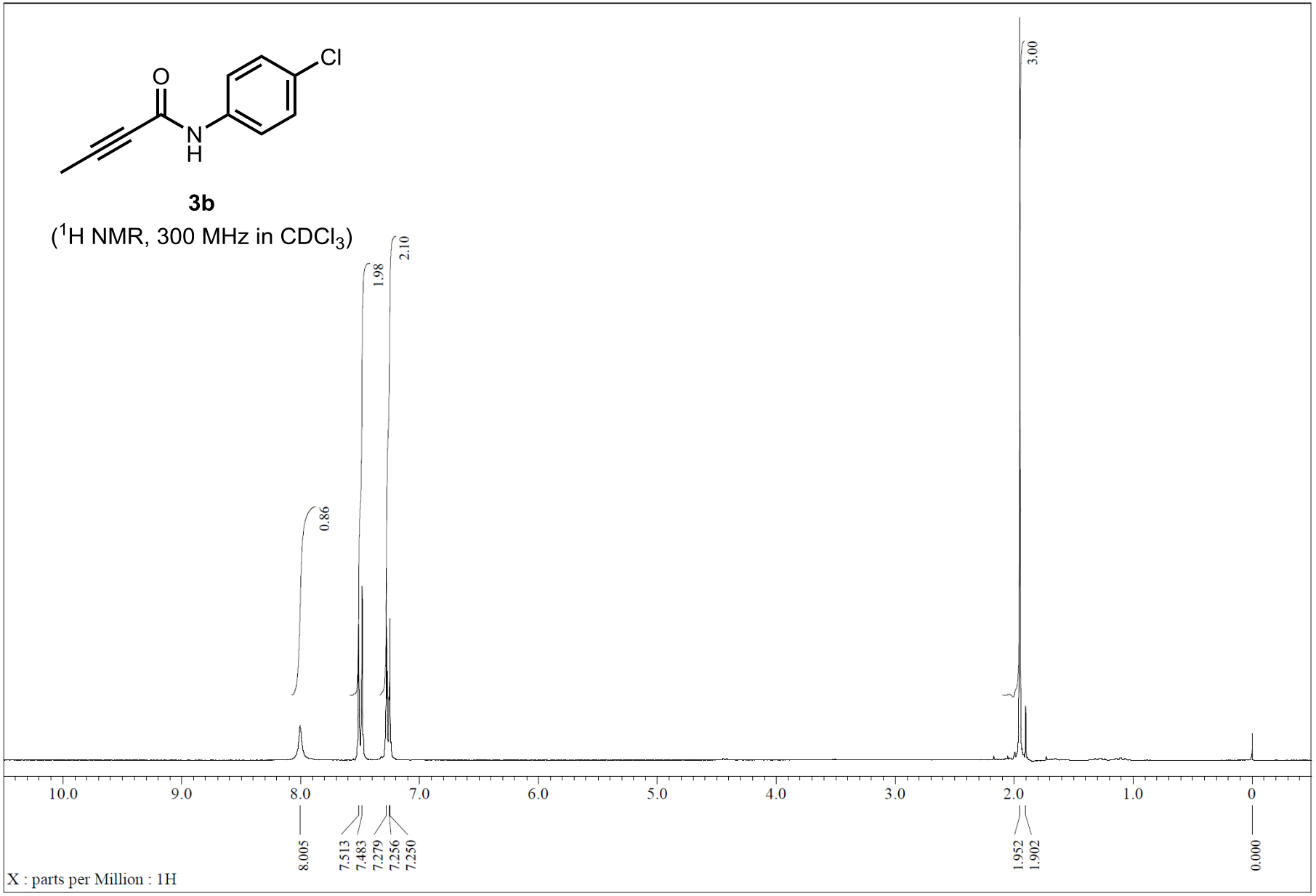
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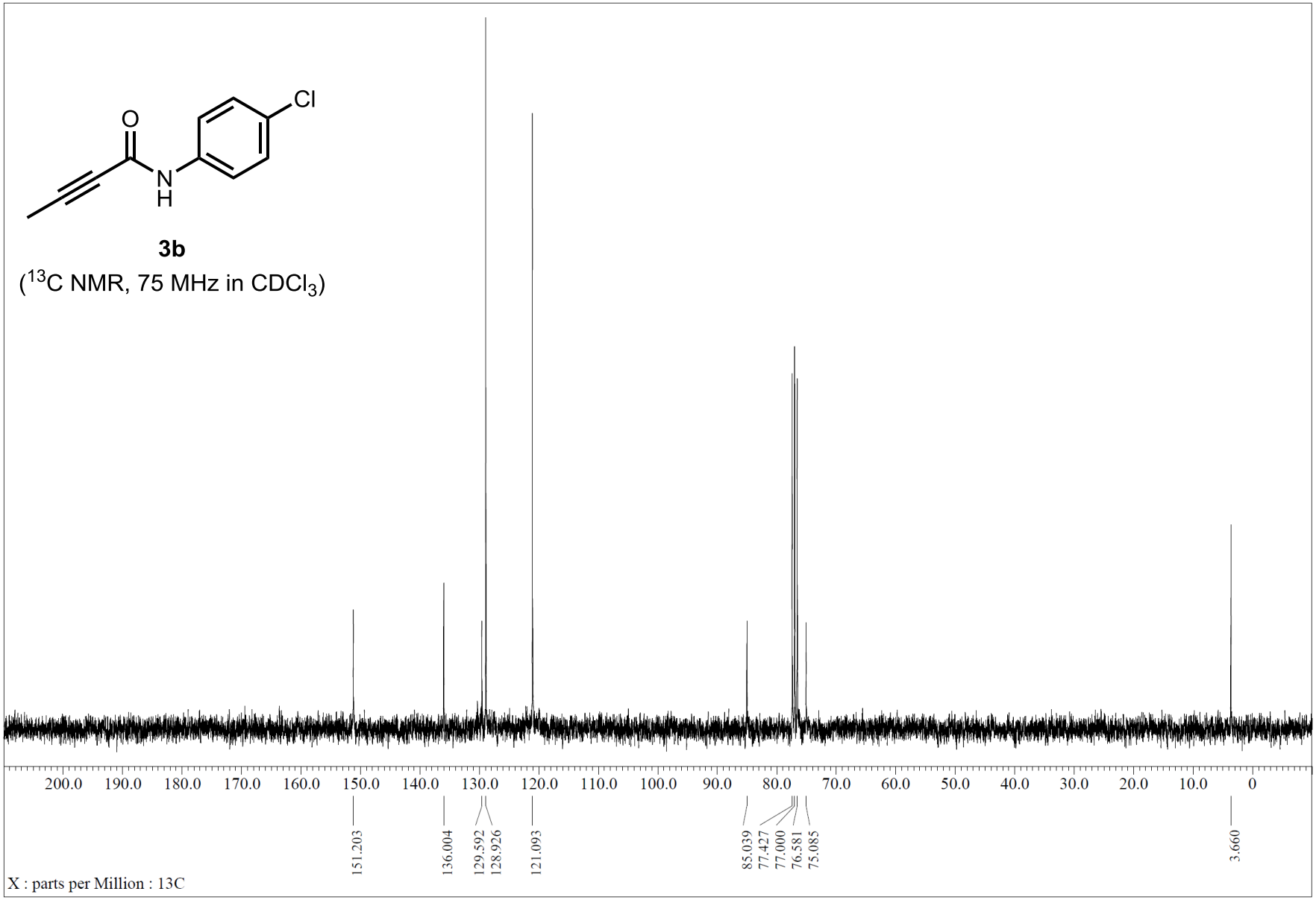
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100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
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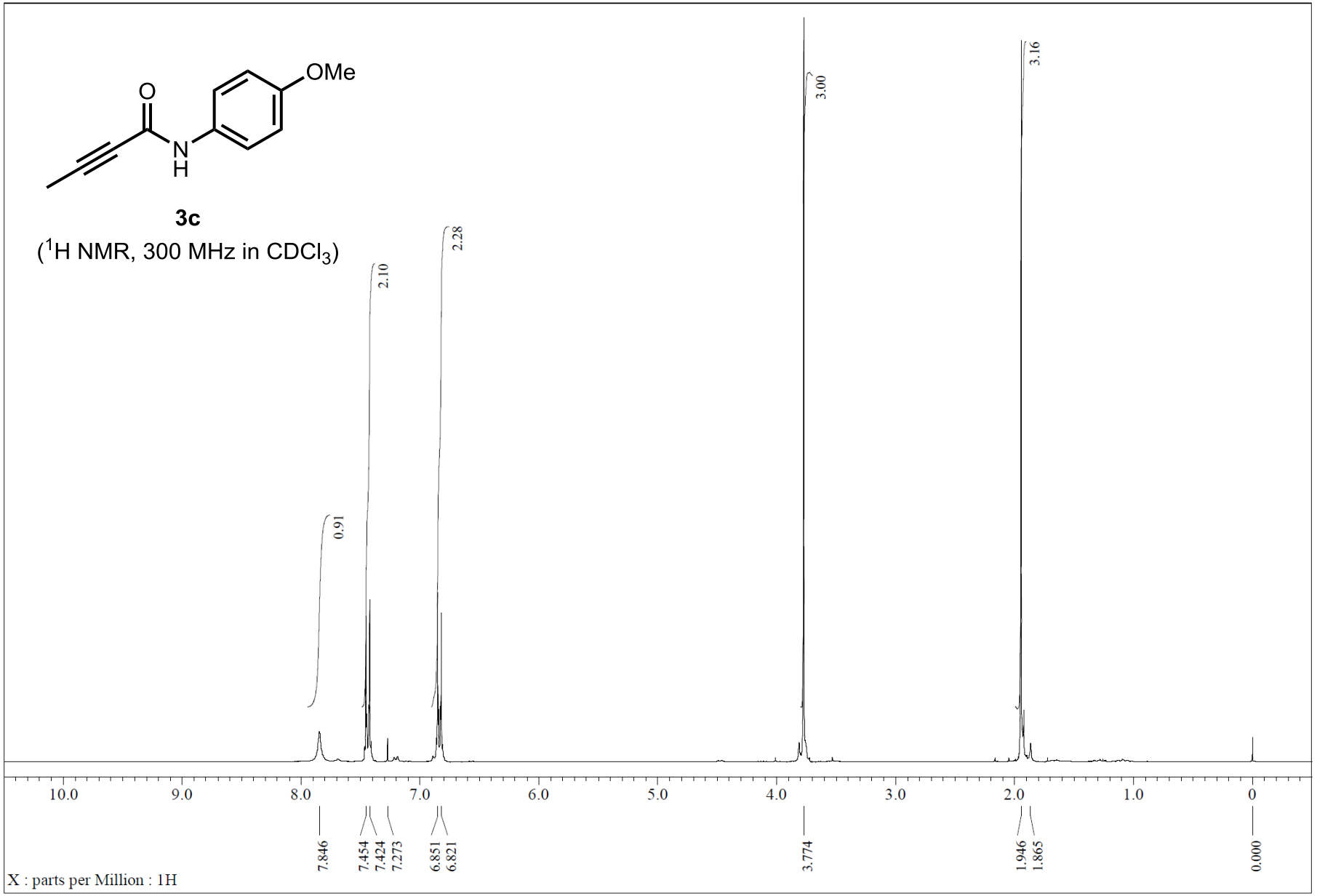
X : parts per Million : 13C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2.0
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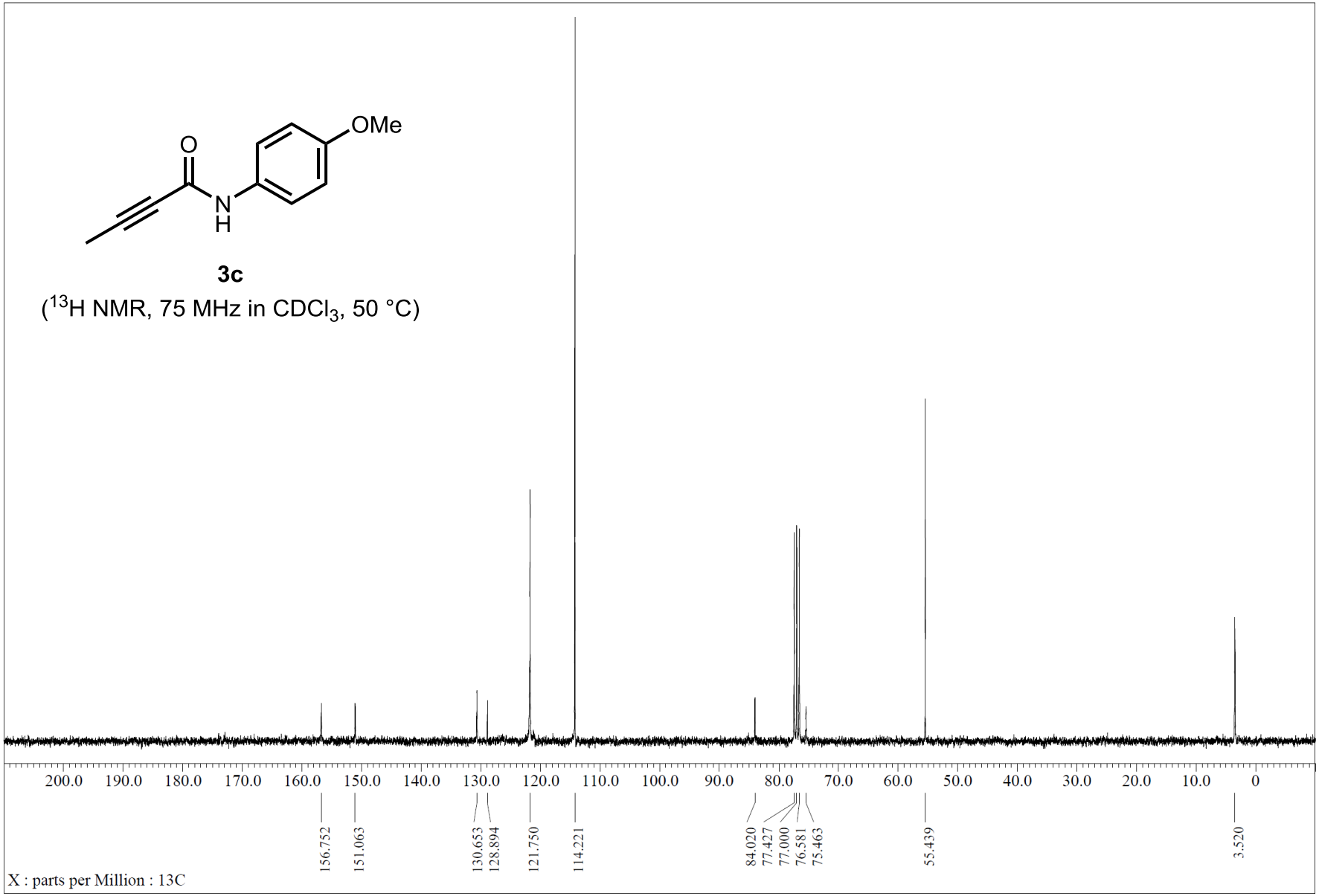
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H
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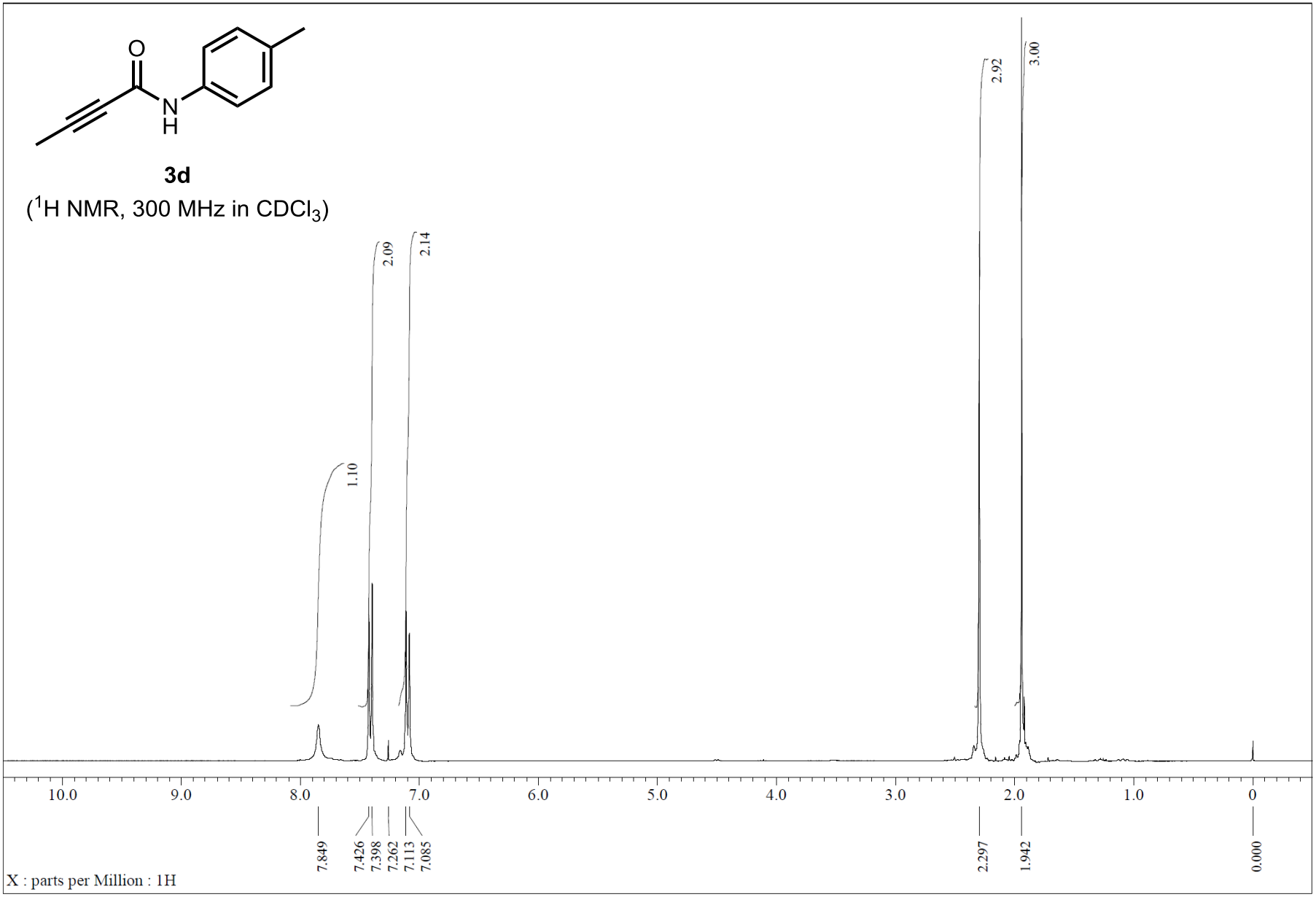
X : parts per Million : 13C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7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
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7.426
7.398
7.262
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7.085
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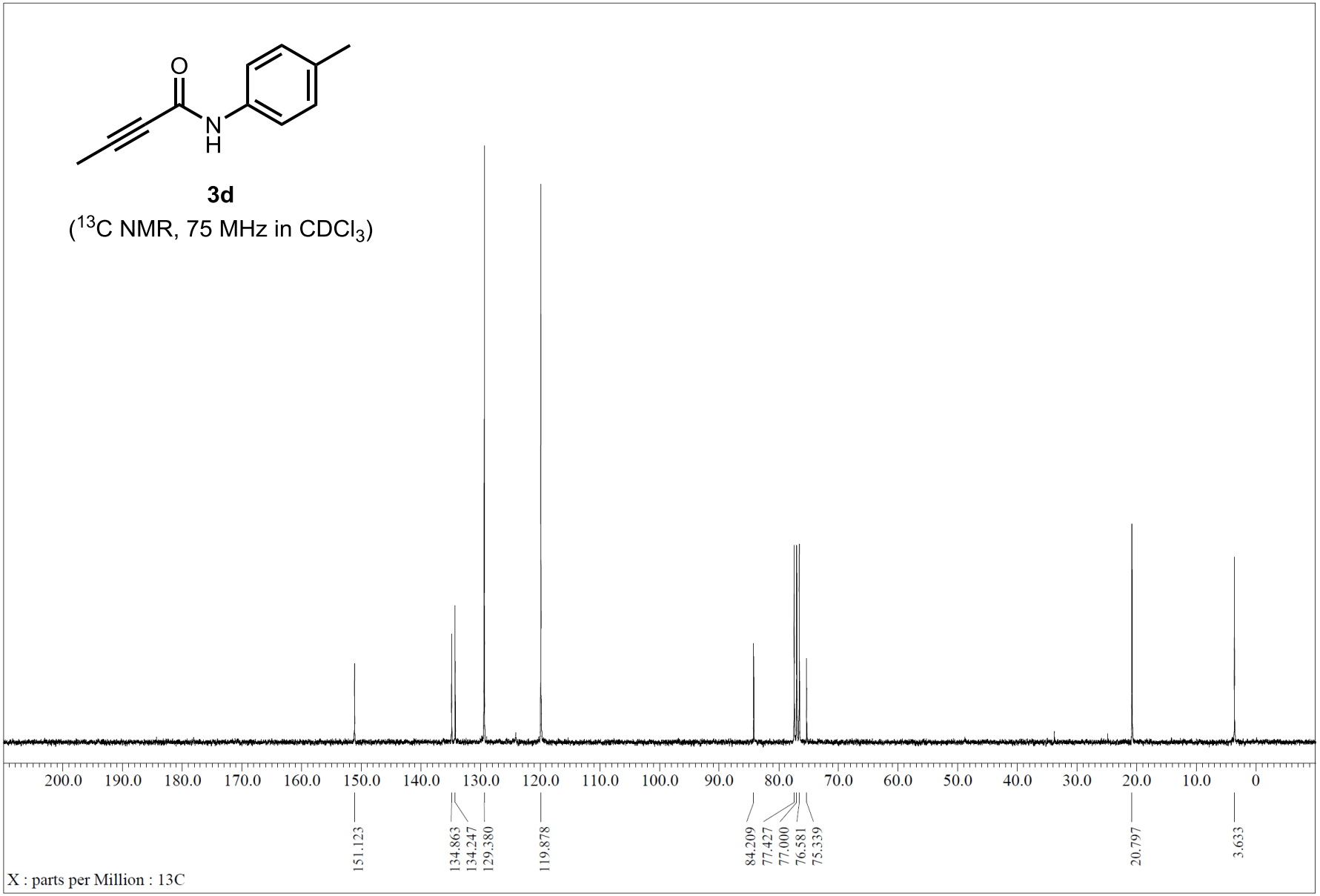
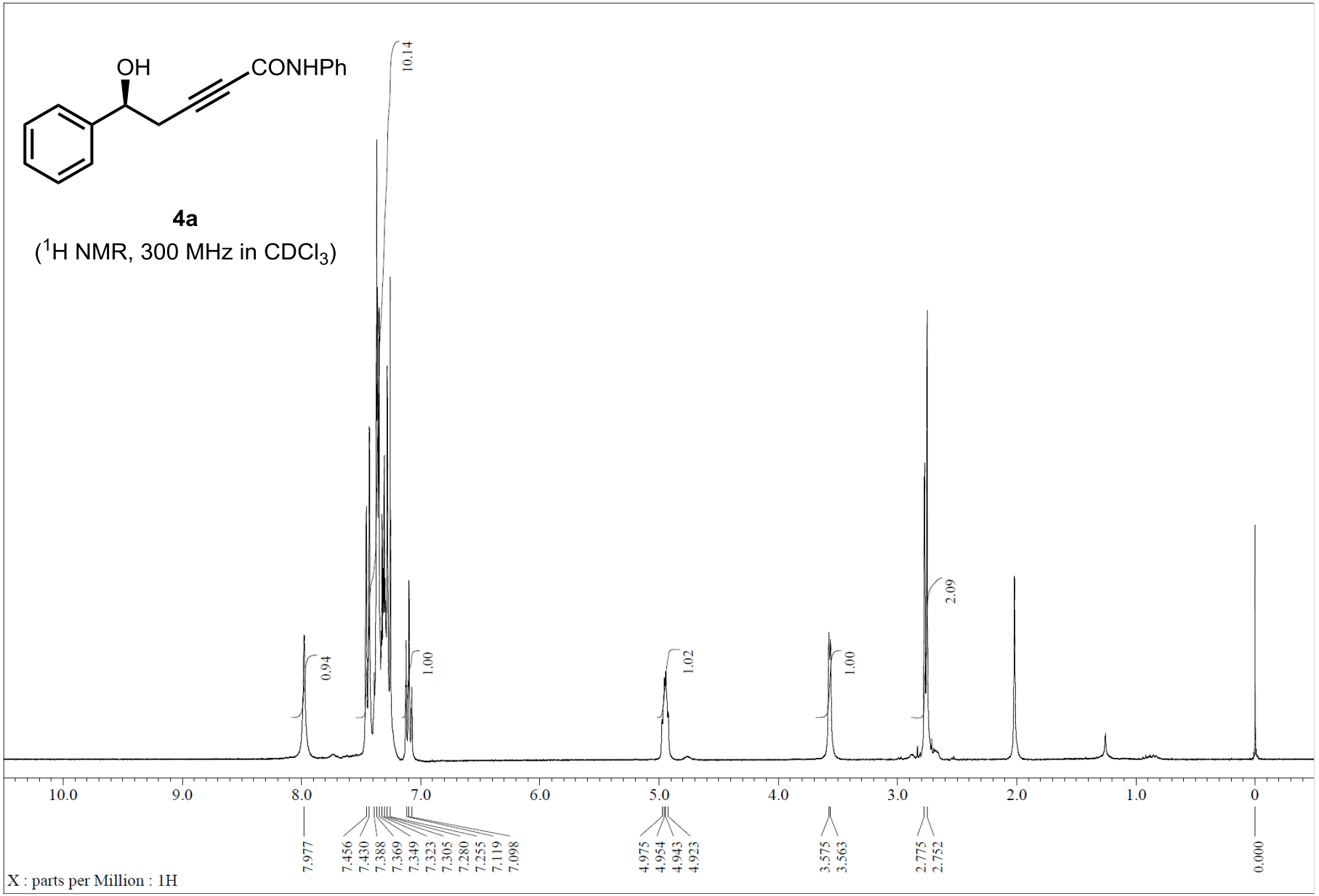
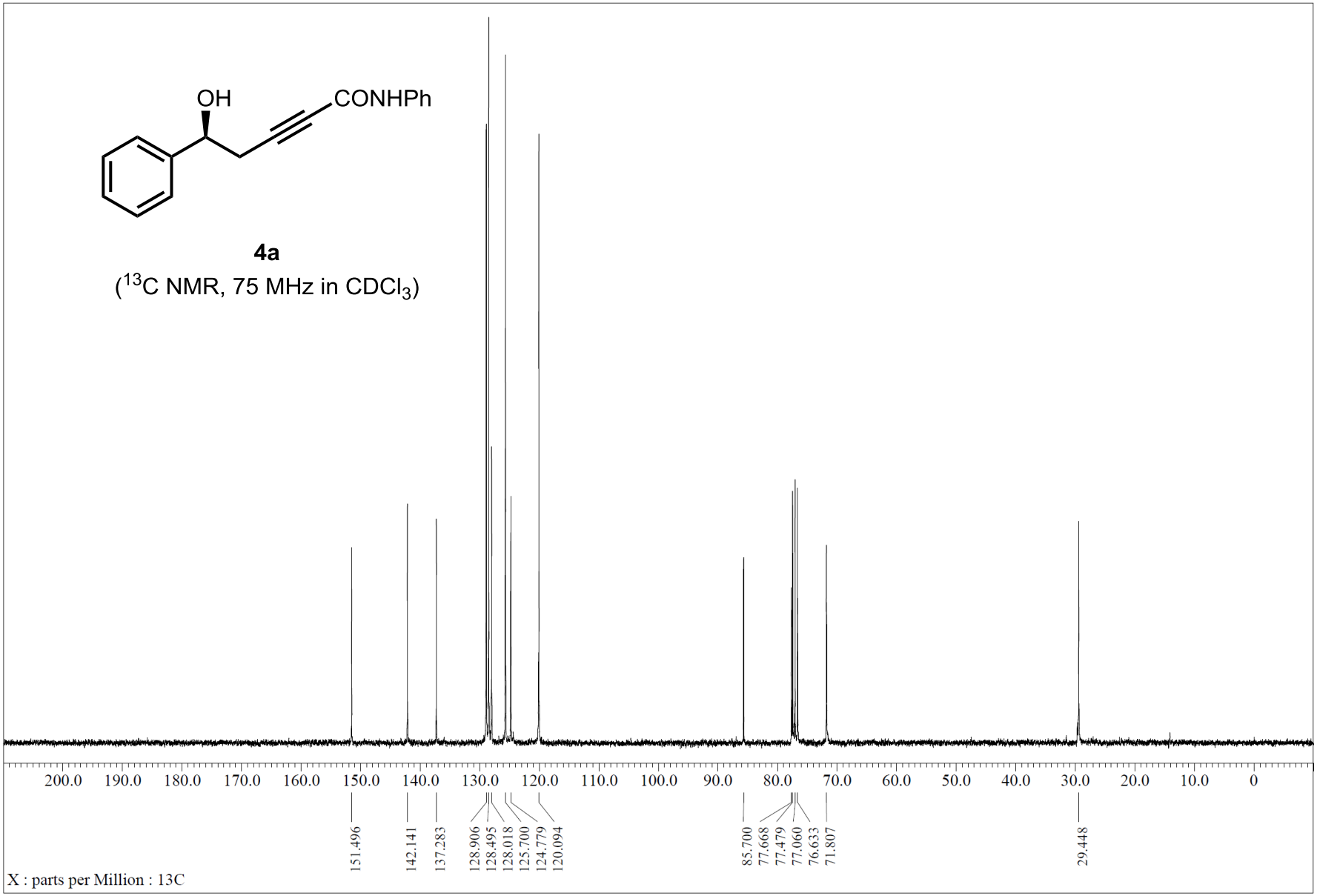
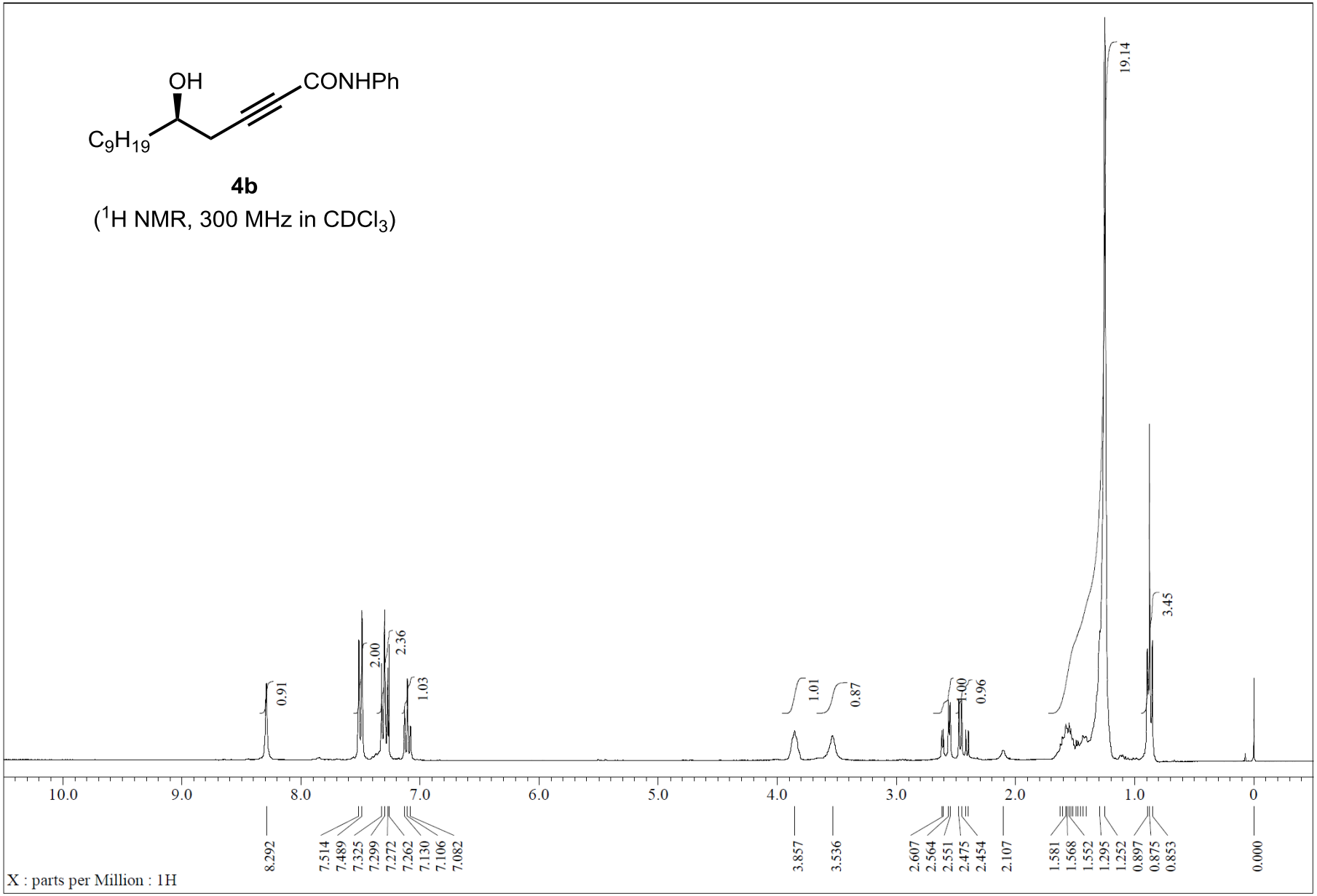
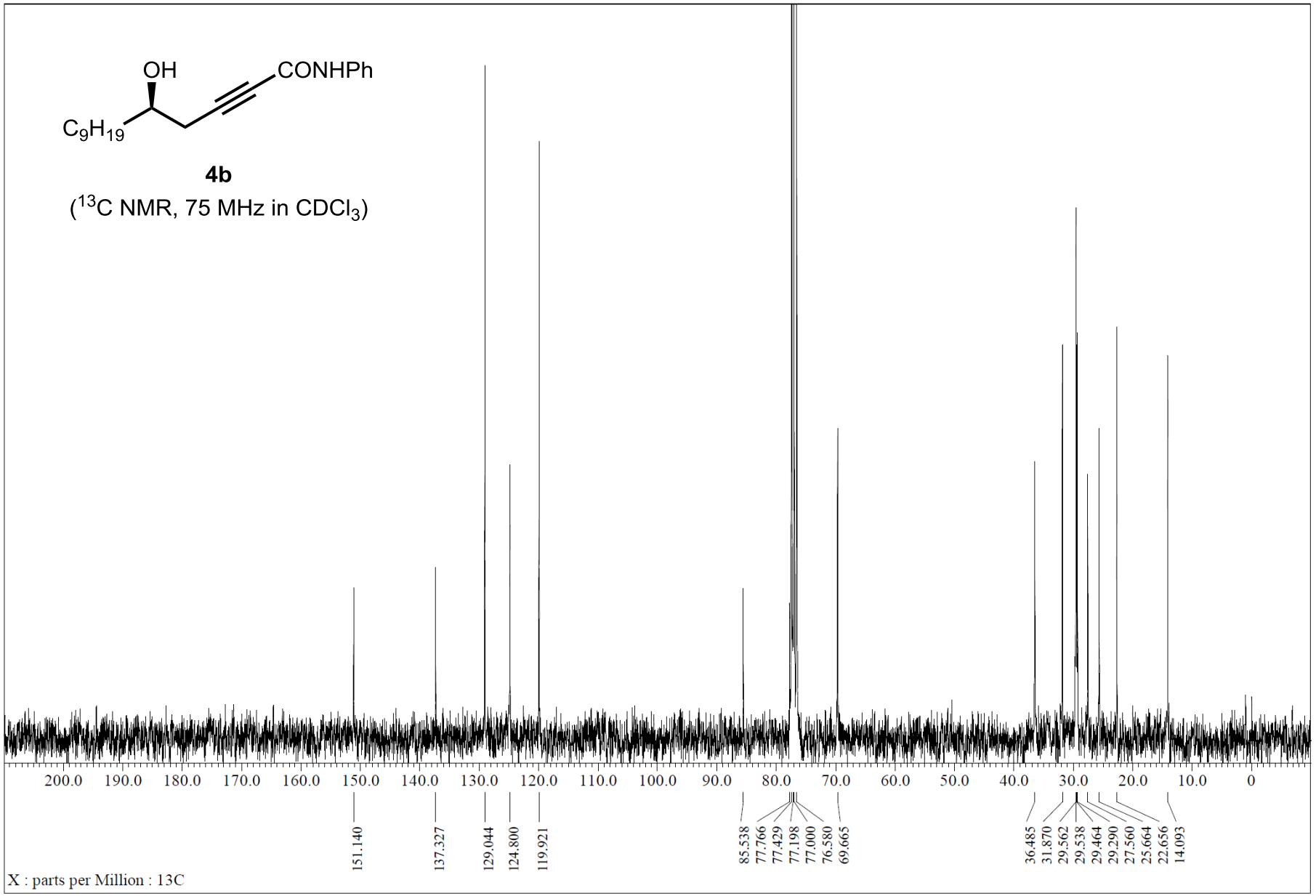
1.942
0.000
X : parts per Million : 1H

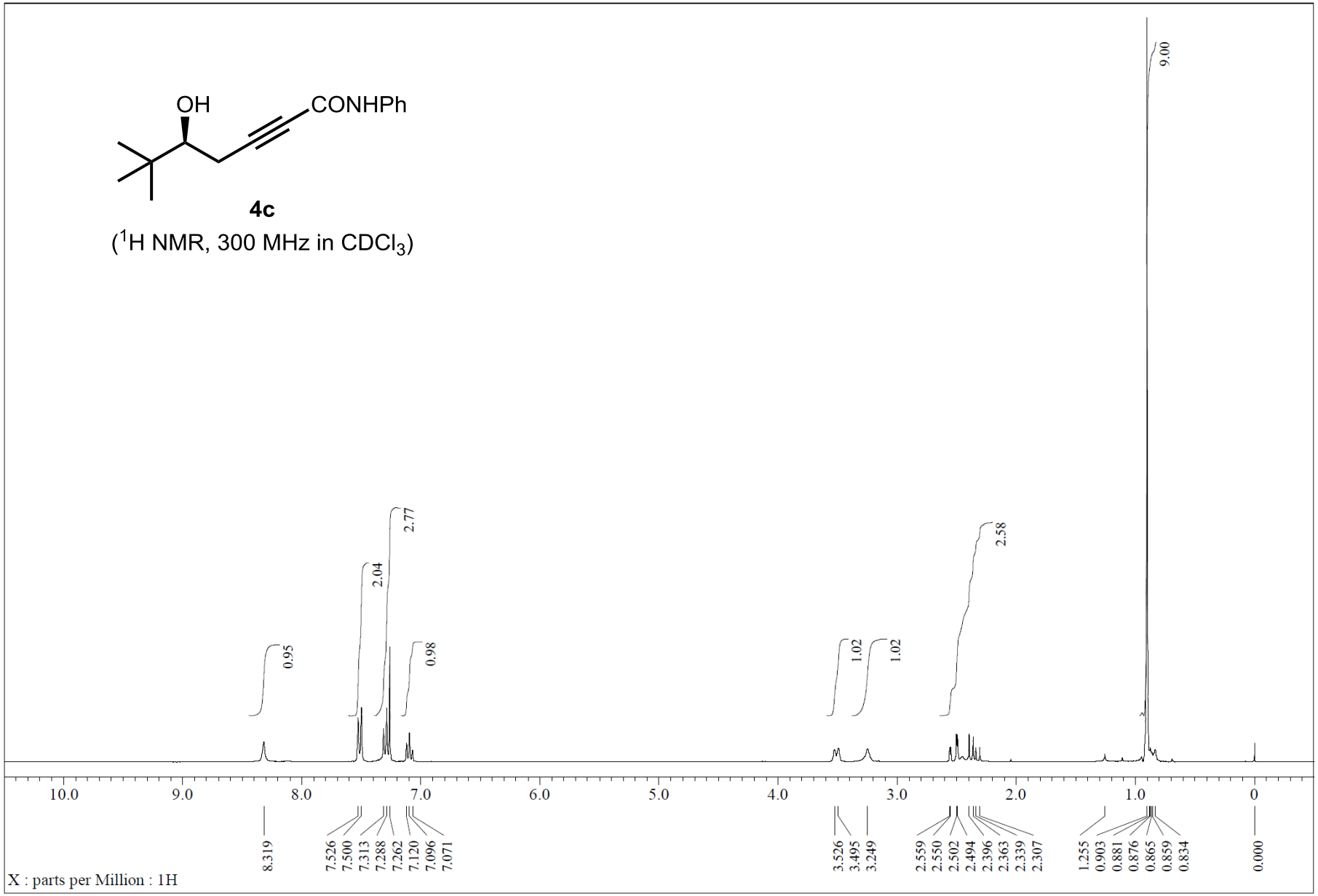

O
N
H
3d
(13C NMR, 75 MHz in CDCl3)
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
151.123
134.863
134.247
129.380
119.878
84.209
77.427
77.000
76.581
75.339
20.797
3.633
X : parts per Million : 13C

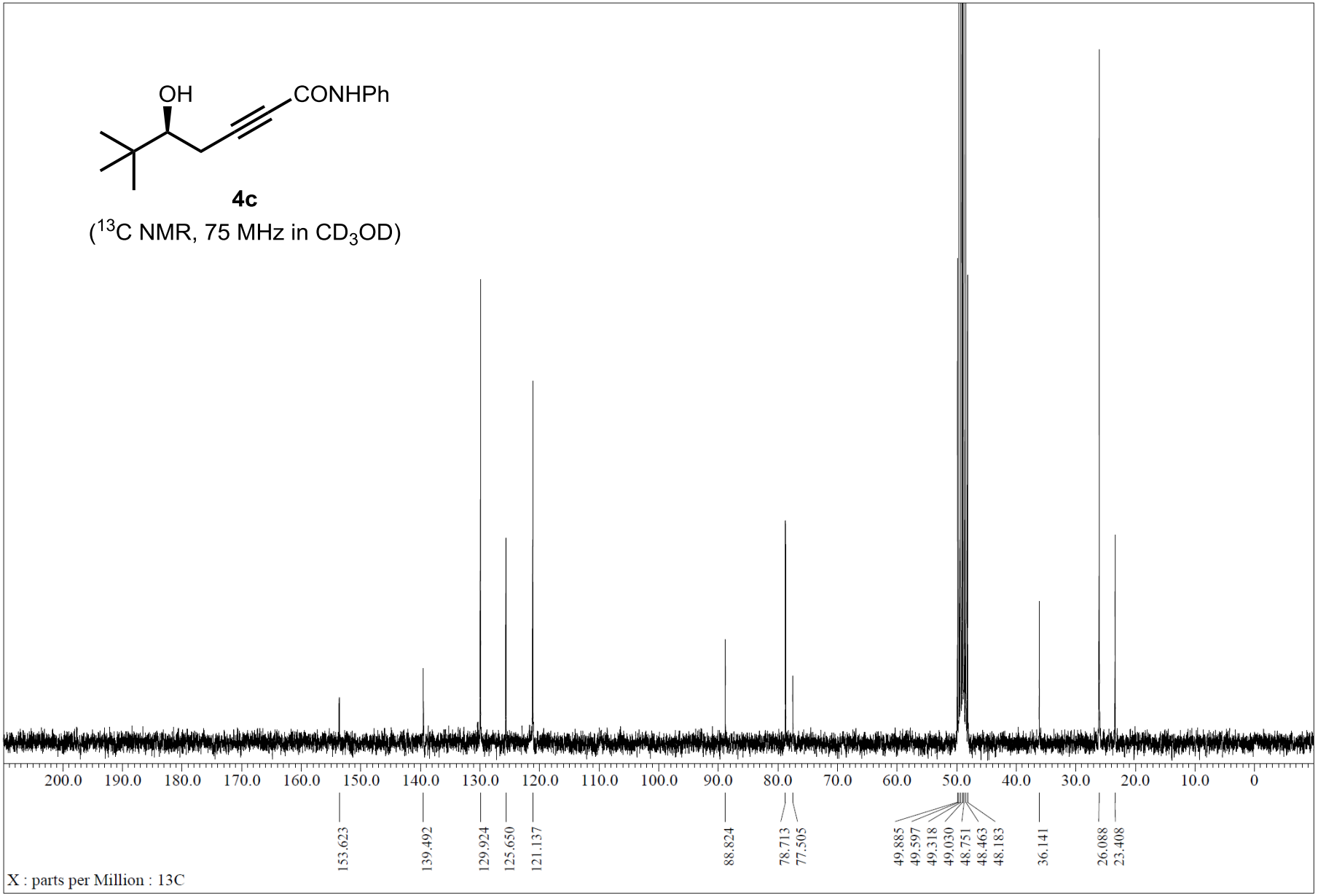

OH
CONHPh
4a
(1H NMR, 300 MHz in CDCl3)
10.14
0.94
1.00
1.02
1.00
2.09
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.977
7.456
7.430
7.388
7.369
7.349
7.323
7.305
7.280
7.255
7.119
7.098
4.975
4.954
4.943
4.923
3.575
3.563
2.775
2.752
0.000
X : parts per Million : 1H

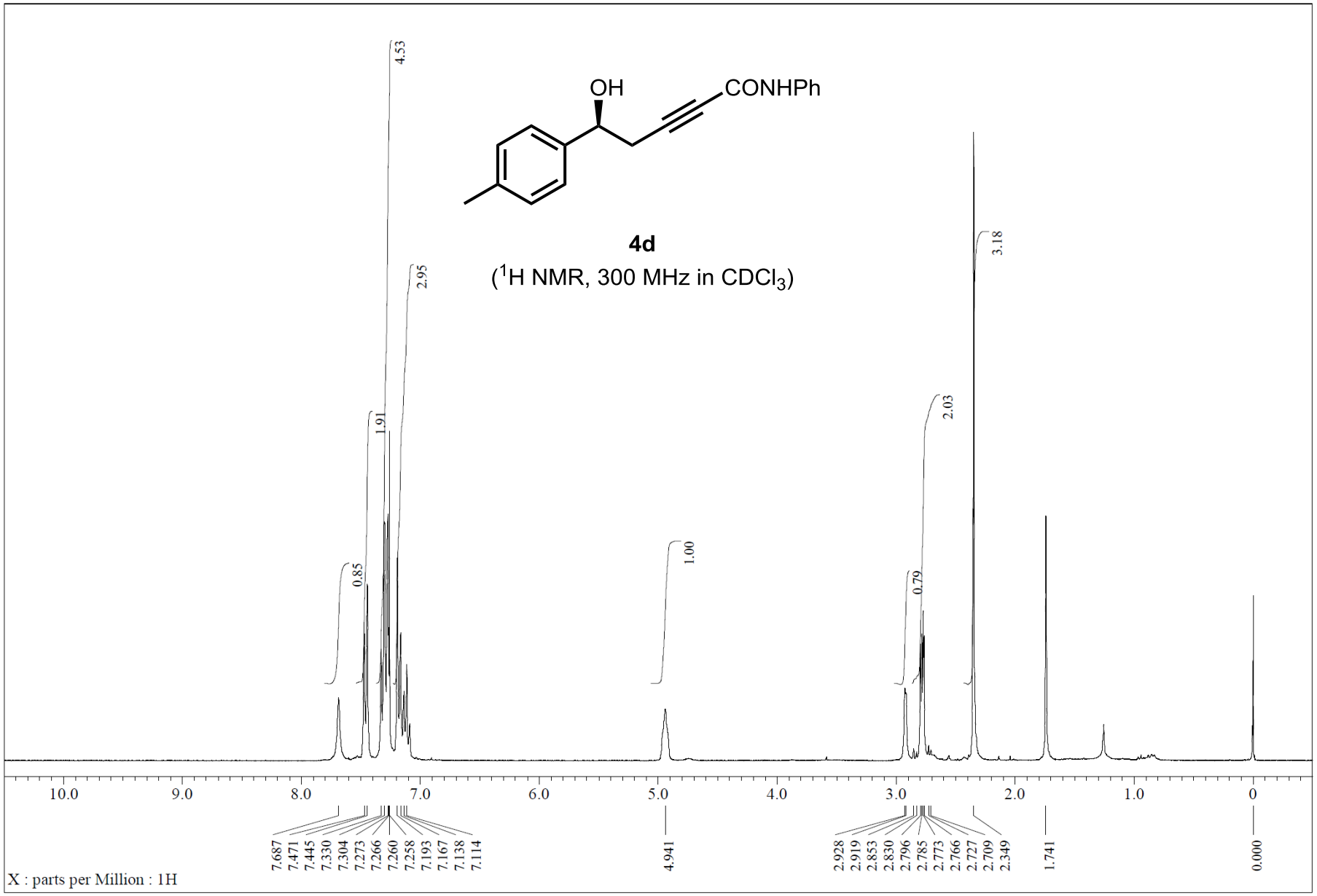

OH
CONHPh
4a
(13C NMR, 75 MHz in CDCl3)
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
151.496
142.141
137.283
128.906
128.495
128.018
125.700
124.779
120.094
85.700
77.668
77.479
77.060
76.633
71.807
29.448
X : parts per Million : 13C

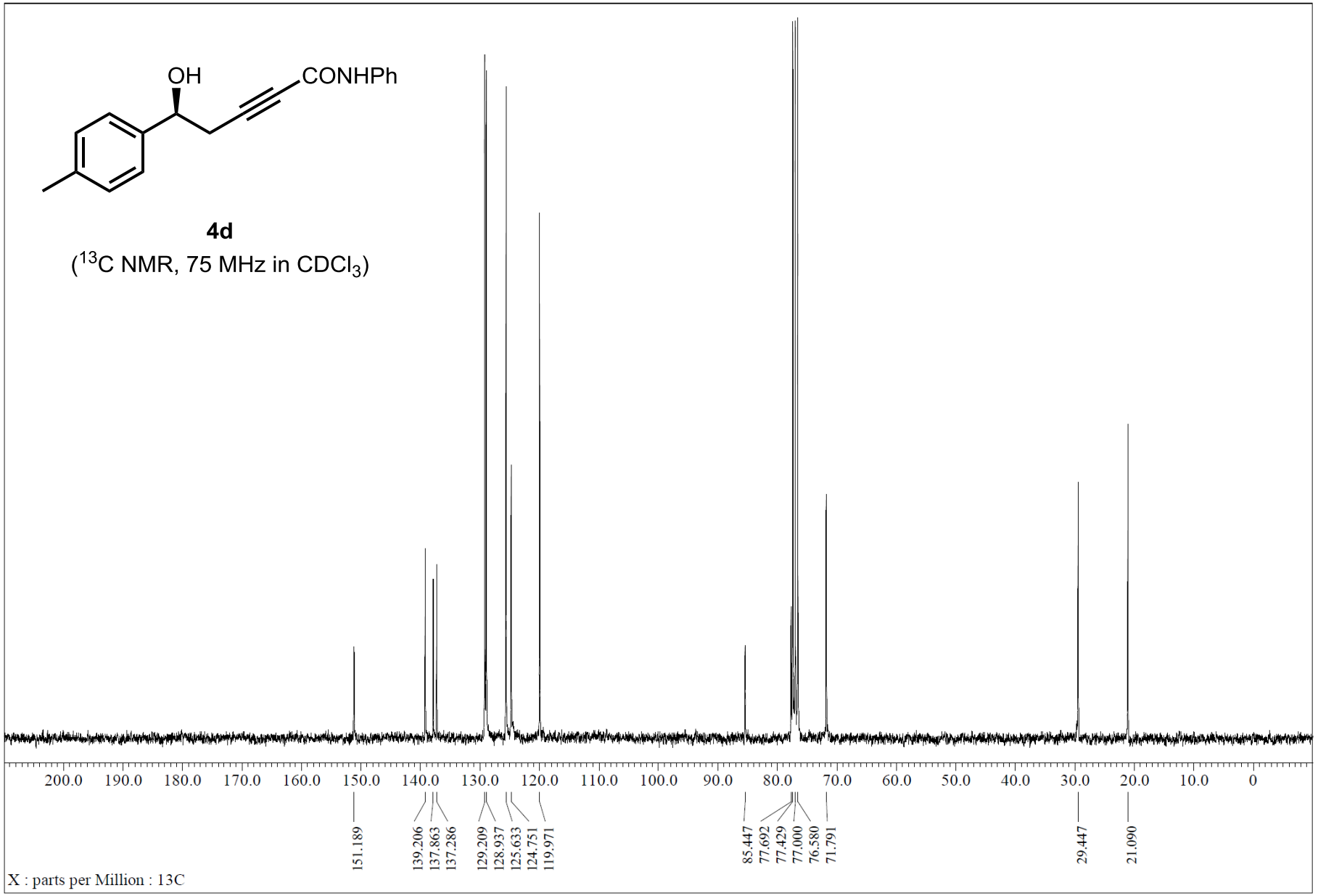

OH
CONHPh
C9H19
4b
(1H NMR, 300 MHz in CDCl3)
19.14
3.45
0.91
2.00
2.36
1.03
1.01
0.87
1.00
0.96
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.292
7.514
7.489
7.325
7.299
7.272
7.262
7.130
7.106
7.082
3.857
3.536
2.607
2.564
2.551
2.475
2.454
2.107
1.581
1.568
1.552
1.295
1.252
0.897
0.875
0.853
0.000
X : parts per Million : 1H

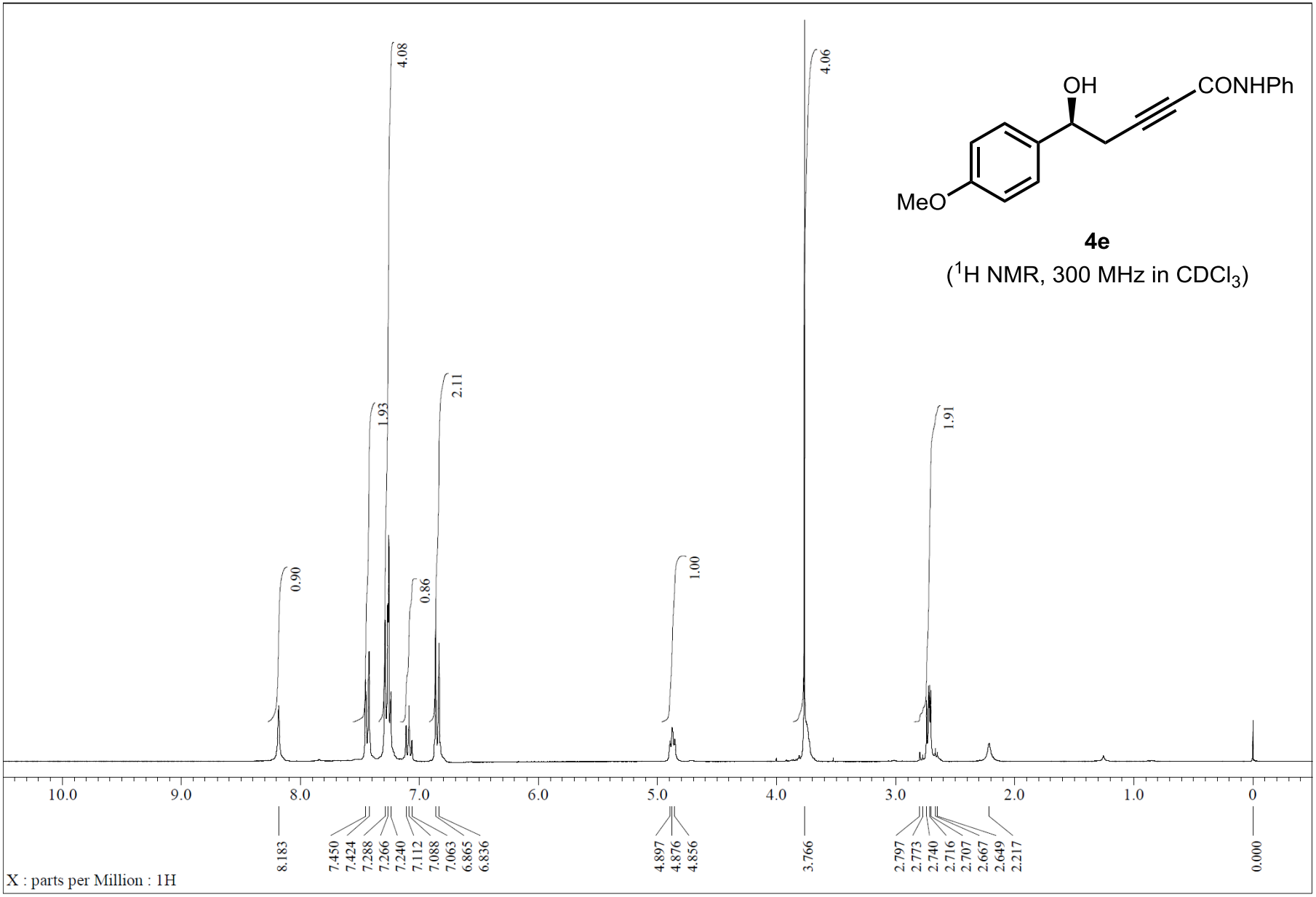

OH
CONHPh
C_9H_{19}
4b
(^{13}C NMR, 75 MHz in $CDCl_3$)
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
151.140
137.327
129.044
124.800
119.921
85.538
77.766
77.429
77.198
77.000
76.580
69.665
36.485
31.870
29.562
29.538
29.464
29.290
27.560
25.664
22.656
14.093
X : parts per Million : 13C

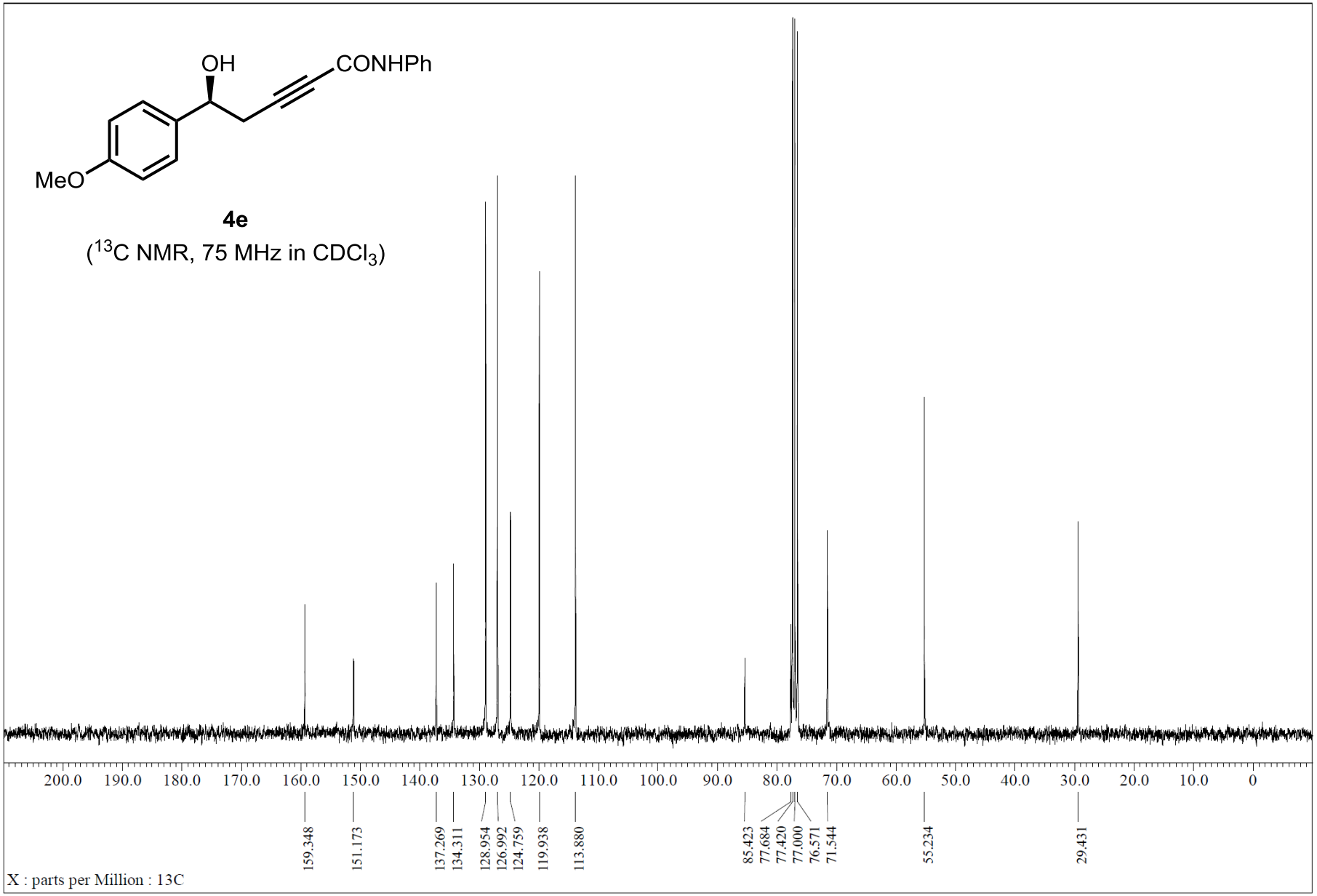

OH
CONHPh
4c
(1H NMR, 300 MHz in CDCl3)
9.00
2.77
2.58
2.04
0.95
0.98
1.02
1.02
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.319
7.526
7.500
7.313
7.288
7.262
7.120
7.096
7.071
3.526
3.495
3.249
2.559
2.550
2.502
2.494
2.396
2.363
2.339
2.307
1.255
0.903
0.881
0.876
0.865
0.859
0.834
0.000
X : parts per Million : 1H

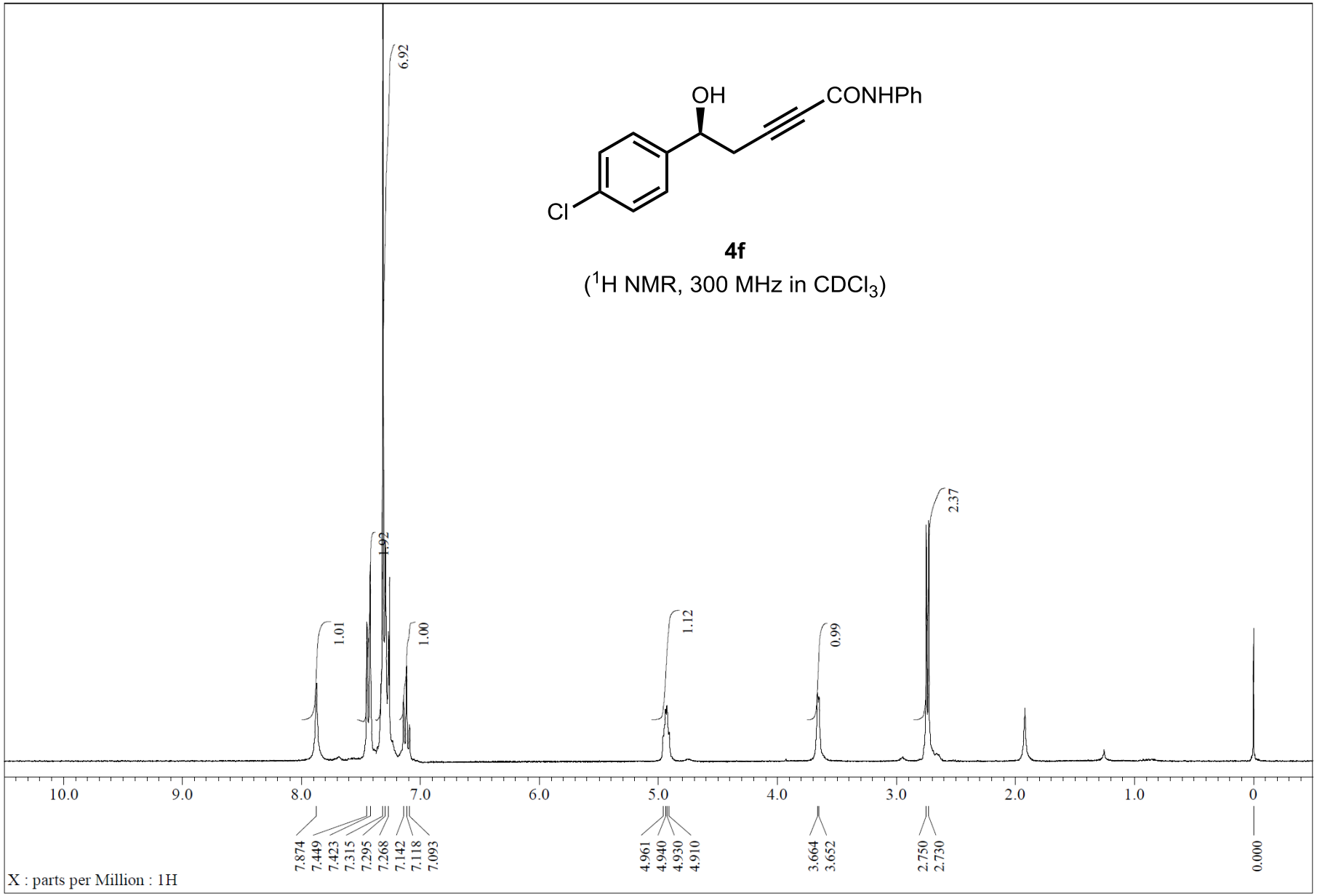

OH
CONHPh
4c
(^{13}C NMR, 75 MHz in CD_3OD)
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
153.623
139.492
129.924
125.650
121.137
88.824
78.713
77.505
49.885
49.597
49.318
49.030
48.751
48.463
48.183
36.141
26.088
23.408
X : parts per Million : 13C

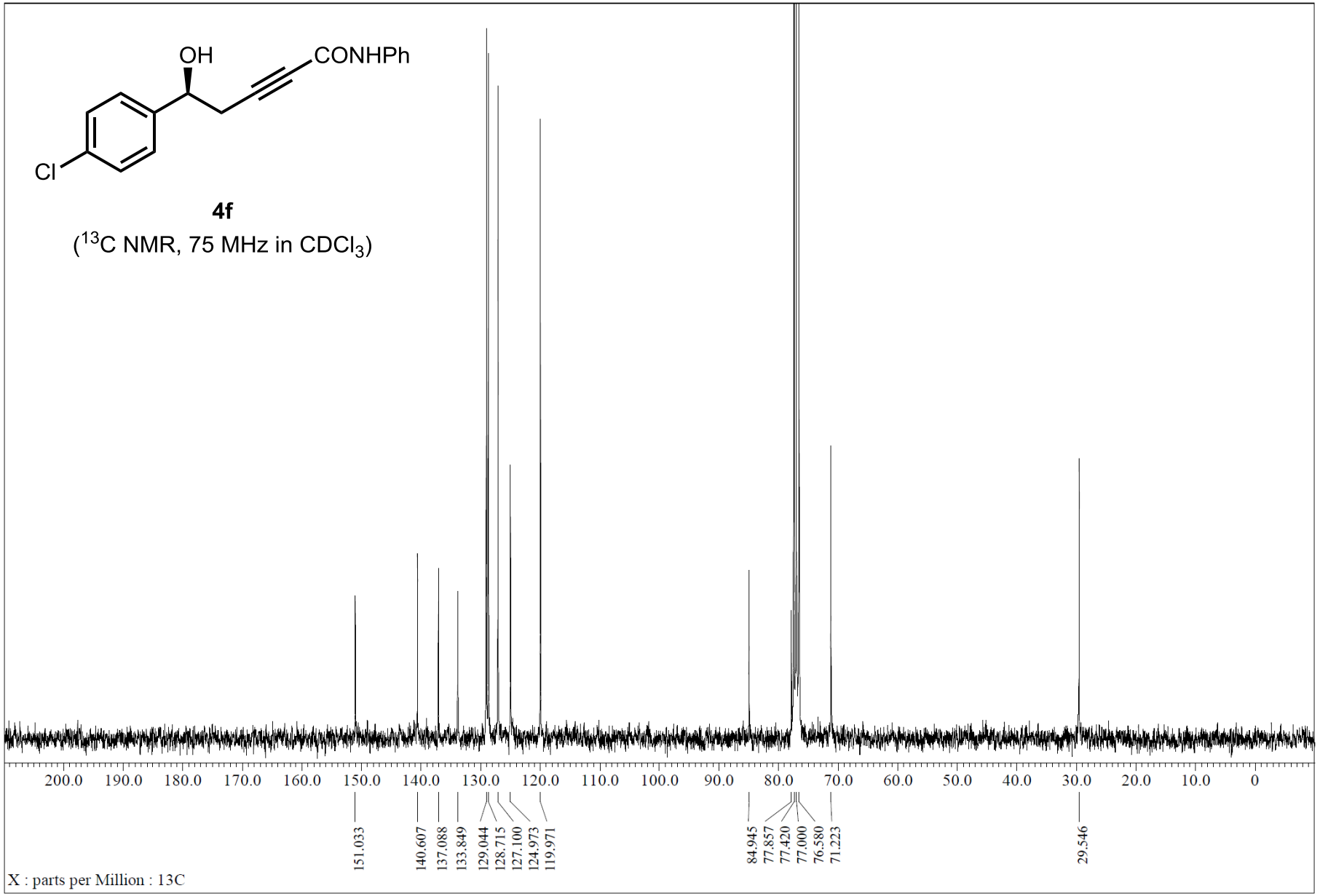

OH
CONHPh
4d
(1H NMR, 300 MHz in CDCl3)
4.53
2.95
1.91
0.85
1.00
0.79
2.03
3.18
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.687
7.471
7.445
7.330
7.304
7.273
7.266
7.260
7.258
7.193
7.167
7.138
7.114
4.941
2.928
2.919
2.853
2.830
2.796
2.785
2.773
2.766
2.727
2.709
2.349
1.741
0.000
X : parts per Million : 1H

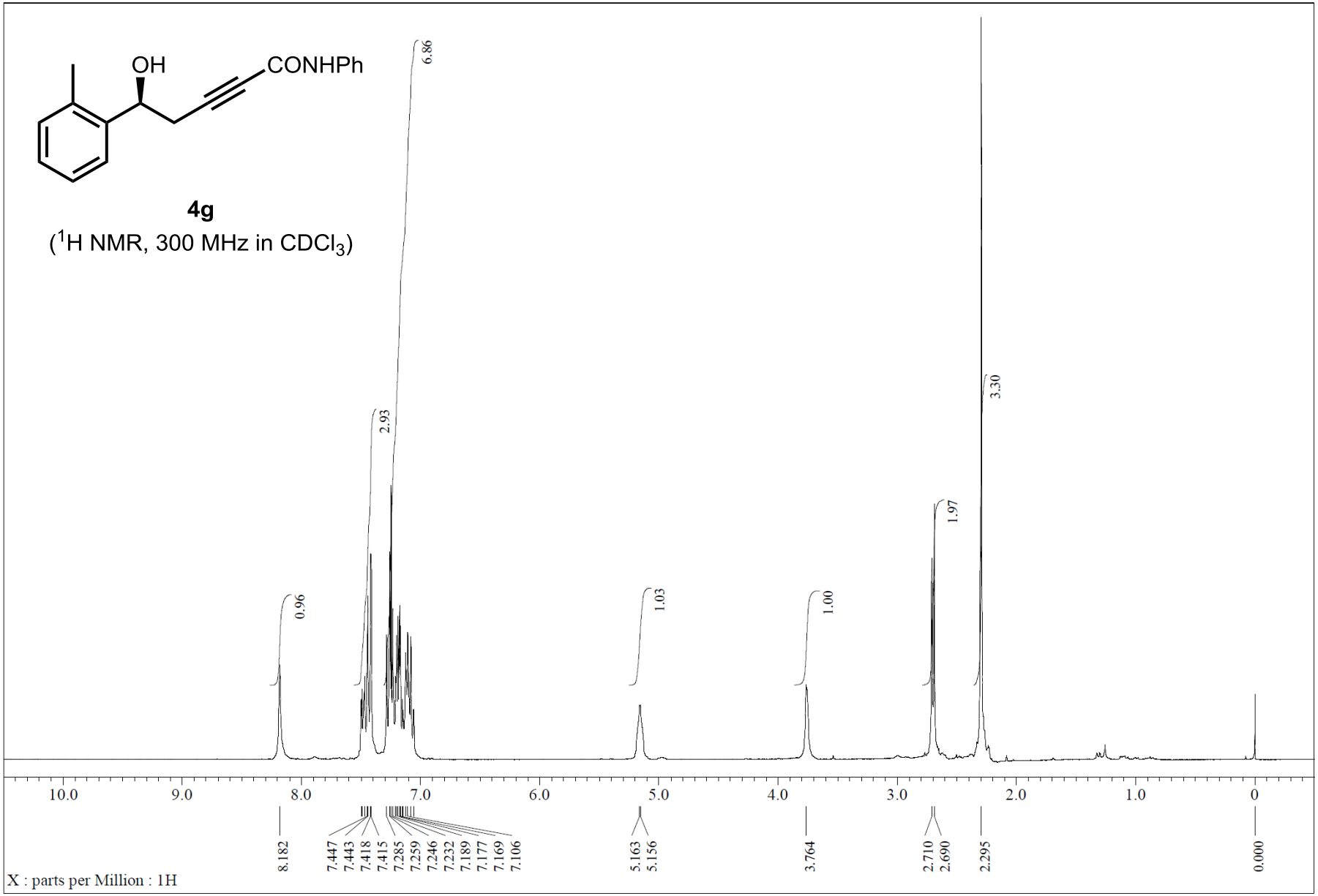

OH
CONHPh
4d
(^{13}C NMR, 75 MHz in $CDCl_3$)
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
151.189
139.206
137.863
137.286
129.209
128.937
125.633
124.751
119.971
85.447
77.692
77.429
77.000
76.580
71.791
29.447
21.090
X : parts per Million : 13C

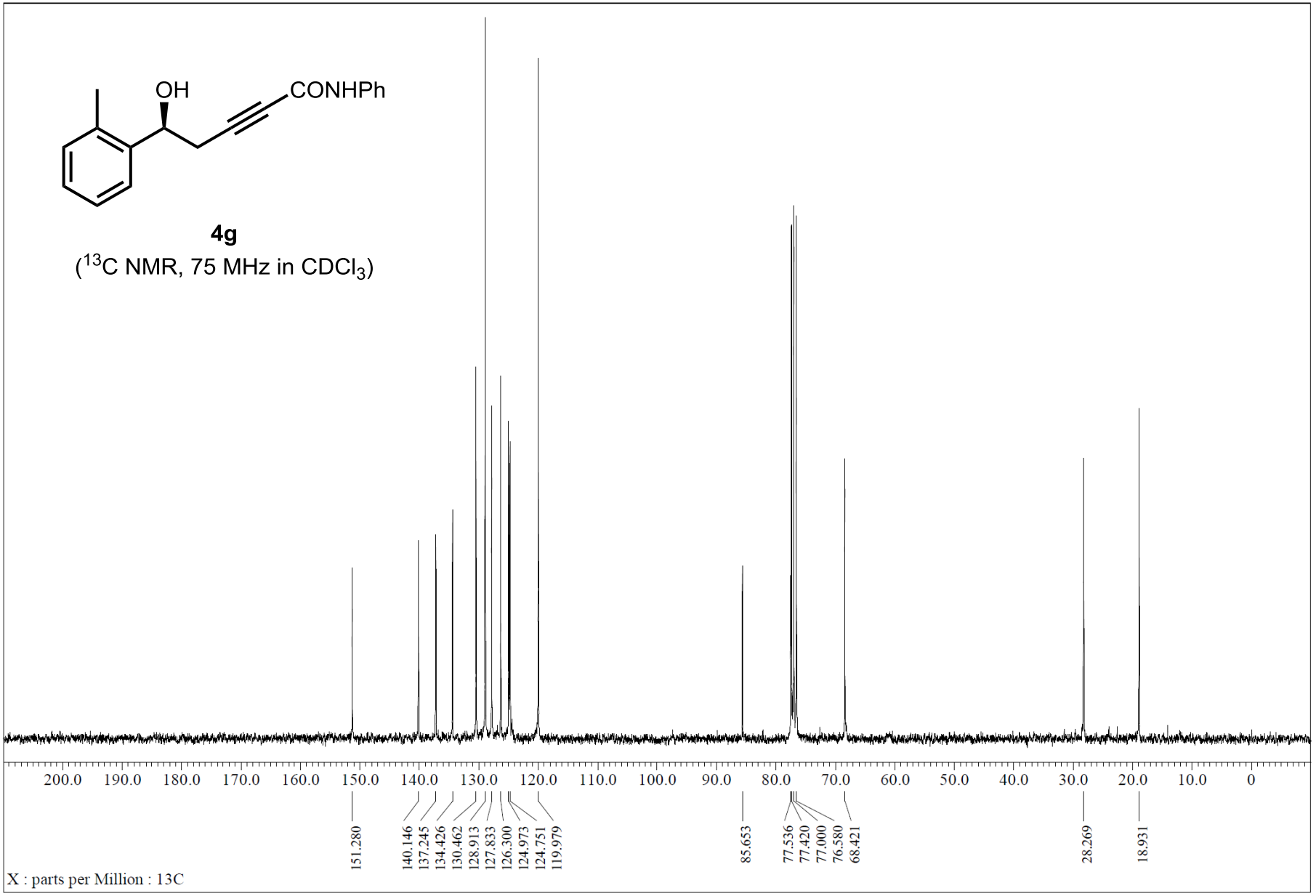

OH
CONHPh
MeO
4e
(1H NMR, 300 MHz in CDCl3)
4.08
4.06
2.11
1.93
1.91
0.90
0.86
1.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.183
7.450
7.424
7.288
7.266
7.240
7.112
7.088
7.063
6.865
6.836
4.897
4.876
4.856
3.766
2.797
2.773
2.740
2.716
2.707
2.667
2.649
2.217
0.000
X : parts per Million : 1H

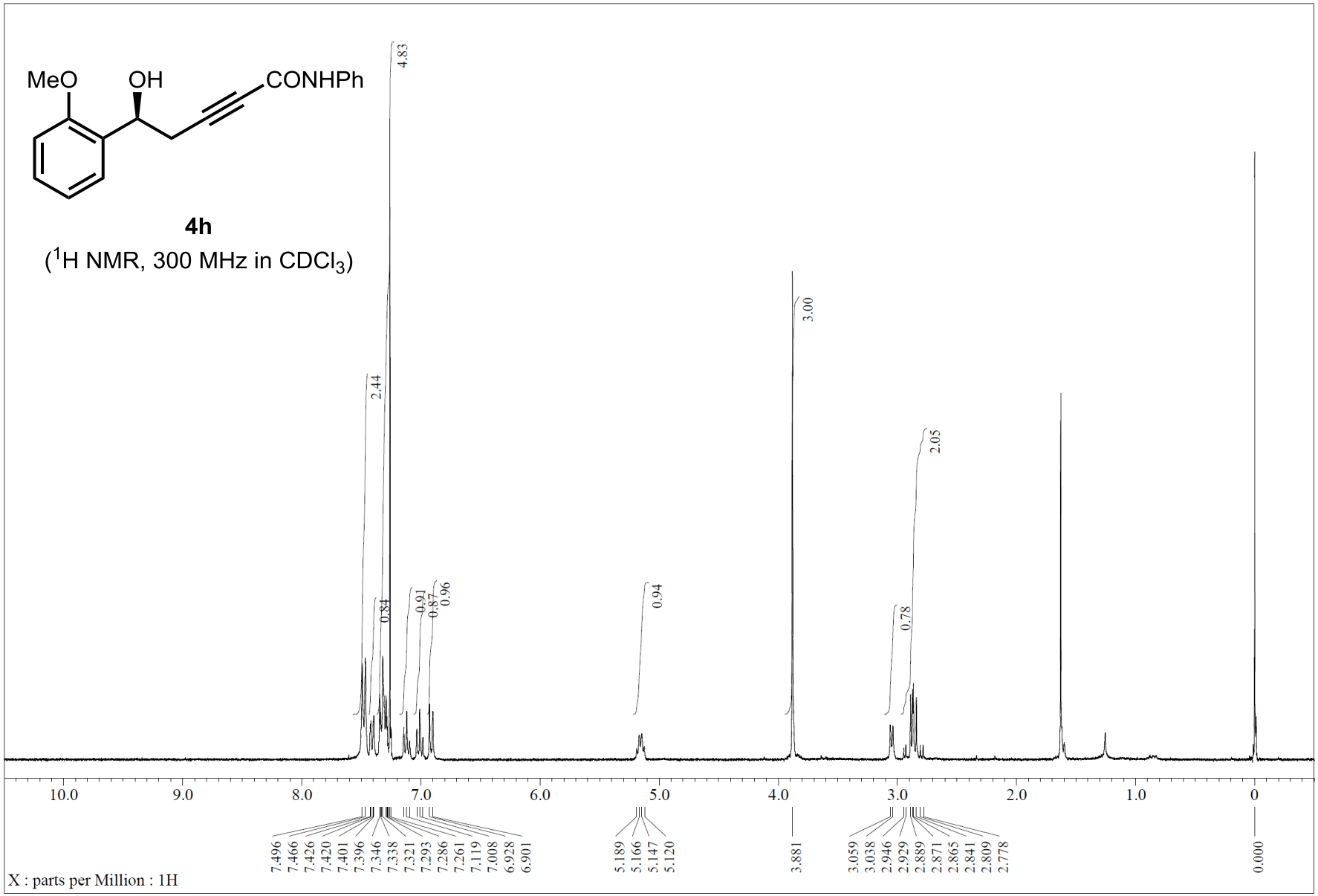

OH
CONHPh
MeO
4e
(13C NMR, 75 MHz in CDCl3)
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
159.348
151.173
137.269
134.311
128.954
126.992
124.759
119.938
113.880
85.423
77.684
77.420
77.000
76.571
71.544
55.234
29.431
X : parts per Million : 13C

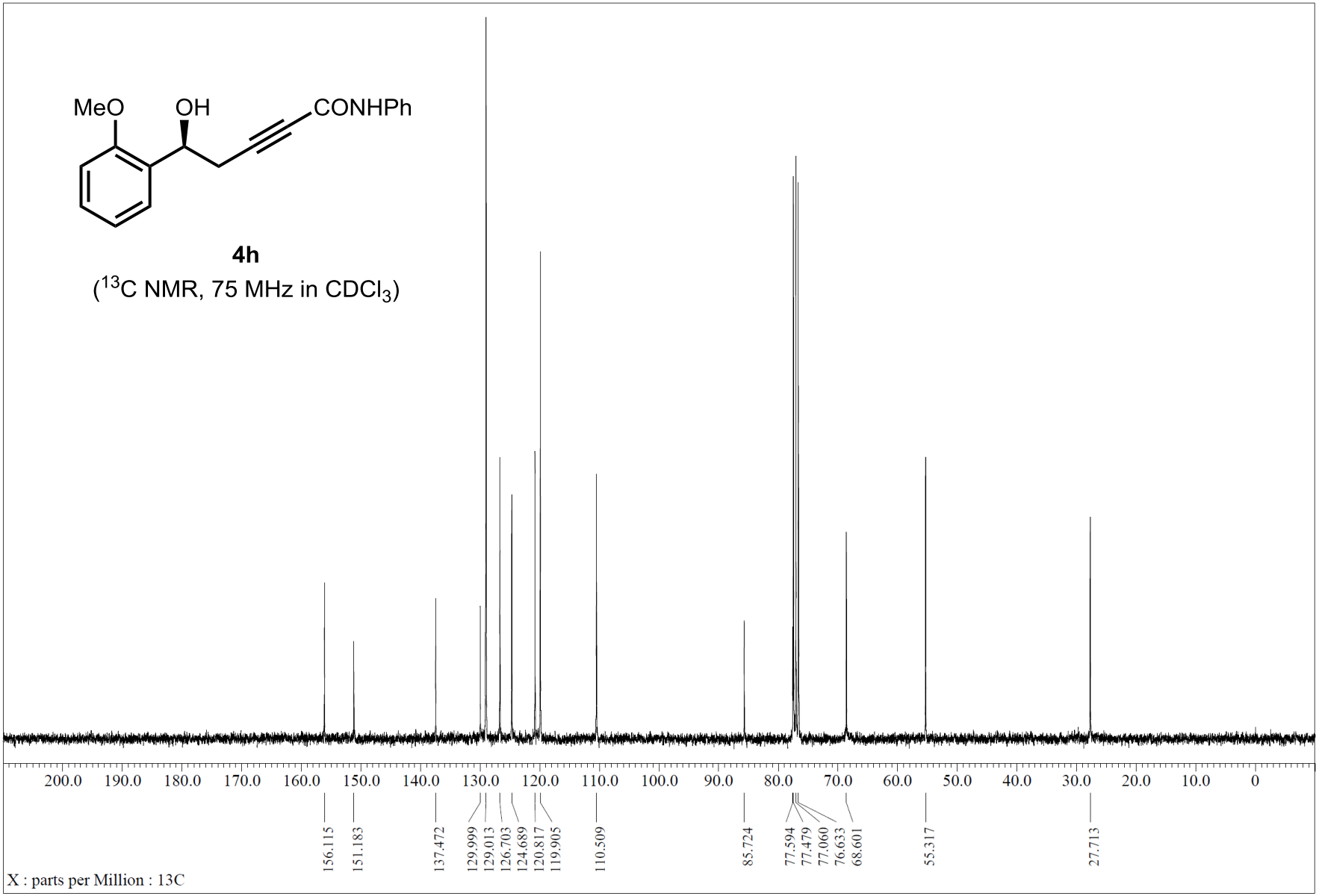

OH
CONHPh
Cl
4f
(1H NMR, 300 MHz in CDCl3)
6.92
1.92
2.37
1.12
1.01
1.00
0.99
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.874
7.449
7.423
7.315
7.295
7.268
7.142
7.118
7.093
4.961
4.940
4.930
4.910
3.664
3.652
2.750
2.730
0.000
X : parts per Million : 1H

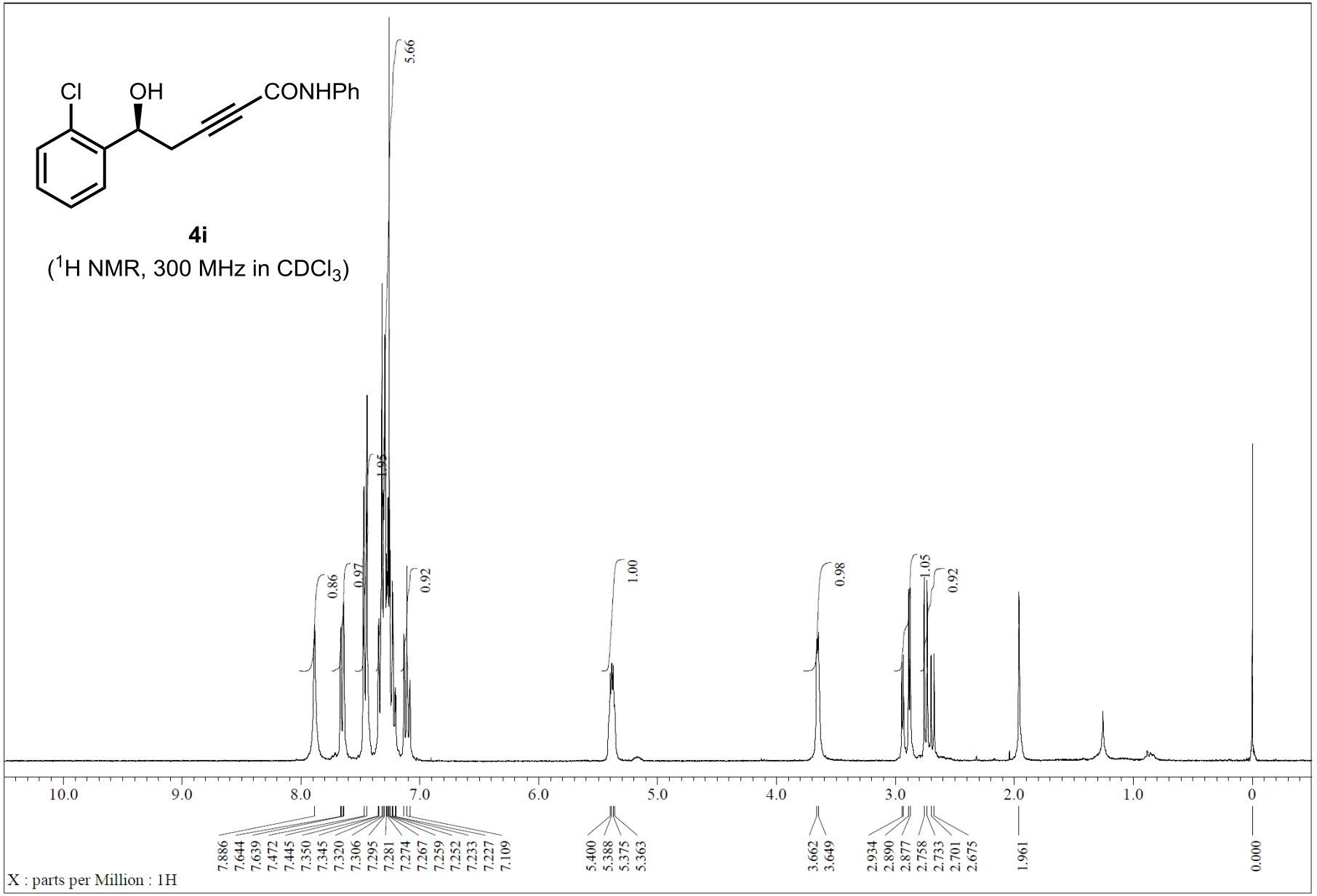

OH
CONHPh
Cl
4f
(^{13}C NMR, 75 MHz in $CDCl_3$)
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
151.033
140.607
137.088
133.849
129.044
128.715
127.100
124.973
119.971
84.945
77.857
77.420
77.000
76.580
71.223
29.546
X : parts per Million : 13C

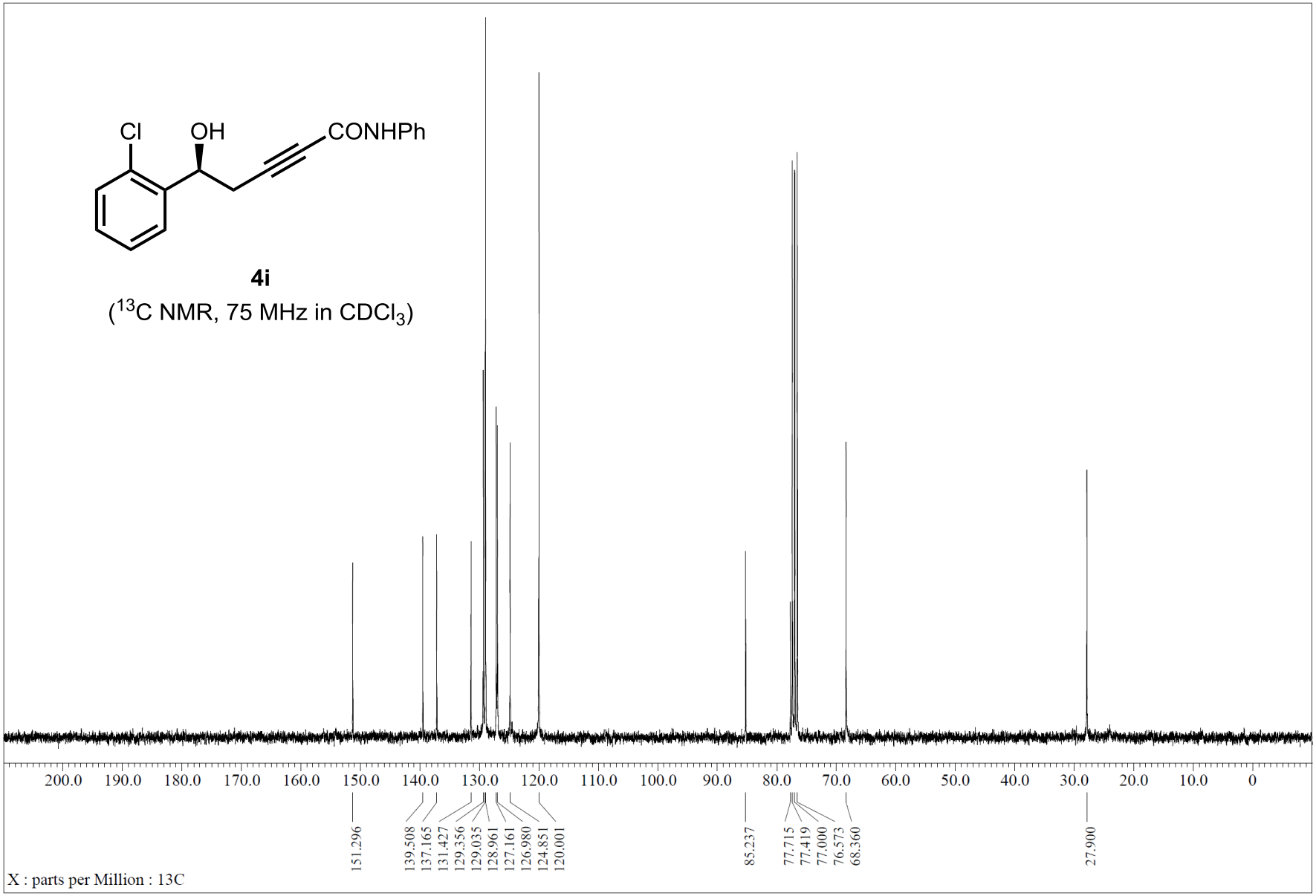

OH
CONHPh
4g
(1H NMR, 300 MHz in CDCl3)
6.86
2.93
0.96
1.03
1.00
1.97
3.30
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.182
7.447
7.443
7.418
7.415
7.285
7.259
7.246
7.232
7.189
7.177
7.169
7.106
5.163
5.156
3.764
2.710
2.690
2.295
0.000
X : parts per Million : 1H

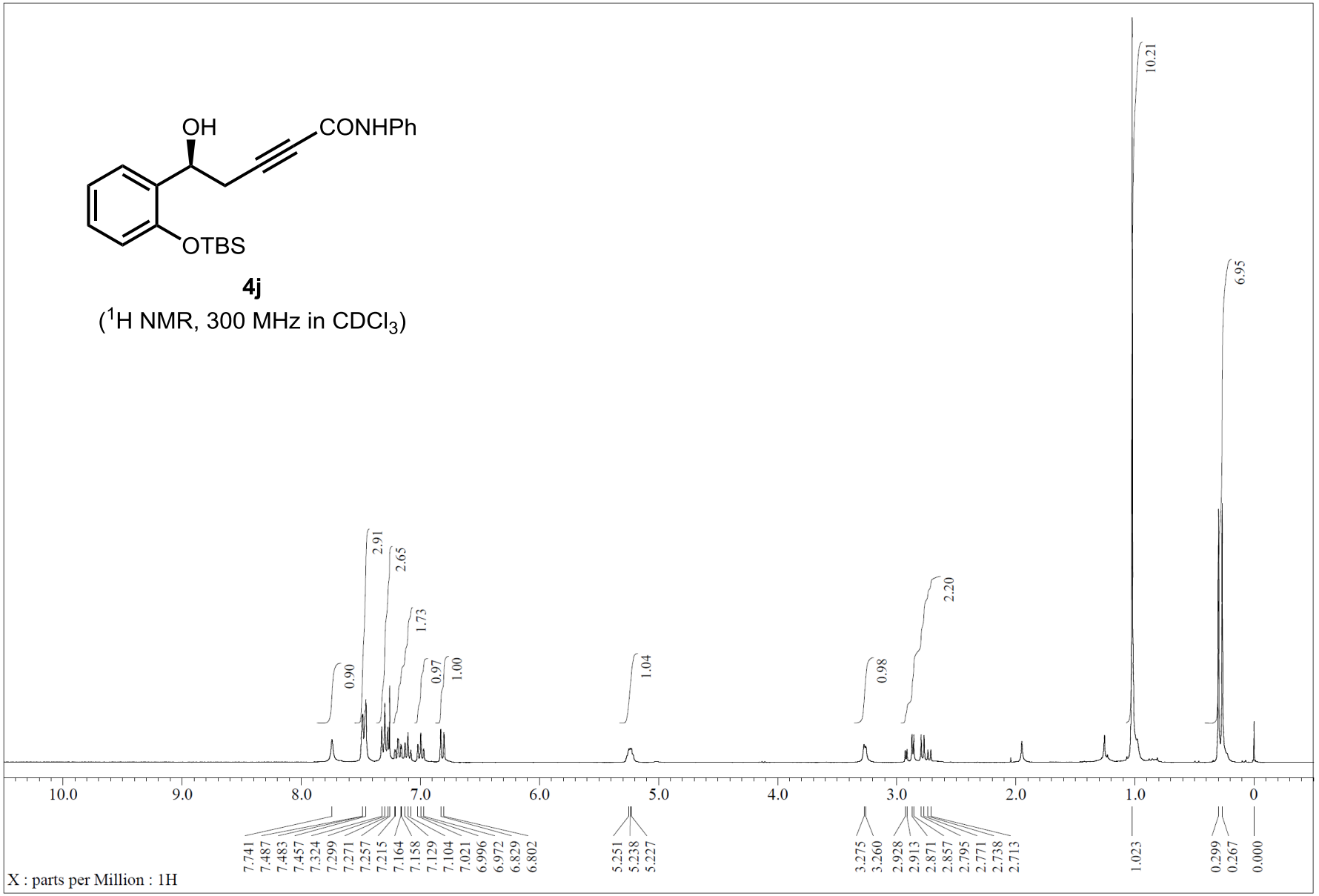

OH
CONHPh
4g
(13C NMR, 75 MHz in CDCl3)
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
151.280
140.146
137.245
134.426
130.462
128.913
127.833
126.300
124.973
124.751
119.979
85.653
77.536
77.420
77.000
76.580
68.421
28.269
18.931
X : parts per Million : 13C

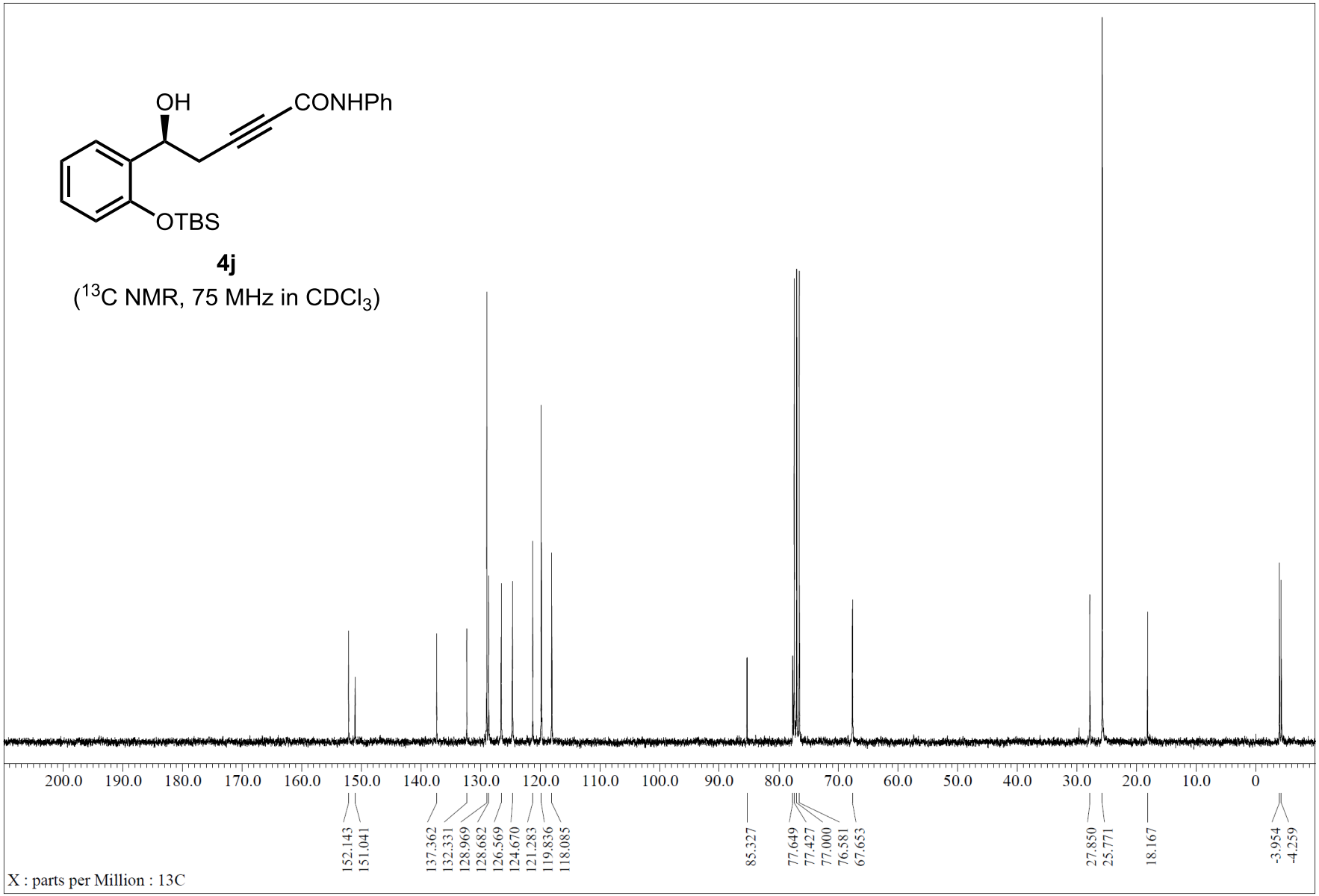

MeO
OH
CONHPh
4h
(1H NMR, 300 MHz in CDCl3)
4.83
2.44
3.00
2.05
0.94
0.84
0.91
0.87
0.96
0.78
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.496
7.466
7.426
7.420
7.401
7.396
7.346
7.338
7.321
7.293
7.286
7.261
7.119
7.008
6.928
6.901
5.189
5.166
5.147
5.120
3.881
3.059
3.038
2.946
2.929
2.889
2.871
2.865
2.841
2.809
2.778
0.000
X : parts per Million : 1H

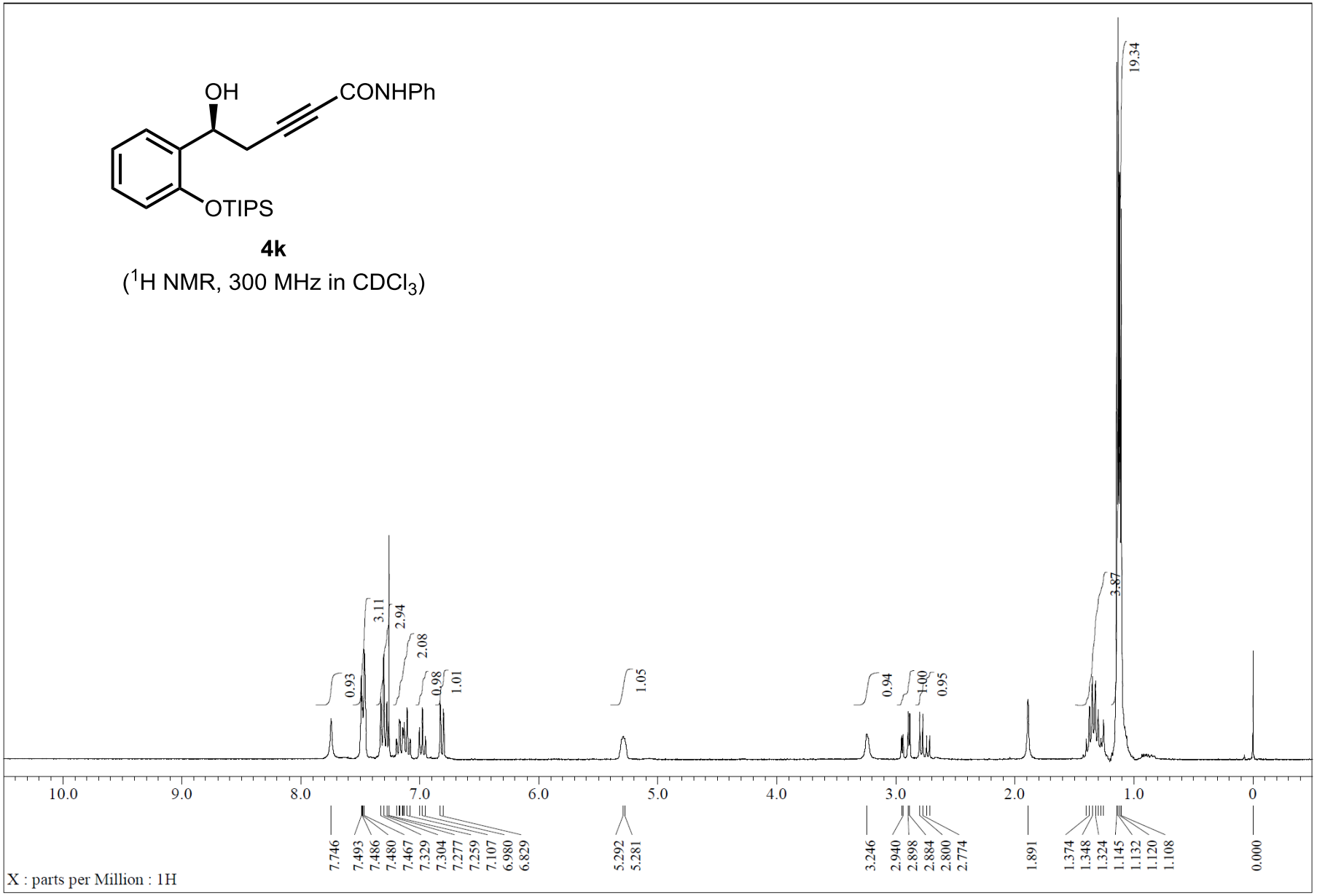

MeO
OH
CONHPh
4h
(13C NMR, 75 MHz in CDCl3)
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
156.115
151.183
137.472
129.999
129.013
126.703
124.689
120.817
119.905
110.509
85.724
77.594
77.479
77.060
76.633
68.601
55.317
27.713
X : parts per Million : 13C

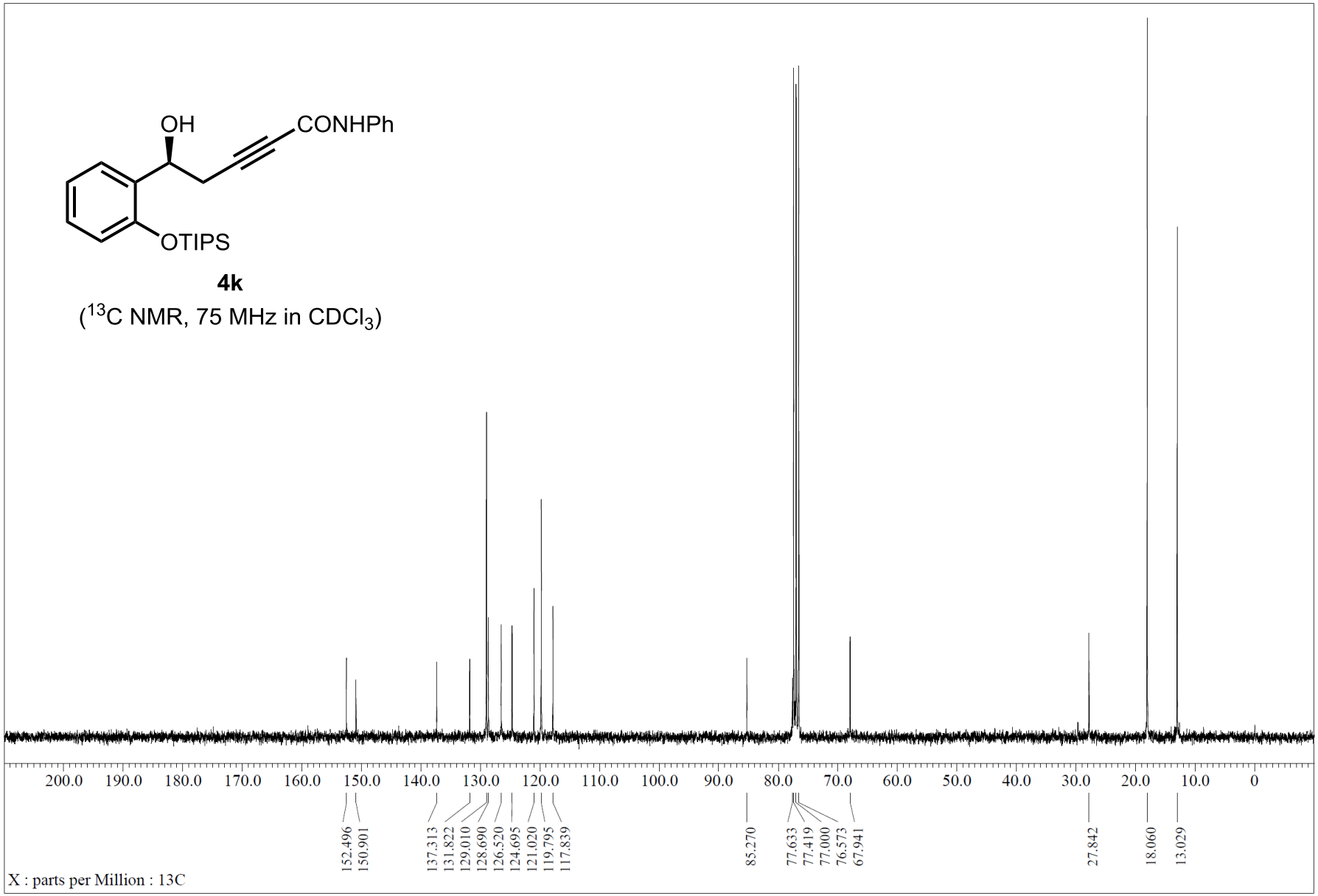

Cl
OH
CONHPh
4i
(1H NMR, 300 MHz in CDCl3)
5.66
1.95
0.86
0.97
0.92
1.00
0.98
1.05
0.92
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.886
7.644
7.639
7.472
7.445
7.350
7.345
7.320
7.306
7.295
7.281
7.274
7.267
7.259
7.252
7.233
7.227
7.109
5.400
5.388
5.375
5.363
3.662
3.649
2.934
2.890
2.877
2.758
2.733
2.701
2.675
1.961
0.000
X : parts per Million : 1H

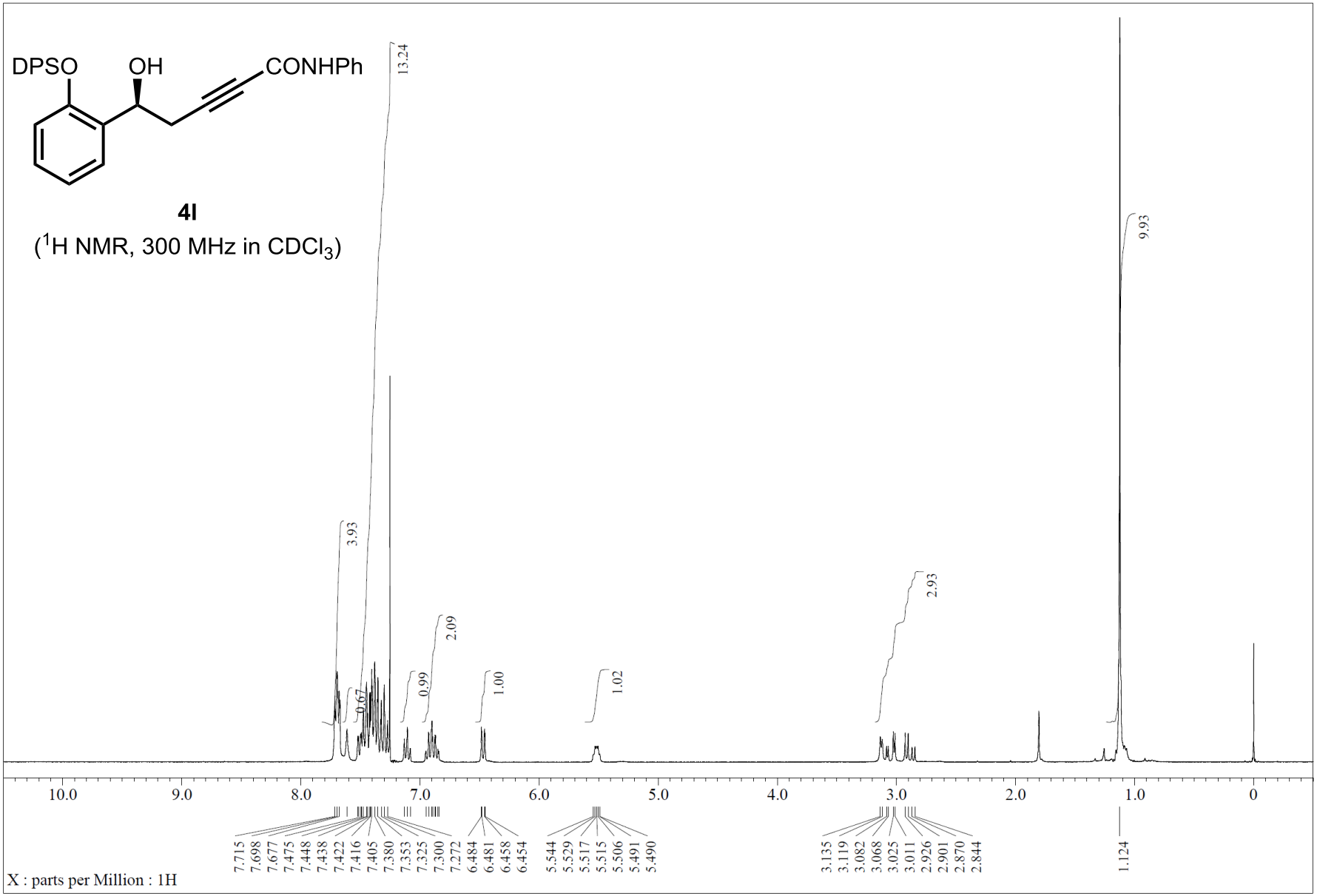

Cl
OH
CONHPh
4i
(13C NMR, 75 MHz in CDCl3)
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
151.296
139.508
137.165
131.427
129.356
129.035
128.961
127.161
126.980
124.851
120.001
85.237
77.715
77.419
77.000
76.573
68.360
27.900
X : parts per Million : 13C

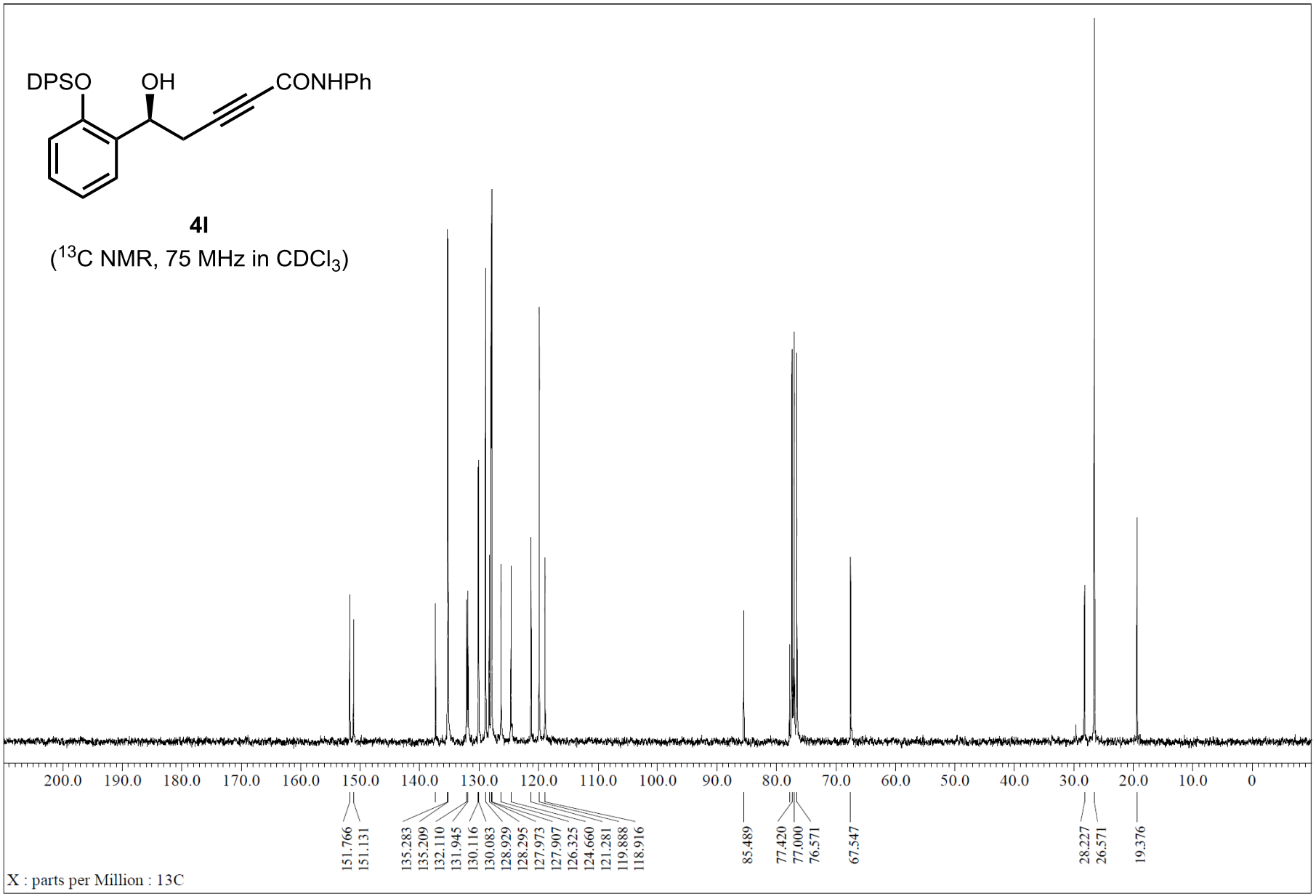

OH
CONHPh
OTBS
4j
(1H NMR, 300 MHz in CDCl3)
10.21
6.95
2.91
2.65
1.73
2.20
0.90
0.97
1.00
1.04
0.98
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.741
7.487
7.483
7.457
7.324
7.299
7.271
7.257
7.215
7.164
7.158
7.129
7.104
7.021
6.996
6.972
6.829
6.802
5.251
5.238
5.227
3.275
3.260
2.928
2.913
2.871
2.857
2.795
2.771
2.738
2.713
1.023
0.299
0.267
0.000
X : parts per Million : 1H

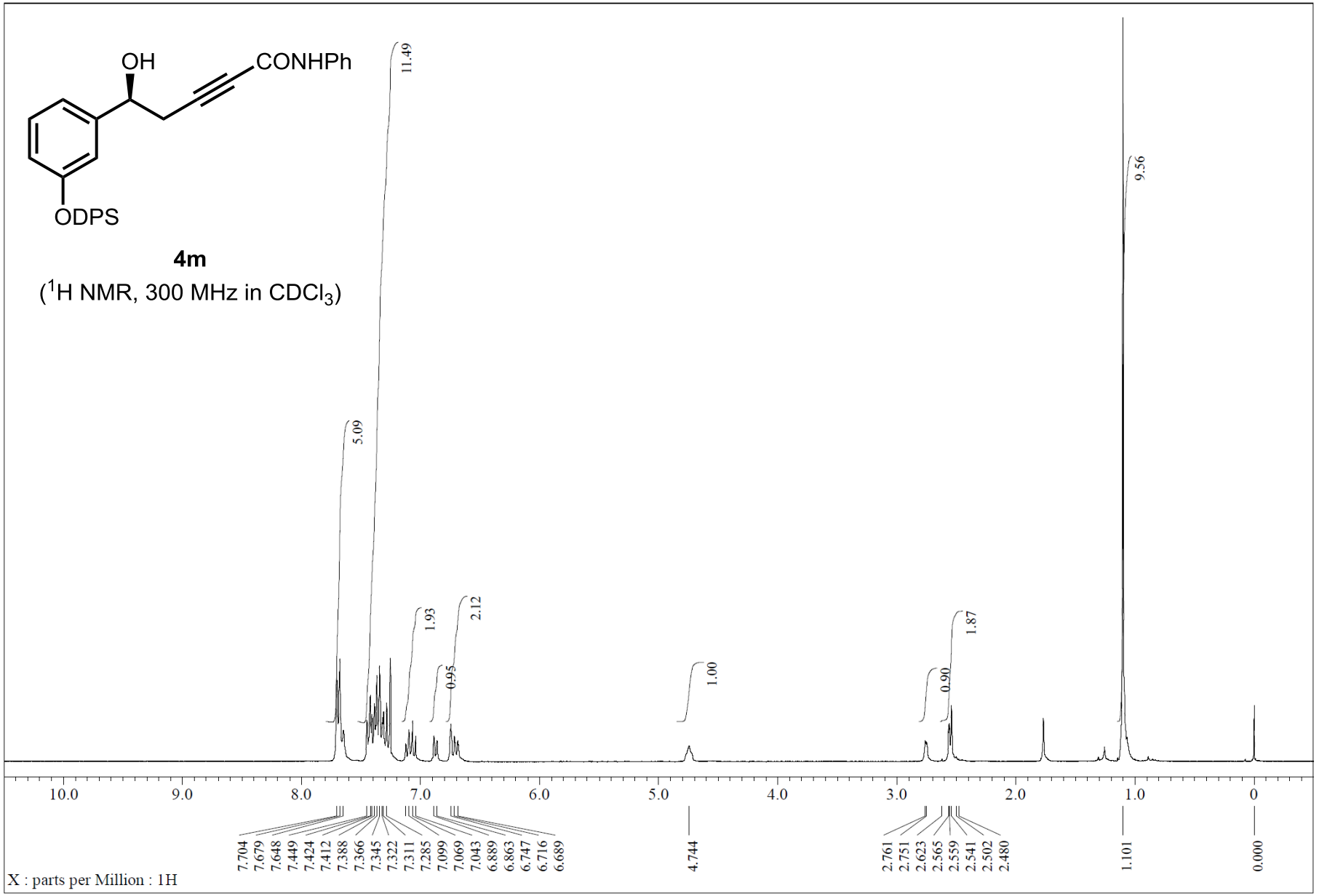

OH
CONHPh
OTBS
4j
(^{13}C NMR, 75 MHz in $CDCl_3$)
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
152.143
151.041
137.362
132.331
128.969
128.682
126.569
124.670
121.283
119.836
118.085
85.327
77.649
77.427
77.000
76.581
67.653
27.850
25.771
18.167
-3.954
-4.259
X : parts per Million : 13C

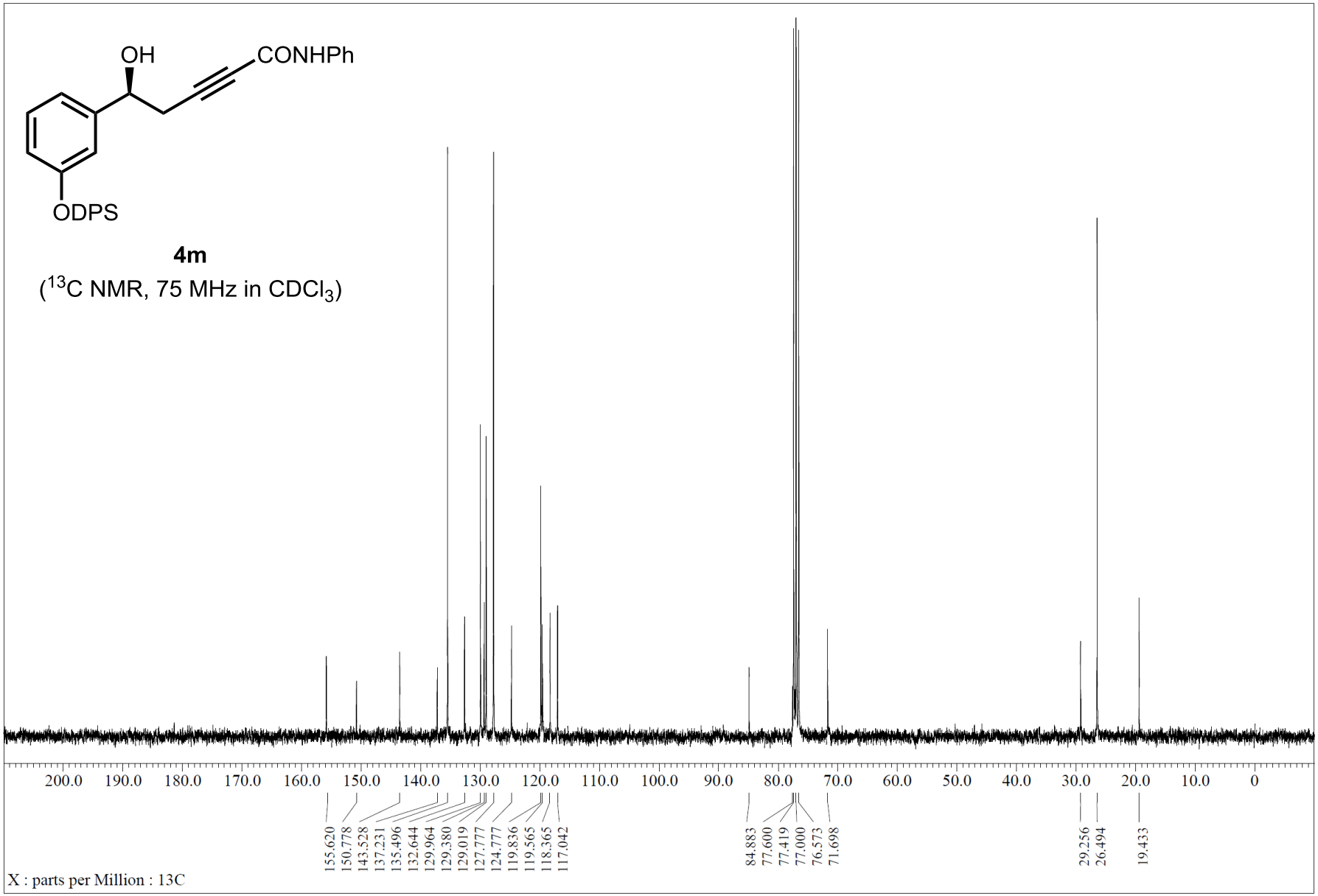

OH
CONHPh
OTIPS
4k
(1H NMR, 300 MHz in CDCl3)
19.34
3.87
3.11
2.94
2.08
0.93
0.98
1.01
1.05
0.94
1.00
0.95
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.746
7.493
7.486
7.480
7.467
7.329
7.304
7.277
7.259
7.107
6.980
6.829
5.292
5.281
3.246
2.940
2.898
2.884
2.800
2.774
1.891
1.374
1.348
1.324
1.145
1.132
1.120
1.108
0.000
X : parts per Million : 1H

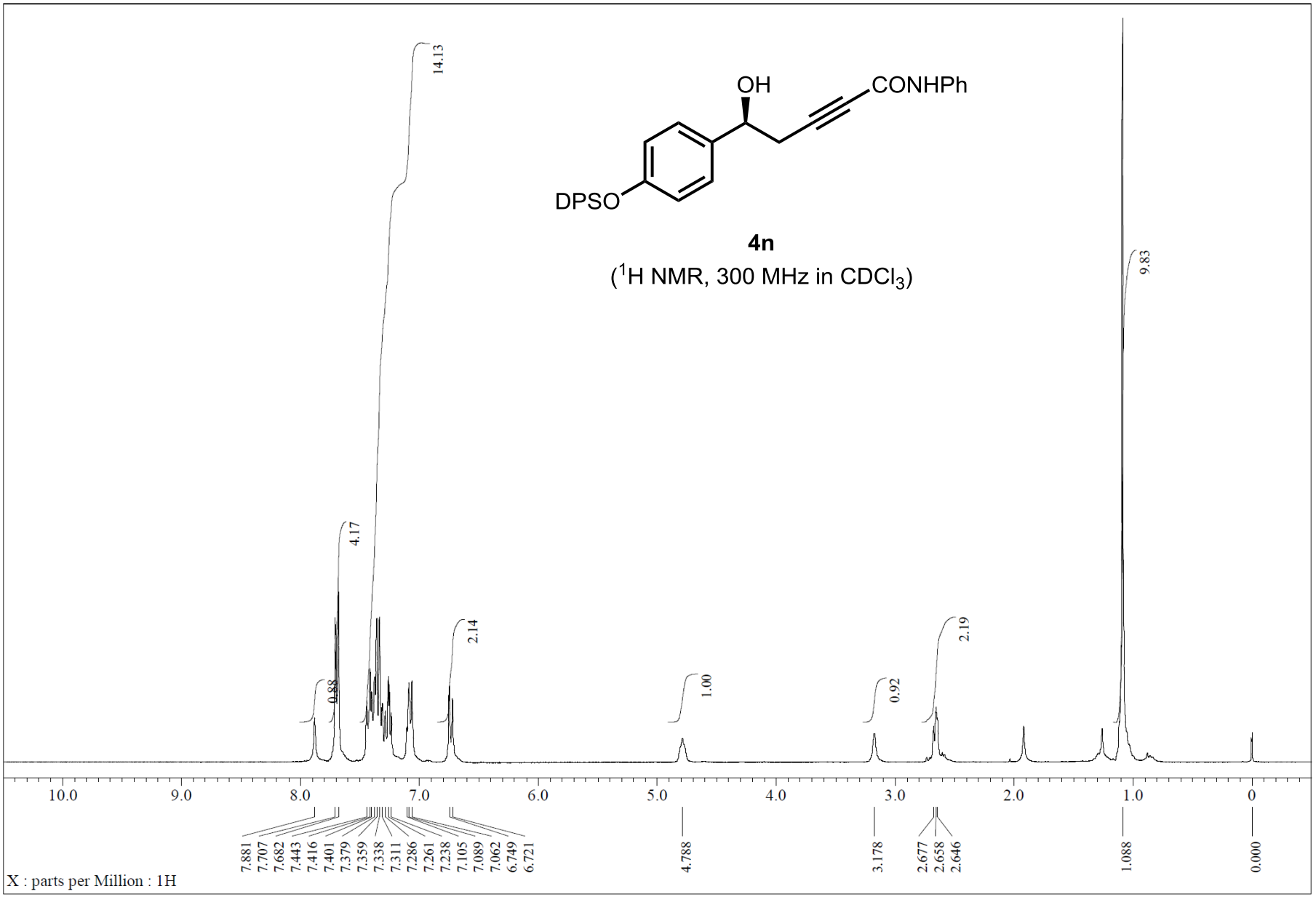

OH
CONHPh
OTIPS
4k
(13C NMR, 75 MHz in CDCl3)
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
152.496
150.901
137.313
131.822
129.010
128.690
126.520
124.695
121.020
119.795
117.839
85.270
77.633
77.419
77.000
76.573
67.941
27.842
18.060
13.029
X : parts per Million : 13C

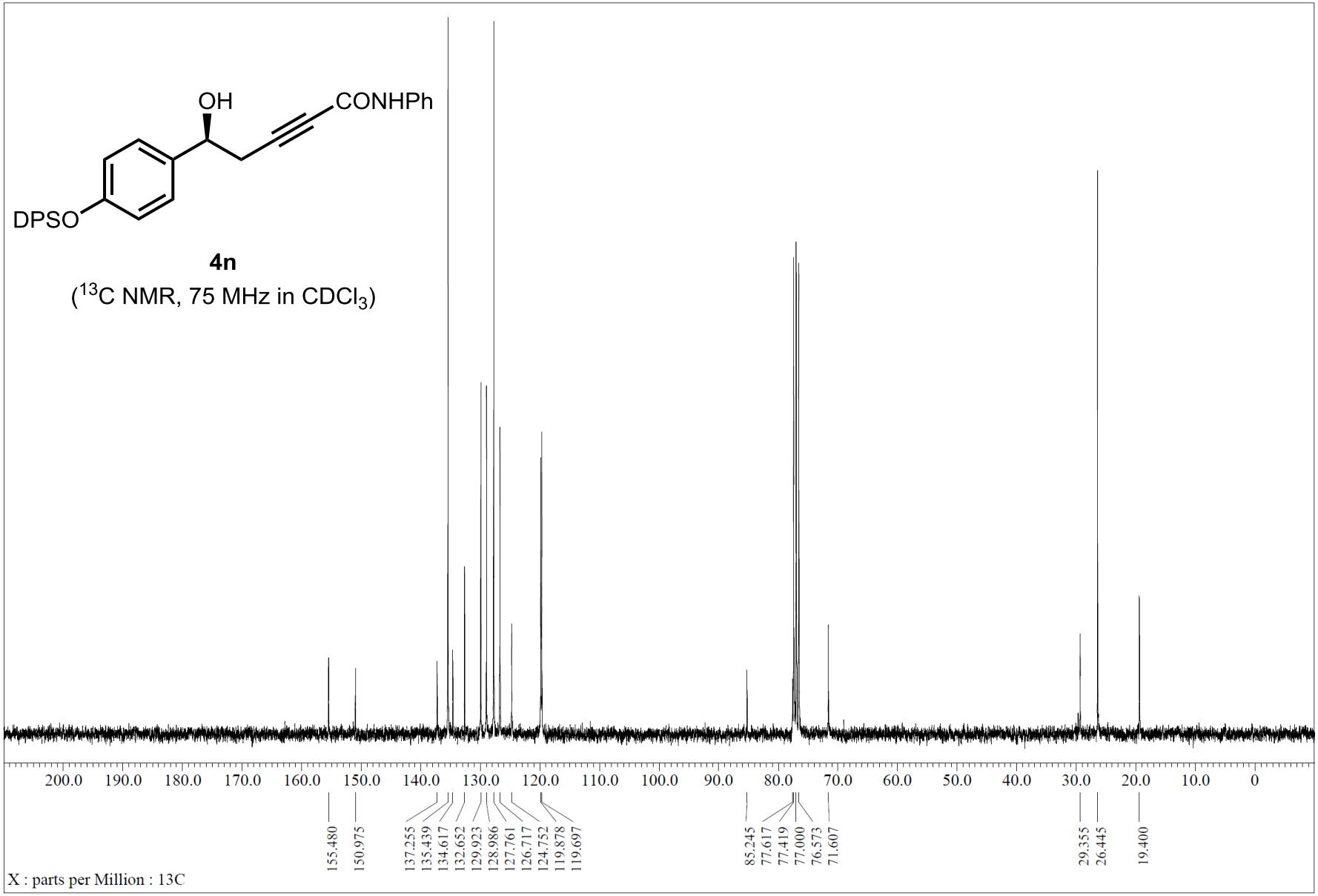

DPSO
OH
CONHPh
4l
(1H NMR, 300 MHz in CDCl3)
13.24
9.93
3.93
2.93
2.09
1.00
1.02
0.99
0.67
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.715
7.698
7.677
7.475
7.448
7.438
7.422
7.416
7.405
7.380
7.353
7.325
7.300
7.272
6.484
6.481
6.458
6.454
5.544
5.529
5.517
5.515
5.506
5.491
5.490
3.135
3.119
3.082
3.068
3.025
3.011
2.926
2.901
2.870
2.844
1.124
X : parts per Million : 1H

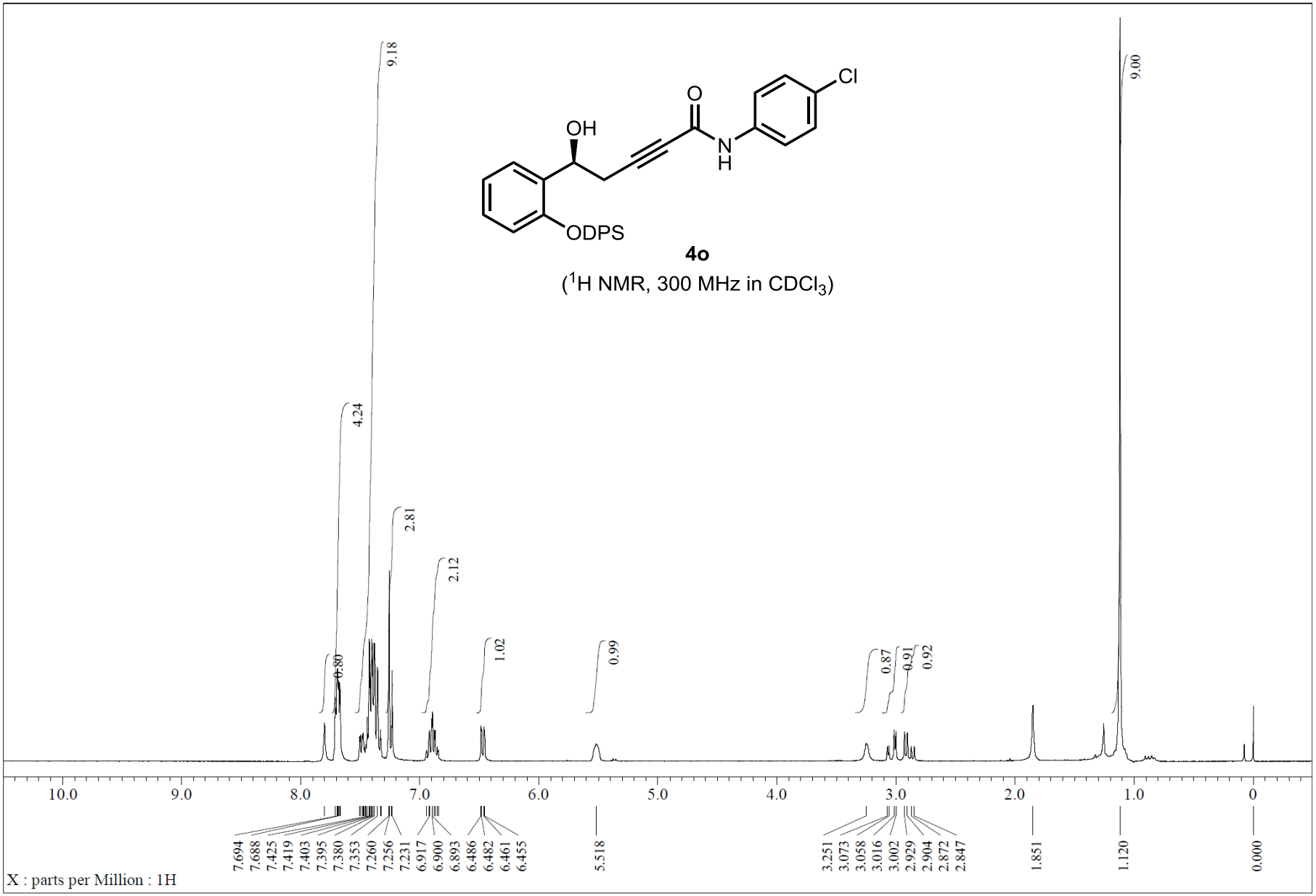

DPSO
OH
CONHPh
4l
(13C NMR, 75 MHz in CDCl3)
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
151.766
151.131
135.283
135.209
132.110
131.945
130.116
130.083
128.929
128.295
127.973
127.907
126.325
124.660
121.281
119.888
118.916
85.489
77.420
77.000
76.571
67.547
28.227
26.571
19.376
X : parts per Million : 13C

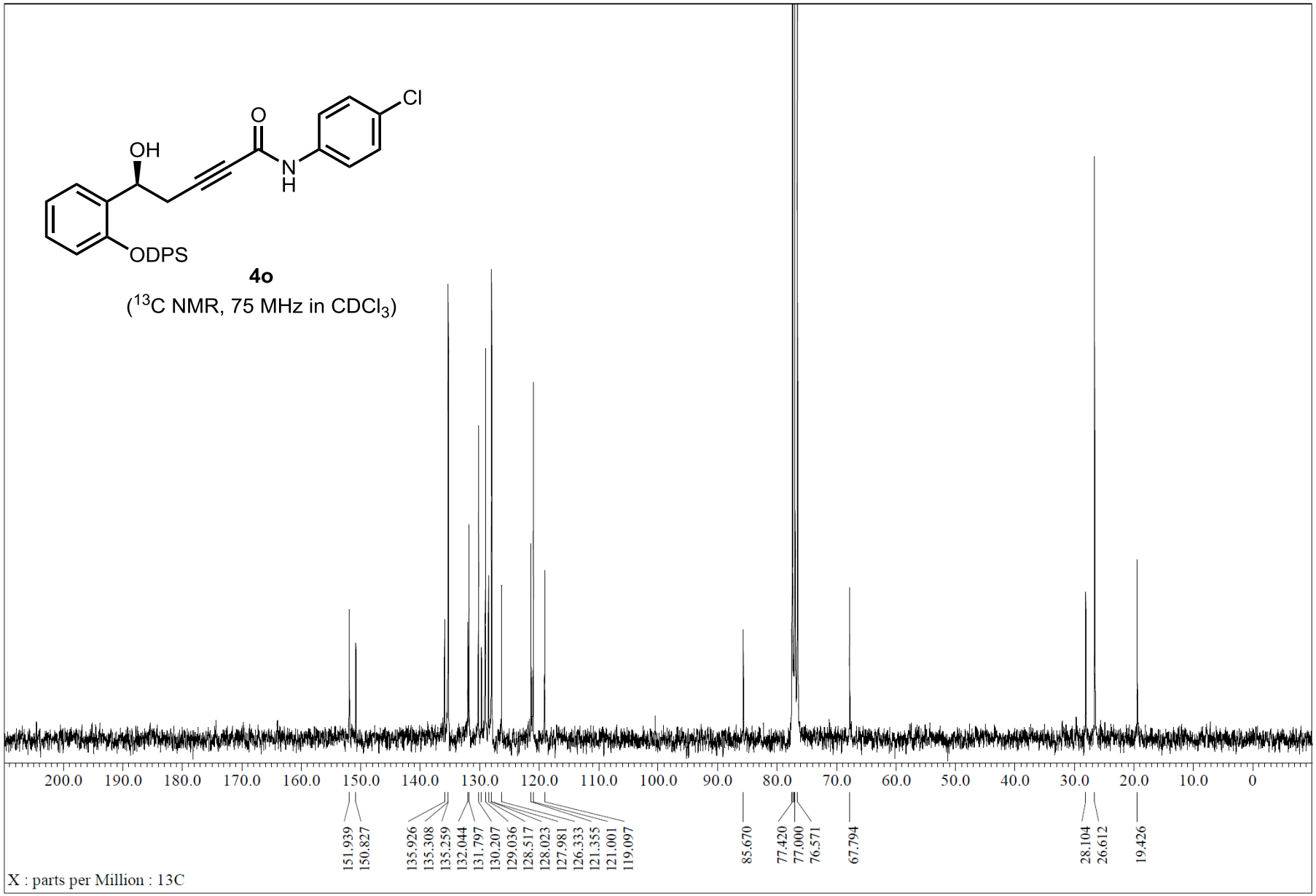

OH
CONHPh
ODPS
4m
(1H NMR, 300 MHz in CDCl3)
11.49
9.56
5.09
1.93
2.12
0.95
1.00
0.90
1.87
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.704
7.679
7.648
7.449
7.424
7.412
7.388
7.366
7.345
7.322
7.311
7.285
7.099
7.069
7.043
6.889
6.863
6.747
6.716
6.689
4.744
2.761
2.751
2.623
2.565
2.559
2.541
2.502
2.480
1.101
0.000
X : parts per Million : 1H

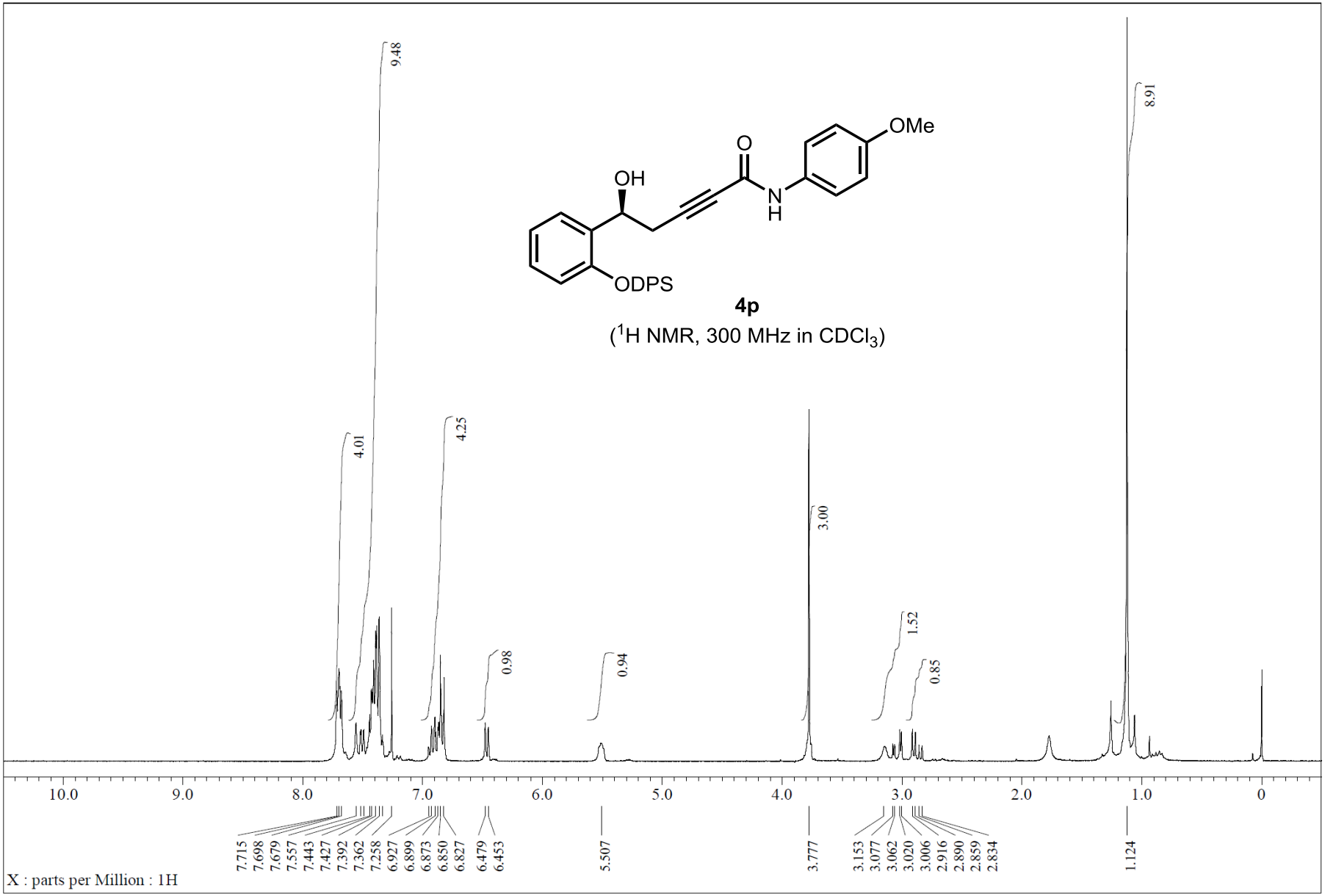

OH
CONHPh
ODPS
4m
(13C NMR, 75 MHz in CDCl3)
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
155.620
150.778
143.528
137.231
135.496
132.644
129.964
129.380
129.019
127.777
124.777
119.836
119.565
118.365
117.042
84.883
77.600
77.419
77.000
76.573
71.698
29.256
26.494
19.433
X : parts per Million : 13C

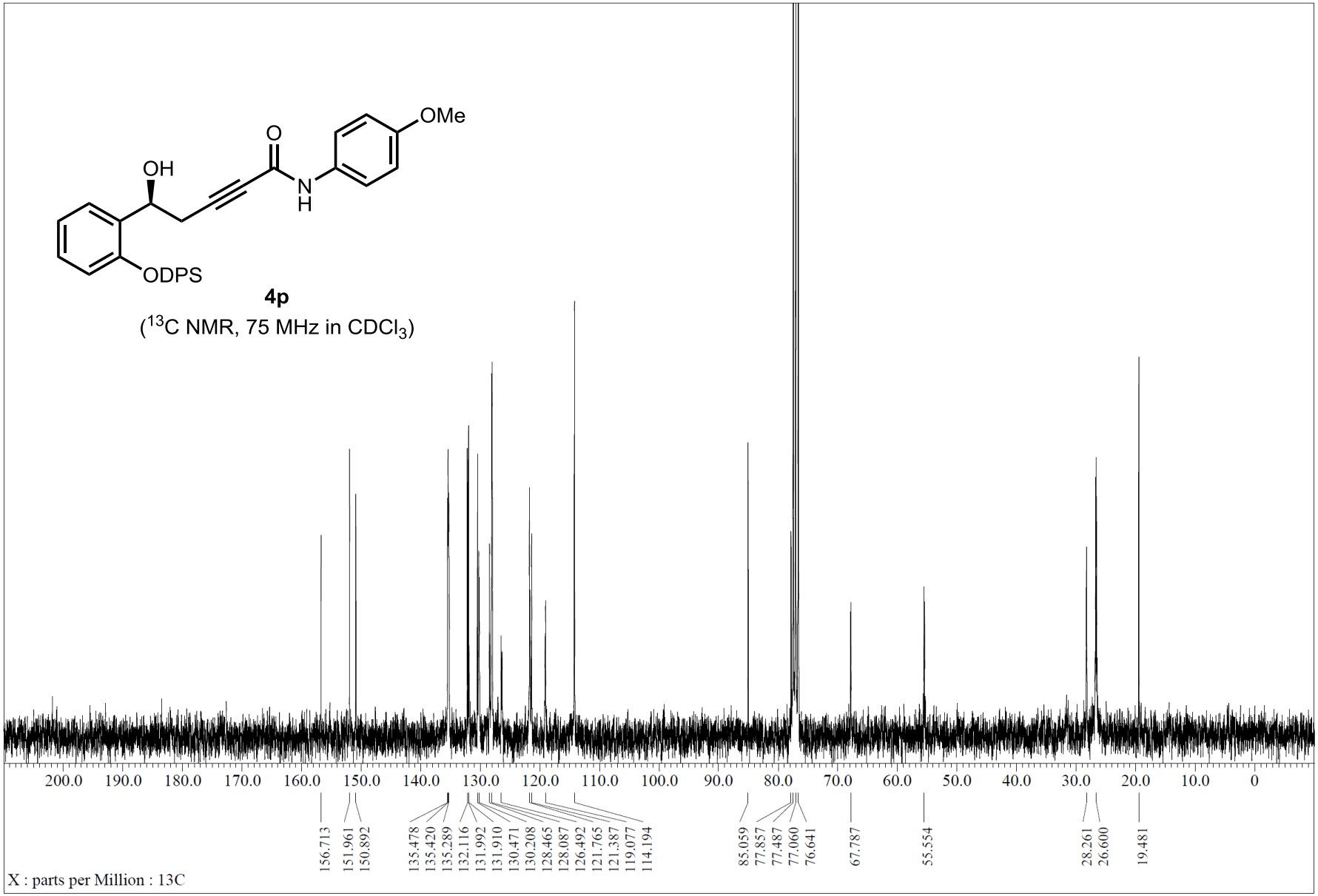

OH
CONHPh
DPSO
4n
(1H NMR, 300 MHz in CDCl3)
14.13
4.17
0.88
2.14
1.00
0.92
2.19
9.83
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.881
7.707
7.682
7.443
7.416
7.401
7.379
7.359
7.338
7.311
7.286
7.261
7.238
7.105
7.089
7.062
6.749
6.721
4.788
3.178
2.677
2.658
2.646
1.088
0.000
X : parts per Million : 1H

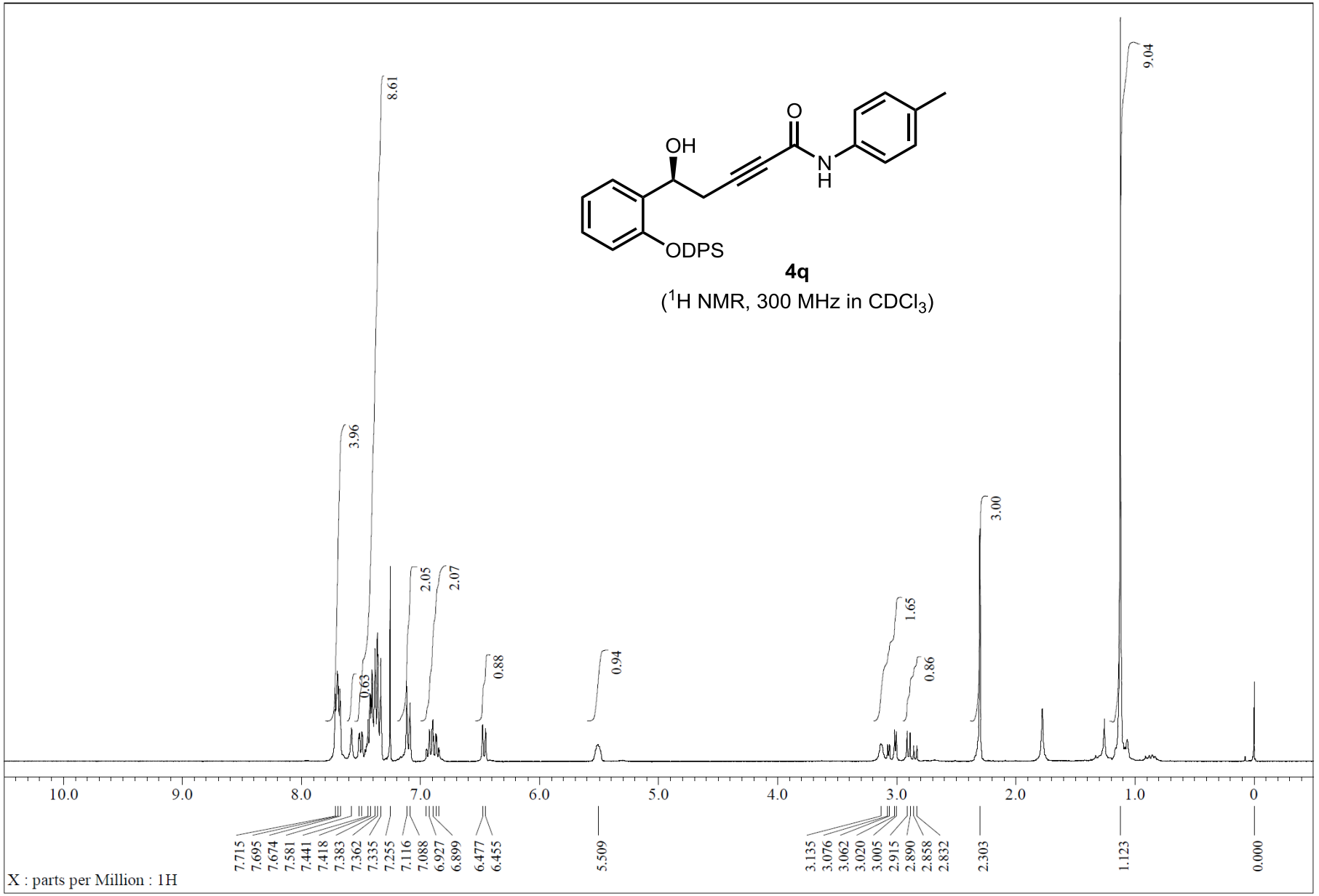

OH
CONHPh
DPSO
4n
(^{13}C NMR, 75 MHz in $CDCl_3$)
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
155.480
150.975
137.255
135.439
134.617
132.652
129.923
128.986
127.761
126.717
124.752
119.878
119.697
85.245
77.617
77.419
77.000
76.573
71.607
29.355
26.445
19.400
X : parts per Million : 13C

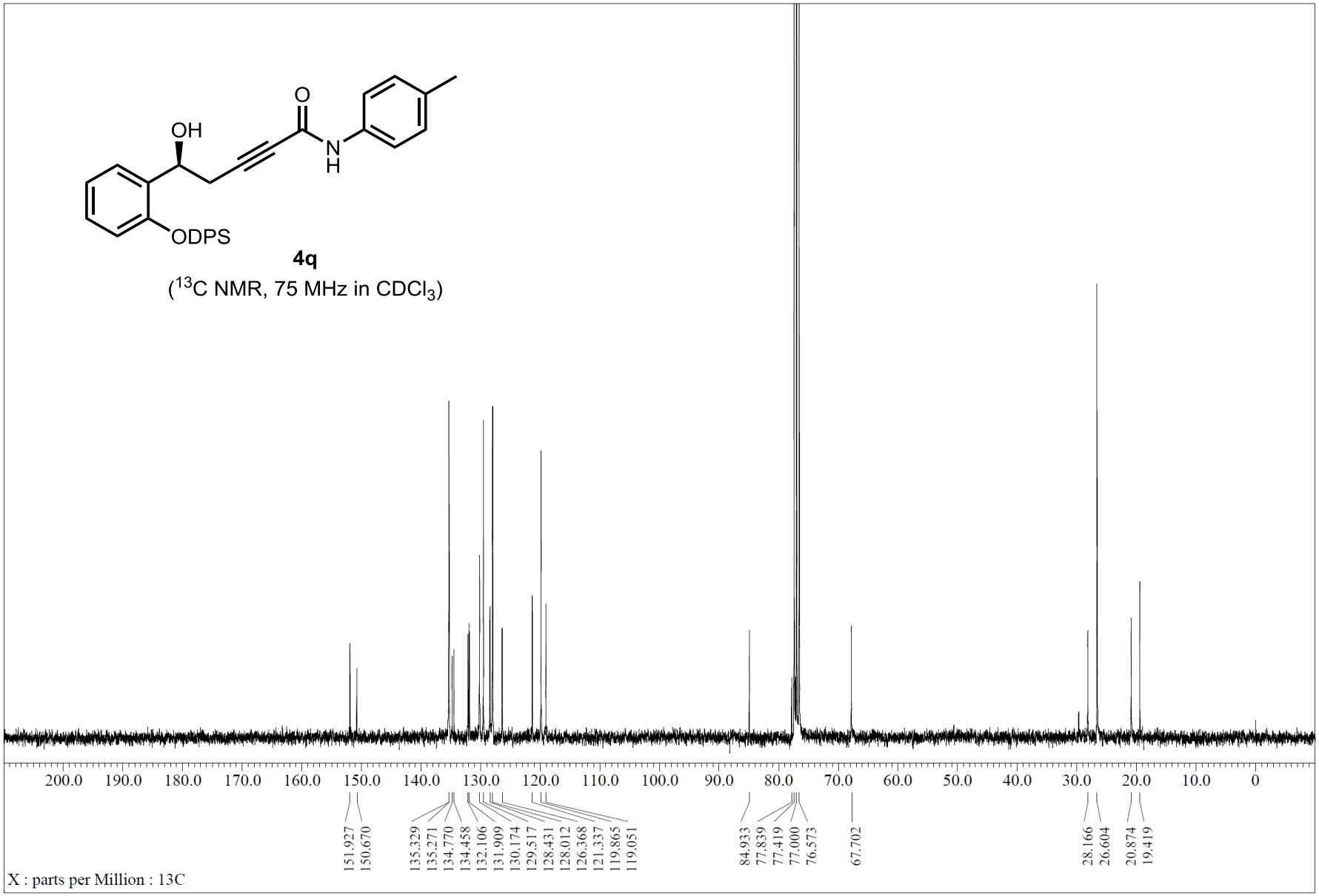

OH
O
N
H
Cl
ODPS
4o
(1H NMR, 300 MHz in CDCl3)
9.18
9.00
4.24
2.81
2.12
1.02
0.99
0.87
0.91
0.92
0.80
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.694
7.688
7.425
7.419
7.403
7.395
7.380
7.353
7.260
7.256
7.231
6.917
6.900
6.893
6.486
6.482
6.461
6.455
5.518
3.251
3.073
3.058
3.016
3.002
2.929
2.904
2.872
2.847
1.851
1.120
0.000
X : parts per Million : 1H

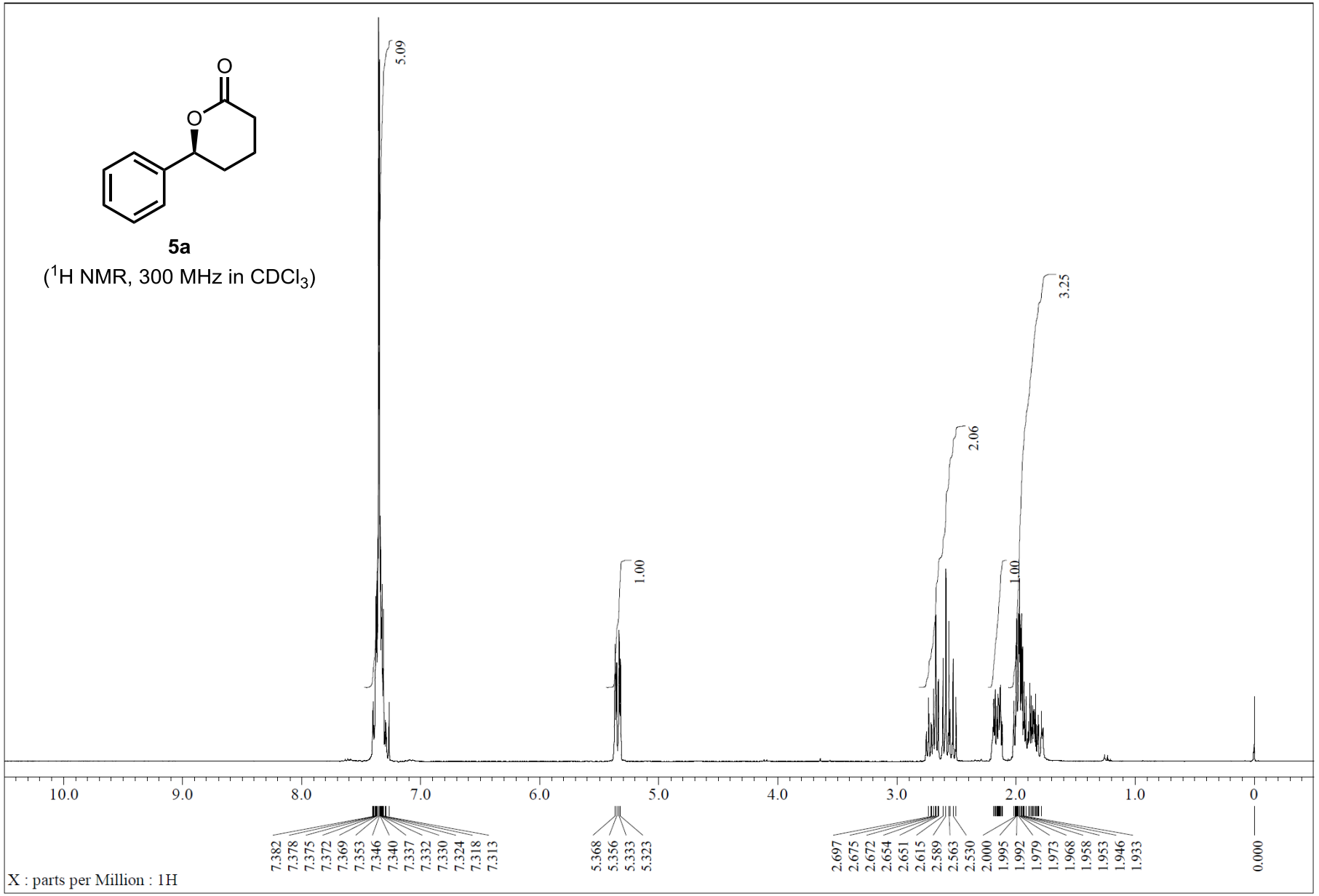

OH
O
N
H
Cl
ODPS
4o
(^{13}C NMR, 75 MHz in $CDCl_3$)
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
151.939
150.827
135.926
135.308
135.259
132.044
131.797
130.207
129.036
128.517
128.023
127.981
126.333
121.355
121.001
119.097
85.670
77.420
77.000
76.571
67.794
28.104
26.612
19.426
X : parts per Million : 13C

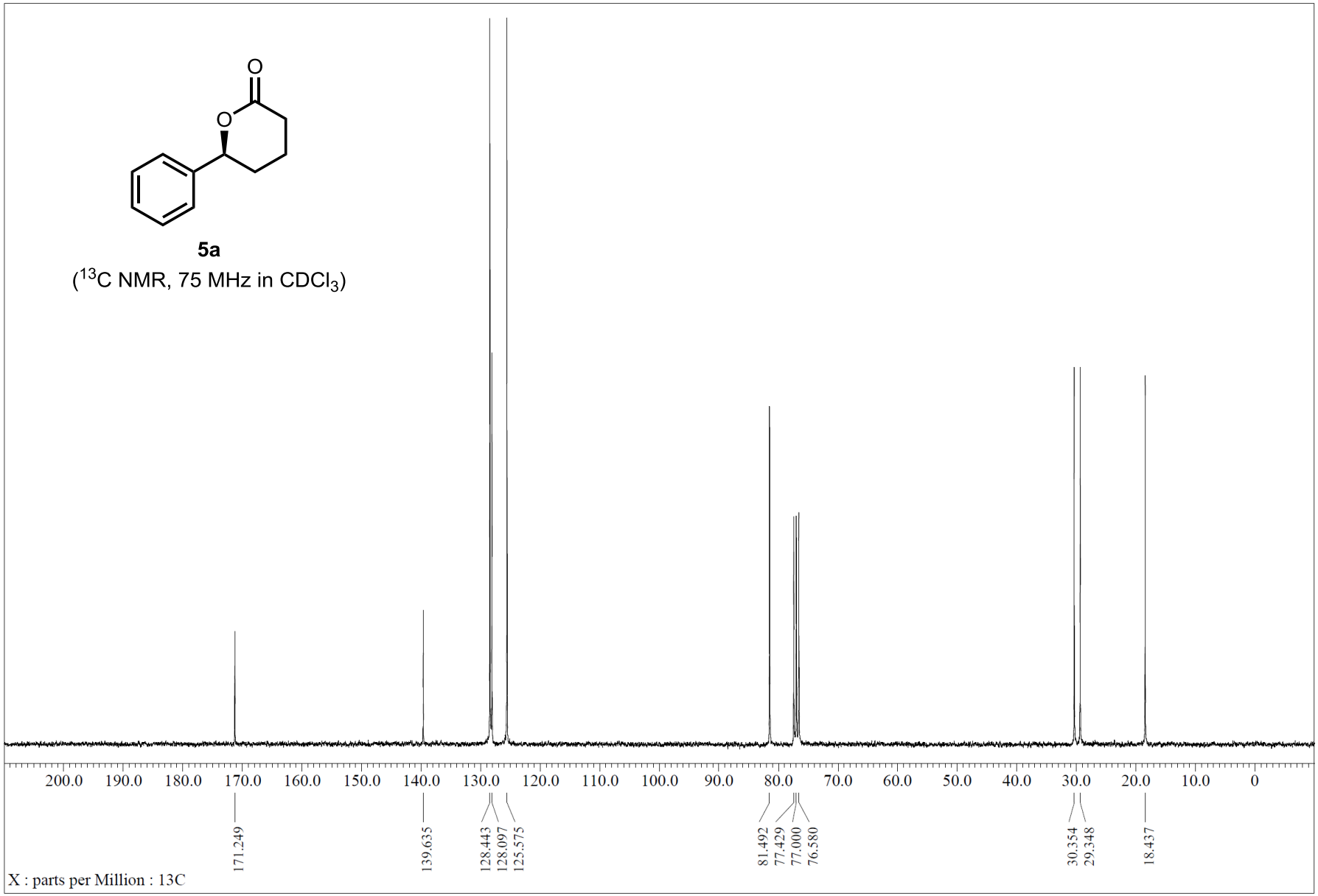

OMe
O
OH
N
H
ODPS
4p
(1H NMR, 300 MHz in CDCl3)
9.48
8.91
4.01
4.25
3.00
1.52
0.98
0.94
0.85
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.715
7.698
7.679
7.557
7.443
7.427
7.392
7.362
7.258
6.927
6.899
6.873
6.850
6.827
6.479
6.453
5.507
3.777
3.153
3.077
3.062
3.020
3.006
2.916
2.890
2.859
2.834
1.124
X : parts per Million : 1H

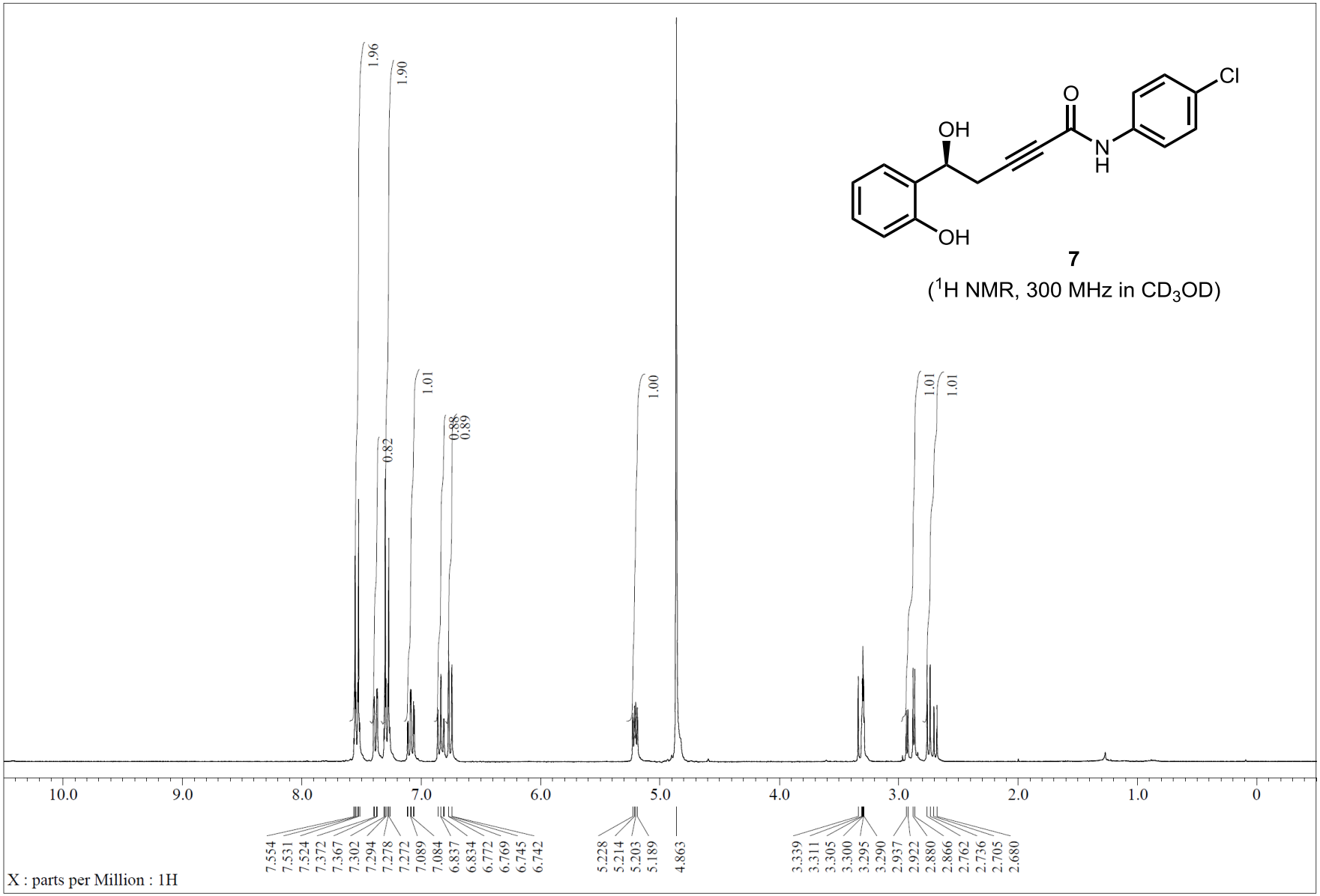

OMe
O
OH
N
H
ODPS
4p
(13C NMR, 75 MHz in CDCl3)
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
156.713
151.961
150.892
135.478
135.420
135.289
132.116
131.992
131.910
130.471
130.208
128.465
128.087
126.492
121.765
121.387
119.077
114.194
85.059
77.857
77.487
77.060
76.641
67.787
55.554
28.261
26.600
19.481
X : parts per Million : 13C

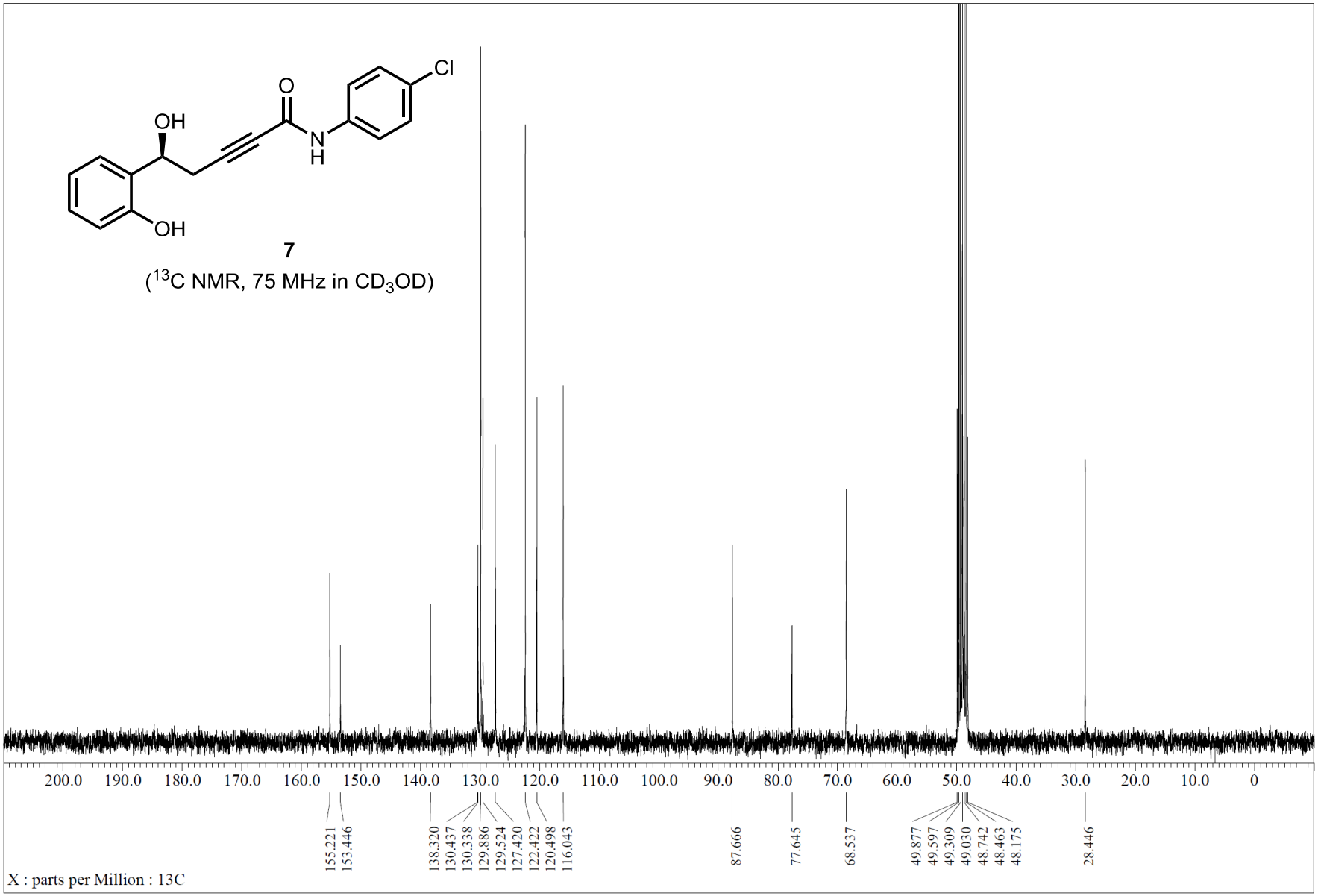

OH
O
N
H
ODPS
4q
(1H NMR, 300 MHz in CDCl3)
8.61
9.04
3.96
0.63
2.05
2.07
0.88
0.94
1.65
0.86
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.715
7.695
7.674
7.581
7.441
7.418
7.383
7.362
7.335
7.255
7.116
7.088
6.927
6.899
6.477
6.455
5.509
3.135
3.076
3.062
3.020
3.005
2.915
2.890
2.858
2.832
2.303
1.123
0.000
X : parts per Million : 1H


OH
O
N
H
ODPS
4q
(13C NMR, 75 MHz in CDCl3)
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
151.927
150.670
135.329
135.271
134.770
134.458
132.106
131.909
130.174
129.517
128.431
128.012
126.368
121.337
119.865
119.051
84.933
77.839
77.419
77.000
76.573
67.702
28.166
26.604
20.874
19.419
X : parts per Million : 13C


5a
(1H NMR, 300 MHz in CDCl3)
5.09
1.00
2.06
1.00
3.25
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.382
7.378
7.375
7.372
7.369
7.353
7.346
7.340
7.337
7.332
7.330
7.324
7.318
7.313
5.368
5.356
5.333
5.323
2.697
2.675
2.672
2.654
2.651
2.615
2.589
2.563
2.530
2.000
1.995
1.992
1.979
1.973
1.968
1.958
1.953
1.946
1.933
0.000
X : parts per Million : 1H

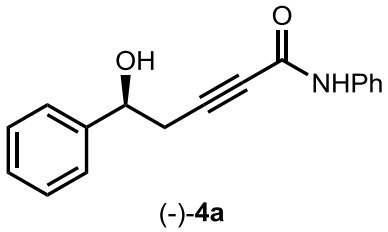

O
O
5a
(^{13}C NMR, 75 MHz in $CDCl_3$)
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
171.249
139.635
128.443
128.097
125.575
81.492
77.429
77.000
76.580
30.354
29.348
18.437
X : parts per Million : 13C


1.96
1.90
1.01
0.88
0.89
0.82
1.00
1.01
1.01
OH
O
N
H
Cl
OH
7
(^{1}H NMR, 300 MHz in CD_3OD)
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.554
7.531
7.524
7.372
7.367
7.302
7.294
7.278
7.272
7.089
7.084
6.837
6.834
6.772
6.769
6.745
6.742
5.228
5.214
5.203
5.189
4.863
3.339
3.311
3.305
3.300
3.295
3.290
2.937
2.922
2.880
2.866
2.762
2.736
2.705
2.680
X : parts per Million : 1H


OH
O
N
H
Cl
OH
7
(13C NMR, 75 MHz in CD3OD)
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
155.221
153.446
138.320
130.437
130.338
129.886
129.524
127.420
122.422
120.498
116.043
87.666
77.645
68.537
49.877
49.597
49.309
49.030
48.742
48.463
48.175
28.446
X : parts per Million : 13C

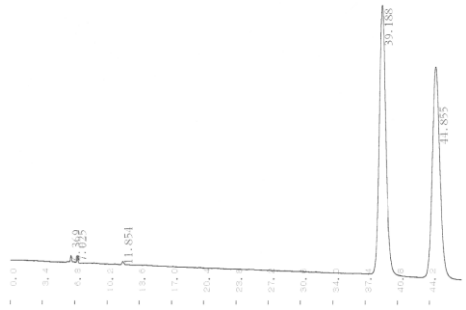
HPLC Chromatographic Conditions

Column: Daicel CHIRALPAK IC (ϕ 0.46 cm, L 25 cm); Eluent: hexane/EtOH = 95/5; Flow rate: 0.5 mL/min; UV detection: 254 nm.



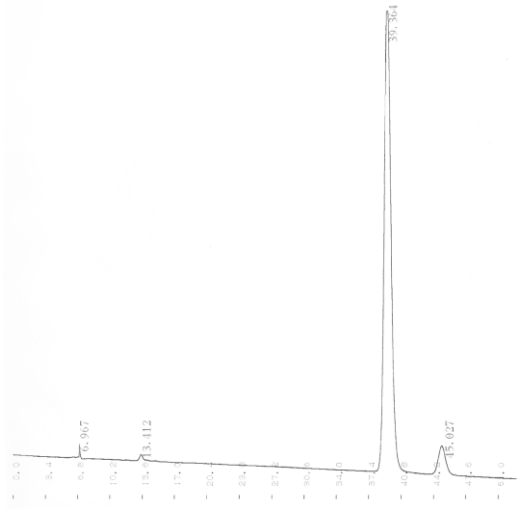
(-)-**4a**

Racemate of **4a**



TIME	AREA	HEIGHT	MK	IDNO	CONC
6.369	925	117			0.2053
7.025	993	138			0.2204
11.854	780	56			0.1731
39.188	236380	4885			52.4543
44.855	211562	3827			46.9469
TOTAL	450640	9023			100

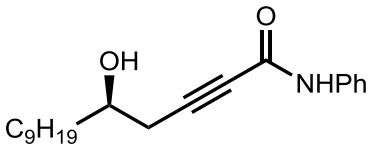
Enantiomerically enriched (-)–**4a** (94:6 er)



TIME	AREA	HEIGHT	MK	IDNO	CONC
6.967	1940	253			0.4273
13.412	2325	104			0.5122
39.364	420415	8553			92.6231
45.027	29219	523			6.4373
TOTAL	453899	9434			100

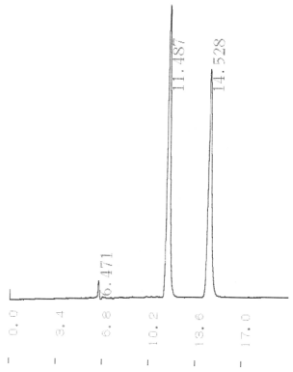
HPLC Chromatographic Conditions

Column: Daicel CHIRALPAK IC (ϕ 0.46 cm, L 25 cm); Eluent: hexane/EtOH = 90/10; Flow rate: 0.5 mL/min; UV detection: 254 nm.



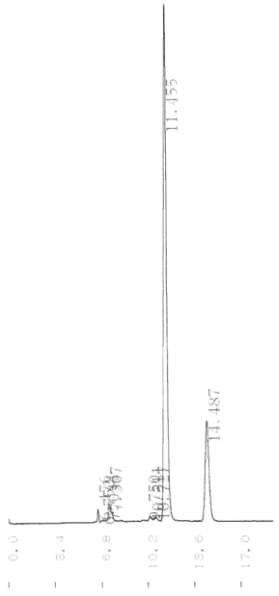
(-)-**4b**

Racemate of **4b**



TIME	AREA	HEIGHT	MK	IDNO	CONC
6.471	1593	224			1.3844
11.487	56757	3663			49.3358
14.528	56692	2861			49.2799
TOTAL	115042	6748			100

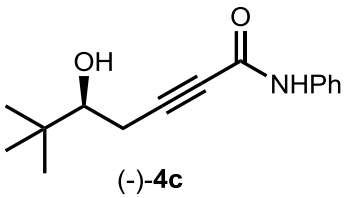
Enantiomerically enriched (-)–**4b** (80:20 er)



TIME	AREA	HEIGHT	MK	IDNO	CONC
6.476	1073	165			0.8201
6.752	232	23			0.1774
7.033	208	19	V		0.1591
7.307	3961	235	V		3.0285
9.75	291	13			0.2228
10.311	857	58	V		0.6549
10.727	741	43	V		0.5663
11.455	98745	6486			75.4937
14.487	24691	1261			18.8773
TOTAL	130799	8304			100

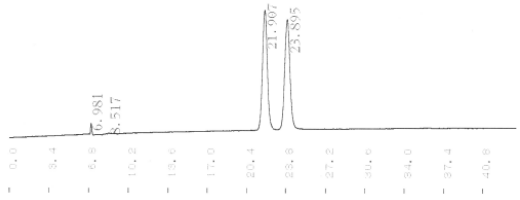
HPLC Chromatographic Conditions

Column: Daicel CHIRALPAK IC (ϕ 0.46 cm, L 25 cm); Eluent: hexane/EtOH = 95/5; Flow rate: 0.5 mL/min; UV detection: 254 nm.



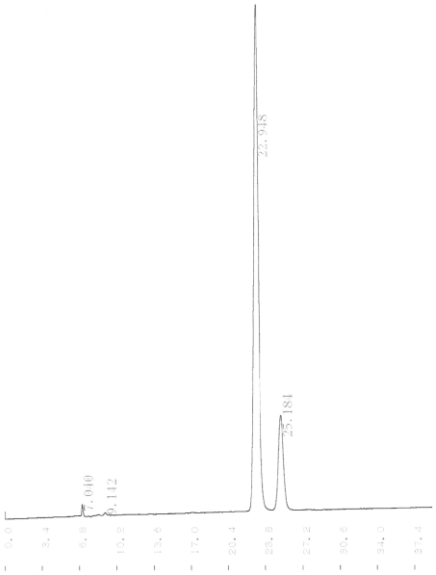
(-)-**4c**

Racemate of **4c**



TIME	AREA	HEIGHT	MK	IDNO	CONC
6.981	1139	164			1.1167
8.517	106	11			0.1041
21.907	50493	1758			49.5095
23.895	50248	1613	V		49.2696
TOTAL	101986	3546			100

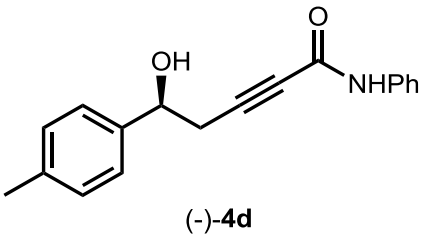
Enantiomerically enriched (-)–**4c** (83:17 er)



TIME	AREA	HEIGHT	MK	IDNO	CONC
7.04	1450	186			0.5116
9.142	511	36			0.1803
22.948	233511	7905			82.3816
25.184	47978	1483	V		16.9265
TOTAL	283451	9610			100

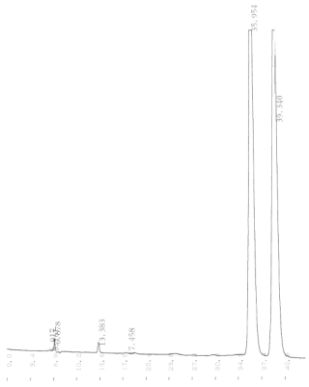
HPLC Chromatographic Conditions

Column: Daicel CHIRALPAK IC (ϕ 0.46 cm, L 25 cm); Eluent: hexane/EtOH = 95/5; Flow rate: 0.5 mL/min; UV detection: 254 nm.



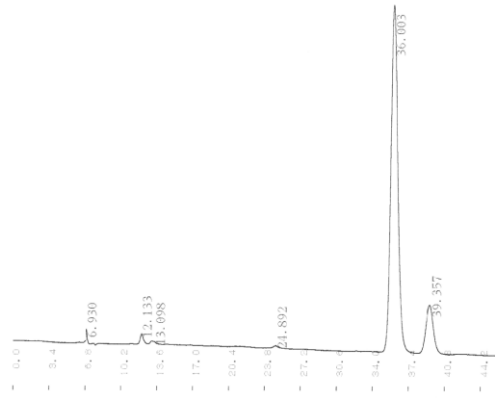
(-)-**4d**

Racemate of **4d**



TIME	AREA	HEIGHT	MK	IDNO	CONC
6.017	83	10			0.0086
6.167	210	11	V		0.0216
6.878	3534	328			0.3641
13.383	4246	264			0.4375
17.458	466	19			0.048
35.954	480867	10440			49.5476
39.34	481110	9582			49.5726
TOTAL	970515	20655			100

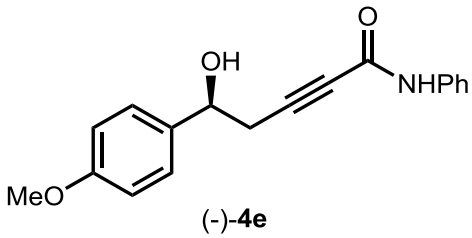
Enantiomerically enriched (-)–**4d** (87:13 er)



TIME	AREA	HEIGHT	MK	IDNO	CONC
6.93	2214	233			0.7268
12.133	3717	169			1.2202
13.098	1334	48	V		0.438
24.892	740	30			0.243
36.003	257780	5628			84.622
39.357	38840	796			12.75
TOTAL	304626	6904			100

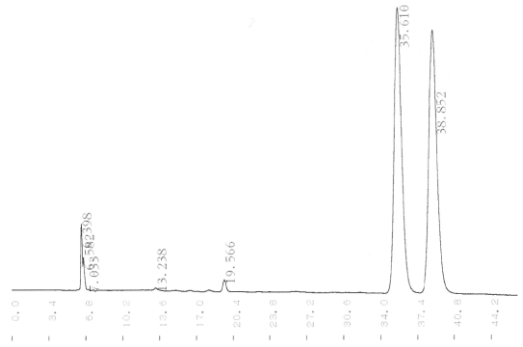
HPLC Chromatographic Conditions

Column: Daicel CHIRALPAK IC (ϕ 0.46 cm, L 25 cm); Eluent: hexane/EtOH = 92/8; Flow rate: 0.5 mL/min; UV detection: 254 nm.



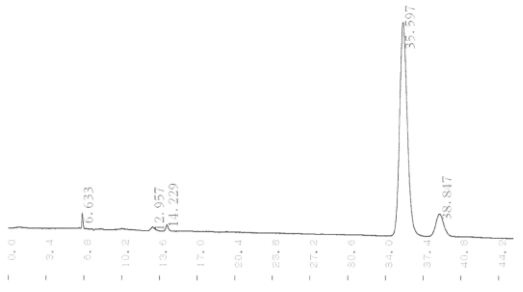
(-)-**4e**

Racemate of **4e**



TIME	AREA	HEIGHT	MK	IDNO	CONC
6.398	9714	1037			2.1221
6.582	4848	514	V		1.0592
7.033	192	18	V		0.0419
13.238	785	38			0.1714
19.566	4196	193			0.9167
35.61	218774	4514			47.7958
38.852	219218	4157	V		47.8928
TOTAL	457727	10472			100

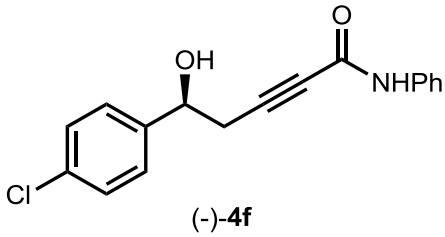
Enantiomerically enriched (-)–**4e** (90:10 er)



TIME	AREA	HEIGHT	MK	IDNO	CONC
6.633	1692	236			0.9352
12.957	1508	60			0.8334
14.229	1689	100			0.9337
35.597	158144	3299			87.4064
38.847	17897	352			9.8914
TOTAL	180930	4047			100

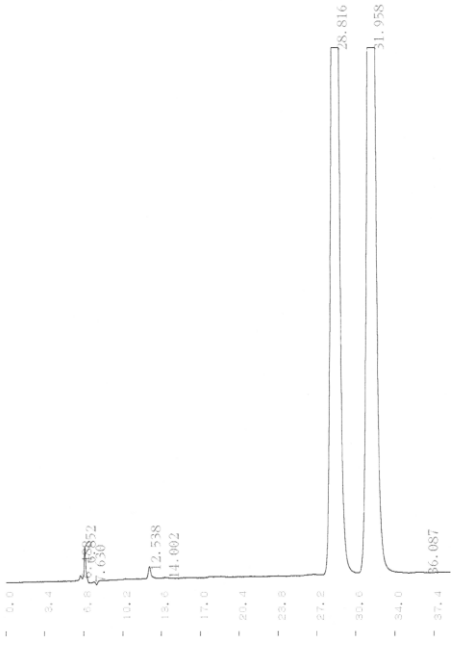
HPLC Chromatographic Conditions

Column: Daicel CHIRALPAK IC (ϕ 0.46 cm, L 25 cm); Eluent: hexane/EtOH = 95/5; Flow rate: 0.5 mL/min; UV detection: 254 nm.



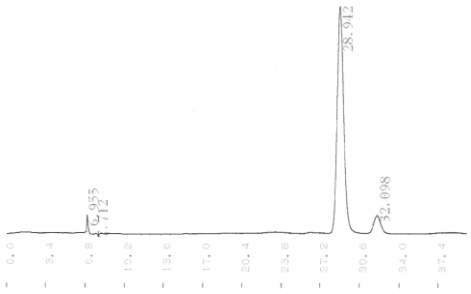
(-)-**4f**

Racemate of **4f**



TIME	AREA	HEIGHT	MK	IDNO	CONC
6.488	1202	86			0.0852
6.852	5632	523	V		0.399
7.63	547	34			0.0388
12.538	2854	175			0.2022
14.002	188	10			0.0133
28.816	698576	17100			49.4953
31.958	701595	15735	V		49.7092
36.087	804	14	V		0.057
TOTAL	1411398	33677			100

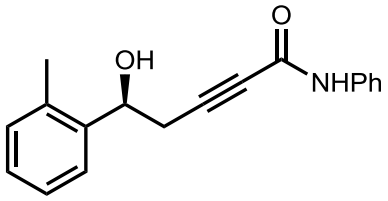
Enantiomerically enriched (-)–**4f** (92:8 er)



TIME	AREA	HEIGHT	MK	IDNO	CONC
6.955	2386	271			1.6427
7.712	355	24			0.2443
28.942	131347	3354			90.4121
32.098	11188	265			7.701
TOTAL	145276	3914			100

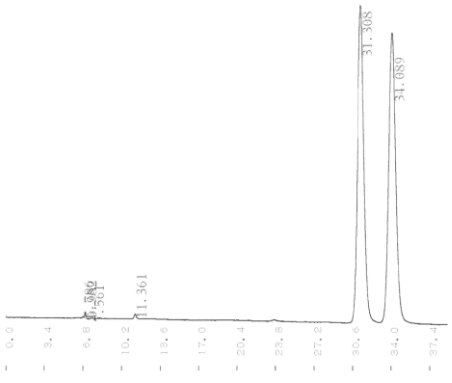
HPLC Chromatographic Conditions

Column: Daicel CHIRALPAK IC (ϕ 0.46 cm, L 25 cm); Eluent: hexane/EtOH = 95/5; Flow rate: 0.5 mL/min; UV detection: 254 nm.



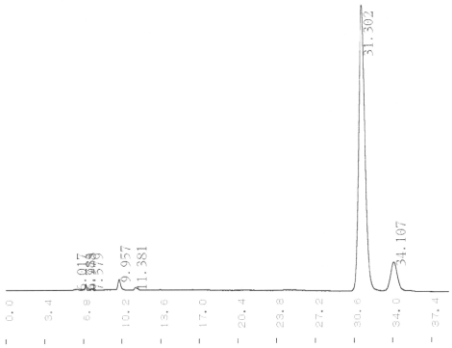
(-)-**4g**

Racemate of **4g**



TIME	AREA	HEIGHT	MK	IDNO	CONC
6.786	258	31			0.0666
6.982	824	107	V		0.2127
7.561	216	14			0.0558
11.361	1041	77			0.2689
31.308	192742	4798			49.7641
34.089	192230	4395	V		49.6318
TOTAL	387311	9422			100

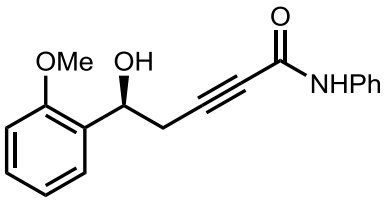
Enantiomerically enriched (-)–**4g** (90:10 er)



TIME	AREA	HEIGHT	MK	IDNO	CONC
6.017	68	8			0.0347
6.783	70	10			0.036
6.978	710	96	V		0.3648
7.579	330	28			0.1695
9.957	2583	154			1.3277
11.381	792	37			0.4072
31.302	171640	4294			88.2335
34.107	18337	436			9.4265
TOTAL	194529	5063			100

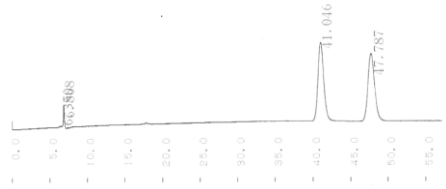
HPLC Chromatographic Conditions

Column: Daicel CHIRALPAK IC (ϕ 0.46 cm, L 25 cm); Eluent: hexane/EtOH = 95/5; Flow rate: 0.5 mL/min; UV detection: 254 nm.



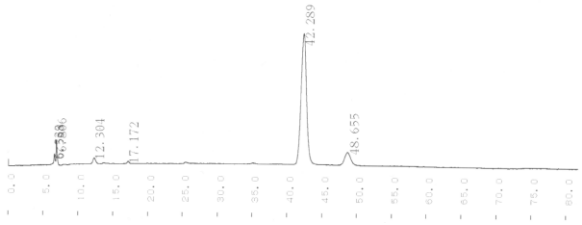
(-)-**4h**

Racemate of **4h**



TIME	AREA	HEIGHT	MK	IDNO	CONC
6.35	504	22			0.3873
6.868	3121	351	V		2.3975
41.046	62900	1185			48.3185
47.787	63652	1022			48.8967
TOTAL	130177	2580			100

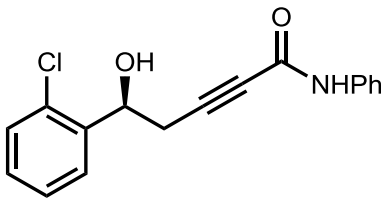
Enantiomerically enriched (-)–**4h** (90:10 er)



TIME	AREA	HEIGHT	MK	IDNO	CONC
6.333	188	18			0.1343
6.568	2078	179	V		1.4875
6.866	3896	406	V		2.7888
12.304	2692	99			1.9265
17.172	721	39			0.5162
42.289	116559	2142			83.4315
48.655	13573	216			9.7152
TOTAL	139707	3098			100

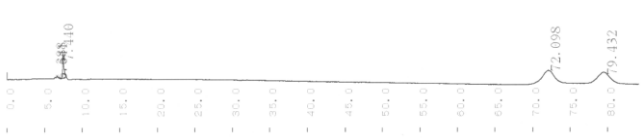
HPLC Chromatographic Conditions

Column: Daicel CHIRALPAK IC (ϕ 0.46 cm, L 25 cm); Eluent: hexane/EtOH = 98/2; Flow rate: 0.5 mL/min; UV detection: 254 nm.



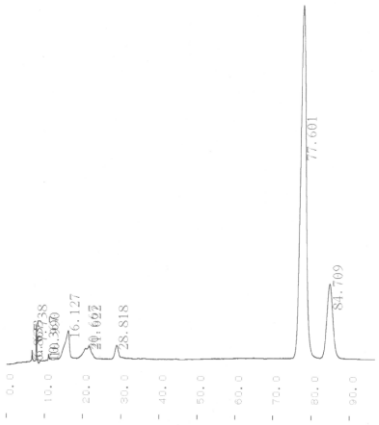
(-)-**4i**

Racemate of **4i**



TIME	AREA	HEIGHT	MK	IDNO	CONC
6.388	221	23			0.5175
6.641	515	43	V		1.208
7.44	5574	389			13.0687
72.098	17914	186			42.0021
79.432	18427	167			43.2037
TOTAL	42651	809			100

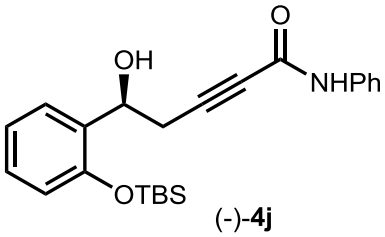
Enantiomerically enriched (-)–**4i** (81:19 er)



TIME	AREA	HEIGHT	MK	IDNO	CONC
6.633	1377	162			0.1839
6.867	279	34	V		0.0372
7.738	6203	565			0.8283
10.367	112	8			0.0149
10.99	1231	89			0.1644
16.127	34922	418			4.6634
20.667	10196	143			1.3615
21.622	13484	183	V		1.8006
28.818	14350	205			1.9163
77.601	542093	5285			72.3897
84.709	124607	1120	V		16.6397
TOTAL	748854	8213			100

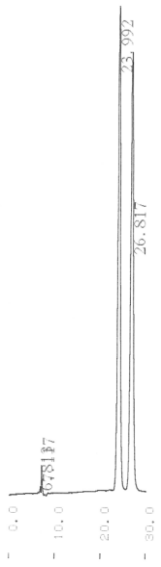
HPLC Chromatographic Conditions

Column: Daicel CHIRALPAK IC (ϕ 0.46 cm, L 25 cm); Eluent: hexane/EtOH = 97/3; Flow rate: 0.5 mL/min; UV detection: 254 nm.



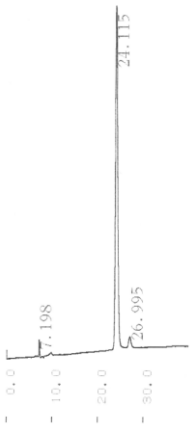
(-)-**4j**

Racemate of **4j**



TIME	AREA	HEIGHT	MK	IDNO	CONC
6.813	643	79			0.1331
7.117	3448	343			0.7135
23.992	238565	6098			49.3743
26.817	240521	5525	V		49.7791
TOTAL	483177	12045			100

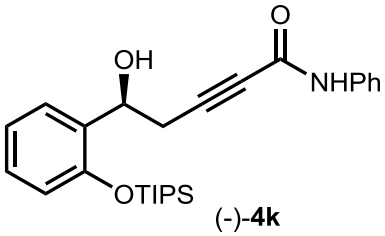
Enantiomerically enriched (-)–**4j** (97:3 er)



TIME	AREA	HEIGHT	MK	IDNO	CONC
7.198	1986	217			1.3013
24.115	145597	4320			95.4079
26.995	5022	134			3.2908
TOTAL	152605	4671			100

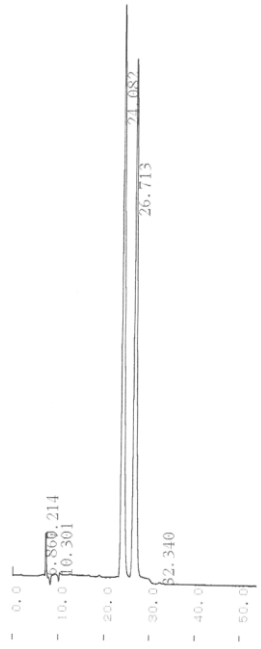
HPLC Chromatographic Conditions

Column: Daicel CHIRALPAK IC (ϕ 0.46 cm, L 25 cm); Eluent: hexane/EtOH = 97/3; Flow rate: 0.5 mL/min; UV detection: 254 nm.



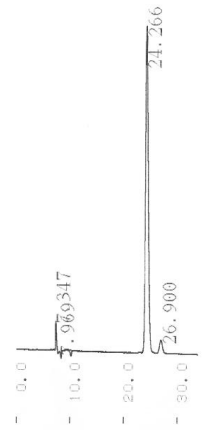
(-)-**4k**

Racemate of **4k**



TIME	AREA	HEIGHT	MK	IDNO	CONC
6.86	133	15			0.0237
7.214	7448	543			1.3303
10.301	1292	72			0.2307
24.082	276428	7198			49.3735
26.713	273824	6521	V		48.9083
32.34	748	19			0.1335
TOTAL	559871	14368			100

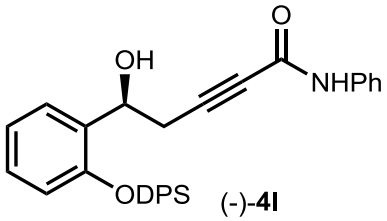
Enantiomerically enriched (-)–**4k** (96:4 er)



TIME	AREA	HEIGHT	MK	IDNO	CONC
7.347	4016	331			3.0074
7.969	899	42			0.6732
24.266	123013	3531			92.1249
26.9	5601	147			4.1945
TOTAL	133529	4051			100

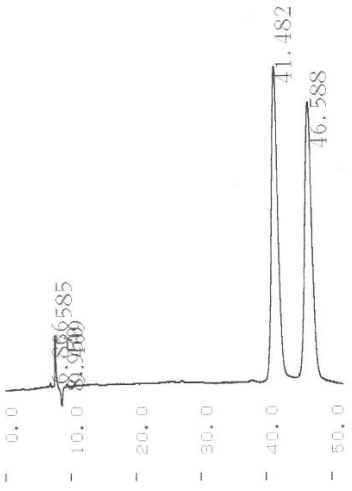
HPLC Chromatographic Conditions

Column: Daicel CHIRALPAK IC (ϕ 0.46 cm, L 25 cm); Eluent: hexane/EtOH = 98/2; Flow rate: 0.5 mL/min; UV detection: 254 nm.



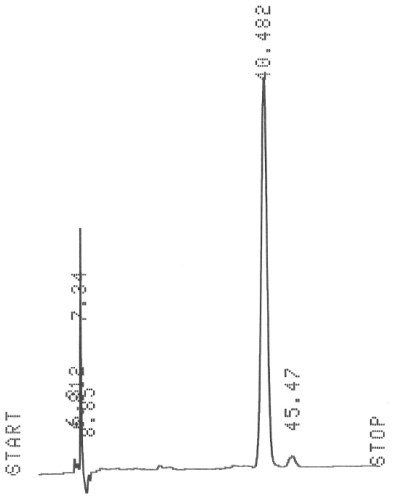
(-)-**4l**

Racemate of **4l**



TIME	AREA	HEIGHT	MK	IDNO	CONC
6.866	340	39			0.0886
7.585	9289	480			2.4207
8.95	2894	108			0.7542
9.409	1119	61	V		0.2915
41.482	186716	2751			48.6608
46.588	183351	2440			47.7841
TOTAL	383708	5878			100

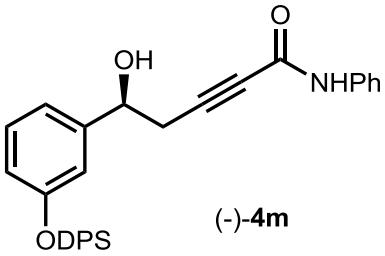
Enantiomerically enriched (-)–**4l** (98:2 er)



TIME	AREA	MK	IDNO	CONC
6.3	2312			0.6331
6.812	4473	V		1.2248
7.34	36686	V		10.0455
8.85	2293			0.6278
40.482	312989			85.7037
45.47	6446			1.765
TOTAL	365199			100

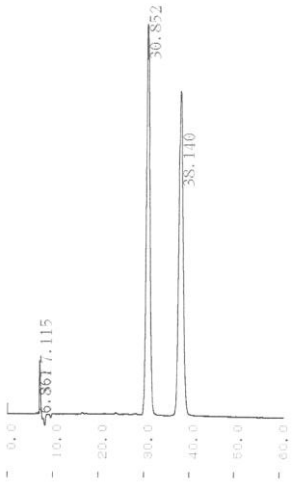
HPLC Chromatographic Conditions

Column: Daicel CHIRALPAK IC (ϕ 0.46 cm, L 25 cm); Eluent: hexane/EtOH = 97/3; Flow rate: 0.5 mL/min; UV detection: 254 nm.



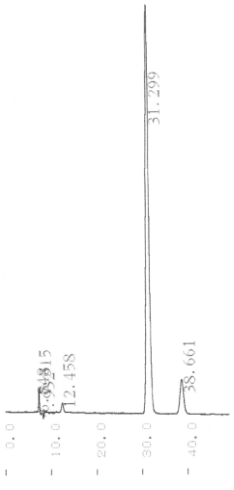
(-)-**4m**

Racemate of **4m**



TIME	AREA	HEIGHT	MK	IDNO	CONC
6.367	678	22			0.1223
6.861	707	58	V		0.1275
7.115	10823	714	V		1.9516
30.852	270742	4922			48.819
38.14	271632	4089			48.9796
TOTAL	554583	9804			100

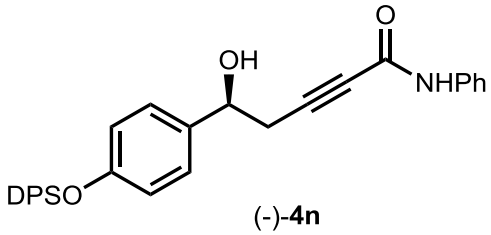
Enantiomerically enriched (-)–**4m** (91:9 er)



TIME	AREA	HEIGHT	MK	IDNO	CONC
6.848	239	23			0.0854
7.315	3930	324	V		1.4032
7.932	967	43			0.3453
12.458	3939	126			1.4062
31.299	245821	5134			87.767
38.661	25188	438			8.9929
TOTAL	280083	6087			100

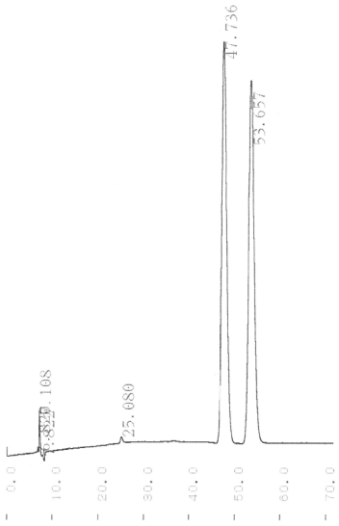
HPLC Chromatographic Conditions

Column: Daicel CHIRALPAK IC (ϕ 0.46 cm, L 25 cm); Eluent: hexane/EtOH = 97/3; Flow rate: 0.5 mL/min; UV detection: 254 nm.



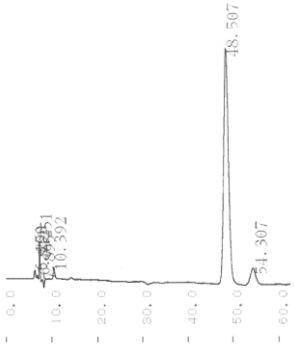
(-)-**4n**

Racemate of **4n**



TIME	AREA	HEIGHT	MK	IDNO	CONC
6.82	695	72			0.0915
7.108	6345	532	V		0.8345
7.822	736	44			0.0968
25.08	2322	76			0.3053
47.736	373304	5041			49.0938
53.657	376986	4545			49.578
TOTAL	760390	10310			100

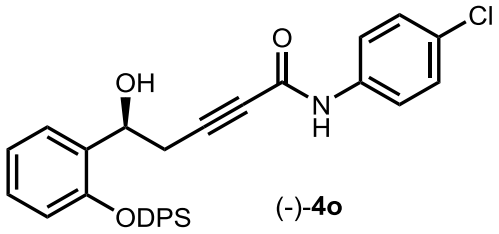
Enantiomerically enriched (-)–**4n** (92:8 er)



TIME	AREA	HEIGHT	MK	IDNO	CONC
6.15	1093	100			0.4417
6.293	1951	125	V		0.7881
6.842	960	71	V		0.3877
7.251	5612	498	V		2.2671
7.895	1121	55			0.4526
10.392	3584	152			1.4479
48.507	215591	2980			87.0875
54.307	17644	215			7.1273
TOTAL	247556	4196			100

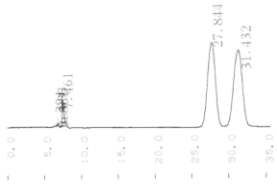
HPLC Chromatographic Conditions

Column: Daicel CHIRALPAK IC (ϕ 0.46 cm, L 25 cm); Eluent: hexane/EtOH = 98/2; Flow rate: 0.5 mL/min; UV detection: 254 nm.



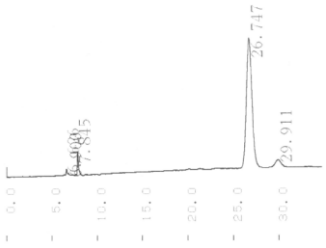
(-)-**4o**

Racemate of **4o**



TIME	AREA	HEIGHT	MK	IDNO	CONC
6.394	250	25			0.1236
6.633	317	31	V		0.1566
6.861	756	72	V		0.3733
7.461	8405	433	V		4.1497
27.844	95739	1294			47.2659
31.432	97086	1177	V		47.9309
TOTAL	202554	3032			100

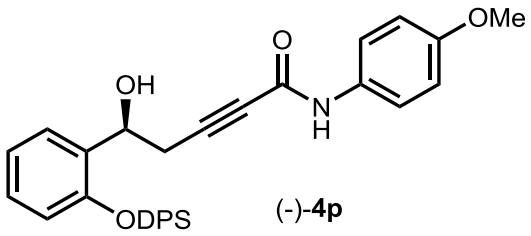
Enantiomerically enriched (-)–**4o** (95:5 er)



TIME	AREA	HEIGHT	MK	IDNO	CONC
6.626	644	80			0.8191
6.9	124	15	V		0.1577
7.845	2813	286			3.5758
26.747	70893	1637			90.1107
29.911	4199	93			5.3367
TOTAL	78673	2111			100

HPLC Chromatographic Conditions

Column: Daicel CHIRALPAK IC (ϕ 0.46 cm, L 25 cm); Eluent: hexane/EtOH = 98/2; Flow rate: 0.5 mL/min; UV detection: 254 nm.

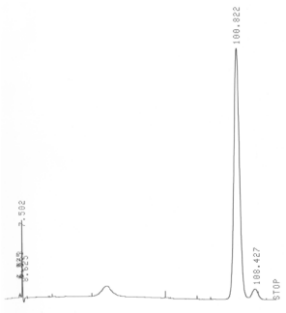


(-)-**4p**

Racemate of **4p**

TIME	AREA	MK	IDNO	CONC
6.3	273			0.0921
6.815	488	V		0.1646
7.737	5610			1.8901
110.125	143062			48.1976
118.983	147390			49.6555
TOTAL	296824			100

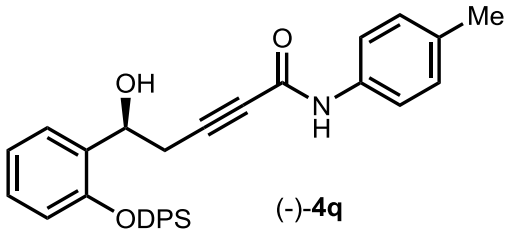
Enantiomerically enriched (-)–**4p** (96:4 er)



TIME	AREA	MK	IDNO	CONC
6.325	693			0.062
6.563	909	V		0.0813
6.8	502	V		0.0449
7.502	19550			1.7481
8.625	225			0.0202
100.822	1057282			94.5388
108.427	39196			3.5048
TOTAL	1118358			100

HPLC Chromatographic Conditions

Column: Daicel CHIRALPAK IC (ϕ 0.46 cm, L 25 cm); Eluent: hexane/EtOH = 98/2; Flow rate: 0.5 mL/min; UV detection: 254 nm.

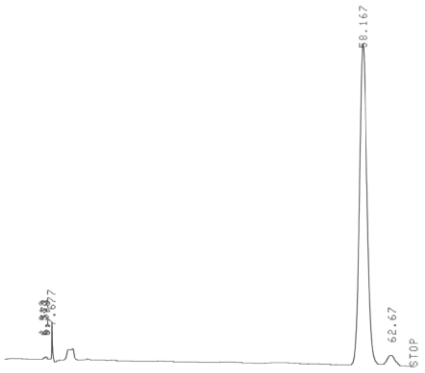


(-)-**4q**

Racemate of **4q**

TIME	AREA	MK	IDNO	CONC
7.672	4127			2.2129
59.65	90036			48.2773
64.467	92334			49.5098
TOTAL	186497			100

Enantiomerically enriched (-)–**4q** (97:3 er)

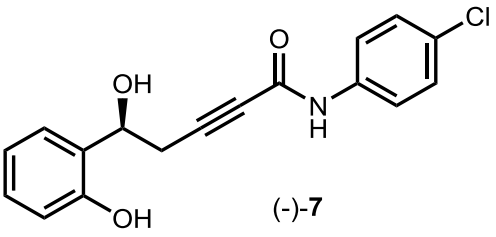


TIME	AREA	MK	IDNO	CONC
6.313	472			0.0843
6.573	569	V		0.1016
6.798	468	V		0.0836
7.677	6165			1.1008
58.167	536965			95.8751
62.67	15428			2.7547
TOTAL	560067			100

HPLC Chromatographic Conditions

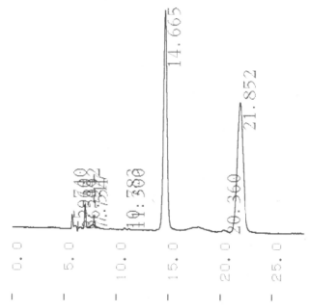
Column: Daicel CHIRALPAK IG (ϕ 0.46 cm, L 25 cm); Eluent: hexane/EtOH = 80/20; Flow rate:

0.5 mL/min; UV detection: 254 nm.



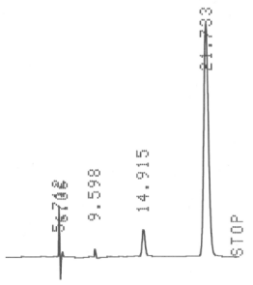
(-)-**7**

Racemate of **7**



TIME	AREA	HEIGHT	MK	IDNO	CONC
5.74	1519	164			1.229
6.992	3318	296	V		2.6848
7.754	1585	62	V		1.2825
14.665	57908	2421			46.8544
21.852	59261	1434			47.9493
TOTAL	123591	4376			100

Enantiomerically enriched (-)–**7** (93:7 er)



TIME	AREA	MK	IDNO	CONC
5.712	4968			4.1051
6.06	3146			2.5991
9.598	1106			0.9138
14.915	7514			6.2084
21.733	104298			86.1736
TOTAL	121032			100