Palladium-catalyzed Three-Component Reaction of 3-(Pinacolatoboryl)ally Acetates, Aldehydes, and Organoboranes: A New Entry to Stereoselective Synthesis of (*Z*)-*anti*-Homoallylic Alcohols

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General

All reactions were carried out in flame-dried glassware under argon atmosphere. Tetrahydrofuran (THF) and diethyl ether were dried over Na with benzophenone-ketyl intermediate as indicator. Triethylamine were purified by distillation from CaH_2. All commercial reagents were used as received unless otherwise noted. **Flash chromatography** was performed with KANTO silica gel 60 (63-210 mm) and KANTO silica gel 60N (63-210 mm). **Thin layer chromatography** was carried out using Merck silica gel 60 F254 TLC plates coated with fluorescent indicator UV254. **NMR spectra** were recorded on JEOL α-GX400 or JNX-ECX500 spectrometer. Chemical shifts (δ) are reported in ppm and coupling constants are reported in Hz with $CDCl_3$ referenced at 7.26 (1H) and 77.16 ppm (13C), respectively. Peak multiplicities are designated by the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad and coupling constants are provided in (J) Hz. The **IR spectra** were recorded on a SHIMADZU FTIR-8400 spectrophotometer. High-resolution mass (**HR-MS**) spectral data were obtained on a JEOL MStation JMS-700. Chiral HPLC was performed on a Waters HPLC (pump: Waters 600 pump, column: Chiralpak AD-H). The specific rotation of a chiral compound was determined on a HORIBA SEPA-500 apparatus and transformed for a given temperature according to the following formula

$$[\alpha]_D^T = \frac{\alpha \cdot 100}{c \cdot d}$$

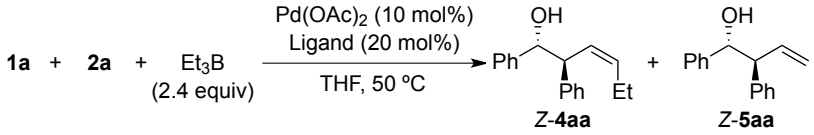
α: measured value for optical rotation; *c*: concentration in g/100 mL; *d*: length of the quartz cuvette in dm; *T*: temperature in °C.

Materials

Substrates (**1a–1k**),[1] (*E*)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl acetate (**1m**),[2] and (*R*)-1-phenylpropargyl alcohol were prepared according to the literature procedure.[3] (*E*)-1-Phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl acetate (**1a**) was synthesized previously[1]. (*R*)-1-phenyl-2-propyn-1-ol was purchased from Aldrich and used as received.

Optimization details

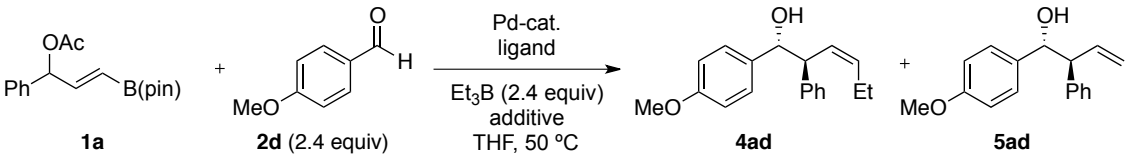
Table S1. Reaction optimization[a]



Entry	ligand	time (h)	**4aa** (%)[b]	*anti*-**4aa**/*syn*-**4aa**[c]	**5aa** [%]
1	PPh_3	2	64	>99:1	14
2	$(p\text{-}FC_6H_4)_3P$	1.5	64	>99:1	14
3	$(p\text{-}MeOC_6H_4)_3P$	2.5	62	>99:1	13
4	$(o\text{-tol})_3P$	2	77	>99:1	6
5	$CyPh_2P$	2	76	>99:1	6
6[d]	$CyPh_2P$	4	75	>99:1	5
7	Cy_3P	18	5	>99:1	0
8	$(n\text{-Bu})_3P$	17	9	>99:1	10
9	*rac*-BINAP	4	0	-	0
10	Xantphos	4	0	-	0

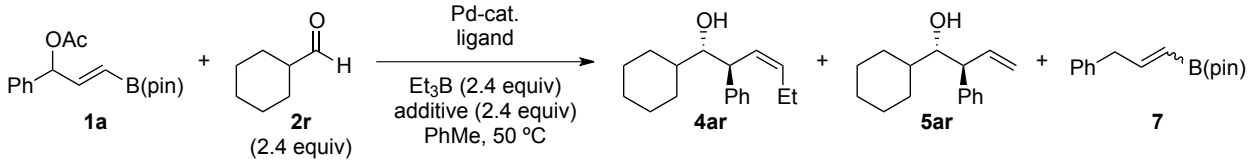
[a] Reaction conditions: **1a** (0.5 mmol), **2a** (1.2 mmol), Et_3B (1.2 mmol), $Pd(OAc)_2$ (10 mol%) and a phosphine ligand (20 mol% as P) in THF (2 mL) at 50 °C. [b] Yield of the isolated product. [c] Determined by NMR analysis. [d] $Pd(OAc)_2$ (5 mol%) and $CyPh_2Ph$ (10 mol%) were used.

Table S2. Reaction optimization



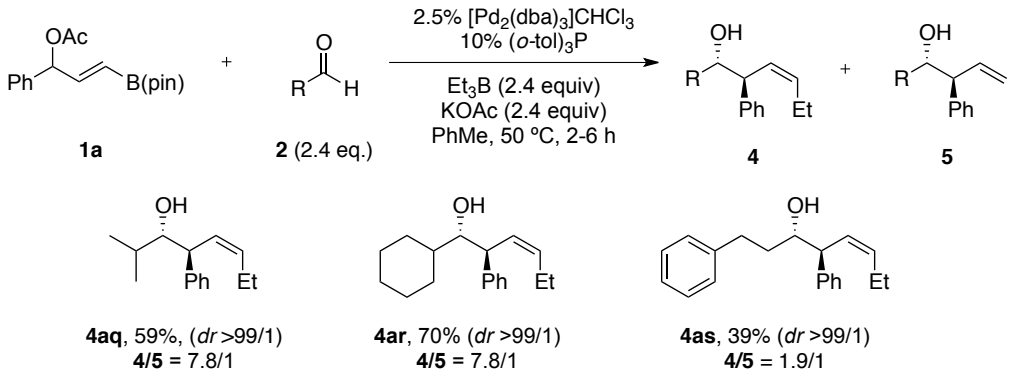
Entry	Pd-cat. (mol%)	ligand (mol%)	additive	time (h)	**4ar** (%)	**5ar** (%)
1	$Pd(OAc)_2$ (10)	$CyPh_2P$ (20)	–	3	76	7
2	$Pd(OAc)_2$ (10)	$t\text{-BuPh}_2P$ (20)	–	4	76	6
3	$Pd(OAc)_2$ (10)	Ph_3P (20)	–	3	58	10
4	$Pd(OAc)_2$ (10)	$(o\text{-tol})_3P$ (20)	–	3	65	7
5	$Pd(OAc)_2$ (5)	$CyPh_2P$ (10)	–	5	74	5
6	$Pd_2(dba)_3CHCl_3$ (5)	$(o\text{-tol})_3P$ (10)	KOAc	3	70	9

Table S3. **Reaction optimization for aliphatic aldehydes: additive effects**

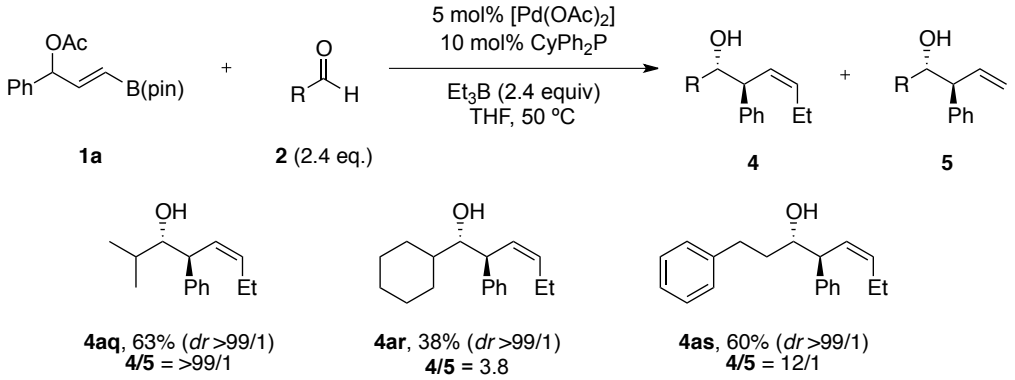


Entry	Pd-cat. (mol%)	ligand (mol%)	additive	time (h)	**4ar** (%)	**5ar** (%)	**7** (%)
1[a]	$Pd(OAc)_2$ (5)	$CyPh_2P$ (10)	–	18	38	10	trace
2	$Pd(OAc)_2$ (5)	$CyPh_2P$ (10)	–	4	37	4	trace
3	$Pd_2(dba)_3CHCl_3$ (2.5)	(*o*-tol)$_3$P (10)	Cs_2CO_3	0.5	41	17	39[b]
4	$Pd_2(dba)_3CHCl_3$ (2.5)	(*o*-tol)$_3$P (10)	KOAc	2.5	70	9	–
5	$Pd_2(dba)_3CHCl_3$ (2.5)	(*o*-tol)$_3$P (10)	NaOAc	3	28	10	17[b]
6	$Pd_2(dba)_3CHCl_3$ (2.5)	(*o*-tol)$_3$P (10)	CsOAc	5	39	20	19[b]

[a] THF was used as a solvent. [b] *E/Z* = 1.6/1. [c] *E/Z* = 1/2.2. [d] *E/Z* = 2.6/1.



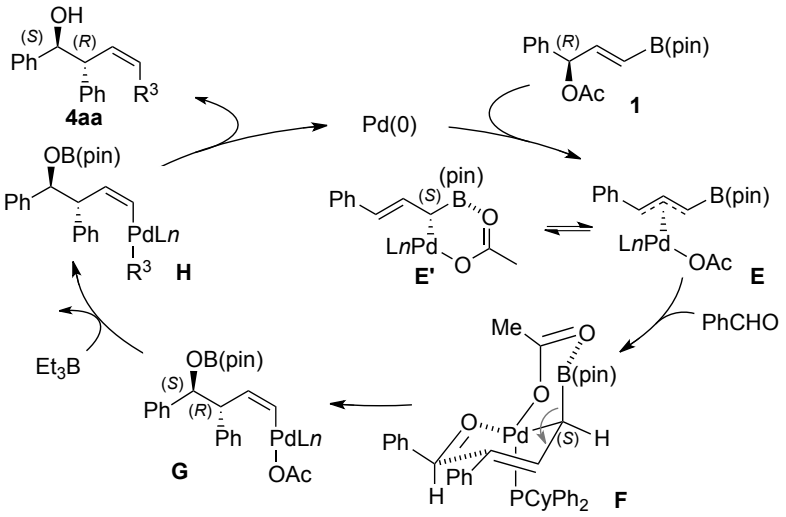
Scheme S1. Additive effects for palladium-catalyzed three-component reaction of **1a**, triethylborane, and aliphatic aldehydes.



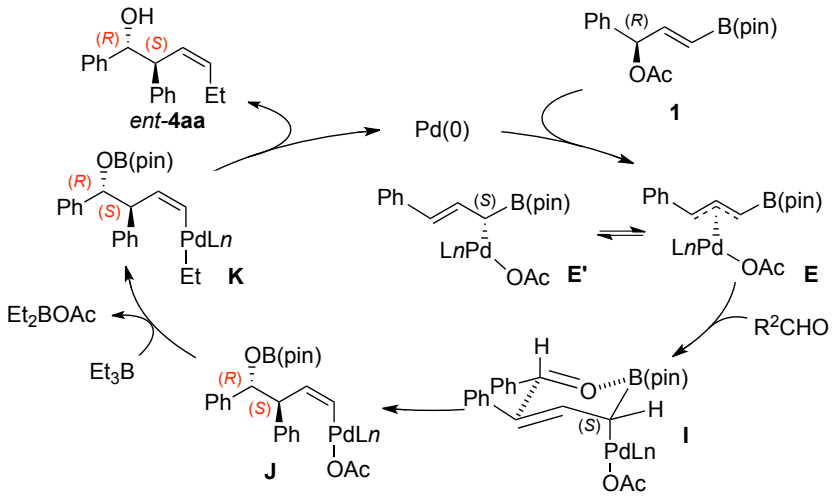
Scheme S2. Pd-catalyzed three-component reaction of **1a**, Et_3B, and aliphatic aldehydes.

Discussion of the reaction mechanism (Scheme 8)

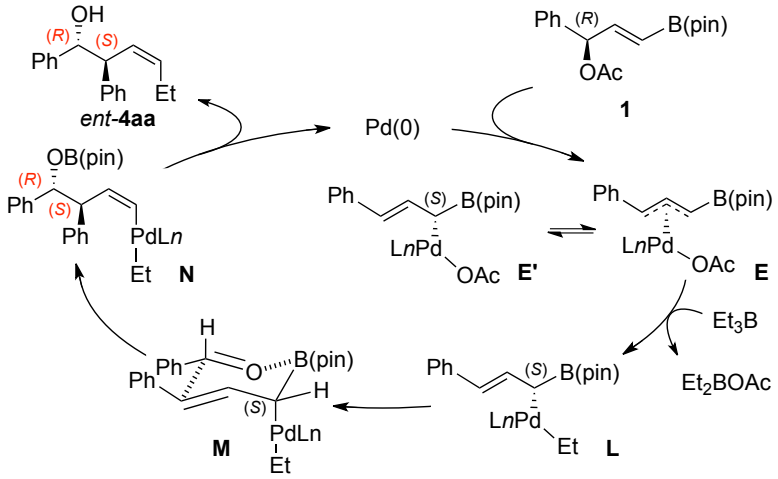
Path A : This reaction mechanism leads to (1*S*, 2*R*)-**4aa**.



Path B: This reaction mechanism leads to (1*R*, 2*S*)-**4aa**.



Path C: This reaction mechanism leads to (1*R*, 2*S*)-**4aa**.

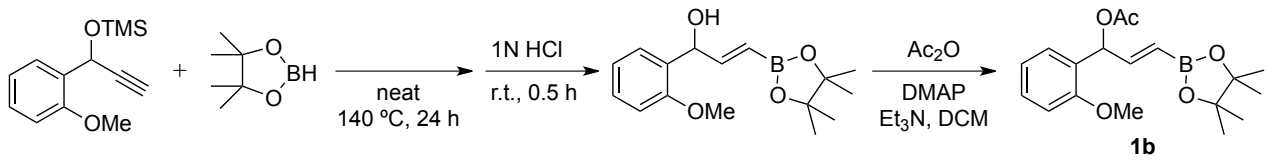


Scheme S3. Plausible reaction mechanisms.

From a mechanistic viewpoint, two other possible reaction paths might be considered (Scheme S3, Paths B and C). One possible reaction mechanism (Path B) consists of 1) oxidative addition of **1** to a palladium complex should lead to a η^3-allylpalladium intermediate **E**. The allylboronate in the allylic *gem*-palladium/boryl intermediate **E′** (depicted in another η^1-allyl form for simplicity) undergoes nucleophilic allylation toward an aldehyde via a closed transition state **I**, where the palladium complex predominantly locates at the axial position to form (*Z*)-vinylpalladium acetate intermediate **J** due to gauche strain of the palladium complex with pinacol ester over $A^{1,3}$ strain. Transmetalation of **J** with an organoborane followed by reductive elimination from a vinylpalladium intermediate **K** gives the desired product **4**. However, this mechanism does not meet the results of chirality transfer experiments.

Another possible reaction mechanism (Path C) is also depicted in scheme 3. The exchange reaction of the alkyl group of the trialkylborane and the acetoxy group of a η^3-allylpalladium intermediate **E** promotes the formation of η^1-allylpalladium intermediate **L**; this undergoes nucleophilic allylation of an aldehyde with allylborane toward an aldehyde via a closed transition state **M** followed by reductive elimination from the intermediate **N** to yield the desired product **4**. However, this mechanism does not meet the results of chirality transfer experiments, either. Thus, the mechanisms that involve paths B and C are unlikely. Overall, the mechanisms through closed six-membered transition state that controlled by an allylboronae do not match the observed chirality transfer.

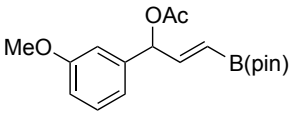
Synthesis and analytical data of substrates (1b–1k)



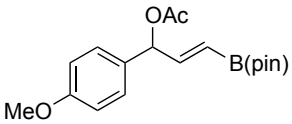
To a solution of crude 1-(2-methoxyphenyl)-3-pinacolatoboryl-2-propen-1-ol (5.0 mmol), DMAP (61.1 mg, 0.5 mmol) and Et_3N (2.1 mL, 15.0 mmol) in dichloromethane (30 mL) was added acetic acid anhydride (946 μL, 10 mmol) at 0 °C under a nitrogen atmosphere. After stirring at room temperature for 2 h, the reaction mixture was quenched with saturated aqueous NH_4Cl. The aqueous phase was extracted with chloroform (2 × 30 mL), and the combined organic extracts were washed with brine (2 × 30 mL). After the organic layer was dried over $MgSO_4$, the solvent was removed under reduced pressure. The residue was purified by neutral silica gel

chromatography (R_f 0.34, EtOAc/hexane = 1/4) to give **1b** as a brown solid (514.5 mg, 31% yield for three steps from 1-(2-methoxyphenyl)-1-trimethylsiloxy-2-proyne).

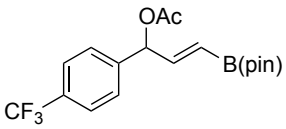
^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.30 (dd, *J* = 1.5, 7.0 Hz, 1H), 7.25 (dt, *J* = 1.5, 7.5 Hz, 1H), 6.93 (t, *J* = 7.5 Hz, 1H), 6.86 (d, *J* = 7.5 Hz, 1H), 6.73 (dd, *J* = 2.0, 4.5 Hz, 1H), 6.68 (dd, *J* = 4.5, 18.0 Hz, 1H), 5.60 (dd, *J* = 1.0, 18.0 Hz, 1H), 3.83 (s, 3H), 2.11 (s, 3H), 1.24 (s, 12H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 169.8, 156.4, 149.3, 129.2, 127.4, 126.9, 120.7, 110.6, 83.4, 70.9, 55.6, 24.9, 24.8, 21.2; **HRMS** (EI) Calcd for $C_{18}H_{25}BO_5$: 332.1795. Found: *m/z* 332.1797.



(*E*)-1-(3-Methoxyphenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl acetate (1c): Purified by silica gel column chromatography (42% yield for three steps, R_f 0.39, EtOAc/hexane = 1/4). Yellow oil, **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.26 (t, *J* = 8.8 Hz, 1H), 6.92 (d, *J* = 7.6 Hz, 1H), 6.87 (t *J* = 1.6 Hz, 1H), 6.83 (ddd, *J* = 0.8, 2.8, 8.8 Hz, 1H), 6.66 (dd, *J* = 5.2, 18.0 Hz, 1H), 6.26 (dd, 1.2, 5.2 Hz, 1H), 5.65 (dd, *J* = 1.2, 18.0 Hz, 1H), 3.80 (s, 3H), 2.11 (s, 3H), 1.25 (s, 12H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 169.9, 159.8, 149.3, 139.9, 129.7, 119.6, 113.6, 113.0, 83.5, 76.6, 55.3, 24.9, 24.8, 21.3; **HRMS** (EI) Calcd for $C_{18}H_{25}BO_5$: 332.1795. Found: *m/z* 332.1790.

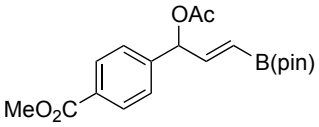


(*E*)-1-(4-Methoxyphenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl acetate (1d): Purified by silica gel column chromatography (25% yield for three steps, R_f 0.53, EtOAc/hexane = 3/7). Yellow oil, **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.25 (d, *J* = 8.5 Hz, 2H), 6.86 (d, *J* = 8.5 Hz, 2H), 6.67 (dd, *J* = 5.0, 18.5 Hz, 1H), 6.25 (dd, *J* = 1.5, 9.5 Hz, 1H), 5.62 (dd, *J* = 1.5, 18.5 Hz, 1H), 3.77 (s, 3H), 2.07 (s, 3H), 1.24 (s, 12H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 169.9, 159.6, 149.6, 130.4, 128.9, 114.0, 83.4, 76.4, 55.3, 24.89, 24.83, 21.1; **HRMS** (EI) Calcd for $C_{18}H_{25}BO_5$: 332.1795. Found: *m/z* 332.1791.

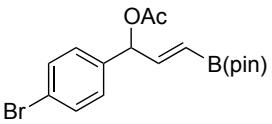


(*E*)-1-(4-Trifluoromethylphenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl acetate (1e): Purified by silica gel column chromatography (60% yield for three steps, R_f 0.42,

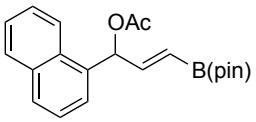
EtOAc/hexane = 1/4). Yellow oil, **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.60 (d, *J* = 8.5 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 2H), 6.64 (dd, *J* = 5.0, 18.0 Hz, 1H), 6.32 (d, *J* = 5.0 Hz, 1H), 5.65 (dd, *J* = 1.5, 18.0 Hz, 1H), 2.13 (s, 3H), 1.25 (s, 12H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 169.8, 148.5, 142.4, 130.5 (q, *J* = 32.9 Hz), 127.7, 125.7 (q, *J* = 270 Hz), 83.7, 76.1, 24.9, 21.2; **HRMS** (EI) Calcd for $C_{18}H_{22}BF_3O_4$: 370.1563. Found: *m/z* 370.1563.



(*E*)-1-(4-Methoxycarbonylphenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl acetate (1f): Purified by silica gel column chromatography (58% yield for three steps, R_f 0.49, EtOAc/hexane = 3/7). Yellow oil, **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.98 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 6.62 (dd, *J* = 5.0, 18.0 Hz, 1H), 6.30 (dd, *J* = 1.5, 5.0 Hz, 1H), 5.64 (dd, *J* =1.5, 18.0 Hz, 1H), 3.87 (s, 3H), 2.10 (s, 3H), 1.22 (s, 12H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 169.7, 166.6, 148.5, 143.3, 129.9, 127.1, 83.6, 76.2, 52.1, 24.8, 24.7, 21.1; **HRMS** (EI) Calcd for $C_{19}H_{25}BO_6$: 360.1744. Found: *m/z* 360.1739.

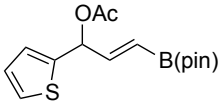


(*E*)-1-(4-Bromophenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl acetate (1g): Purified by silica gel column chromatography (53% yield for three steps, R_f 0.49, EtOAc/hexane = 1/4). Yellow oil, **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.47 (d, *J* = 8.5 Hz, 2H), 7.21 (d, *J* = 8.5 Hz, 2H), 6.63 (dd, *J* = 5.0, 18.0 Hz, 1H), 6.23 (dd, *J* = 1.5, 5.0 Hz, 1H), 5.63 (dd, *J* = 1.5, 18.0 Hz, 1H), 2.10 (s, 3H), 1.25 (s, 12H); **^{13}C NMR** ($CDCl_3$, 125 MHz) *δ* 169.8, 148.8, 137.4, 131.8, 129.2, 122.3, 83.6, 76.1, 24.9, 24.8, 21.1; **HRMS** (EI) Calcd for $C_{17}H_{22}BBrO_4$: 380.0795. Found: *m/z* 380.0800.

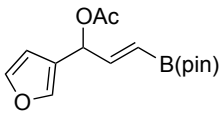


(*E*)-1-(2-Naphthyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl acetate (1h): Purified by silica gel column chromatography (72% yield for three steps, R_f 0.41, EtOAc/hexane = 1/4). Yellow amorphous, **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.11 (dd, *J* = 1.2, 8.0 Hz, 1H), 7.87 (dd, *J* =

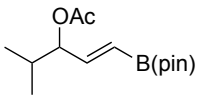
2.0, 7.6 Hz, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.57-7.44 (m, 4H), 7.04 (dd, J = 1.6, 4.4 Hz, 1H), 6.85 (dd, J = 4.4, 18.4 Hz, 1H), 5.70 (dd, J = 2.0, 18.4 Hz, 1H), 2.14 (s, 3H), 1.24 (s, 12H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 170.1, 149.2, 134.1, 134.0, 130.8, 129.1, 128.9, 126.5, 125.9, 125.4, 123.9, 83.6, 77.3, 74.2, 24.9, 24.8, 21.2; **HRMS** (EI) Calcd for $C_{21}H_{25}BO_4$: 352.1846. Found: *m/z* 352.1846.



(*E*)-1-(2-Thienyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl acetate (1i): Purified by silica gel column chromatography (40% yield for three steps, R_f 0.40, EtOAc/hexane = 1/4). Yellow oil, **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.28 (dd, J = 1.3, 5.2 Hz, 1H), 7.05 (d, J = 3.2 Hz, 1H), 6.96 (dd, J = 3.2, 5.2 Hz, 1H), 6.73 (dd, J = 5.2, 18.0 Hz, 1H), 6.56 (dd, J = 1.2, 5.2 Hz, 1H), 5.73 (dd, J = 1.2, 18.0 Hz, 1H), 2.08 (s, 3H), 1.25 (s, 12H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 169.7, 148.3, 141.0, 126.8, 126.7, 126.2, 83.6, 71.8, 24.9, 24.8, 21.1; **HRMS** (EI) Calcd for $C_{15}H_{21}BO_4S$: 308.1254. Found: *m/z* 308.1250.



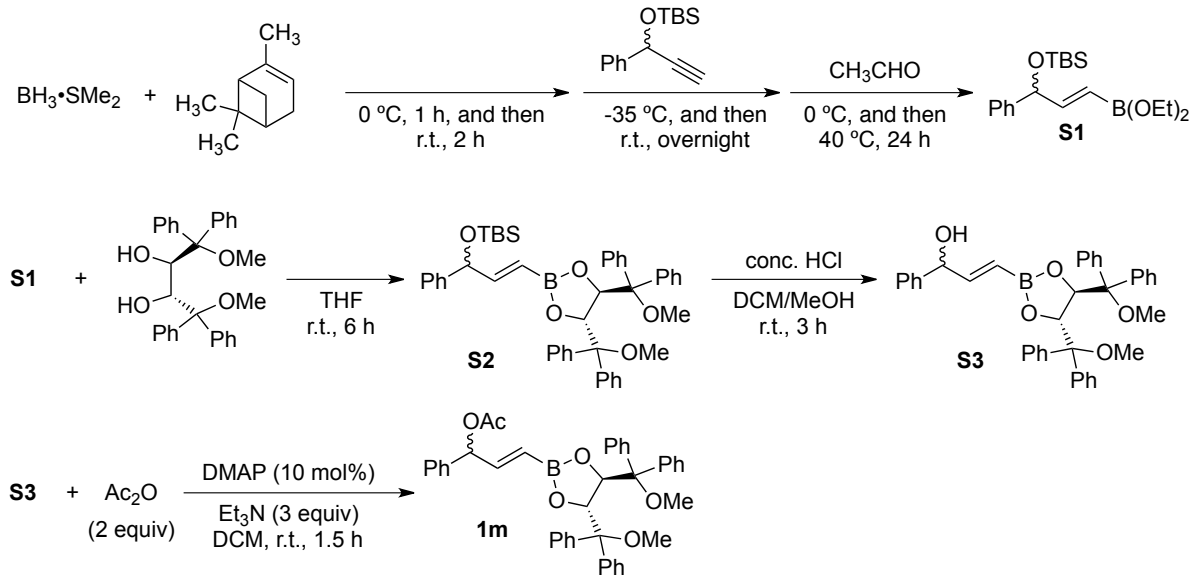
(*E*)-1-(3-Furyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl acetate (1j): Purified by silica gel column chromatography (26% yield for three steps, R_f 0.41, EtOAc/hexane = 1/4). Yellow oil, **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.42-7.34 (m, 2H), 6.66 (dd, J = 5.2, 17.6 Hz, 1H), 6.37 (dd, J = 1.2, 1.6 Hz, 1H), 6.29 (dd, J = 1.2, 5.2 Hz, 1H), 5.68 (dd, J = 1.6, 17.6 Hz, 1H), 2.08 (s, 3H), 1.26 (s, 12H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 170.0, 148.3, 143.4, 141.0, 123.1, 109.6, 83.6, 69.3, 24.9, 24.8, 21.2; **HRMS** (EI) Calcd for $C_{15}H_{21}BO_5$: 292.1482. Found: *m/z* 292.1484.



(*E*)-1-(3-*iso*-Propyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-acetoxy-4-methyl-pent-1-ene (1k): Purified by silica gel column chromatography (44% yield for three steps, R_f 0.46, EtOAc/hexane = 1/4). Yellow oil, **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 6.47 (dd, J = 5.5, 18.0 Hz, 1H), 5.54 (dd, J = 1.5, 18.0 Hz, 1H), 5.12 (dt, J = 1.5, 5.5 Hz, 1H), 2.07 (s, 3H), 1.90 (m, 1H), 1.26 (d, J = 2.0 Hz, 12H), 0.91 (dd, J = 1.5, 6.5 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 170.2, 148.7,

83.2, 79.3, 31.6, 24.7, 24.6, 20.9, 18.2, 17.6; **HRMS** (EI) Calcd for $C_{14}H_{25}BO_4$: 268.1846. Found: *m/z* 268.1846.

Synthesis of (4*R*,5*R*)-(*E*)-1-phenyl-3-[4,5-bis{methoxy(diphenyl)methyl}-1,3,2-dioxaborolan-2-yl]allyl acetate (1m)



Synthesis of S2.

A procedure reported by Miyaura was used to prepare **S1**.[4] A 100 mL two neck round bottom-flask was charged with THF (5 mL) and BH_3•SMe_2 (885.1 mg, 11.6 mmol). α-Pinene (3.43 g, 25.2 mmol) was then added dropwise at 0 °C. The mixture was stirred for 1 h at 0 °C and an additional 2 h at room temperature to give a white suspension of diisopinocampheylborane. After being cooled to -35 °C, 3-(*tert*-butyldimethylsilyloxy)-3-phenylpropyne (2.04 g, 8.3 mmol) was slowly added, and the resulting mixture was stirred for 1 h at -35 °C, slowly warmed to room temperature, and stirred for overnight. Acetaldehyde (14 mL, 250.5 mmol) was added at 0 °C, and the mixture was then refluxed for 24 h. The evaporation of the excess acetaldehyde and other volatile in vacuo gave a yellow oil of the crude **S1**. The crude **S1** was directly treated with (2*R*,3*R*)-1,4-dimethoxy-1,1,4,4-tetraphenyl-2,3-butandiol[6] (30 mmol) in THF (5 mL) for 6 h at room temperature. The evaporation of the solvent followed by silica gel column chlomatography (R_f 0.66, EtOAc/hexane = 4/1, TLC stain: *p*-anisaldehyde) gave **S2** as a mixture of diastereomer (*d.r.* = 1:1) (2.55 g, 49%).

Fluffy white solid, **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.41-7.13 (m, 50H), 6.20 (dd, *J* = 5.5, 18.5 Hz, 1H), 6.17 (dd, *J* = 5.5, 18.5 Hz, 1H), 5.41 (dd, *J* = 2.0, 18.5 Hz, 1H), 5.37 (s, 2H), 5.35 (s, 2H),

5.34 (dd, J = 2.0, 18.5 Hz, 1H), 5.03 (m, 2H), 3.03 (s, 6H), 3.01 (s, 6H), 0.88 (s, 9H), 0.86 (s, 9H), -0.002 (s, 3H), -0.008 (s, 3H), -0.04 (s, 3H), -0.06 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 154.9, 154.8, 143.0, 141.5, 141.3, 141.2, 141.1, 129.8, 128.54, 128.52, 128.21, 128.17, 127.96, 127.93, 127.65, 127.62, 127.4, 127.2, 127.1, 126.3, 126.2, 83.43, 83.41, 77.7, 77.6, 76.8, 76.5, 51.9, 26.03, 26.0, 18.5, 18.46, -4.4, -4.5, -4.8.

Synthesis of S3.

A procedure reported by Pietruszka was used to prepare **S3**.[5, 6] **S2** was deprotected by dissolving alkenylboronic ester **S2** (487.7 mg, 0.72 mmol) in a minimum amount of CH_2Cl_2 (10 mL) and MeOH (30 mL). Concentrated hydrochloric acid (1 mL) in MeOH (10 mL) was then added dropwise at room temperature and stirred for 3 h at room temperature. Upon completion of the reaction, saturated aqueous sodium hydrogencarbonate (10 mL) was added and the volume of the solvent reduced under reduced pressure. Water was added and the aqueous layer extracted with Et_2O (2 × 20 mL). The combined organic layers were washed with saturated brine, dried over $MgSO_4$, and concentrated. The residue was purified by neutral silica gel column chromatography (R_f 0.46, EtOAc/hexane = 4/1, TLC stain: *p*-anisaldehyde) to give **S3** as a mixture of diastereomer (1.70 g, 95%). The spectral data of **S3** are consistent with those of the literature.[5]

Fluffy white solid, **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.37-7.16 (m, 25H), 6.29 (dd, J = 5.2, 17.6 Hz, 1H), 5.39 (dd, J = 1.6, 8.0 Hz, 1H), 5.35 (s, 2H), 5.06 (m, 1H), 3.02 (s, 6H), 1.81 (d, J = 3.6 Hz, 1H); **Distinguishable diastereomer peaks**: **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 5.36 (s, 2H), 5.35 (dd, J = 1.6, 8.0 Hz, 1H), 1.79 (d, J = 3.6 Hz, 1H).

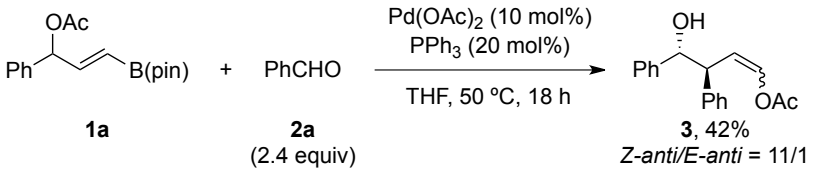
Synthesis of 1m.

To a solution of **S3** (1.70 g, 2.85 mmol), DMAP (34.9 mg, 0.285 mmol) and Et_3N (1.19 mL, 8.55 mmol) in CH_2Cl_2 (15 mL) was added acetic acid anhydride (540 μL, 5.7 mmol) at 0 °C. After stirring at room temperature for 1.5 h, the reaction mixture was quenched with saturated aqueous NH_4Cl. The aqueous phase was extracted with $CHCl_3$ (2 × 20 mL), and the combined organic extracts were washed with brine (2 × 20 mL). After the organic layer was dried over $MgSO_4$, the solvent was removed under reduced pressure. The residue was purified by neutral silica gel chromatography (R_f 0.39, EtOAc/hexane = 1/4) to give **1m** as a mixture of diastereomer (1.40 g, 77%).

Fluffy white solid, **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.38-7.17 (m, 50H), 6.20 (dd, J = 4.8, 18.0 Hz, 1H), 6.21 (dd, J = 4.8, 18.0 Hz, 1H), 6.12 (dd, J = 1.6, 4.8 Hz, 1H), 6.10 (dd, J = 1.6, 4.8 Hz, 1H),

6.12 (dd, J = 1.6, 4.8 Hz, 1H), 5.35 (s, 4H), 5.27 (dd, J = 8.8, 18.0 Hz, 1H), 5.29 (dd, J = 1.6, 18.0 Hz, 1H), 3.00 (s, 12H), 2.04 (s, 3H), 2.03 (s, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 169.8, 149.2, 149.0, 141.3, 141.1, 138.4, 138.3, 129.8, 128.6, 128.5, 128.4, 128.3, 127.9, 127.7, 127.6, 127.5, 127.4, 118.0, 83.4, 77.8, 77.7, 76.5, 76.4, 51.9, 21.2.

Palladium-catalyzed allylation of benzaldehyde with 1-alkenylboronate 1a (Scheme 1)

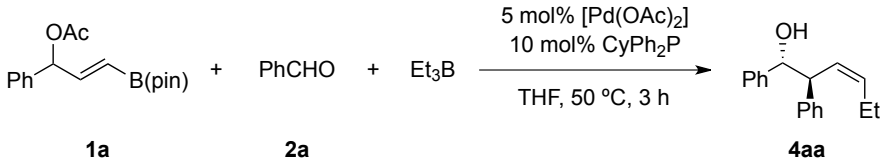


A 10 mL two neck round-bottom flask was charged with $Pd(OAc)_2$ (11.2 mg, 0.1 mmol), Ph_3P (26.4 mg, 0.2 mmol), and THF (1 mL). The mixture was stirred at room temperature for 0.5 h, and a THF (1 mL) solution of **1a** (151.1 mg, 0.5 mmol) and benzaldehyde (**2a**) (123 μL, 1.2 mmol) was then added. The reaction mixture was stirred at 50 °C for 18 h. Upon completion of the reaction, the reaction mixture was diluted with EtOAc (20 mL) and washed with saturated NH_4Cl (2 × 20 mL), saturated $NaHCO_3$ (2 × 20 mL), and brine (2 × 20 mL). The combined organic layers were dried over $MgSO_4$ and concentrated. The residue was purified by silica gel chromatography (R_f 0.23, EtOAc/hexane = 1/4) to give **3** as a yellow oil (59.3 mg, 42%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.27-7.14 (m, 11 H), 5.40 (dd, J = 6.4, 10.4 Hz, 1H), 4.92 (d, J = 6.4 Hz, 1H), 4.16 (dd, J = 6.4, 10.4 Hz, 1H), 2.01 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 167.7, 142.1, 140.9, 135.8, 128.6, 128.4, 128.1, 127.6, 126.9, 126.5, 112.0, 77.8, 49.6, 20.7; **HRMS** (EI) Calcd for $C_{18}H_{18}O_3$: 282.1256. Found: *m/z* 282.1255.

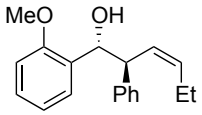
Distinguishable *syn* isomer peaks (*E-anti*-**3**): **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 5.87 (dd, J = 9.6, 12.4 Hz, 1H), 4.86 (d, J = 6.8 Hz, 1H), 3.55 (dd, J = 6.8, 9.6 Hz, 1H), 2.10 (s, 3H).

General procedure for palladium-catalyzed three-component reaction (Scheme 2)

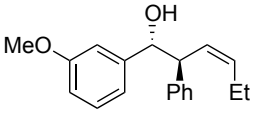


A 10 mL two neck round-bottom flask was charged with $Pd(OAc)_2$ (5.6 mg, 0.05 mmol), $CyPh_2P$ (13.4 mg, 0.1 mmol), and THF (1 mL). The mixture was stirred at room temperature for 0.5 h, and a THF (1 mL) solution of **1a** (151.1 mg, 0.5 mmol), benzaldehyde (**2a**) (123 μL, 1.2 mmol), and Et_3B (1.2 mmol, 0.97 M hexane solution) was then added. The reaction mixture was stirred at 50 °C for 3 h. Upon completion of the reaction, the reaction mixture was diluted with EtOAc (20 mL) and washed with saturated NH_4Cl (2 × 20 mL), saturated $NaHCO_3$ (2 × 20 mL), and brine (2 × 20 mL). The combined organic layers were dried over $MgSO_4$ and concentrated. The residue was purified by silica gel chromatography (R_f 0.48, EtOAc/hexane = 1/4) to give **4aa** as a yellow oil (94.6 mg, 75%). The spectral data of **4aa** are consistent with those of the literature.[8]

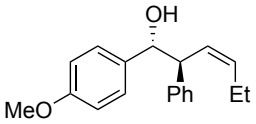
The ratio of compounds **4** and **5** was determined by NMR analysis of the crude mixtures. Compounds **5aa**,[8] **5ab**,[8] **5ad**,[8] **5ae**,[8] **5ag**,[9] **5ai**,[9] **5aq**,[10] **5ar**,[8] **5as**,[11] **5da**,[12] **5ga**,[13] and **5ma**[14] were known compounds. Other compounds **5ac**, **5ah**, **5ak**, **5an**, **5ca**, **5fa**, **5ia**, **5ja** could not be isolated.



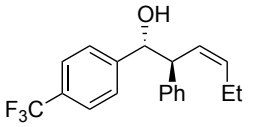
***anti*-(*Z*)-1-(2-Methoxyphenyl)-2-phenylpent-3-en-1-ol (4ab)**: Purified by silica gel column chromatography (96.0 mg, 68% yield, R_f 0.37, EtOAc/hexane = 1/4). Yellow oil, **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.24-7.12 (m, 7H), 6.87 (dt, J = 0.8, 8.0 Hz, 1H), 6.78 (dm, J = 8.0 Hz, 1H), 5.88 (ddt, J = 10.0, 10.8, 1.6 Hz, 1H), 5.57 (ddt, J = 0.8, 10.8, 7.2 Hz, 1H), 5.13 (t, J = 6.0 Hz, 1H), 4.09 (dd, J = 6.0, 10.0 Hz, 1H), 3.75 (s, 3H), 2.53 (d, J = 6.0 Hz, 1H), 1.91 (quint, J = 7.2 Hz, 1H), 1.90 (quint, J = 7.2 Hz, 1H), 0.77 (t, J = 7.2 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 156.4, 142.7, 134.6, 130.5, 128.3, 128.2, 127.9, 127.7, 126.3, 74.4, 55.3, 49.6, 20.9, 14.0; **HRMS** (EI) Calcd for $C_{19}H_{22}O_2$: 282.1620. Found: *m/z* 282.1625.



***anti*-(*Z*)-1-(3-Methoxyphenyl)-2-phenylpent-3-en-1-ol (4ac)**: Purified by silica gel column chromatography (114.4 mg, 81% yield, R_f 0.40, EtOAc/hexane = 1/4). Yellow oil, **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.24-7.05 (m, 6H), 6.76-6.66 (m, 2H), 5.84 (ddt, *J* = 10.4, 10.8, 1.6 Hz, 1H), 5.68 (dt, *J* = 10.8, 7.2 Hz, 1H), 4.79 (d, *J* = 7.2 Hz, 1H), 3.85 (dd, *J* = 7.2, 10.4 Hz, 1H), 3.69 (s, 3H), 2.26 (d, *J* = 2.0 Hz, 1H), 2.11-1.98 (m, 2H), 0.88 (t, *J* = 7.2 Hz, 3H).
The spectral data of **4ac** are consistent with those of the literature.[7]

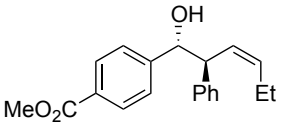


***anti*-(*Z*)-1-(4-Methoxyphenyl)-2-phenylpent-3-en-1-ol (4ad)**: Purified by silica gel column chromatography (101.7 mg, 72% yield, R_f 0.40, EtOAc/hexane = 1/4). Yellow oil, **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.20 (tm, *J* = 8.0 Hz, 2H), 7.13 (m, 1H), 7.05-7.09 (m, 4H), 6.72-6.75 (dm, *J* = 9.5 Hz, 2H), 5.82 (ddt, *J* = 10.0, 11.0, 1.5 Hz, 1H), 5.67 (ddt, *J* = 1.0, 11.0, 7.5 Hz, 1H), 4.76 (d, *J* = 7.5 Hz, 1H), 3.84 (dd, *J* = 7.5, 10.0 Hz, 1H), 3.74 (s, 3H), 2.14-2.01 (m, 2H), 0.90 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 158.7, 141.5, 135.4, 134.1, 128.26, 128.24, 128.0, 127.7, 126.3, 113.2, 77.4, 55.1, 52.3, 20.9, 13.9; **HRMS** (EI) Calcd for $C_{19}H_{22}O_2$: 282.1620. Found: *m/z* 282.1622.



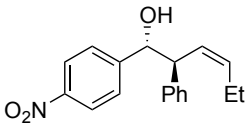
***anti*-(*Z*)-1-(4-Trifluoromethylphenyl)-2-phenylpent-3-en-1-ol (4ae)**: Purified by silica gel column chromatography (120.1 mg, 75% yield, R_f 0.42, EtOAc/hexane = 1/4). Yellow oil, **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.46 (d, *J* = 8.0 Hz, 2H), 7.22-7.27 (m, 4H), 7.18 (dm, *J* = 7.5 Hz, 1H), 7.07-7.09 (m, 2H), 5.82 (ddt, *J* = 10.5, 11.0, 1.5 Hz, 1H), 5.70 (ddt, *J* = 1.0, 11.0, 7.5 Hz, 1H), 4.87 (dd, *J* = 2.0, 7.5 Hz, 1H), 3.83 (dd, *J* = 7.5, 10.5 Hz, 1H), 2.34 (d, *J* = 2.0 Hz, 1H), 2.04 (quint, *J* = 7.5 Hz, 1H), 2.03 (quint, *J* = 7.5 Hz, 1H), 0.87 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 146.1, 140.9, 136.4, 129.5 (q, *J* = 31.6 Hz), 128.7, 128.3, 127.1, 127.0, 126.8, 124.9 (q, *J* = 3.6 Hz), 124.3 (q, *J* = 270 Hz), 77.4, 52.4, 21.0, 13.9; **HRMS** (EI) Calcd for $C_{19}H_{19}F_3O$: 320.1388. Found: *m/z* 320.1394.

Distinguishable *syn* isomer peaks (*syn*-**4ae**): **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 5.53 (ddt, *J* = 11.0, 10.5, 2.0 Hz, 1H), 5.33 (ddt, *J* = 1.0, 11.0, 7.0 Hz, 1H), 0.62 (t, *J* = 7.5 Hz, 3H).



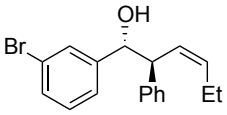
***anti*-(*Z*)-1-(4-Methoxycarbonylphenyl)-2-phenylpent-3-en-1-ol (4af)**: Purified by silica gel column chromatography (122.6 mg, 79% yield, R_f 0.29, EtOAc/hexane = 1/4). Yellow oil, **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.88 (dm, *J* = 8.5 Hz, 2H), 7.21 (tm, *J* = 8.5 Hz, 4H), 7.15 (dm, *J* = 8.5 Hz, 1H), 7.06 (dm, *J* = 7.0 Hz, 2H), 5.82 (ddt, *J* = 10.0, 11.0, 1.5 Hz, 1H), 5.68 (dt, *J* = 11.0, 7.0 Hz, 1H), 4.86 (br d, *J* = 7.0 Hz, 1H), 3.88 (s, 3H), 3.84 (dd, *J* = 7.0, 10.0 Hz, 1H), 2.35 (br s, 1H), 2.04 (quint, *J* = 7.5, 1H), 2.03 (quint, *J* = 7.5, 1H), 0.87 (t, *J* = 7.5 Hz, 3H) **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 167.1, 147.4, 141.0, 136.1, 129.2, 129.1, 128.5, 128.2, 127.2, 126.7, 126.6, 77.6, 52.4, 52.0, 21.0, 14.0; **HRMS** (EI) Calcd for $C_{20}H_{22}O_3$: 310.1569. Found: *m/z* 310.1565.

Distinguishable *syn* isomer peaks (*syn*-**4af**): **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 5.54 (ddt, *J* = 10.0, 11.0, 1.5 Hz, 1H), 0.64 (d, *J* = 7.5 Hz, 3H).

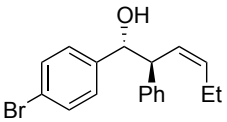


***anti*-(*Z*)-1-(4-Methoxycarbonylphenyl)-2-phenylpent-3-en-1-ol (4ag)**: Purified by silica gel column chromatography (107.0 mg, 72% yield, R_f 0.44, EtOAc/hexane = 1/4). Brown oil, **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 8.04-8.06 (dm, *J* = 9.0 Hz, 2H), 7.29 (dm, *J* = 9.0 Hz, 2H), 7.25-7.21 (m, 2H), 7.18 (dm, *J* = 7.5 Hz, 1H), 7.06 (dm, *J* = 7.0 Hz, 1H), 5.81 (ddt, *J* = 10.0, 10.5, 1.5 Hz, 1H), 5.85 (dt, *J* = 10.5, 7.5 Hz, 1H), 4.89 (br d, *J* = 7.5 Hz, 1H), 3.79 (dd, *J* = 7.5, 10.0 Hz, 1H), 2.45 (d, *J* = 1.5 Hz, 1H), 2.04 (quint, *J* = 7.5, 1H), 2.03 (quint, *J* = 7.5, 1H), 0.88 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 149.5, 147.2, 140.4, 136.9, 128.8, 128.2, 127.5, 127.1, 126.7, 123.1, 77.2, 52.6, 21.1, 14.0; **HRMS** (EI) Calcd for $C_{18}H_{19}NO_3$: 297.1365. Found: *m/z* 297.1370.

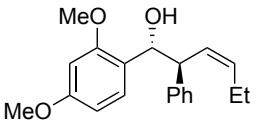
Distinguishable *syn* isomer peaks (*syn*-**4ag**): **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 8.17 (dm, *J* = 9.0 Hz, 2H), 7.49 (dm, *J* = 9.0 Hz, 2H), 5.56 (ddt, *J* = 9.5, 11.5, 1.5 Hz, 1H), 5.36 (ddt, *J* = 1.0, 11.5, 7.5 Hz, 1H), 4.93 (dm, *J* = 9.5 Hz, 1H), 1.80 (dquint, *J* = 1.5, 7.5 Hz, 1H), 1.67 (dquint, *J* = 1.5, 7.5 Hz, 1H), 0.65 (t, *J* = 7.5 Hz, 3H).



***anti*-(*Z*)-1-(3-Bromophenyl)-2-phenylpent-3-en-1-ol (4ah)**: Purified by silica gel column chromatography (121.9 mg, 73% yield, R_f 0.45, EtOAc/hexane = 1/4). Yellow oil, **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.37 (br s, 1H), 7.31 (dm, *J* = 5.6 Hz, 1H), 7.25-7.21 (m, 2H), 7.18 (m, 1H), 7.09 (dm, *J* = 6.4 Hz, 2H), 6.93 (dm, *J* = 6.4 Hz, 1H), 6.88 (dm, *J* = 6.4 Hz, 1H), 5.81 (ddt, *J* = 8.4, 8.8, 1.2 Hz, 1H), 5.69 (dt, *J* = 8.8, 6.0 Hz, 1H), 4.77 (d, *J* = 6.0 Hz, 1H), 3.81 (dd, *J* = 6.0, 8.4 Hz, 1H), 2.28 (d, *J* = 1.6 Hz, 1H), 2.043 (quint, *J* = 6.0 Hz, 1H), 2.041 (quint, *J* = 6.0 Hz, 1H), 0.882 (t, *J* = 6.0 Hz, 3H), 0.880 (t, *J* = 6.0 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 144.4, 141.1, 136.3, 130.5, 129.6, 129.4, 128.6, 128.3, 127.1, 126.8, 125.4, 122.2, 77.4, 52.4, 21.1, 14.0; **HRMS** (EI) Calcd for $C_{18}H_{19}BrO$: 330.0619. Found: *m/z* 330.0622.

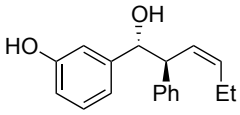


***anti*-(*Z*)-1-(4-Bromophenyl)-2-phenylpent-3-en-1-ol (4ai)**: Purified by silica gel column chromatography (91.1 mg, 55% yield, R_f 0.44, EtOAc/hexane = 1/4). Yellow oil, **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.32 (dm, *J* = 8.4 Hz, 2H), 7.25-7.20 (m, 2H), 7.16 (m, 1H), 7.06 (dm, *J* = 6.8 Hz, 2H), 7.02 (dm, *J* = 8.4 Hz, 2H), 5.81 (ddt, *J* = 10.0, 11.2, 1.2 Hz, 1H), 5.69 (dt, *J* = 11.2, 7.6 Hz, 1H), 4.76 (dd, *J* = 2.0, 8.0 Hz, 1H), 3.79 (dd, *J* = 8.0, 10.0 Hz, 1H), 2.29 (d, *J* = 2.0 Hz, 1H), 2.06 (dquint, *J* = 1.2, 7.6 Hz, 1H), 2.05 (dquint, *J* = 1.2, 7.6 Hz, 1H), 0.89 (t, *J* = 7.6 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 141.1, 141.0, 136.3, 131.0, 128.6, 128.4, 128.3, 127.4, 126.7, 121.2, 77.4, 52.5, 21.1, 14.0; **HRMS** (EI) Calcd for $C_{18}H_{19}BrO$: 330.0619. Found: *m/z* 330.0625.

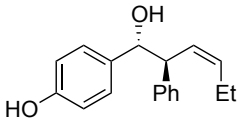


***anti*-(*Z*)-1-(2,4-Dimethoxyphenyl)-2-phenylpent-3-en-1-ol (4aj)**: Purified by silica gel column chromatography (98.4 mg, 63% yield, R_f 0.58, EtOAc/hexane = 3/7). Yellow oil, **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.24-7.09 (m, 6H), 6.39 (dd, *J* = 2.4, 8.4 Hz, 1H), 6.35 (d, *J* = 2.4 Hz, 1H), 5.87 (ddt, *J* = 10.0, 10.8, 1.6 Hz, 1H), 5.58 (ddt, *J* = 0.8, 10.8, 7.6 Hz, 1H), 5.04 (dd, *J* = 5.2, 6.4 Hz, 1H), 4.05 (dd, *J* = 6.4, 10.0 Hz, 1H), 3.76 (s, 3H), 3.71 (s, 3H), 2.47 (d, *J* = 5.2 Hz, 1H), 1.952 (dquint, *J* = 1.6, 7.6 Hz, 1H), 1.948 (dquint, *J* = 1.6, 7.6 Hz, 1H), 0.82 (t, *J* = 7.6 Hz, 3H); **^{13}C**

NMR ($CDCl_3$, 100 MHz) δ 160.0, 157.5, 142.7, 134.5, 128.5, 128.3, 128.23, 128.20, 126.2, 123.0, 104.0, 98.4, 74.1, 55.4, 55.3, 49.9, 21.0, 14.0; **HRMS** (EI) Calcd for $C_{20}H_{24}O_3$: 312.1725. Found: *m/z* 312.1725.

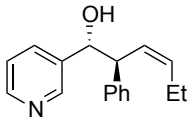


***anti*-(*Z*)-1-(3-Hydroxyphneyl)-2-phenylpent-3-en-1-ol (4ak)**: Purified by silica gel column chromatography (93.1 mg, 65% yield, R_f 0.40, EtOAc/hexane = 3/7). Yellow oil, **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.21 (t, *J* = 7.5 Hz, 2H), 7.15 (m, 1H), 7.11-7.08 (m, 2H), 7.04 (t, *J* = 7.5 Hz, 1H), 6.70-6.61 (m, 3H), 5.81 (ddt, 10.0, 10.5, 1.5 Hz, 1H), 5.67 (dt, *J* = 10.5, 7.5 Hz, 1H), 5.51 (br s, 1H), 4.76 (d, *J* = 7.0 Hz, 1H), 3.85 (dd, *J* = 7.0, 10.5 Hz, 1H), 2.46 (br s, 1H), 2.06 (dquint, *J* = 1.5, 7.5 Hz, 1H), 2.03 (dquint, *J* = 1.5, 7.5 Hz, 1H), 0.88 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 155.4, 143.7, 141.4, 135.9, 129.1, 128.5, 128.3, 127.6, 126.6, 119.2, 114.5, 113.6, 77.8, 52.2, 21.1, 14.0; **HRMS** (EI) Calcd for $C_{18}H_{20}O_2$: 268.1463. Found: *m/z* 268.1460.



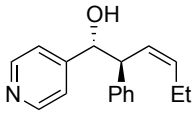
***anti*-(*Z*)-1-(4-Hydroxyphneyl)-2-phenylpent-3-en-1-ol (4al)**: Purified by silica gel column chromatography (79.2 mg, 59% yield, R_f 0.31, EtOAc/hexane = 3/7). Colorless solid, **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.19 (tm, *J* = 6.0 Hz, 2H), 7.13 (tm, *J* = 6.0 Hz, 1H), 7.05 (dm, *J* = 6.0 Hz, 2H), 7.01 (dm, *J* = 6.8 Hz, 2H), 6.64 (dm, *J* = 6.8 Hz, 2H), 5.82 (ddt, *J* = 8.0, 8.8, 1.2 Hz, 1H), 5.68 (dt, *J* = 5.6, 8.8 Hz, 1H), 4.96 (br s, 1H), 4.74 (d, *J* = 6.4 Hz, 1H), 3.83 (dd, *J* = 6.4, 8.0 Hz. 1H), 2.30 (br s, 1H), 2.12 (dquint, *J* = 1.2, 6.0 Hz, 1H), 2.05 (dquint, *J* = 1.2, 6.0 Hz, 1H), 0.91 (t, *J* = 6.0 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 154.9, 141.5, 135.8, 134.2, 128.47, 128.40, 128.1, 126.5, 114.9, 77.7, 52.6, 21.1, 14.1; **HRMS** (EI) Calcd for $C_{18}H_{20}O_2$: 268.1463. Found: *m/z* 268.1465.

Distinguishable *syn* isomer peaks (*syn*-**4al**): **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 5.50 (ddt, *J* = 10.0, 10.5, 1.5 Hz, 1H), 5.28 (dt, *J* = 7.5, 10.5, 1H), 0.68 (t, *J* = 7.5 Hz, 3H).



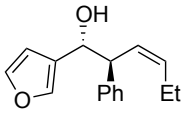
***anti*-(*Z*)-1-(3-Pyridyl)-2-phenylpent-3-en-1-ol (4am)**: Purified by silica gel column chromatography (73.5 mg, 58% yield, R_f 0.35, EtOAc/hexane = 1/2). Colorless solid, **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.40 (dd, *J* = 1.6, 4.8 Hz, 1H), 8.33 (d, *J* = 2.4 Hz, 1H), 7.50 (dt, *J* = 7.6, 2.0 Hz, 1H), 7.25-7.12 (m, 4H), 7.07 (dm, *J* = 6.8 Hz, 2H), 5.82 (ddt, *J* = 10.0, 10.8, 1.2 Hz, 1H), 5.71 (dt, *J* = 10.8, 7.2 Hz, 1H), 4.84 (d, *J* = 7.2 Hz, 1H), 3.83 (dd, *J* = 7.2, 10.0 Hz, 1H), 2.049 (quint, *J* = 7.2 Hz, 1H), 2.047 (quint, *J* = 7.2 Hz, 1H), 0.88 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 148.6, 148.4, 140.8, 137.7, 136.3, 134.3, 128.7, 128.3, 127.1, 126.9, 123.0, 75.8, 52.5, 21.0, 14.0; **HRMS** (EI) Calcd for $C_{17}H_{19}NO$: 253.1467. Found: *m/z* 253.1460.

Distinguishable *syn* isomer peaks (*syn*-**4am**): **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 5.52 (m, 1H), 5.32 (m, 1H), 0.64 (t, *J* = 7.2 Hz, 3H).

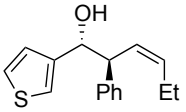


(*Z*)-1-(4-Pyridyl)-2-phenylpent-3-en-1-ol (4an): Purified by silica gel column chromatography (81.1 mg, 64% yield, R_f 0.35, EtOAc/hexane = 1/2). Colorless solid, *anti*-**4an** was obtained as a mixture of diastereomer. *anti*-**4an**: **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.43 (dd, *J* = 1.2, 4.8 Hz, 2H), 7.31-7.17 (m, 3H), 7.12-7.04 (m, 4H), 5.56 (ddt, *J* = 1.6, 10.0, 10.8, 1H), 5.37 (ddt, *J* = 1.6, 7.2, 10.8 Hz, 1H), 4.80 (d, *J* = 6.8 Hz, 1H), 3.80 (dd, *J* = 6.8, 10.0 Hz, 1H), 2.02 (dquint, *J* = 1.6, 7.2 Hz, 2H), 0.86 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 151.4, 149.3, 140.9, 136.4, 128.7, 128.3, 127.0, 126.7, 121.7, 76.6, 52.0, 21.1, 14.0; **HRMS** (EI) Calcd for $C_{17}H_{19}NO$: 253.1467. Found: *m/z* 253.1464.

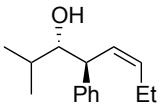
Distinguishable *syn* isomer peaks (*syn*-**4an**): **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.52 (dd, *J* = 1.2, 4.8 Hz, 2H), 7.38-7.33 (m, 2H), 7.31-7.17 (m, 5H), 5.55 (ddt, *J* = 1.6, 9.6, 11.2 Hz, 1H), 5.36 (dt, *J* = 7.2, 9.6 Hz, 1H), 4.81 (d, *J* = 9.6 Hz, 1H), 3.83 (t, *J* = 9.6 Hz, 1H), 1.82 (duint, *J* = 1.6, 7.2 Hz, 1H), 1.71 (dquint, *J* = 1.6, 7.2 Hz, 1H), 0.65 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 151.3, 149.4, 140.8, 134.5, 129.1, 128.5, 127.3, 127.2, 122.2, 76.8, 52.2, 21.8, 13.7.



***anti*-(*Z*)-1-(3-Furyl)-2-phenylpent-3-en-1-ol (4ao)**: Purified by silica gel column chromatography (87.2 mg, 72% yield, R_f 0.40, EtOAc/hexane = 1/4). Yellow oil, **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.23-7.28 (m, 3H), 7.17-7.21 (m, 2H), 7.16 (dm, *J* = 8.0 Hz, 2H), 6.16 (s, 1H), 5.79 (ddt, *J* = 9.5, 11.0, 1.5 Hz, 1H), 5.69 (dt, *J* = 11.0, 7.5 Hz, 1H), 4.82 (d, *J* = 7.5 Hz, 1H), 3.83 (dd, *J* = 7.5, 9.5 Hz, 1H), 2.16 (d, *J* = 2.5 Hz, 1H), 2.04-2.19 (m, 2H), 0.94 (t, *J* = 7.5 Hz, 3H) **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 142.7, 141.6, 139.8, 135.8, 128.6, 128.3, 128.1, 126.7, 126.6, 108.9, 70.9, 51.5, 21.1, 14.1; **HRMS** (EI) Calcd for $C_{16}H_{18}O_2$: 242.1307. Found: *m/z* 242.1305.

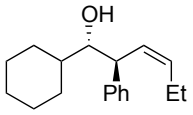


***anti*-(*Z*)-1-(3-Thienyl)-2-phenylpent-3-en-1-ol (4ap)**: Purified by silica gel column chromatography (95.6 mg, 74% yield, R_f 0.43, EtOAc/hexane = 1/4). Yellow oil, **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.27-7.22 (m, 2H), 7.20-7.16 (m, 2H), 7.14-7.10 (m, 2H), 6.97 (ddd, *J* = 0.5, 1.0, 2.5 Hz, 1H), 6.86 (dd, *J* = 1.0, 5.0 Hz, 1H), 5.82 (ddt, *J* = 10.0, 11.0, 1.5 Hz, 1H), 5.68 (ddt, *J* = 0.5, 11.0, 7.0 Hz, 1H), 4.93 (dd, *J* = 1.5, 7.0 Hz, 1H), 3.87 (dd, *J* = 7.5, 10.0 Hz, 1H), 2.25 (d, *J* = 1.5 Hz, 1H), 2.12 (dquint, *J* = 1.5, 7.5 Hz, 1H), 2.05 (dquint, *J* = 1.5, 7.5 Hz, 1H), 0.91 (t, *J* = 7.5 Hz, 3H); **^{13}CNMR** ($CDCl_3$, 125 MHz) δ 143.5, 141.6, 135.7, 128.5, 128.3, 127.9, 126.6, 126.1, 125.2, 121.5, 74.4, 52.0, 21.1, 14.1; **HRMS** (EI) Calcd for $C_{16}H_{18}OS$: 258.1078. Found: *m/z* 258.1083.



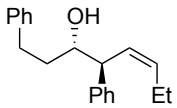
***anti*-(*Z*)-2-Methyl-4-phenyloct-5-en-3-ol (4aq)**: Purified by silica gel column chromatography (68.8 mg, 63% yield, R_f 0.55, EtOAc/hexane = 1/4). Yellow oil, **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.33-7.28 (m, 2H), 7.24-7.20 (m, 3H), 5.71 (ddt, *J* = 9.5, 11.0, 1.5 Hz, 1H), 5.64 (dt, *J* = 7.0, 11.0 Hz, 1H), 3.75 (dd, *J* = 7.0, 9.5 Hz, 1H), 3.56 (ddd, *J* = 2.5, 4.5, 7.0 Hz, 1H), 2.15 (dquint, *J* = 1.5, 7.5 Hz, 1H), 2.09 (dquint, *J* = 1.5, 7.5 Hz, 1H), 1.66 (d, *J* = 3.0 Hz, 1H), 1.58 (m, 1H), 0.948 (t, *J* = 7.5 Hz, 3H), 0.946 (d, *J* = 6.5 Hz, 3H), 0.93 (d, *J* = 6.5 Hz, 3H).

The spectral data of **4aq** are consistent with those of the literature.[7]

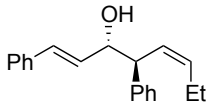


***anti*-(*Z*)-1-Cyclohexyl-2-phenylpent-3-en-1-ol (4ar)**: Purified by silica gel column chromatography (90.4 mg, 70% yield, R_f 0.60, EtOAc/hexane = 1/4). Yellow oil, **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.34-7.28 (m, 2H), 7.25-7.20 (m, 3H), 5.73 (ddt, *J* = 9.2, 10.8, 1.2 Hz, 1H), 5.67 (dt, *J* = 10.8, 7.2 Hz, 1H), 3.83 (dd, *J* = 6.4, 9.2 Hz, 1H), 3.57 (m, 1H), 2.16 (dquint, *J* = 1.2, 7.2 Hz, 1H), 2.08 (dquint, *J* = 1.2, 7.2 Hz, 1H), 1.92 (m, 1H), 1.80-1.58 (m, 5H), 1.33-1.10 (m, 6H), 0.97 (t, *J* = 7.2 Hz, 3H).

The spectral data of **4ar** are consistent with those of the literature.[7]



***anti*-(*Z*)-1-Phenyl-4-phenyloct-5-en-3-ol (4as)**: Purified by silica gel column chromatography (84.1 mg, 60% yield, R_f 0.43, EtOAc/hexane = 1/4). Yellow oil, **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.32-7.11 (m, 10H), 5.72-5.71 (m, 2H), 3.75-3.80 (m, 1H), 3.62 (t, *J* = 8.0 Hz, 1H), 2.84 (ddd, *J* = 7.0, 8.5, 14.0 Hz, 1H), 2.62 (ddd, *J* = 7.0, 8.5, 14.0 Hz, 1H), 2.06-2.21 (m, 2H), 1.84 (d, *J* = 2.5 Hz, 1H), 1.73-1.66 (m, 2H), 0.96 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 142.3, 142.2, 135.5, 128.8, 128.5, 128.4, 128.0, 126.6, 125.8, 74.2, 50.5, 36.0, 32.2, 21.1, 14.2; **HRMS** (EI) Calcd for $C_{20}H_{24}O$: 280.1827. Found: *m/z* 280.1827.



***anti*-(1*E*, 5*Z*)-1,4-Diphenylocta-1,5-dien-3-ol (4at)**: Purified by silica gel column chromatography (103.0 mg, 74% yield, R_f 0.46, EtOAc/hexane = 1/4). Yellow oil, **4at** was obtained as a mixture of diastereomer.

Major diastereomer (*anti*-**4at**): **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.39-7.19 (m, 10H), 6.53 (dd, *J* = 1.5, 16.0 Hz, 1H), 6.11 (dd, *J* = 6.0, 16.0 Hz, 1H), 5.80 (ddt, *J* = 9.5, 11.0, 1.5 Hz, 1H), 5.69 (dt, *J* = 11.0, 7.5 Hz, 1H), 4.46 (dd, *J* = 6.0, 6.5 Hz, 1H), 3.79 (dd, *J* = 6.5, 9.5 Hz, 1H), 2.18 (dquint, *J* = 1.5, 7.0 Hz, 1H), 2.10 (dquint, *J* = 1.5, 7.0 Hz, 1H), 1.95 (br s, 1H), 0.95 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 141.5, 136.9, 135.5, 131.0, 129.9, 128.7, 128.5, 128.4, 127.9, 127.6, 126.7, 126.5, 75.9, 50.9, 21.2, 14.2.

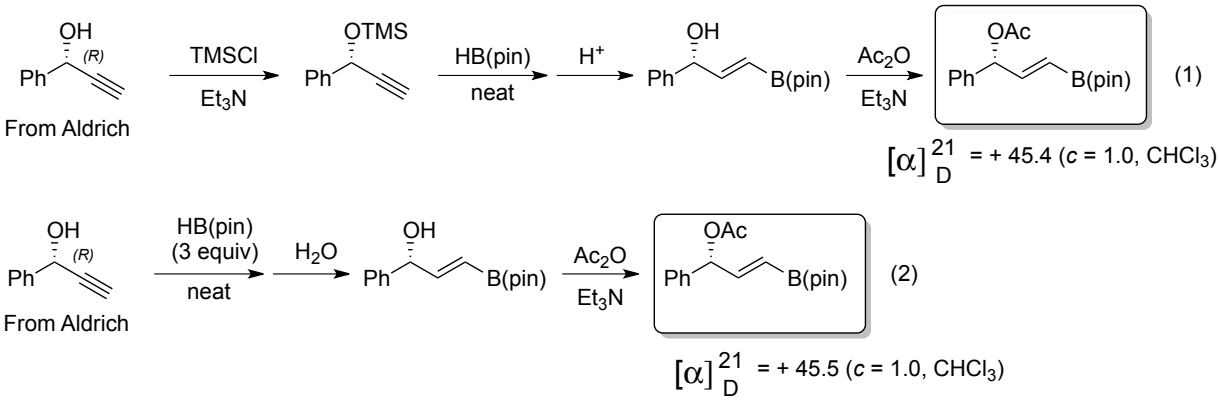
Distinguishable *syn* isomer peaks (*syn*-**4at**): **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.37-7.21 (m, 10H), 6.63 (d, *J* = 16.0 Hz, 1H), 6.24 (dd, *J* = 6.0, 16.0 Hz, 1H), 5.65 (t, *J* = 11.0 Hz, 1H), 5.56 (dt, *J* = 11.0, 7.5 Hz, 1H), 4.51 (t, *J* = 8.0 Hz, 1H), 3.82 (t, *J* = 8.0 Hz, 1H), 2.04-2.20 (m, 2H), 1.72 (br s, 1H), 0.90 (t, *J* = 7.5 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 141.6, 136.9, 134.4, 131.2, 129.9, 128.9, 128.6, 128.4, 127.8, 127.6, 126.9, 126.6, 76.0, 50.9, 21.2, 14.0

The spectral data of *syn*-**4at** are consistent with those of the literature.[7]

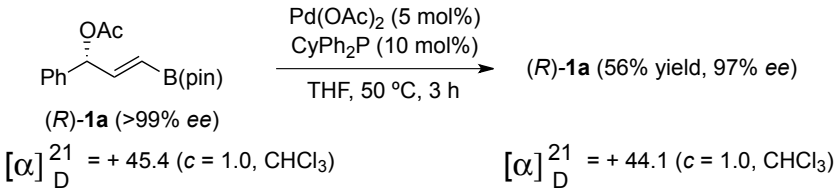
Determination of enantiomeric excess, relative configuration, and absolute configuration

The optical rotation of (*R*)-**1a**:

Substrate (*R*)-**1a** was prepared by two methods (eqs 1 and 2). The optical rotation values are shown below.

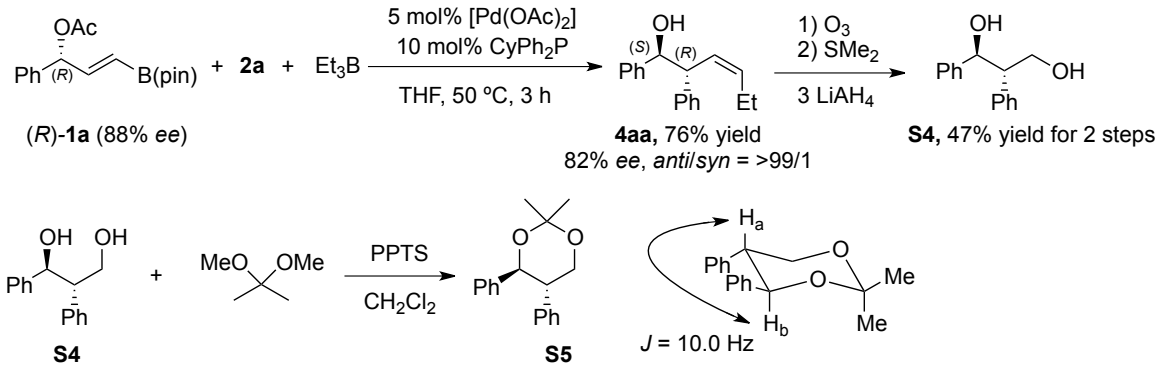


$Pd(OAc)_2$ (4.4 mg, 5 mol%) and $CyPh_2P$ (10.7 mg, 10 mol%) in THF (1 mL) was stirred at room temperature for 0.5 h. To this solution was added (*R*)-**1a** in THF (1 mL). After stirring at 50 °C for 3 h, the reaction mixture was diluted with EtOAc (10 mL) and washed with saturated NH_4Cl (2 × 10 mL) and brine (2 × 10 mL). The organic layers were dried over $MgSO_4$ and concentrated. The residue was purified by silica gel chromatography to give (*R*)-**1a** as a yellow oil (26.4 mg, 56%). The enantiomeric excess (*ee* %) of recovered (*R*)-**1a** was calculated by measuring the specific rotation. The background racemization of (*R*)-**1a** by the processes of oxidative addition and reductive elimination is comparatively slow under present condition.



The absolute configuration of product **4aa** by chirality transfer reaction was determined by derivatization to give a literature known material.[6] The diol **S4** was converted to the corresponding acetonide **S5**, and the coupling constant (J = 10.0 Hz) between H_a and H_b on 1H NMR spectra of **S5** indicated that the relative stereochemistry of the substituents on the 1,3-dioxane ring of **S5** was *anti*-orientation. [7, 15]

Compound S5. To a solution of **S4** (54.1 mg, 0.24 mmol) in CH_2Cl_2 (2 mL) were added 2,2-dimethoxypropane (150 μL, 1.2 mmol) and PPTS (6.3 mg, 25 μmol) at 0 °C, and the mixture was stirred at room temperature for 2.5 h. To the mixture was added saturated NH_4Cl aqueous solution at 0 °C, and the aqueous layer was extracted with AcOEt. The organic layer was washed with brine (2 × 20 mL). The combined organic layers were dried over $MgSO_4$ and concentrated. The residue was purified by silica gel chromatography to give **S5** as a colorless solid (55.0 mg, 87%). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.24-7.13 (m, 8H), 7.06-7.02 (m, 2H), 5.05 (d, J = 10.0 Hz, 1H), 4.25 (t, J = 11.6 Hz, 1H), 4.00 (dd, J = 4.8, 11.6 Hz, 1H), 3.08 (dt, J = 5.6, 11.2 Hz, 1H), 1.75 (s, 3H), 1.61 (s, 3H).

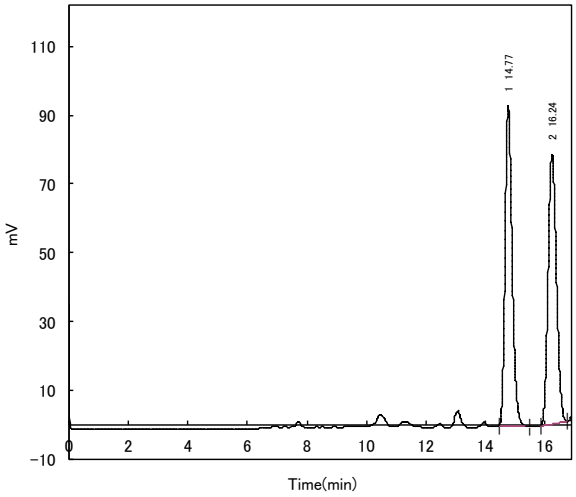


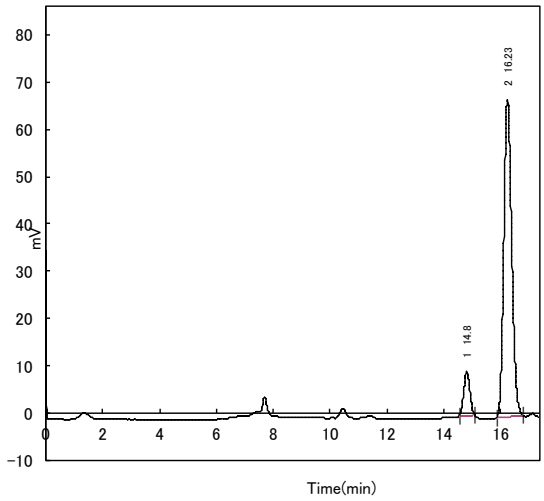
Determination of enantiomeric excess of **4aa**: **HPLC:** Rt = 14.8 min (*1R,2S* isomer) and 16.2 min (*1S,2R* isomer); Chiralcel AD-H, *n*-Hexane: *i*-PrOH = 95: 5, flow: 1.0 mL/min, λ = 254 nm, 91% *er*.

(3*Z*, *1S, 2R*)-1,2-Diphenylhex-3-en-1-ol (*1S, 2R*)-**4aa**: $[\alpha]_D^{18} = -50.6$ (c = 1.01, acetone).

Reference for (3*Z*, *1R, 2S*)-1,2-Diphenylhex-3-en-1-ol (*1R, 2S*)-**4aa** (99% *ee*): $[\alpha]_D^{20} = +65.4$ (c = 1.01, acetone)[7]

HPLC Analysis of 4aa (Scheme 7)





No.	Rt	Area	Area(%)	Height
1	14.77	1520388.859	50	92967
2	16.24	1520391.107	50	78552
		3040779.965	100	171519

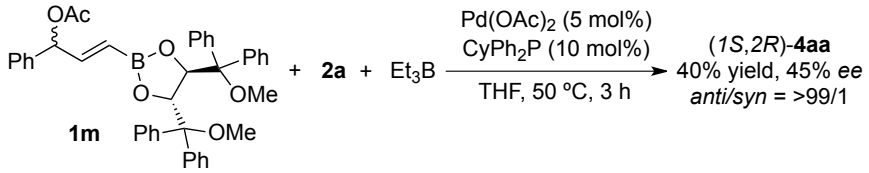
No.	Rt	Area	Area(%)	Height
1	14.8	135333.925	9.4792	9284
2	16.23	1292361.491	90.5208	67160
		1427695.416	100	76444

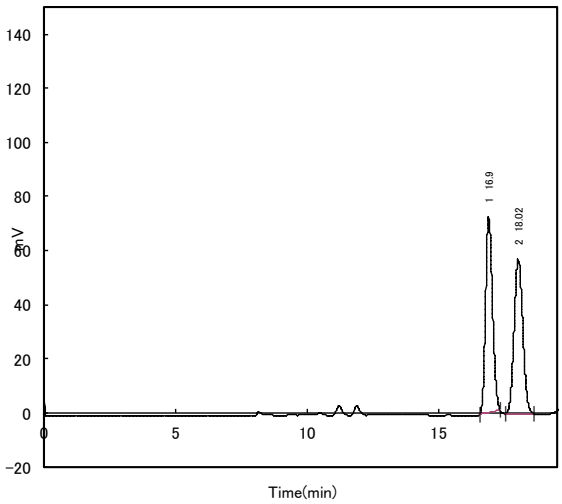
To a solution of **4aa** (141.8 mg, 0.587 mmol, *Z/E* = >99/1, 81% *ee*) in CH_2Cl_2 (20 mL) at –78 °C was bubbled a stream of O_3 until the reaction was complete by TLC analysis. Upon completion of the reaction, Me_2S (1.6 mL) was added at –78 °C and the mixture allowed to warm to rt and stirred for 2 h. The mixture was concentrated in vacuo. The residue dissolved in anhydrous THF (10 mL), $LiAlH_4$ (66.8 mg, 1.76 mmol) was then added at 0 °C and the reaction was stirred for 1 hour. The mixture was diluted with Et_2O (10 mL) and washed with 10% aqueous solution of Rochelle's salt (2 × 10 mL) and brine (2 × 10 mL). The combined organic layers were dried over $MgSO_4$ and concentrated. The residue was purified by silica gel chromatography to give (*1S,2S*)-1,2-diphenylpropane-1,3-diol (**S4**) as a white solid (63.0 mg, 47%).

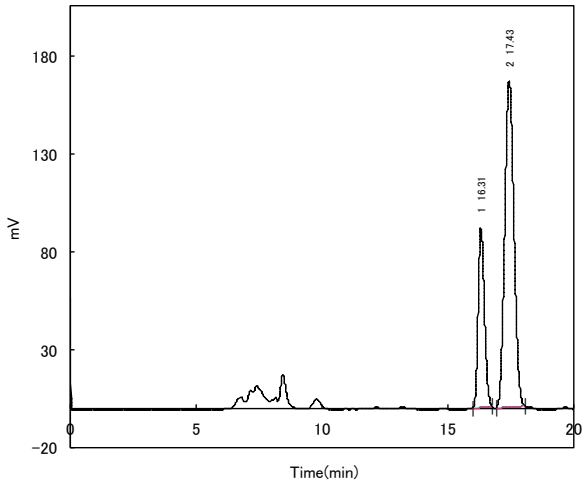
(*1S,2S*)-1,2-Diphenylpropane-1,3-diol: $[\alpha]_D^{18} = +56.4$ (c = 0.40, acetone), [lit.[6] $[\alpha]_D^{20} = +67.0$ (c = 0.55, acetone)]

References for ***ent*-S4**: $[\alpha]_D^{20} = -52$ (c = 0.40, acetone)[17a], $[\alpha]_D^{20} = -64$ (c = 0.90, acetone)[16b].

HPLC Analysis of 4aa (Scheme 7)

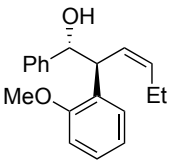




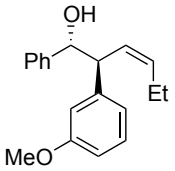


No.	Rt	Area	Area(%)	Height
1	16.9	1322469.329	50.154	72560
2	18.02	1314350.25	49.846	57548
		2636819.579	100	130108

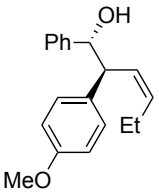
No.	Rt	Area	Area(%)	Height
1	16.31	1592504.55	27.3574	92709
2	17.43	4228605.65	72.6426	167258
		5821110.2	100	259967



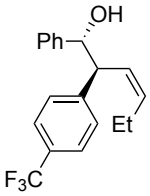
***anti*-(*Z*)-1-Phenyl-2-(2-methoxyphenyl)pent-3-en-1-ol (4ba)**: Purified by silica gel column chromatography (90.0 mg, 63% yield, R_f 0.39, EtOAc/hexane = 1/4). Yellow oil, **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.25-7.12 (m, 7H), 6.85 (dt, *J* = 0.8, 10.0 Hz, 1H), 6.78 (dm, *J* = 10.0 Hz, 1H), 5.89 (ddt, *J* = 10.0, 10.4, 2.0 Hz, 1H), 5.59 (ddt, *J* = 0.8, 10.4, 7.2 Hz, 1H), 4.94 (dd, *J* = 2.4, 6.4 Hz, 1H), 4.37 (dd, *J* = 6.4, 10.0 Hz, 1H), 3.72 (s, 3H), 2.36 (d, *J* = 2.4 Hz, 1H), 1.991 (dq, *J* = 2.0, 7.2 Hz, 1H), 1,986 (dq, *J* = 2.0, 7.2 Hz, 1H), 0.82 (t, *J* = 7.2Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 156.8, 142.5, 135.5, 130.3, 129.2, 127.7, 127.5, 127.1, 127.0, 126.6, 120.7, 110.8, 76.6, 55.5, 45.5, 21.1, 14.0; **HRMS** (EI) Calcd for $C_{19}H_{22}O_2$: 282.1620. Found: *m/z* 282.1619.



***anti*-(*Z*)-1-Phenyl-2-(3-methoxyphenyl)pent-3-en-1-ol (4ca)**: Purified by silica gel column chromatography (98.8 mg, 70% yield, R_f 0.34, EtOAc/hexane = 1/4). Yellow oil, **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.25-7.11 (m, 6H), 6.68-6.71 (m, 2H), 6.62 (m, 1H), 5.82 (ddt, *J* = 10.4, 11.2, 1.2 Hz, 1H), 5.66 (ddt, *J* = 1.2, 11.2, 7.6 Hz, 1H), 4.81 (dd, *J* = 1.2, 6.8 Hz, 1H), 3.84 (dd, *J* = 6.8, 10.4 Hz, 1H), 3.71 (s, 3H), 2.25 (d, *J* = 2.4 Hz, 1H), 2.04 (dquint, *J* = 1.2, 7.6 Hz, 1H), 2.03 (dquint, *J* = 1.2, 7.6 Hz, 1H), 0.87 (t, *J* = 7.6 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 159.5, 143.2, 142.1, 135.8, 129.4, 127.9, 127.5, 127.4, 126.7, 120.7, 114.2, 111.8, 77.9, 55.2, 52.4, 21.0, 14.0; **HRMS** (EI) Calcd for $C_{19}H_{22}O_2$: 282.1620. Found: *m/z* 282.1620.

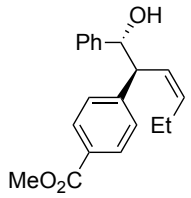


***anti*-(*Z*)-1-Phenyl-2-(4-methoxyphenyl)pent-3-en-1-ol (4da)**: Purified by silica gel column chromatography (101.7 mg, 72% yield, R_f 0.53, EtOAc/hexane = 3/7). Yellow oil, **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.25-7.15 (m, 5H), 6.99 (dm, *J* = 8.5 Hz, 2H), 6.75 (dm, *J* = 8.5 Hz, 2H), 5.80 (ddt, *J* = 10.0, 10.5, 1.5 Hz, 1H), 5.65 (dt, *J* = 10.5, 7.5 Hz, 1H), 4.77 (d, *J* = 7.0 Hz, 1H), 3.84 (dd, *J* = 7.0, 10.0 Hz, 1H), 3.75 (s, 3H), 2.25 (br s, 1H), 2.05 (dquint, *J* = 1.5, 7.5 Hz, 1H), 2.04 (dquint, *J* = 1.5, 7.5 Hz, 1H), 0.88 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 158.2, 142.1, 135.5, 133.6, 129.2, 128.0, 127.9, 127.4, 126.7, 113.8, 78.1, 55.2, 51.5, 21.0, 14.1; **HRMS** (EI) Calcd for $C_{19}H_{22}O_2$: 282.1620. Found: *m/z* 282.1616.

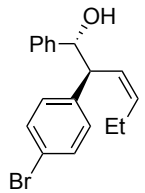


***anti*-(*Z*)-1-Phenyl-2-(4-trifluoromethylphenyl)pent-3-en-1-ol (4ea)**: Purified by silica gel column chromatography (113.7 mg, 71% yield, R_f 0.43, EtOAc/hexane = 1/4). Yellow oil, **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.46 (d, *J* = 8.0 Hz, 2H), 7.25-7.13 (m, 7 H), 5.82 (ddt, *J* = 10.0, 10.5, 1.5 Hz, 1H), 5.70 (ddt, *J* = 0.5, 10.5, 7.5 Hz, 1H), 4.82 (d, *J* = 7.5 Hz, 1H), 3.93 (dd, *J* = 7.5, 10.0

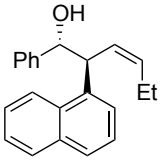
Hz, 1H), 2.24 (s, 1H), 2.06 (dquint, J = 1.5, 7.5 Hz, 1H), 1.99 (dquint, J = 1.5, 7.5 Hz, 1H), 0.87 (t, J = 7.5 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 145.8, 141.7, 136.4, 128.7, 128.7 (q, J = 31.6 Hz), 128.1, 127.8, 127.0, 126.6, 125.3 (q, J = 3.6 Hz), 124.3 (q, J = 270.0 Hz), 77.9, 52.2, 21.1, 13.9; **HRMS** (EI) Calcd for $C_{19}H_{19}F_3O$: 320.1388. Found: *m/z* 320.1388.



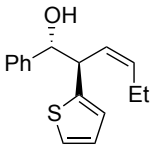
***anti*-(*Z*)-1-Phenyl-2-(4-methoxycarbonylphenyl)pent-3-en-1-ol (4fa)**: Purified by silica gel column chromatography (121.1 mg, 78% yield, R_f 0.49, EtOAc/hexane = 3/7). Colorless solid, **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.86 (dm, J = 8.5 Hz, 2H), 7.23-7.16 (m, 5 H), 7.13 (dm, J = 8.5 Hz, 2H), 5.83 (tt, J = 10.5, 1.5 Hz, 1H), 5.70 (dt, J = 10.5, 7.5 Hz, 1H), 4.81 (d, J = 7.5 Hz, 1H), 3.92 (dd, J = 7.5, 10.5 Hz, 1H), 3.87 (s, 3H), 2.32 (br s, 1H), 2.08 (dquint, J = 1.5, 7.5 Hz, 1H), 2.01 (dquint, J = 1.5, 7.5 Hz, 1H), 0.87 (t, J = 7.5 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 167.1, 147.1, 141.7, 129.7, 128.4, 128.3, 128.1, 127.7, 127.3, 126.7, 77.9, 52.6, 52.1, 21.1, 14.0; **HRMS** (EI) Calcd for $C_{20}H_{22}O_3$: 310.1569. Found: *m/z* 310.1565.



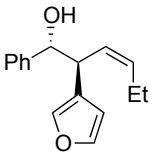
***anti*-(*Z*)-1-Phenyl-2-(4-bromophenyl)pent-3-en-1-ol (4ga)**: Purified by silica gel column chromatography (124.2 mg, 75% yield, R_f 0.48, EtOAc/hexane = 1/4). Yellow oil, **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.32 (d, J = 8.5 Hz, 2H), 7.25-7.13 (m, 5H), 6.94 (dm, J = 8.5 Hz, 2H), 5.78 (ddt, J = 10.0, 11.0, 1.5 Hz, 1H), 5.68 (dt, J = 11.0, 7.5 Hz, 1H), 4.76 (d, J = 7.5 Hz, 1H), 3.83 (dd, J = 7.5, 10.0 Hz, 1H), 2.24 (br s, 1H), 2.05 (dquint, J = 1.5 7.5 Hz, 1H), 2.01 (dquint, J = 1.5 7.5 Hz, 1H), 0.87 (t, J = 7.5 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 141.8, 140.7, 136.1, 131.4, 130.1, 128.1, 127.6, 127.3, 126.7, 120.3, 77.9, 51.8, 21.1, 14.0; **HRMS** (EI) Calcd for $C_{18}H_{19}BrO$: 330.0619. Found: *m/z* 330.0625.



***anti*-(*Z*)-1-Phenyl-2-(2-naphthyl)pent-3-en-1-ol (4ha)**: Purified by silica gel column chromatography (115.0 mg, 76% yield, R_f 0.41, EtOAc/hexane = 1/4). Yellow oil, **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.07 (d, *J* = 8.4 Hz, 1H), 7.83 (dd, *J* = 2.0, 7.2 Hz, 1H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.54 (dm, *J* = 7.2 Hz, 1H), 7.51-7.42 (m, 3H), 7.31 (dm, *J* = 7.2 Hz, 2H), 7.20 (tm, *J* = 7.2 Hz, 2H), 7.14 (m, 1H), 6.02 (ddt, *J* = 9.6, 10.8, 1.6 Hz, 1H), 5.63 (dt, *J* = 11.2, 7.6 Hz, 1H), 5.09 (dd, *J* = 2.0, 5.6 Hz, 1H), 4.81 (dd, *J* = 5.6, 9.6 Hz, 1H), 2.18 (d, *J* = 2.8 Hz, 1H), 2.00 (dquint, *J* = 1.6, 7.6 Hz, 1H), 1.94 (dquint, *J* = 1.6, 7.6 Hz, 1H), 0.78 (t, *J* = 7.6 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 142.3, 138.3, 135.6, 134.1, 131.4, 129.1, 128.0, 127.4, 127.3, 126.3, 126.0, 125.8, 125.5, 122.8, 76.8, 46.2. 21.3, 13.9; **HRMS** (EI) Calcd for $C_{22}H_{22}O$: 302.1671. Found: *m/z* 302.1670.

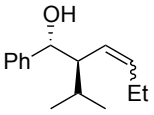


***anti*-(*Z*)-1-Phenyl-2-(2-thienyl)pent-3-en-1-ol (4ia)**: Purified by silica gel column chromatography (89.1 mg, 69% yield, R_f 0.43, EtOAc/hexane = 1/4). Yellow oil, **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.30-7.21 (m, 5H), 7.13 (dm, *J* = 5.0 Hz, 1H), 6.88 (ddm, *J* = 4.0, 5.0 Hz, 1H), 6.70 (dm, *J* = 3.5 Hz, 1H), 5.73 (ddt, *J* = 9.5, 10.5, 1.5 Hz, 1H), 5.65 (dt, *J* = 10.5, 7.5 Hz, 1H), 4.87 (dd, *J* = 2.0, 6.5 Hz, 1H), 4.20 (dd, *J* = 6.5, 9.5 Hz, 1H), 2.28 (d, *J* = 2.0 Hz, 1H), 2.01 (dquint, *J* = 1.5, 7.5 Hz, 1H), 1.95 (dquint, *J* = 1.5, 7.5 Hz, 1H), 0.84 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 144.6, 141.7, 135.8, 128.0, 127.6, 126.9, 126.8, 126.7, 124.7, 123.8, 78.1, 47.3, 21.0, 13.9; **HRMS** (EI) Calcd for $C_{16}H_{18}OS$: 258.1078. Found: *m/z* 258.1076.



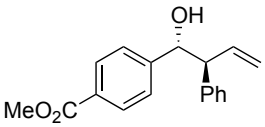
***anti*-(*Z*)-1-Phenyl-2-(3-furyl)pent-3-en-1-ol (4ja)**: Purified by silica gel column chromatography (60.6 mg, 50% yield, R_f 0.43, EtOAc/hexane = 1/4). Yellow oil, **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.32-7.21 (m, 6H), 7.08 (m, 1H), 6.13 (m, 1H), 5.65 (dt, *J* = 11.2, 7.2 Hz, 1H), 5.60 (ddt, *J* = 8.8, 11.2, 1.2 Hz, 1H), 4.73 (dd, *J* = 2.4, 6.4 Hz, 1H), 3.85 (dd, *J* = 6.4, 8.8 Hz, 1H), 2.21 (d, *J* = 2.4Hz,

1H), 2.03 (dquint, J = 1.2, 7.6 Hz, 1H), 1.97 (dquint, J = 1.2, 7.6 Hz, 1H), 0.86 (t, J = 7.6 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 142.8, 142.0, 139.8, 135.6, 128.1, 127.6, 126.9, 126.6, 124.8, 110.2, 77.2, 42.9, 21.0, 14.1; **HRMS** (EI) Calcd for $C_{16}H_{18}O_2$: 242.1307. Found: *m/z* 242.1307.



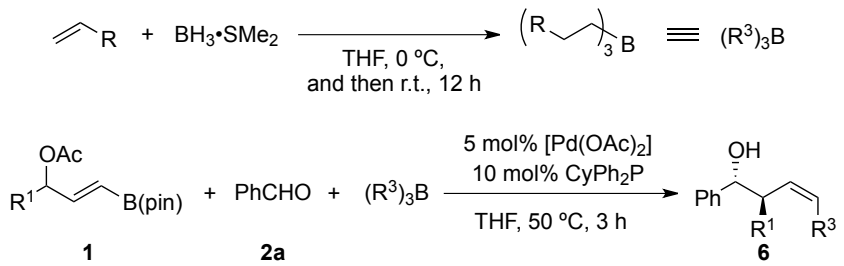
***anti*-(*Z*)-1-Phenyl-2-(*iso*-propyl)pent-3-en-1-ol (4ka)**: Purified by silica gel column chromatography (41.5 mg, 38% yield, R_f 0.46, EtOAc/hexane = 1/4). Yellow oil, **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.37-7.32 (m, 4H), 7.29-7.26 (m, 1H), 5.76 (tt, J = 7.5, 11.0 Hz, 1H), 5.36 (ddt, J = 1.5, 11.0 Hz, 1.5 Hz, 1H), 4.59 (d, J = 8.0 Hz, 1H), 2.53 (dddd, J = 1.0, 4.5, 8.0, 11.0 Hz, 1H), 2.03 (dquint, J = 1.5, 7.5 Hz, 1H), 1.97 (dquint, J = 1.5, 7.5 Hz, 1H), 1.50 (dseptet, J = 4.5, 6.5 Hz, 1H), 0.90 (t, J = 7.5 Hz, 3H), 0.85 (d, J = 6.5 Hz 3H), 0.83 (d, J = 6.5 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 143.2, 137.9, 128.3, 127.6, 126.9, 125.6, 75.3, 51.6, 28.3, 22.0, 21.2, 17.5, 14.2; **HRMS** (EI) Calcd for $C_{15}H_{22}O$: 218.1671. Found: *m/z* 218.1670.

Distinguishable *syn* isomer peaks (*syn*-**4ka**): **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 0.58 (t, J = 7.6 Hz, 3H).

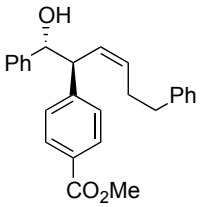


***anti*-1-(4-Methoxycarbonylphenyl)but-3-en-1-ol (5af)**: Purified by silica gel column chromatography (9.9 mg, 7% yield, R_f 0.18, EtOAc/hexane = 1/4). Yellow oil, **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.87 (dm, J = 8.8 Hz, 2H), 7.24-7.13 (m, 5H), 7.03 (dm, J = 8.8 Hz, 2H), 6.24 (ddd, J = 8.8, 10.8, 17.2 Hz, 1H), 5.29 (dm, J = 10.8 Hz, 1H), 5.24 (dm, J = 17.2 Hz, 1H), 4.89 (dd, J = 2.4, 8.0 Hz, 1H), 3.88 (s, 3H), 3.51 (dd, J = 8.0, 8.8 Hz, 1H), 2.38 (d, J =2.4 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 167.1, 147.1, 140.2, 137.4, 129.3, 129.2, 128.6, 128.4, 127.0, 126.8, 119.0, 77.0, 59.4, 52.2; **HRMS** (EI) Calcd for $C_{18}H_{18}O_3$: 282.1256. Found: *m/z* 282.1256.

General procedure for the palladium-catalyzed three-component reaction (Scheme 6)

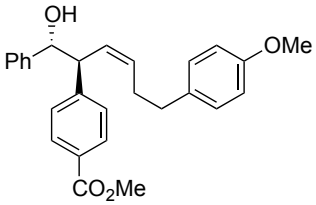


To a solution of BH_3•SMe_2 (4.95 mmol) in THF (2.5 mL) was added dropwise to a degassed alkene (1.5 mmol) at 0 ºC. After addition, the reaction mixture was warmed to room temperature and stirred for 12 hours. Upon completion of the reaction (checked by NMR), the solvent was removed under reduced pressure to give a trialkylborane, which was used for next reaction without further purification. A 10 mL two neck round-bottom flask was charged with $Pd(OAc)_2$ (5.6 mg, 0.05 mmol), $CyPh_2P$ (13.4 mg, 0.1 mmol), and THF (1 mL). The mixture was stirred at room temperature for 0.5 h, and a THF (1 mL) solution of **1f** (180.1 mg, 0.5 mmol), benzaldehyde (**2a**) (123 μL, 1.2 mmol), and trialkylboranes (1.5 mmol) in THF (1.5 mL) was then added successively. The reaction mixture was stirred at 50 °C for 3 h. Upon completion of the reaction, the reaction mixture was diluted with EtOAc (20 mL) and washed with saturated NH_4Cl (2 × 20 mL), saturated $NaHCO_3$ (2 × 20 mL), and brine (2 × 20 mL). The combined organic layers were dried over $MgSO_4$ and concentrated. The residue was purified by silica gel chromatography to give **6a** (102.2 mg, 53%).

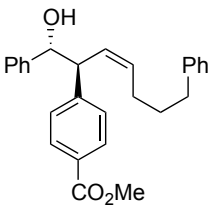


***anti*-(*Z*)-1,6-diphenyl-2-(4-metoxycarbonylphenyl)hex-3-en-1-ol (6a)**: Purified by silica gel column chromatography (102.4 mg, 53% yield, R_f 0.46, EtOAc/hexane = 1/4). Colorless solid (Mp 117.5-118.5 °C), **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.78 (d, *J* = 8.0 Hz, 2H), 7.21-7.07 (m, 6H), 7.05-6.99 (m, 6H), 5.81 (dd, *J* = 9.5, 11.0 Hz, 1H), 5.63 (dt, *J* = 11.0, 7.5 Hz, 1H), 4.70 (dm, *J* = 7.0 Hz, 1H), 3.79 (s, 3H), 3.80 (m, 1H), 2.45 (t, *J* = 7.5 Hz, 2H), 2.27 (q, *J* = 7.5 Hz, 1H), 2.23 (q, *J* = 7.5 Hz, 1H), 2.17 (d, *J* = 2.0 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 16.7.1, 147.0, 141.8,

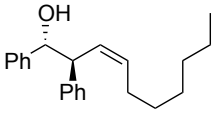
141.6, 133.3, 129.7, 128.6, 128.49, 128.46, 128.43, 128.3, 128.1, 127.7, 126.6, 126.0, 77.9, 52.5, 52.1, 35.5, 29.7; **HRMS** (EI) Calcd for $C_{26}H_{26}O_3$: 386.1882. Found: *m/z* 386.1880.



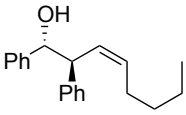
***anti*-(*Z*)-1-Phenyl-2-(4-metoxycarbonylphenyl)-6-(4-methoxyphenyl)hex-3-en-1-ol (6b)**: Purified by silica gel column chromatography (96.6 mg, 50% yield, R_f 0.46, EtOAc/hexane = 1/4). Yellow solid, **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.87 (dm, *J* = 8.8 Hz, 2H), 7.24-7.16 (m, 3H), 7.14-7.08 (m, 4H), 7.01 (dm, *J* = 8.8 Hz, 2H), 5.90 (dd, *J* = 9.6, 10.8 Hz, 1H), 5.72 (dt, *J* = 10.8, 7.2 Hz, 1H), 4.81 (dd, *J* = 2.0, 7.2 Hz, 1H), 3.88 (s, 3H), 3.85 (dd, *J* = 7.2, 9.6 Hz, 1H), 3.79 (s, 3H), 2.49 (t, *J* = 7.2 Hz, 2H), 2.27 (d, *J* = 2.4 Hz, 1H), 2.03 (q, *J* = 7.2 Hz, 2H), 1.54 (quint, *J* = 7.2 Hz, 1), 1.53 (quint, *J* = 7.2 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 167.1, 157.8, 147.1, 141.7, 134.4, 134.3, 129.7, 129.4, 128.5, 128.4, 128.2, 128.1, 127.7, 126.7, 113.8, 78.0, 55.4, 52.6, 52.1, 34.5, 31.2, 27.2; **HRMS** (EI) Calcd for $C_{27}H_{28}O_4$: 416.1988. Found: *m/z* 416.1994.



***anti*-(*Z*)-1,6-Diphenyl-2-(4-metoxycarbonylphenyl)hept-3-en-1-ol (6c)**: Purified by silica gel column chromatography (110.1 mg, 55% yield, R_f 0.46, EtOAc/hexane = 1/4). Colorless solid (Mp 90.0-91.5 °C), **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.86 (dm, *J* = 8.4 Hz, 2H), 7.29-7.17 (m, 6H), 7.14-7.07 (6 H), 5.09 (dd, *J* = 9.6, 11.2 Hz, 1H), 5.73 (dt, *J* = 11.2, 7.2 Hz, 1H), 4.81 (*J* = 7.2, 2.0 Hz, 1H), 3.88 (s, 3H), 3.85 (dd, *J* = 7.2, 9.6 Hz, 1H), 2.51 (t, *J* = 7.2 Hz, 1H), 2.22 (br s, 1H), 2.05 (dt, *J* = 1.2, 7.2 Hz, 1H), 2.03 (dt, *J* = 1.2, 7.2 Hz, 1H), 1.63-1.51 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.1, 147.1, 142.2, 141.7, 134.2, 129.7, 128.6, 128.5, 128.4, 128.3, 128.1, 127.7, 126.7, 125.8, 78.0, 77.5, 52.6, 52.1, 35.4, 31.0, 29.2; **HRMS** (EI) Calcd for $C_{27}H_{28}O_3$: 400.2038. Found: *m/z* 400.2040.

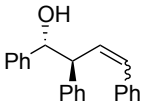


***anti*-(*Z*)-1-Phenyl-2-phenyl-dec-3-en-1-ol (6d)**: Purified by silica gel column chromatography (81.7 mg, 53% yield, R_f 0.43, EtOAc/hexane = 1/4). Yellow oil, **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.24-7.12 (m, 8H), 7.08 (dm, *J* = 7.0 Hz, 2H), 5.87 (ddt, *J* = 10.0, 10.5, 1.0 Hz, 1H), 5.68 (dt, *J* = 10.5, 7.0 Hz, 1H), 4.82 (dd, *J* = 1.5, 7.5 Hz, 1H), 3.87 (dd, *J* = 7.5, 10.0 Hz, 1H), 2.26 (d, *J* = 2.0 Hz, 1H), 2.03 (dq, *J* = 1.0, 7.5 Hz, 2H), 1.28-1.17 (m, 8H), 0.86 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 142.1, 141.6, 134.4, 128.5, 128.4, 128.3, 128.0, 127.5, 126.7, 126.6, 78.1, 52.6, 31.8, 29.5, 29.1, 27.8, 22.7, 14.2;



***anti*-(*Z*)-1-Phenyl-2-phenyl-oct-3-en-1-ol (6e)**: Purified by silica gel column chromatography (77.1 mg, 55% yield, R_f 0.43, EtOAc/hexane = 1/4). Yellow oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.24-7.12 (m, 8H), 7.10-7.07 (m, 2H), 5.87 (ddt, *J* = 1.5, 10.0, 11.0 Hz, 1H), 5.68 (dt, *J* = 7.5, 11.0 Hz, 1H), 4.82 (d, *J* = 7.5 Hz, 1H), 3.87 (dd, *J* = 7.5, 10.0 Hz, 1H), 2.26 (br s, 1H), 2.07-2.00 (m, 2H), 1.28-1.20 (m, 4H), 0.84 (t, *J* = 7.5 Hz, 3H).

The spectral data of **6e** are consistent with those of the literature.[16a]



***anti*-(*Z*)-1,2,3-Triphenylbut-3-en-1-ol (6h)**: Commercially available Ph_3B (0.25M in THF) was use. (*Z*)-*anti*-**6h** was obtained as a mixture of (*Z*)-*anti*-**6h** and (*E*)-*anti*-**6h**. A small amount of (*E*)-*anti*-**6h** was obtained as a pure form. Purified by silica gel column chromatography (135.2 mg, 90% yield, R_f 0.39, EtOAc/hexane = 1/4). Yellow oil, (*E*)-*anti*-**6h**: **^{1}H NMR** ($CDCl_3$, 500 MHz) δ 7.38 (dm, *J* = 8.0 Hz, 2H), 7.31 (tm, *J* = 7.5 Hz, 2H), 7.25-7.12 (m, 11H), 6.63 (dd, *J* = 7.5, 15.5 Hz, 1H), 6.54 (d, *J* = 15.5 Hz, 1H), 4.95 (dd, *J* = 2.5, 7.5 Hz, 1H), 3.72 (t, *J* = 7.5 Hz, 1H), 2.32 (br s, 1H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 142.0, 141.0, 137.1, 133.6, 129.2, 128.7, 128.6, 128.53, 128.1, 127.7, 127.64, 126.8, 126.5, 77.8, 58.3; **HRMS** (EI) Calcd for $C_{22}H_{20}O$: 300.1514. Found: *m/z* 300.1514.

Distinguishable (*Z*)-isomer peaks ((*Z*)-*anti*-**6h**): **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.39-7.10 (m, 15H), 6.73 (d, *J* = 11.6 Hz, 1H), 6.22 (dd, *J* = 10.8, 11.6 Hz, 1H), 4.90 (dd, *J* = 2.0, 1H), 4.13 (dd,

J = 7.2, 10.8 Hz, 1H), 2.18 (br s, 1H); **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 141.8, 141.2, 136.9, 132.5, 130.6, 128.8, 128.48, 128.3, 128.1, 127.58, 127.1, 126.7, 78.6, 52.4.

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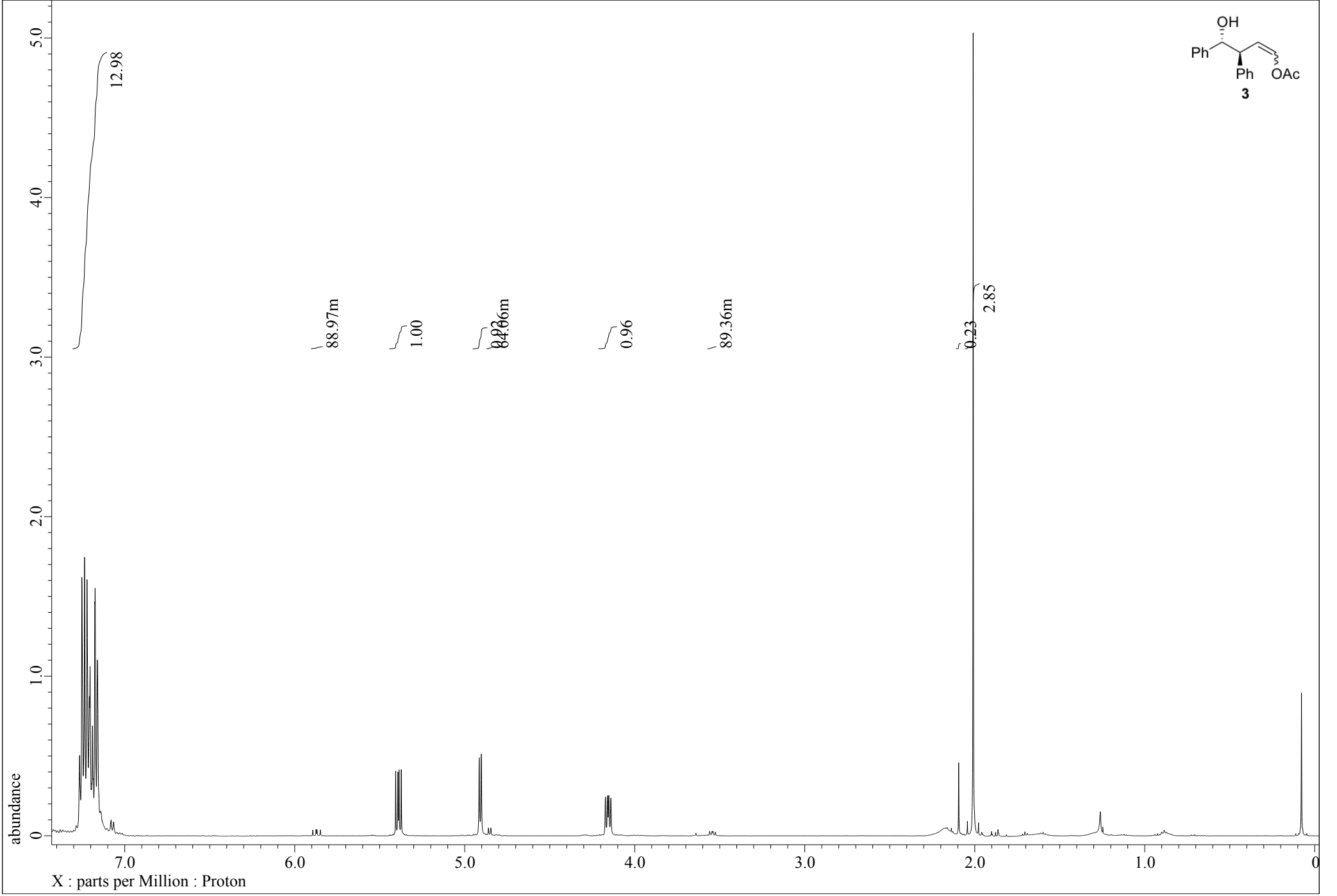
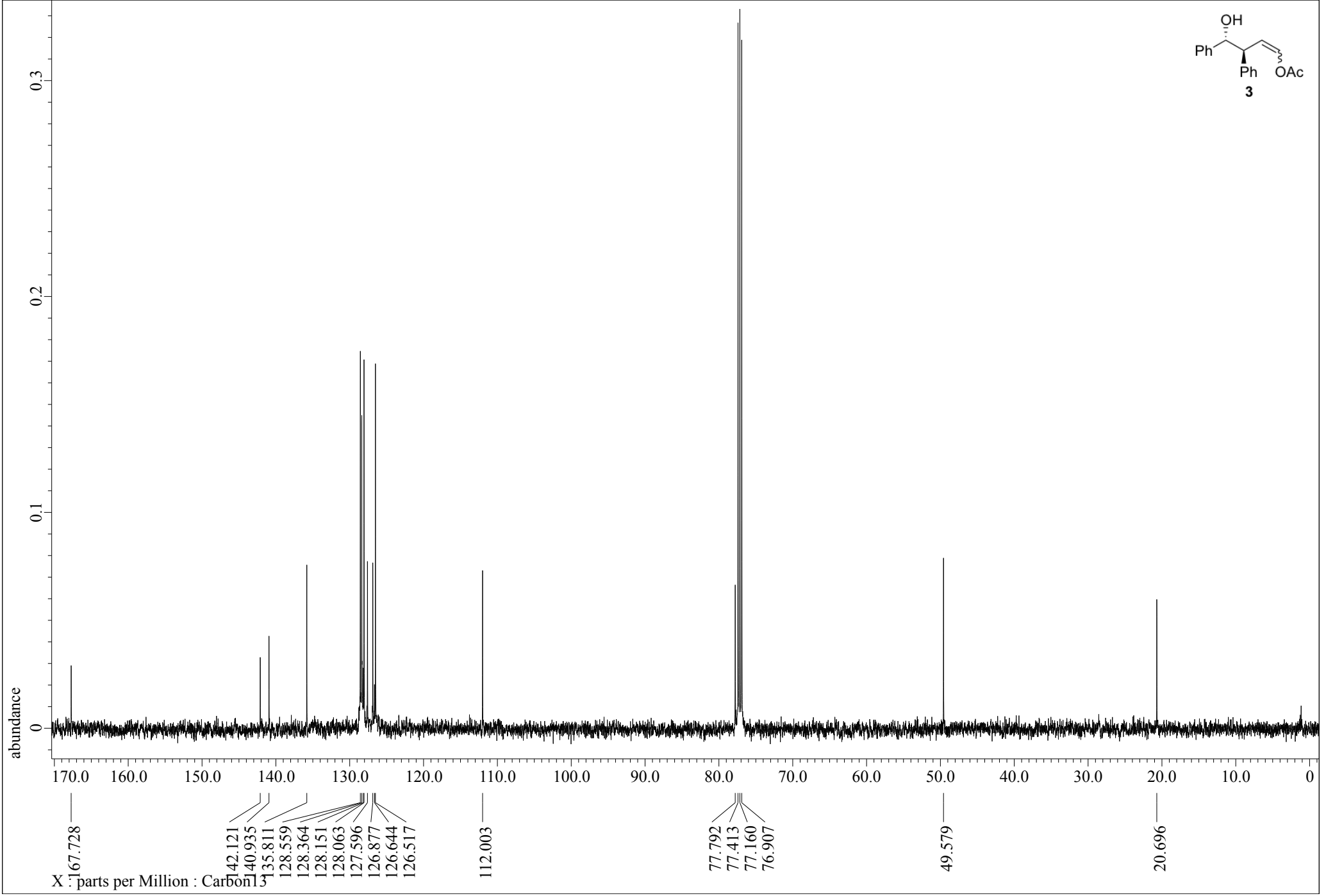
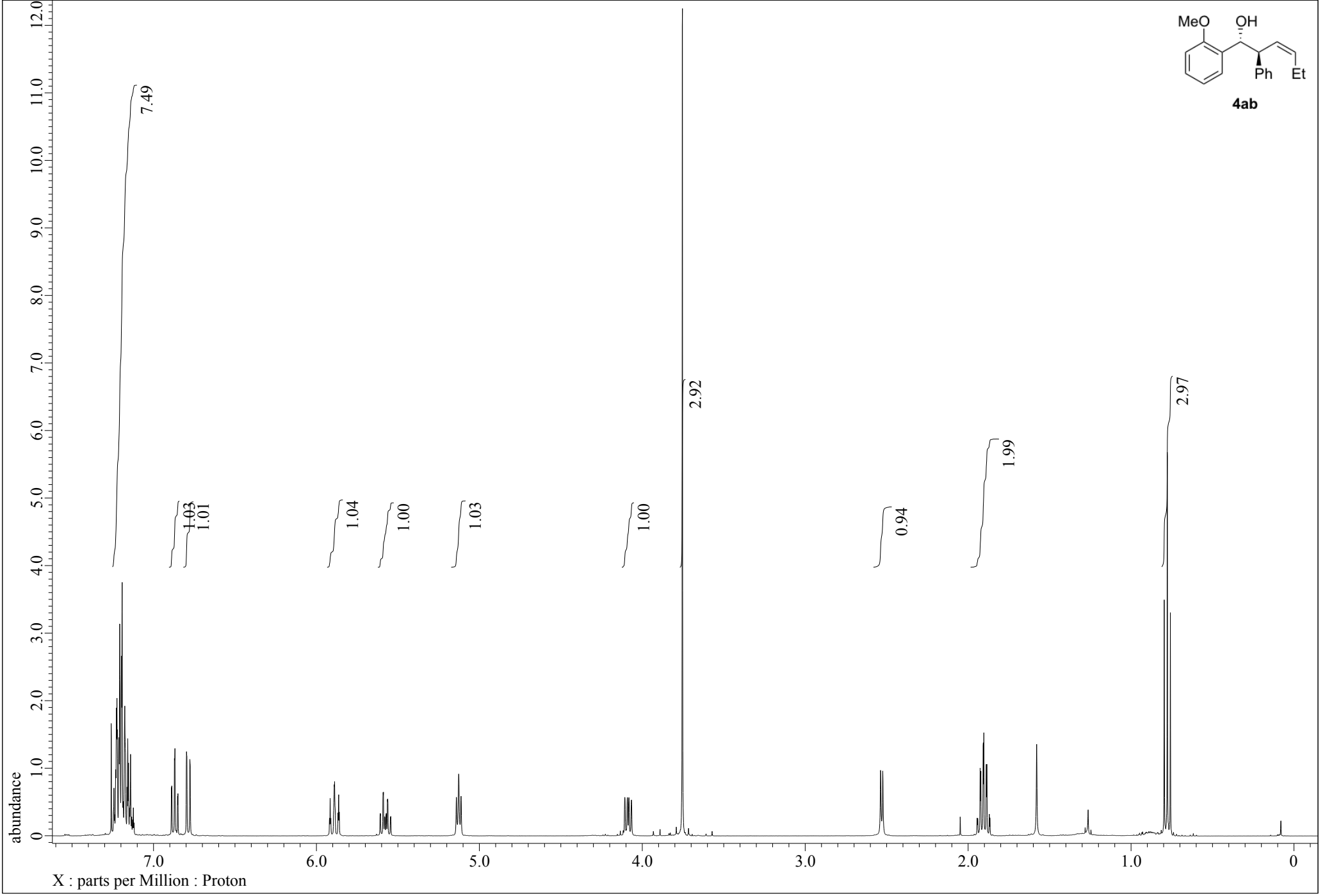
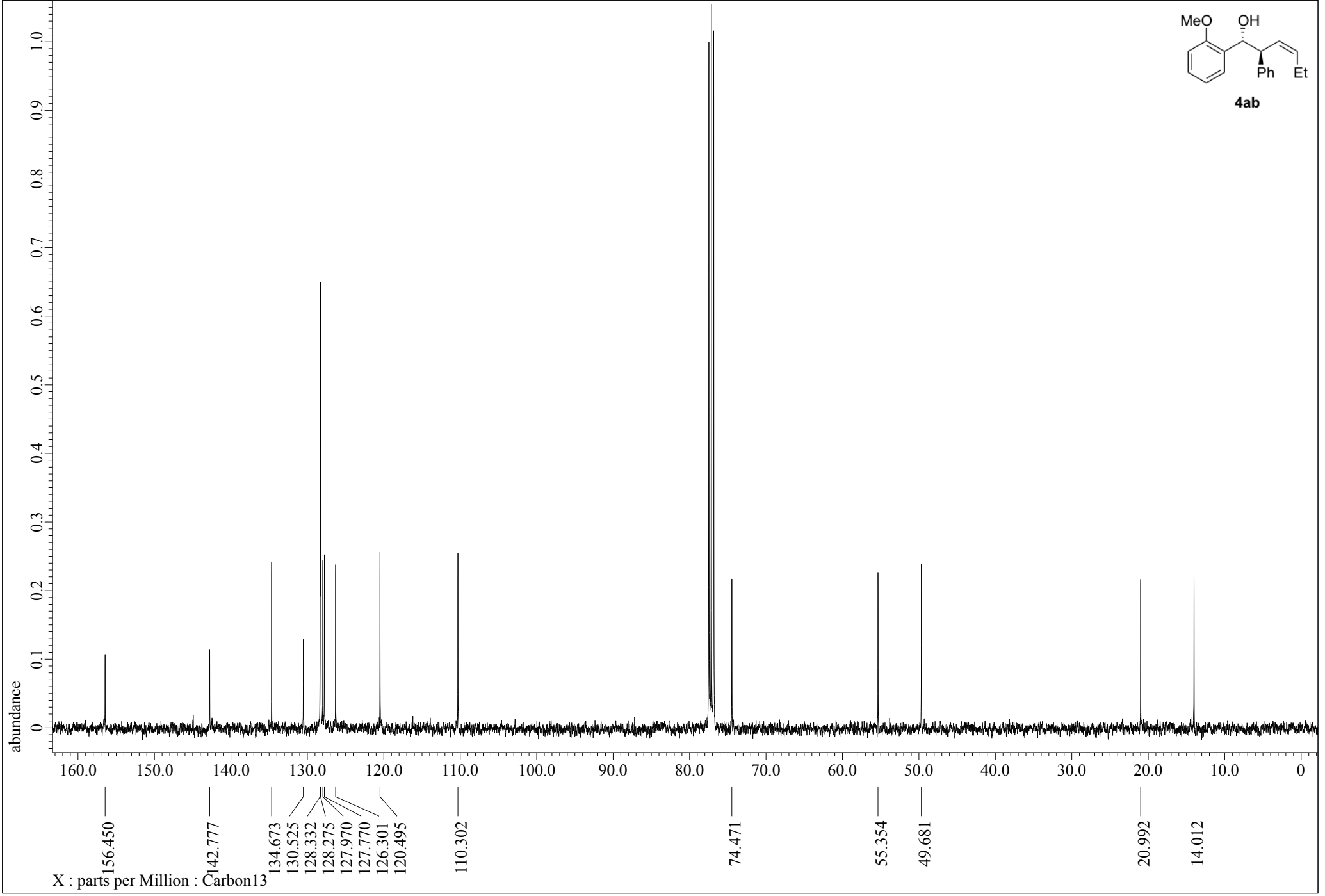
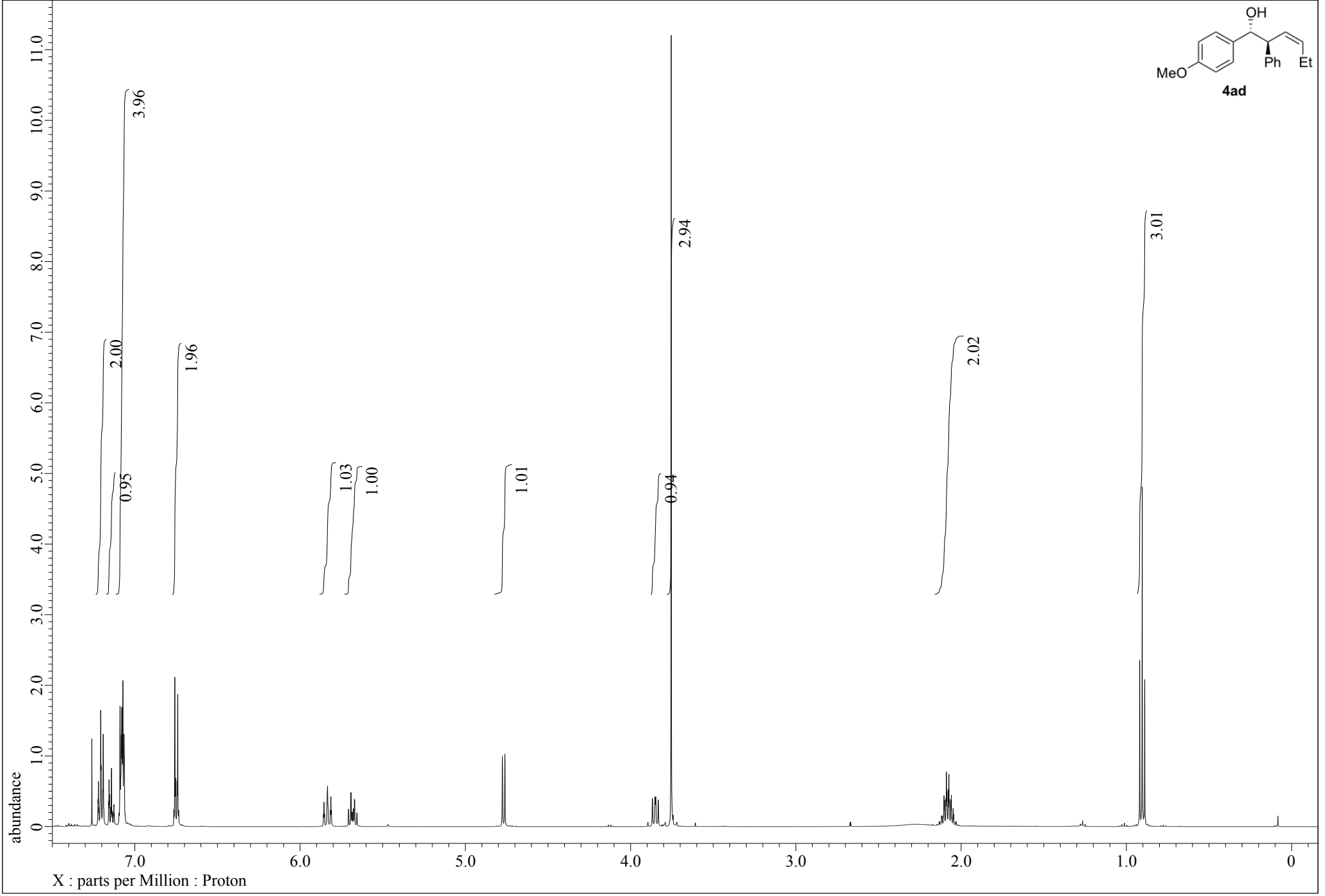
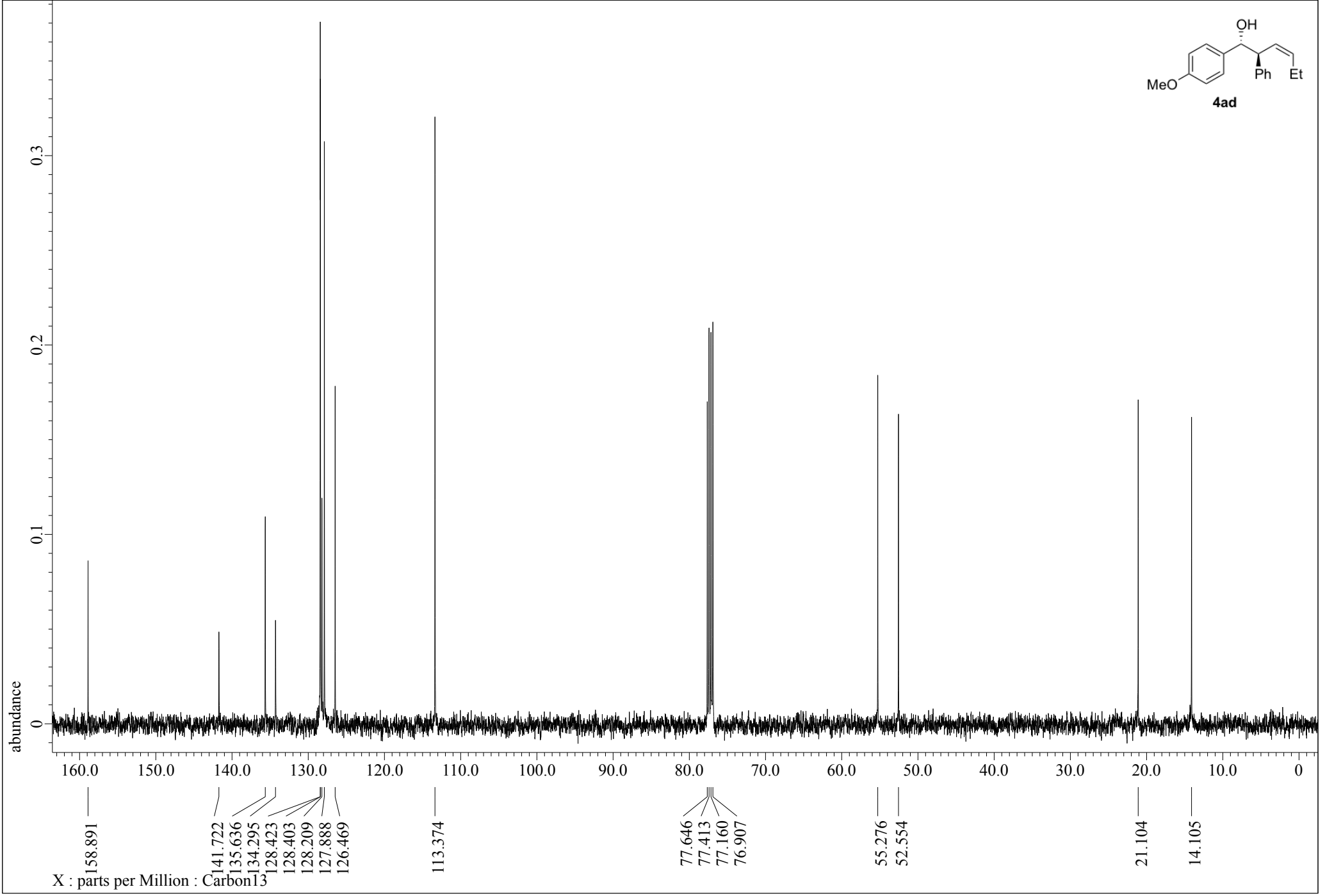

OH
Ph
Ph
OAc
3
12.98
88.97m
1.00
0.96
89.36m
0.23
2.85
abundance
X : parts per Million : Proton

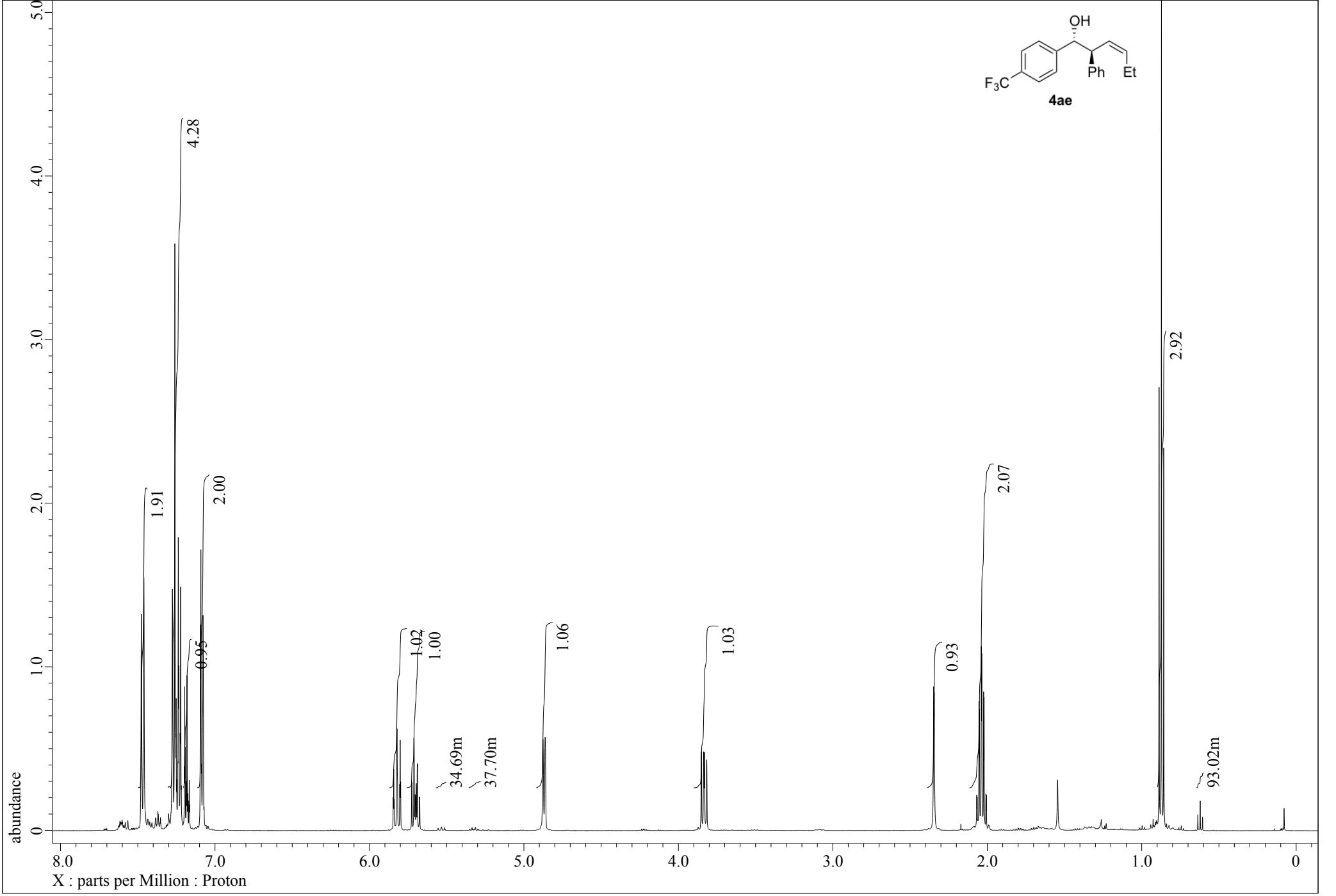

OH
Ph
Ph
OAc
3
abundance
0.3
0.2
0.1
0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
167.728
142.121
140.935
135.811
128.559
128.364
128.151
128.063
127.596
126.877
126.644
126.517
112.003
77.792
77.413
77.160
76.907
49.579
20.696
X : parts per Million : Carbon13

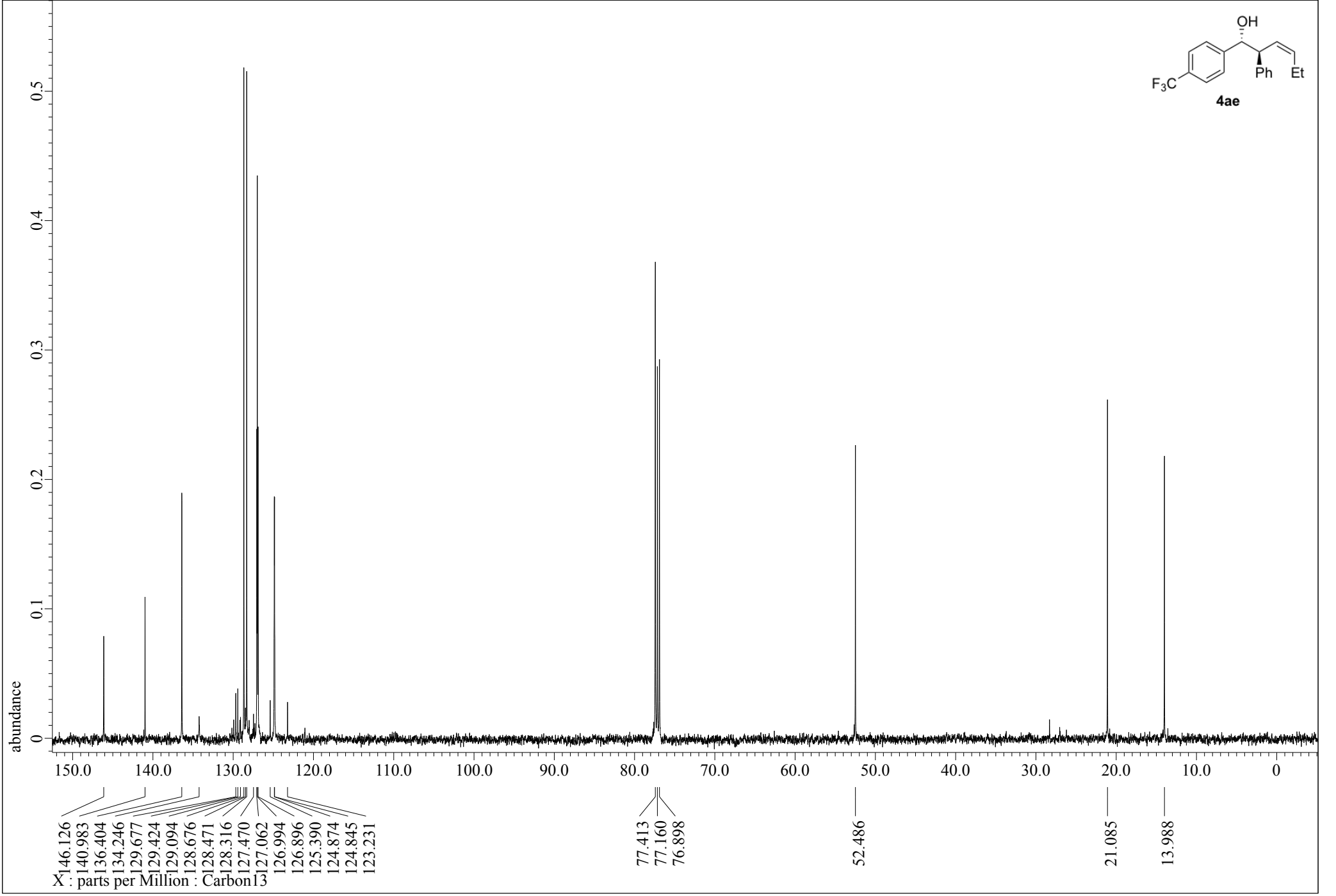

MeO
OH
Ph
Et
4ab
7.49
1.03
1.01
1.04
1.00
1.03
1.00
2.92
0.94
1.99
2.97
abundance
X : parts per Million : Proton

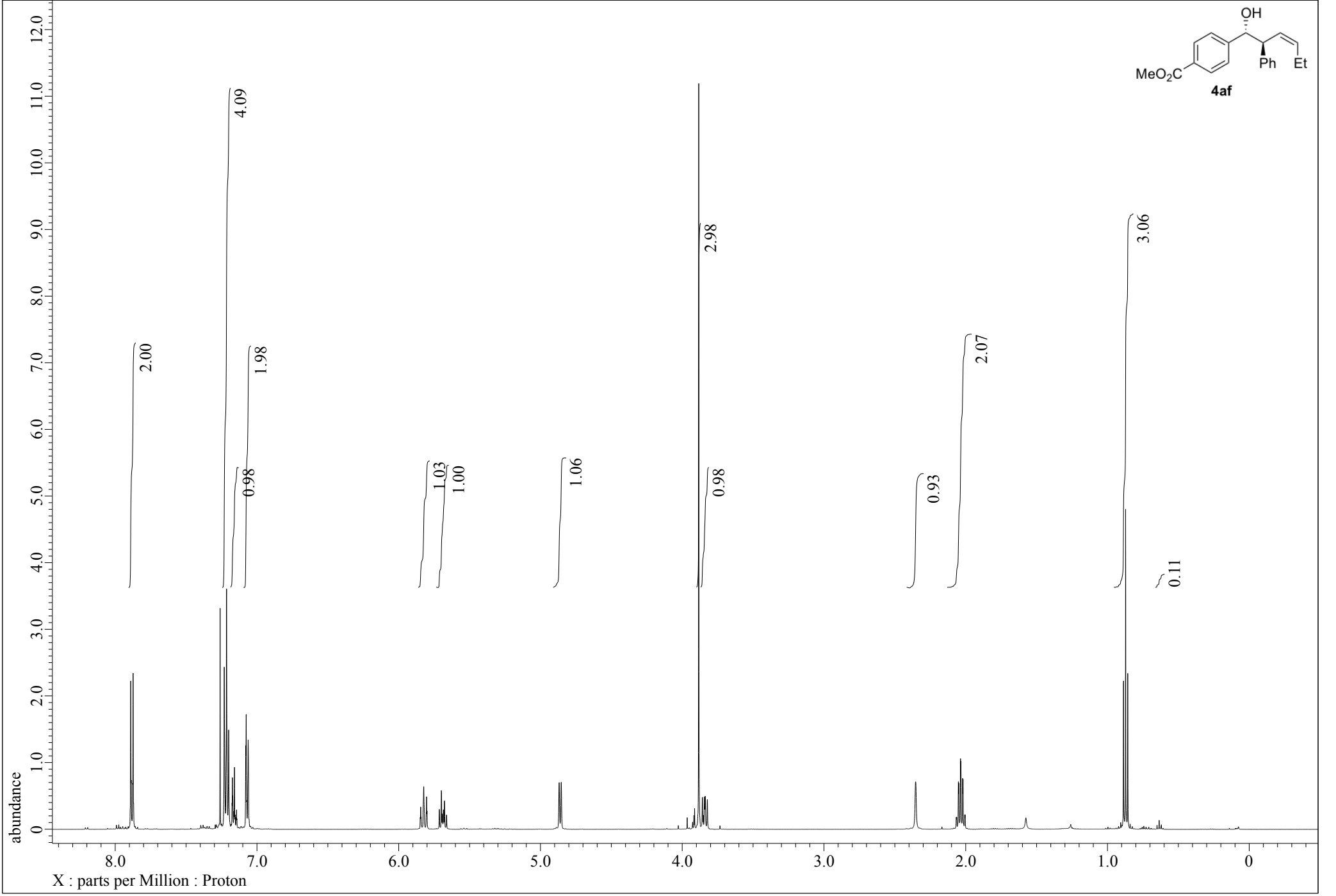

MeO
OH
Ph
Et
4ab
abundance
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
156.450
142.777
134.673
130.525
128.332
128.275
127.970
127.770
126.301
120.495
110.302
74.471
55.354
49.681
20.992
14.012
X : parts per Million : Carbon13

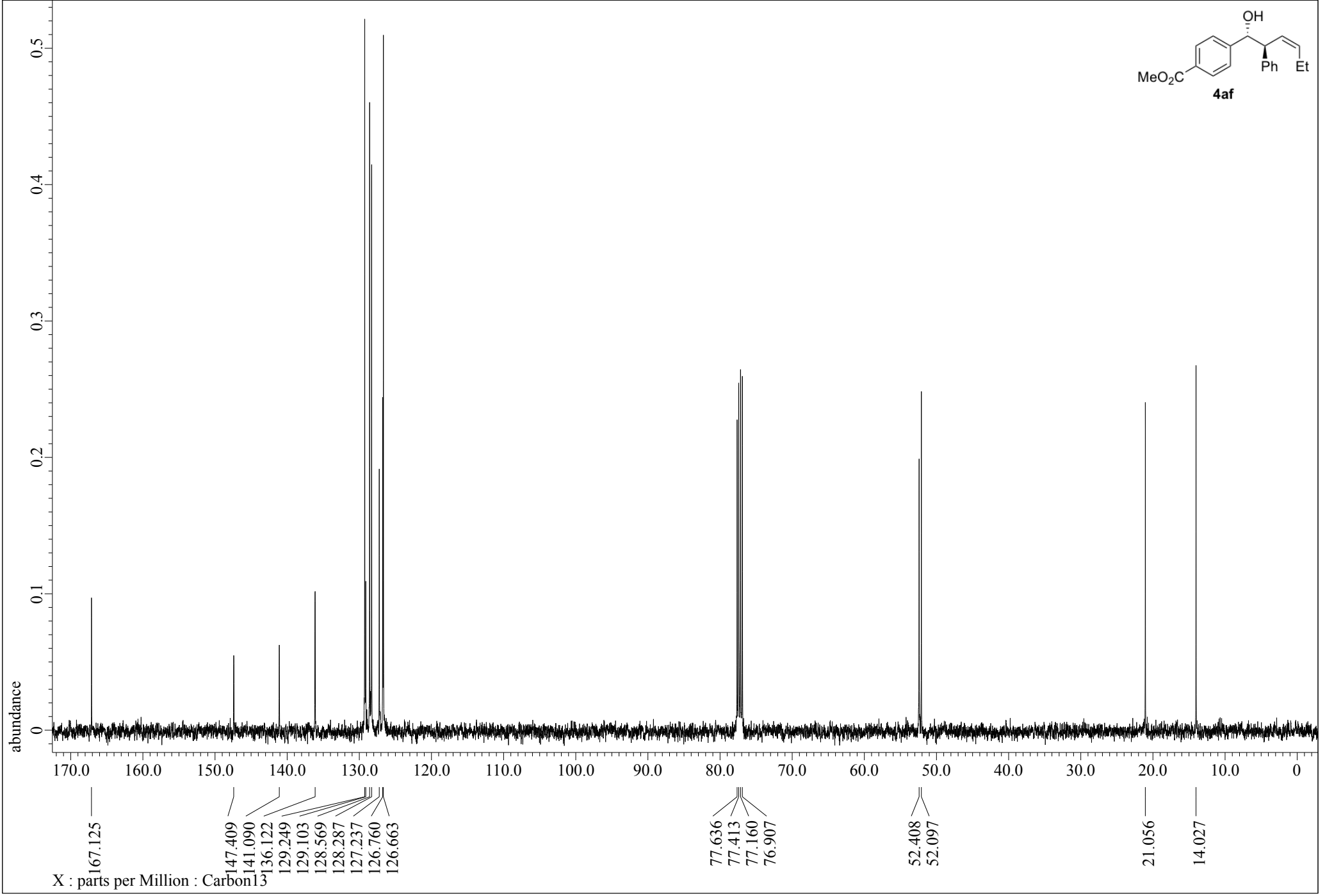

OH
MeO
Ph
Et
4ad
3.96
2.00
0.95
1.96
1.03
1.00
1.01
0.94
2.94
2.02
3.01
abundance
X : parts per Million : Proton


OH
MeO
Ph
Et
4ad
abundance
0.3
0.2
0.1
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
158.891
141.722
135.636
134.295
128.423
128.403
128.209
127.888
126.469
113.374
77.646
77.413
77.160
76.907
55.276
52.554
21.104
14.105
X : parts per Million : Carbon13


OH
Ph
Et
F3C
4ae
4.28
1.91
2.00
0.95
1.02
1.00
34.69m
37.70m
1.06
1.03
0.93
2.07
2.92
93.02m
abundance
X : parts per Million : Proton


OH
Ph
Et
F3C
4ae
abundance
0
0.1
0.2
0.3
0.4
0.5
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
146.126
140.983
136.404
134.246
129.677
129.424
129.094
128.676
128.471
128.316
127.470
127.062
126.994
126.896
125.390
124.874
124.845
123.231
77.413
77.160
76.898
52.486
21.085
13.988
X : parts per Million : Carbon13


OH
MeO2C
Ph
Et
4af
2.00
4.09
1.98
0.98
1.03
1.00
1.06
2.98
0.98
0.93
2.07
3.06
0.11
abundance
X : parts per Million : Proton


OH
MeO2C
Ph
Et
4af
abundance
0.5
0.4
0.3
0.2
0.1
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
167.125
147.409
141.090
136.122
129.249
129.103
128.569
128.287
127.237
126.760
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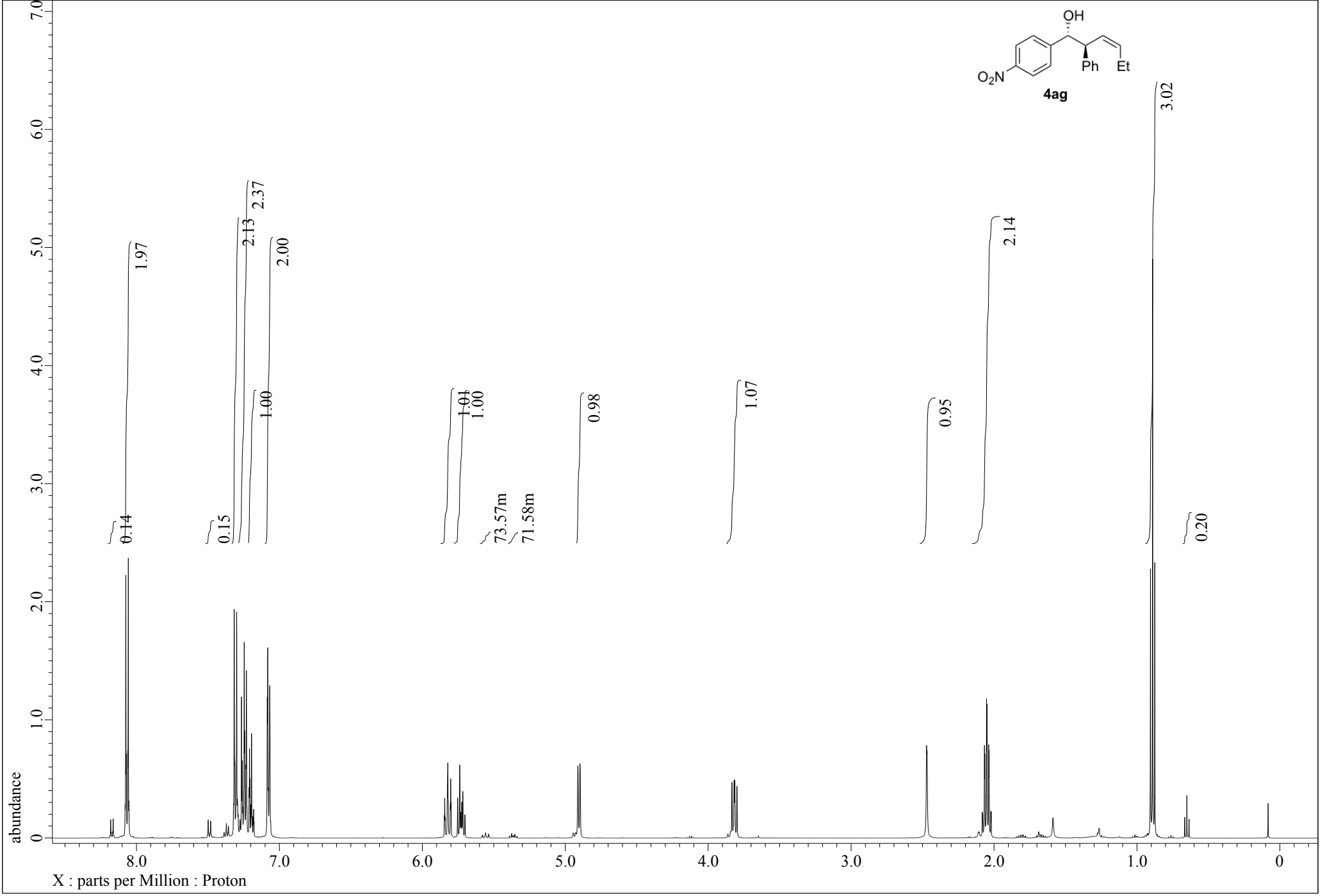
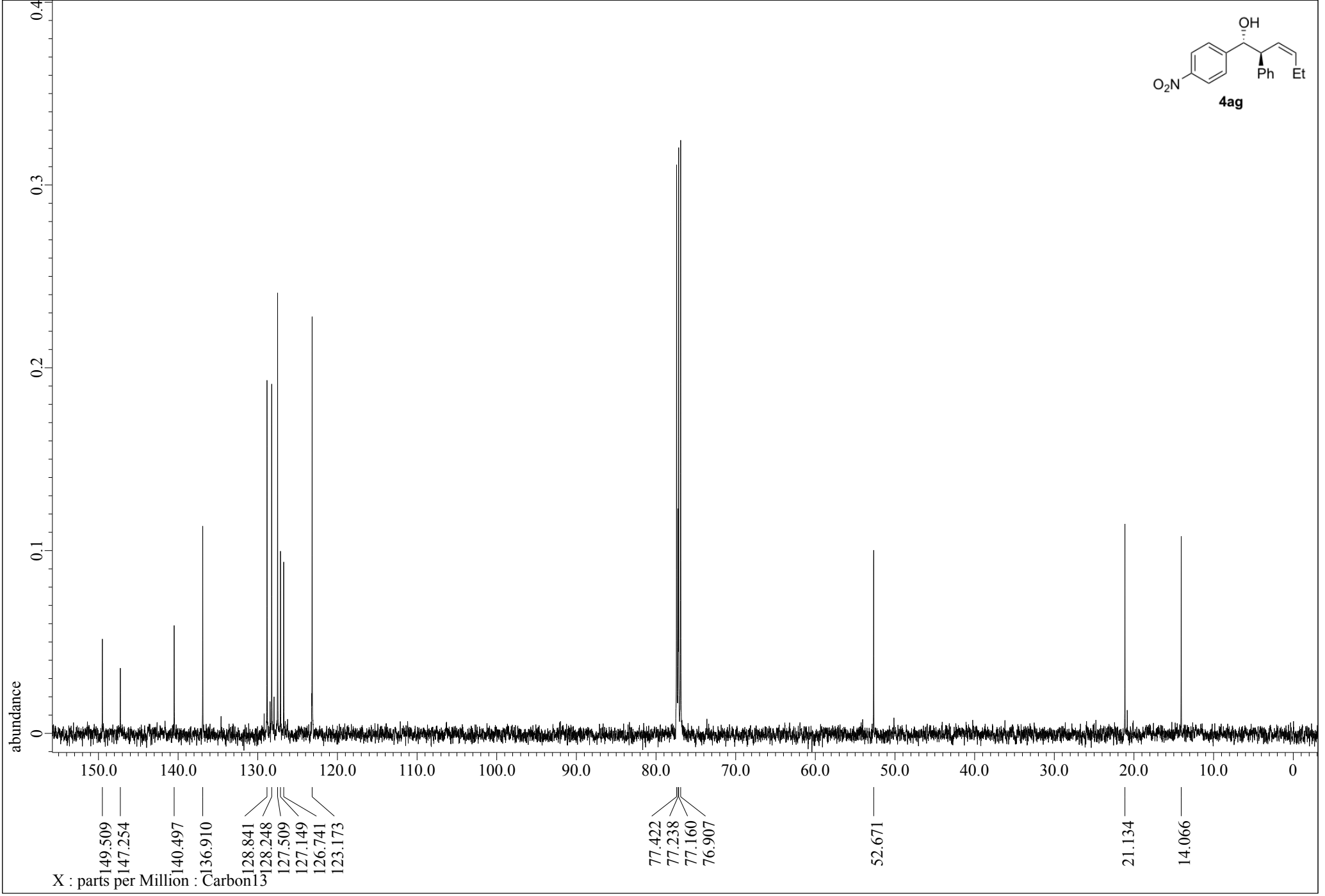
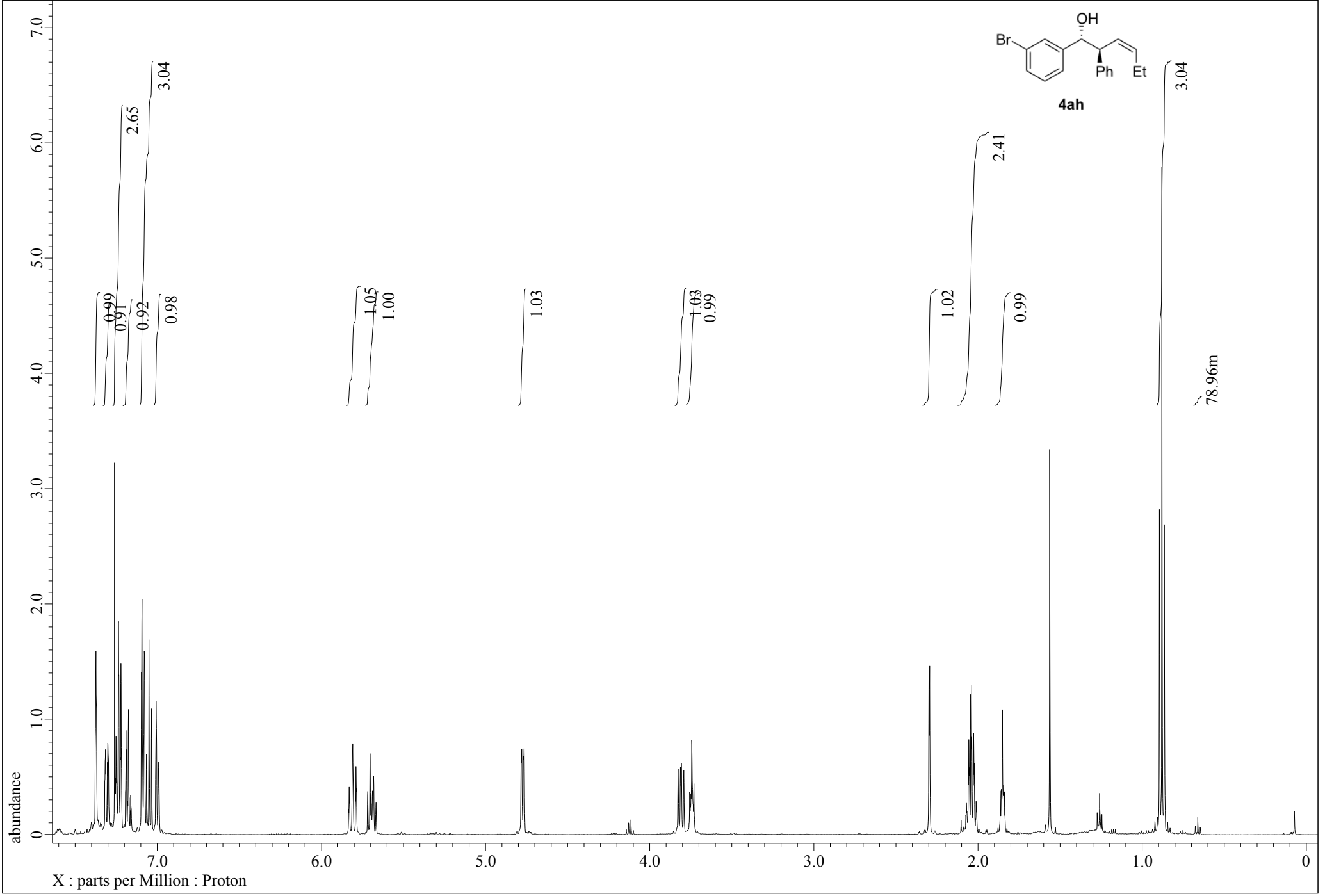
77.636
77.413
77.160
76.907
52.408
52.097
21.056
14.027
X : parts per Million : Carbon13


OH
O2N
Ph
Et
4ag
1.97
0.14
0.15
2.13
2.37
1.00
2.00
1.01
1.00
73.57m
71.58m
0.98
1.07
0.95
2.14
3.02
0.20
abundance
X : parts per Million : Proton


OH
O2N
Ph
Et
4ag
abundance
0.4
0.3
0.2
0.1
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
149.509
147.254
140.497
136.910
128.841
128.248
127.509
127.149
126.741
123.173
77.422
77.238
77.160
76.907
52.671
21.134
14.066
X : parts per Million : Carbon13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Br
Ph
Et
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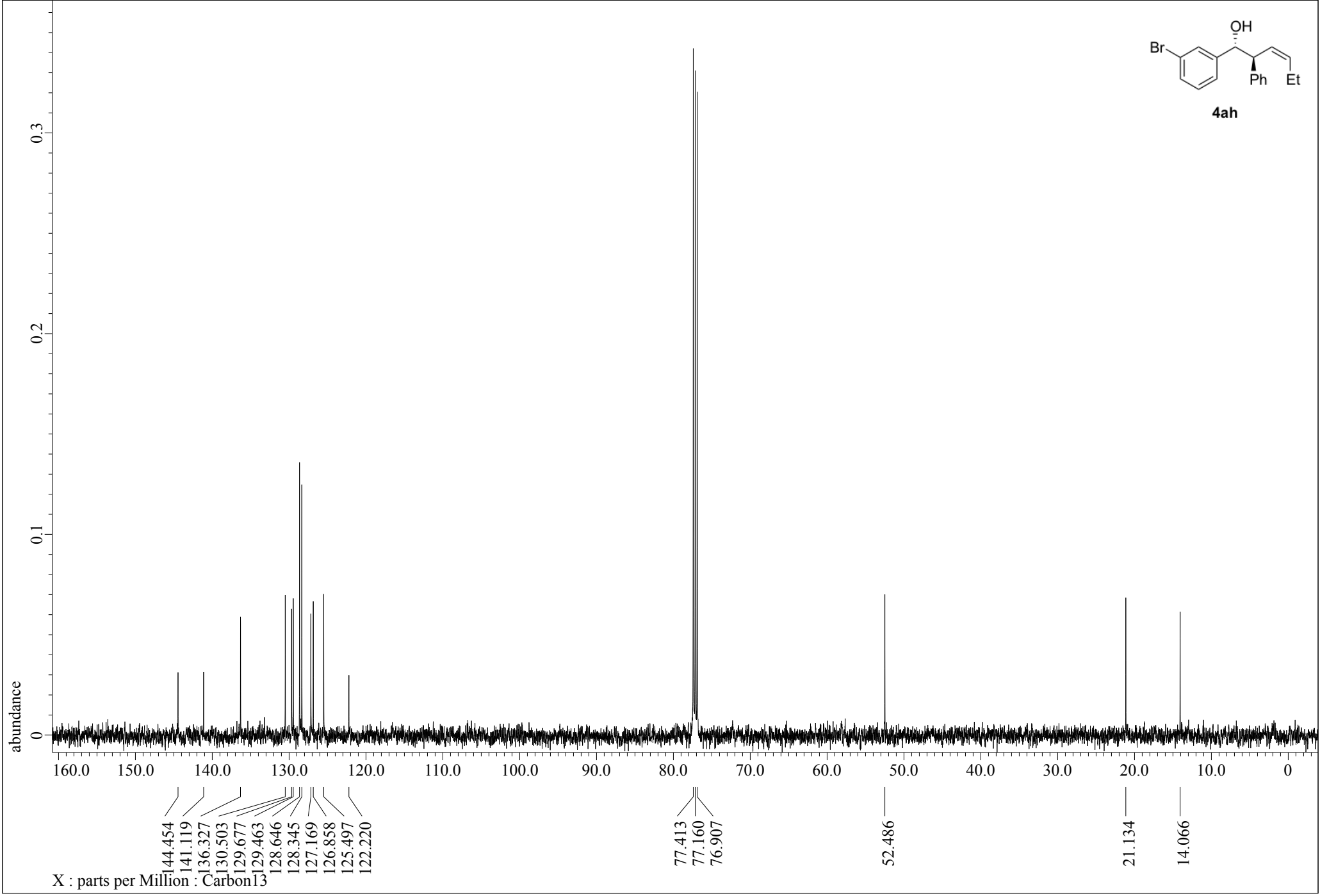
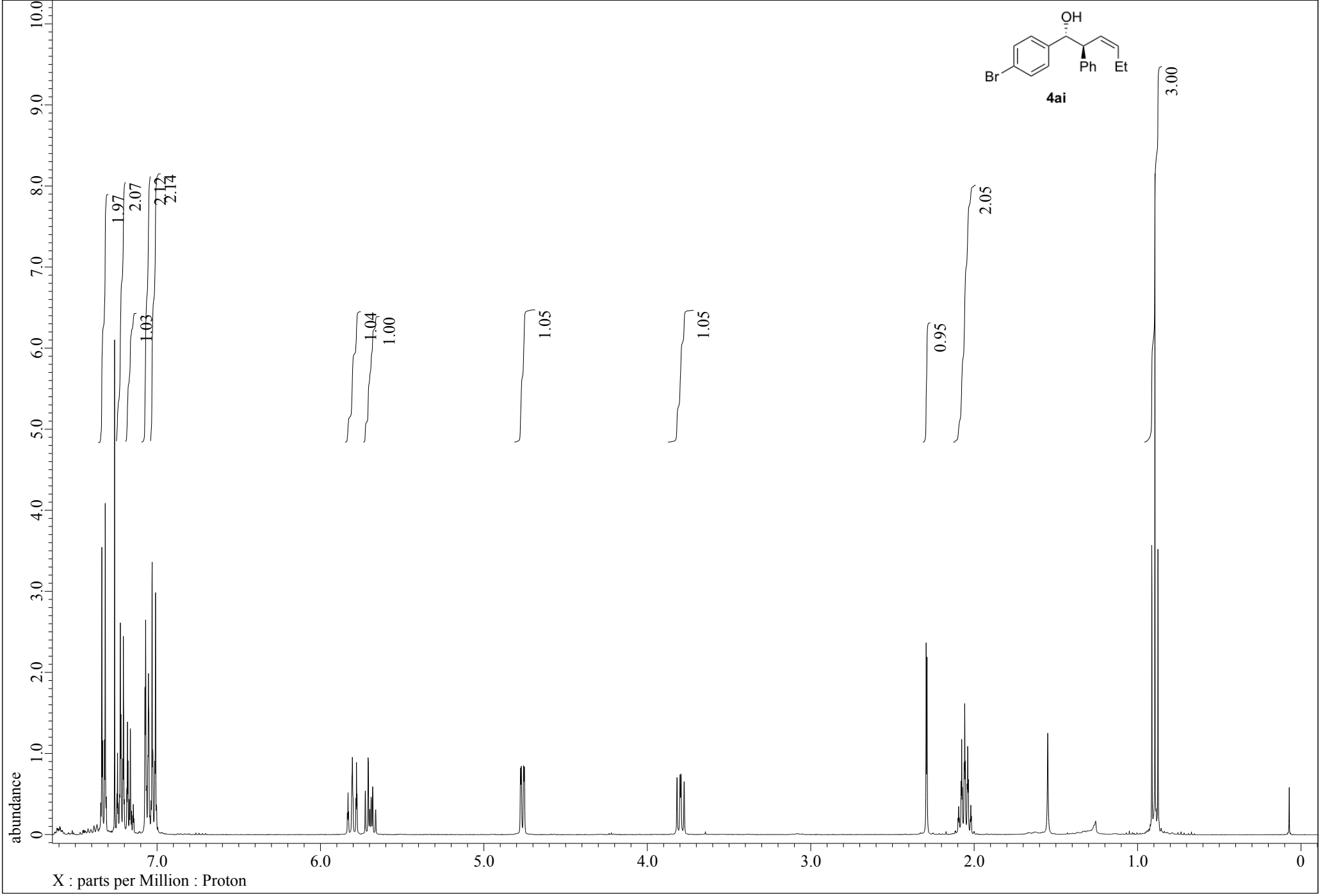
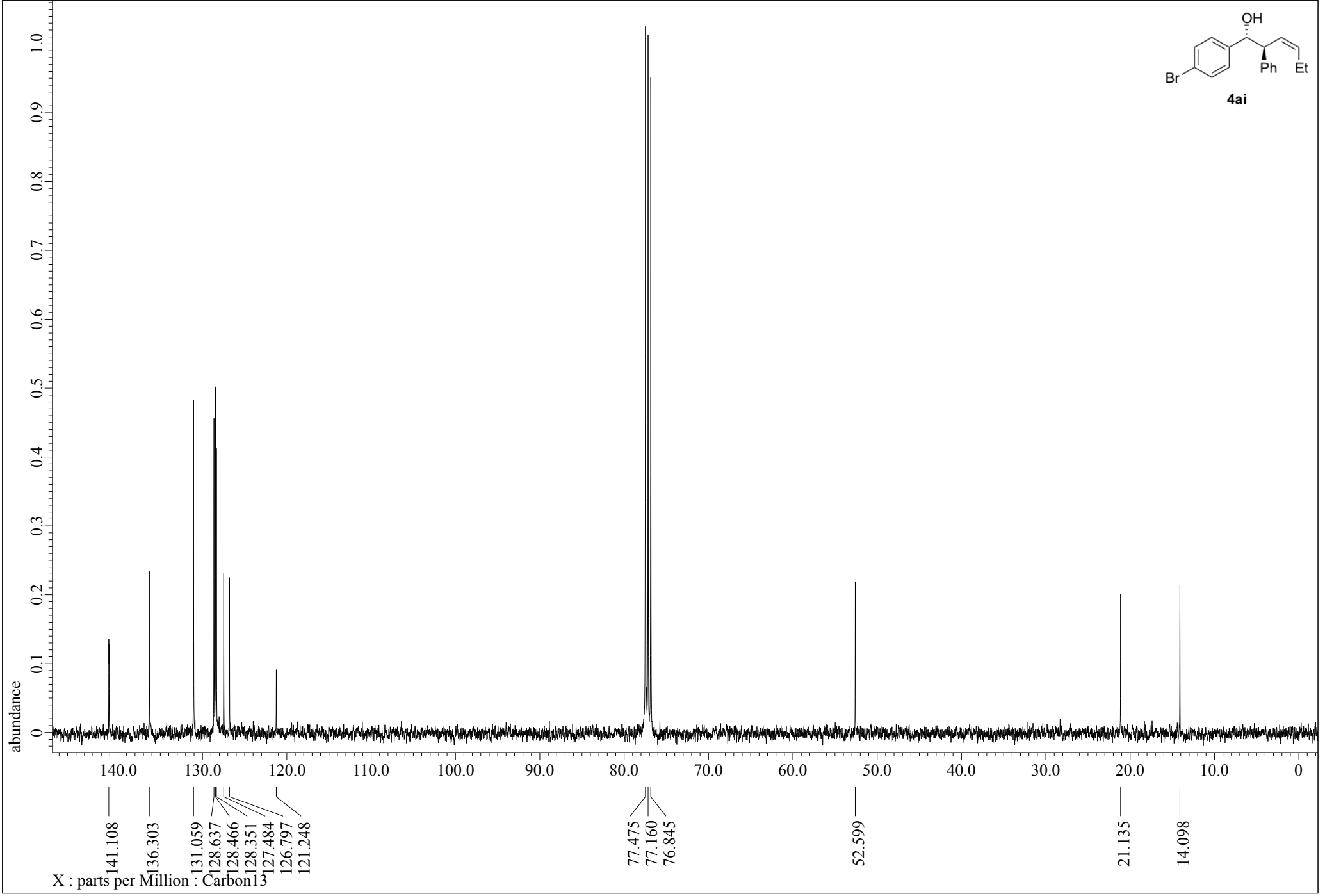
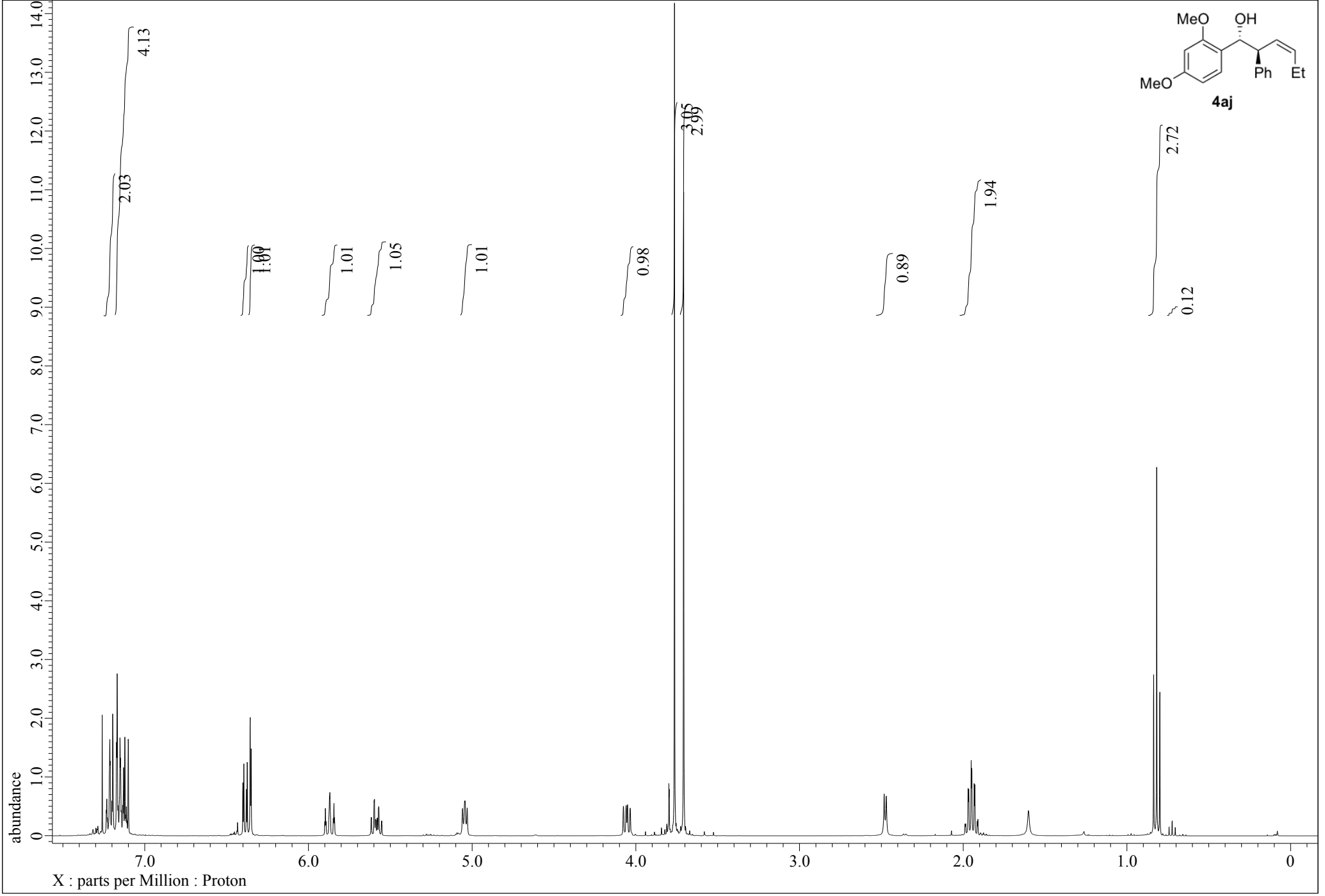
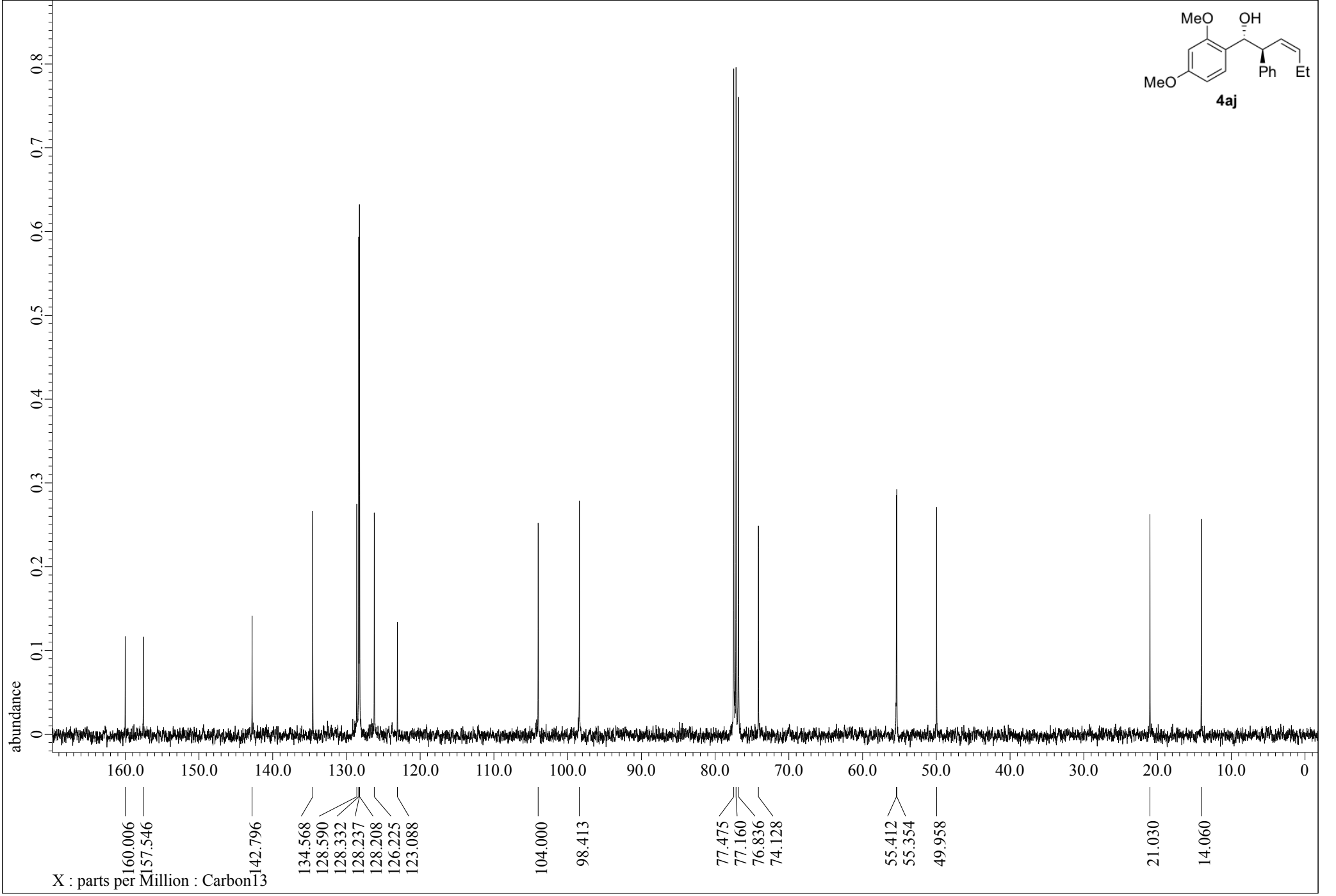
3.04
2.65
0.99
0.91
0.92
0.98
1.05
1.00
1.03
1.03
0.99
1.02
2.41
0.99
3.04
78.96m
abundance
X : parts per Million : Proton


OH
Br
Ph
Et
4ah
abundance
0.3
0.2
0.1
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
144.454
141.119
136.327
130.503
129.677
129.463
128.646
128.345
127.169
126.858
125.497
122.220
77.413
77.160
76.907
52.486
21.134
14.066
X : parts per Million : Carbon13


OH
Br
Ph
Et
4ai
1.97
2.07
1.03
2.12
2.14
1.04
1.00
1.05
1.05
0.95
2.05
3.00
abundance
X : parts per Million : Proton


OH
Br
Ph
Et
4ai
abundance
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
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
141.108
136.303
131.059
128.637
128.466
128.351
127.484
126.797
121.248
77.475
77.160
76.845
52.599
21.135
14.098
X : parts per Million : Carbon13


MeO
OH
MeO
Ph
Et
4aj
4.13
2.03
1.00
1.01
1.01
1.05
1.01
0.98
3.05
2.99
0.89
1.94
2.72
0.12
abundance
X : parts per Million : Proton


MeO
OH
MeO
Ph
Et
4aj
abundance
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
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
160.006
157.546
142.796
134.568
128.590
128.332
128.237
128.208
126.225
123.088
104.000
98.413
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76.836
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55.412
55.354
49.958
21.030
14.060
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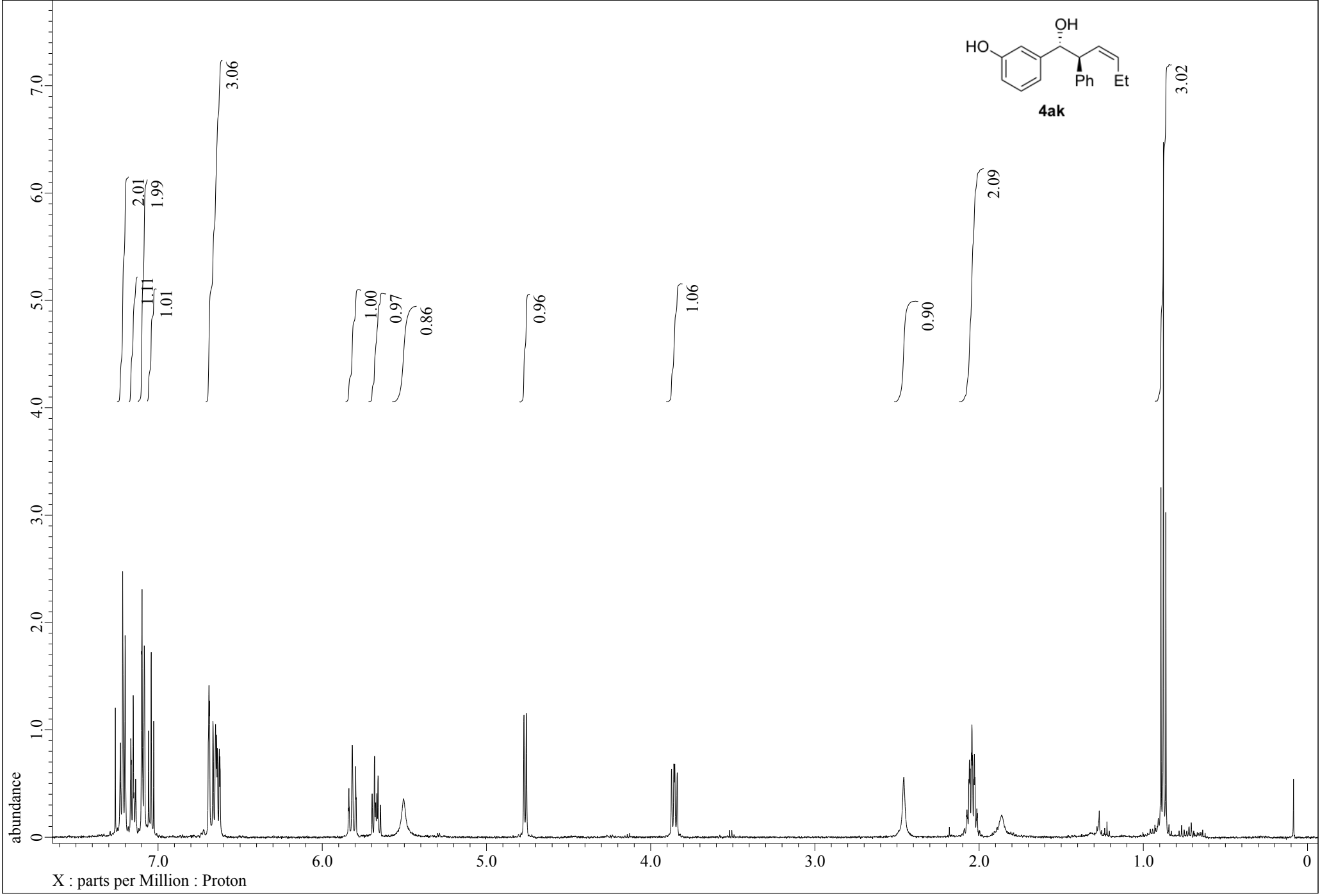
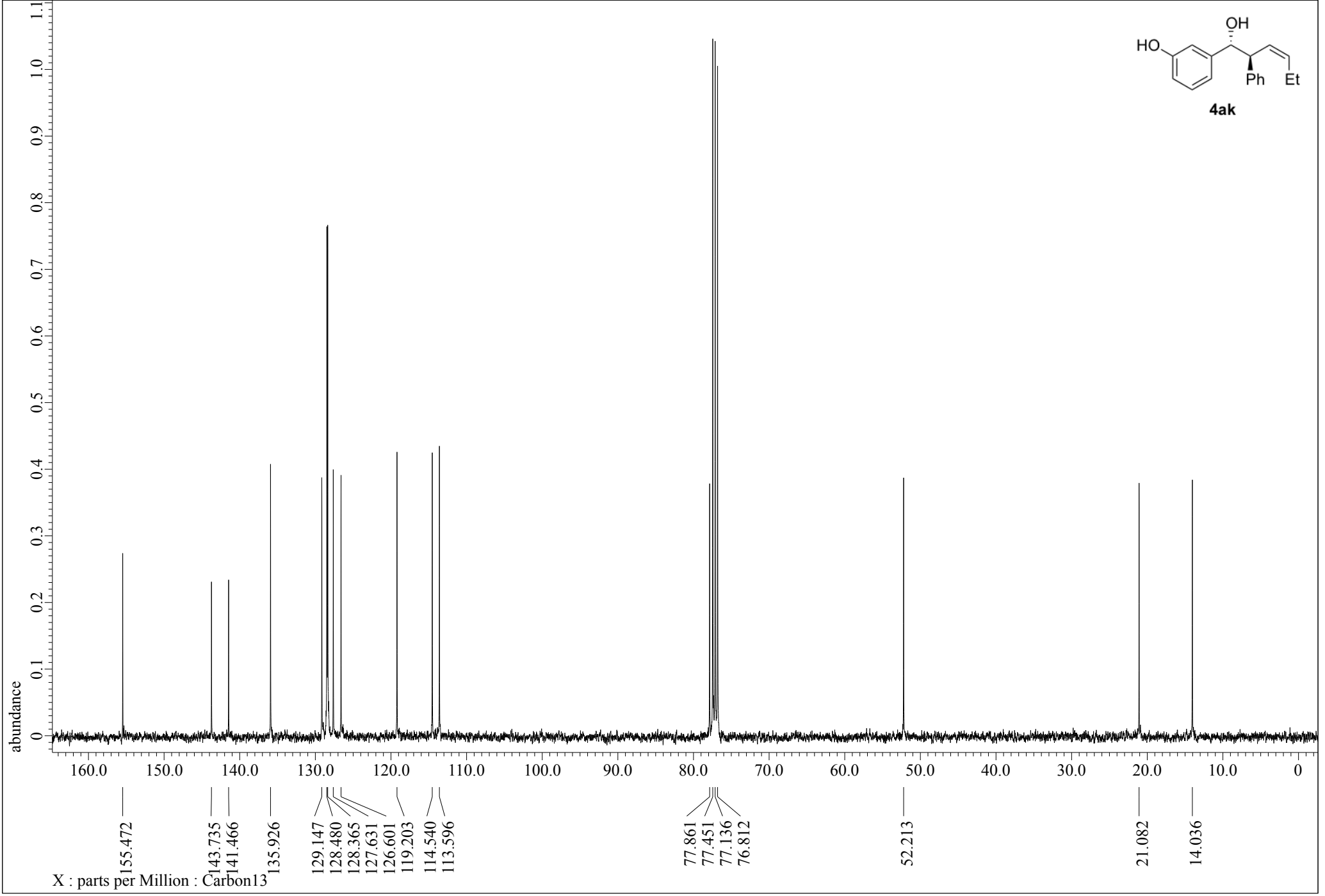
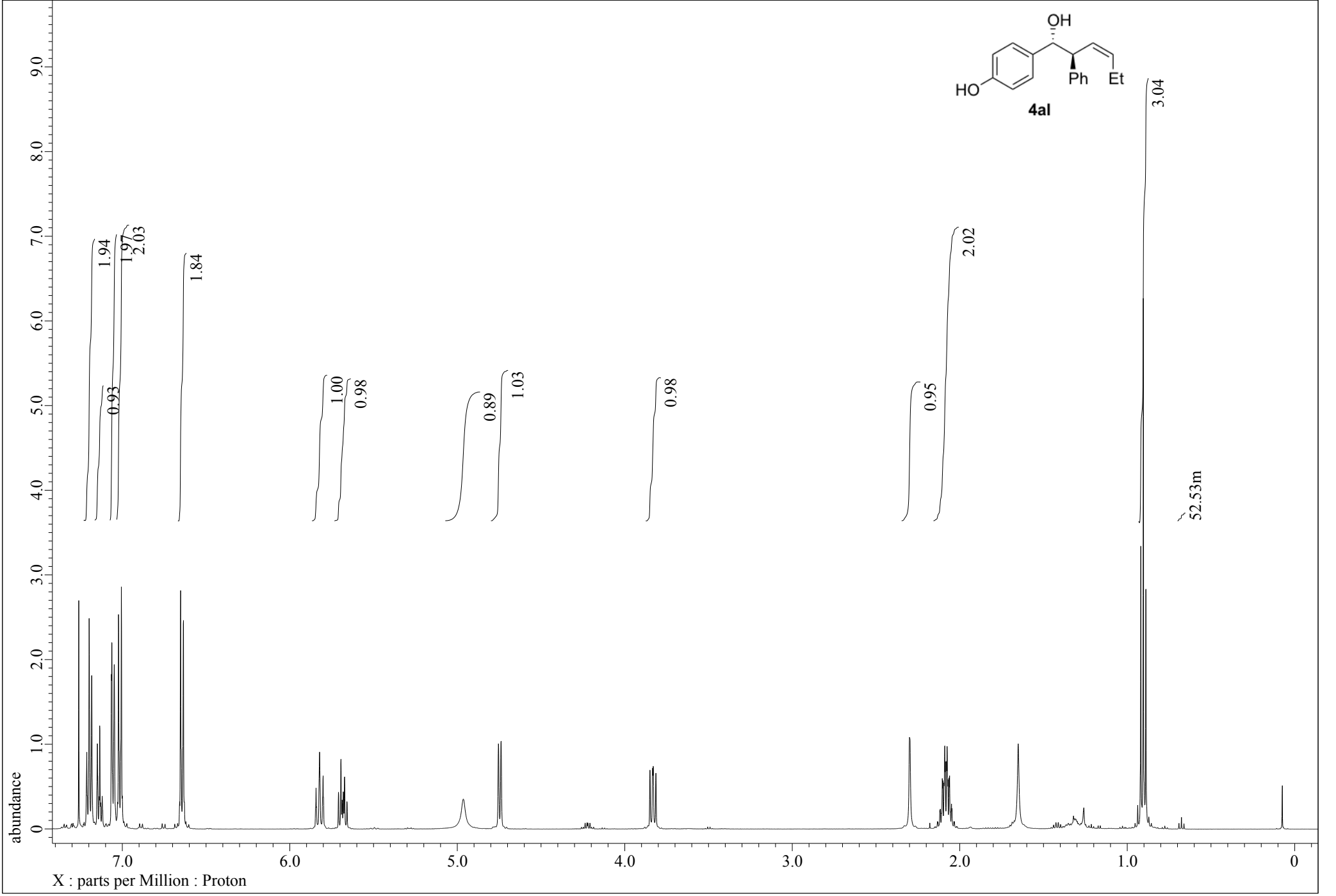
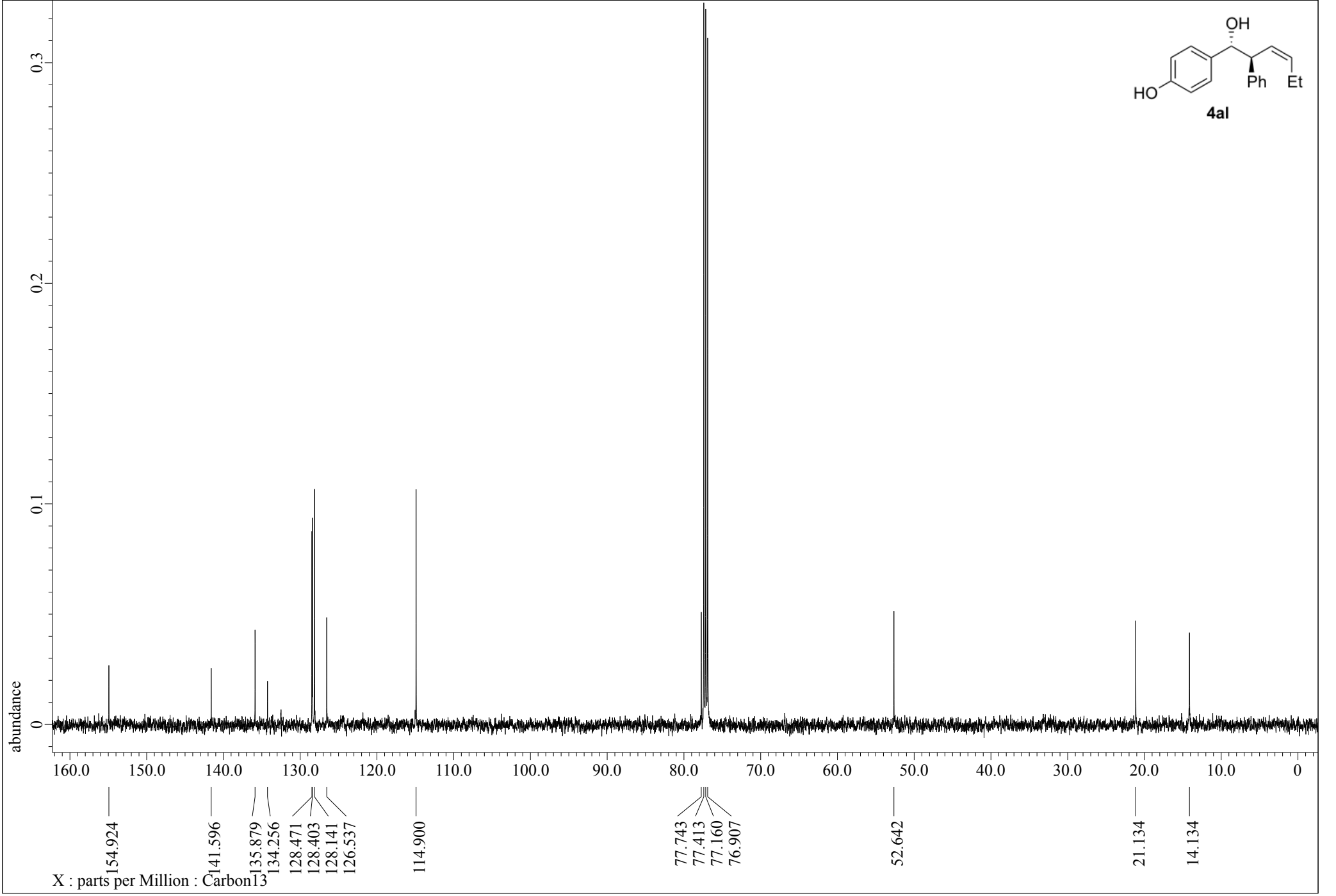
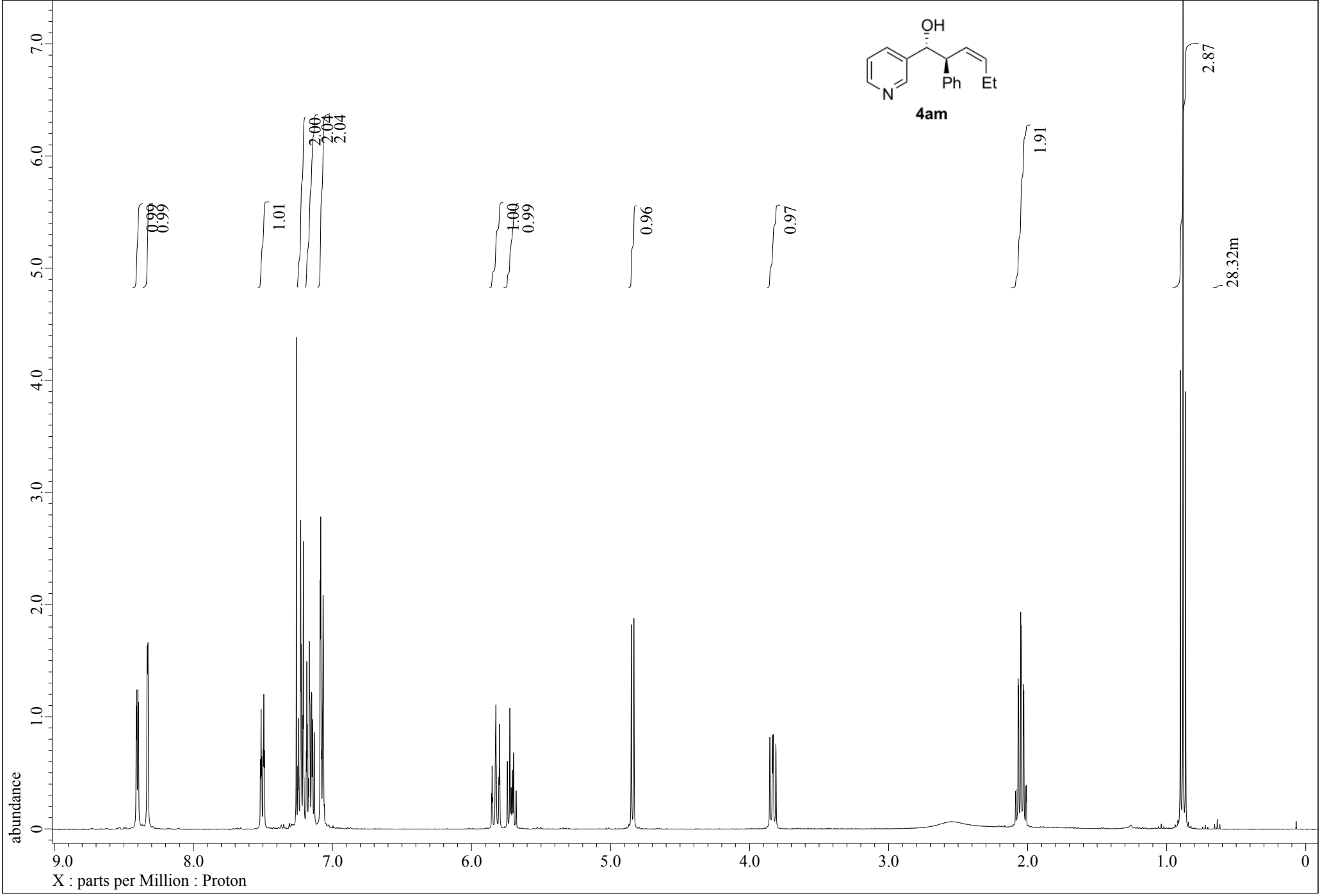
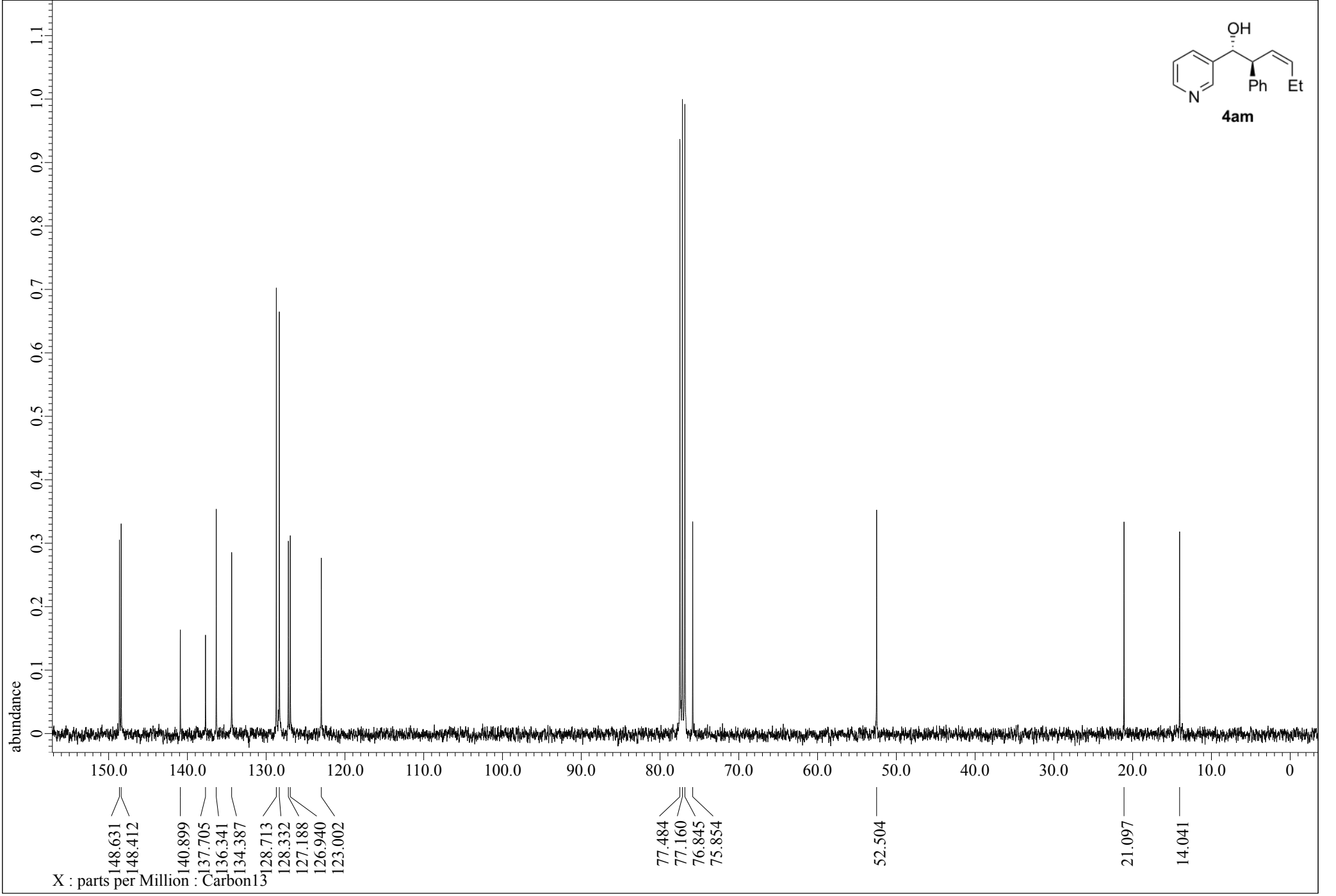

OH
HO
Ph
Et
4ak
3.06
2.01
1.99
1.11
1.01
1.00
0.97
0.86
0.96
1.06
0.90
2.09
3.02
abundance
X : parts per Million : Proton

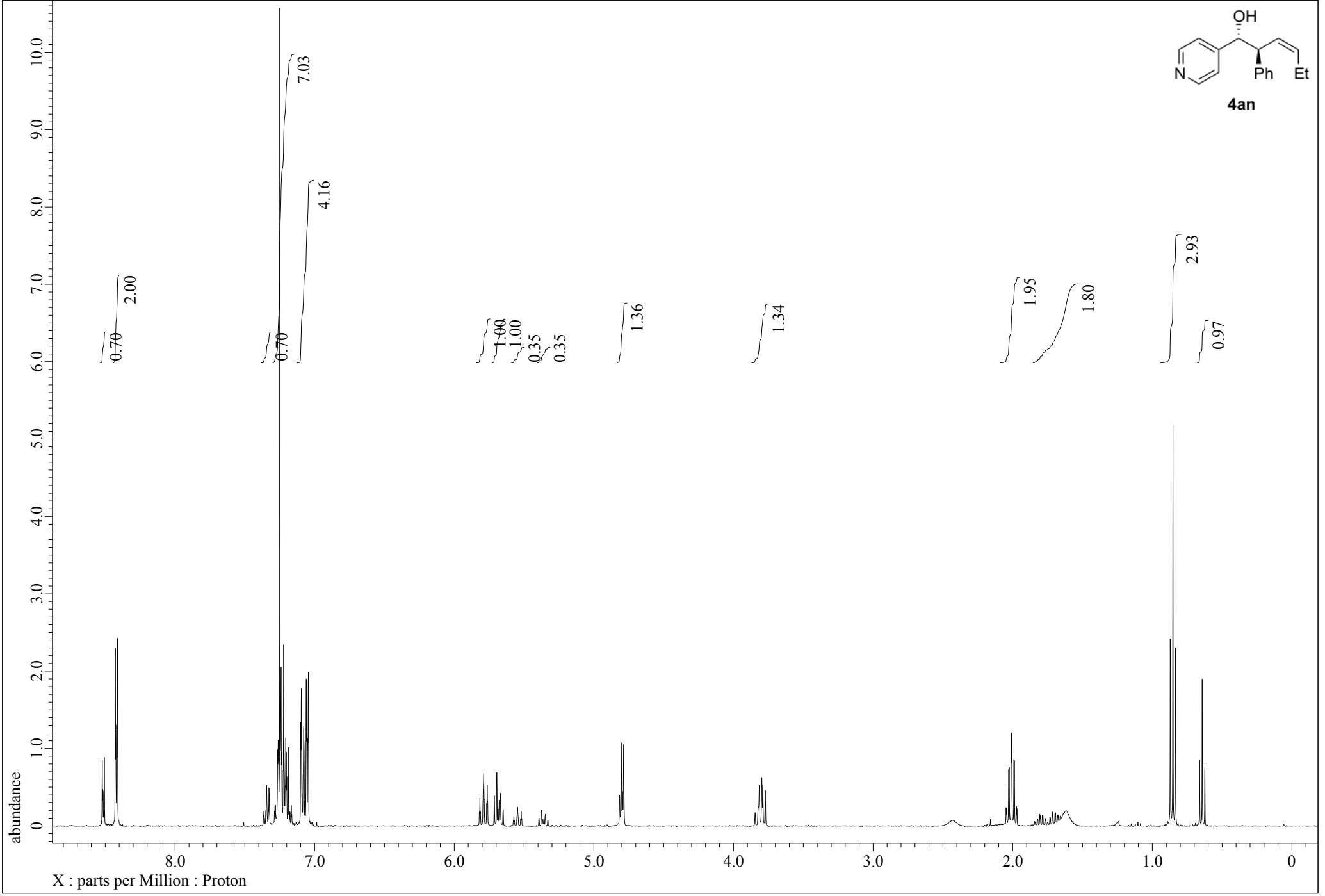

OH
HO
Ph
Et
4ak
abundance
155.472
143.735
141.466
135.926
129.147
128.480
128.365
127.631
126.601
119.203
114.540
113.596
77.861
77.451
77.136
76.812
52.213
21.082
14.036
X : parts per Million : Carbon13

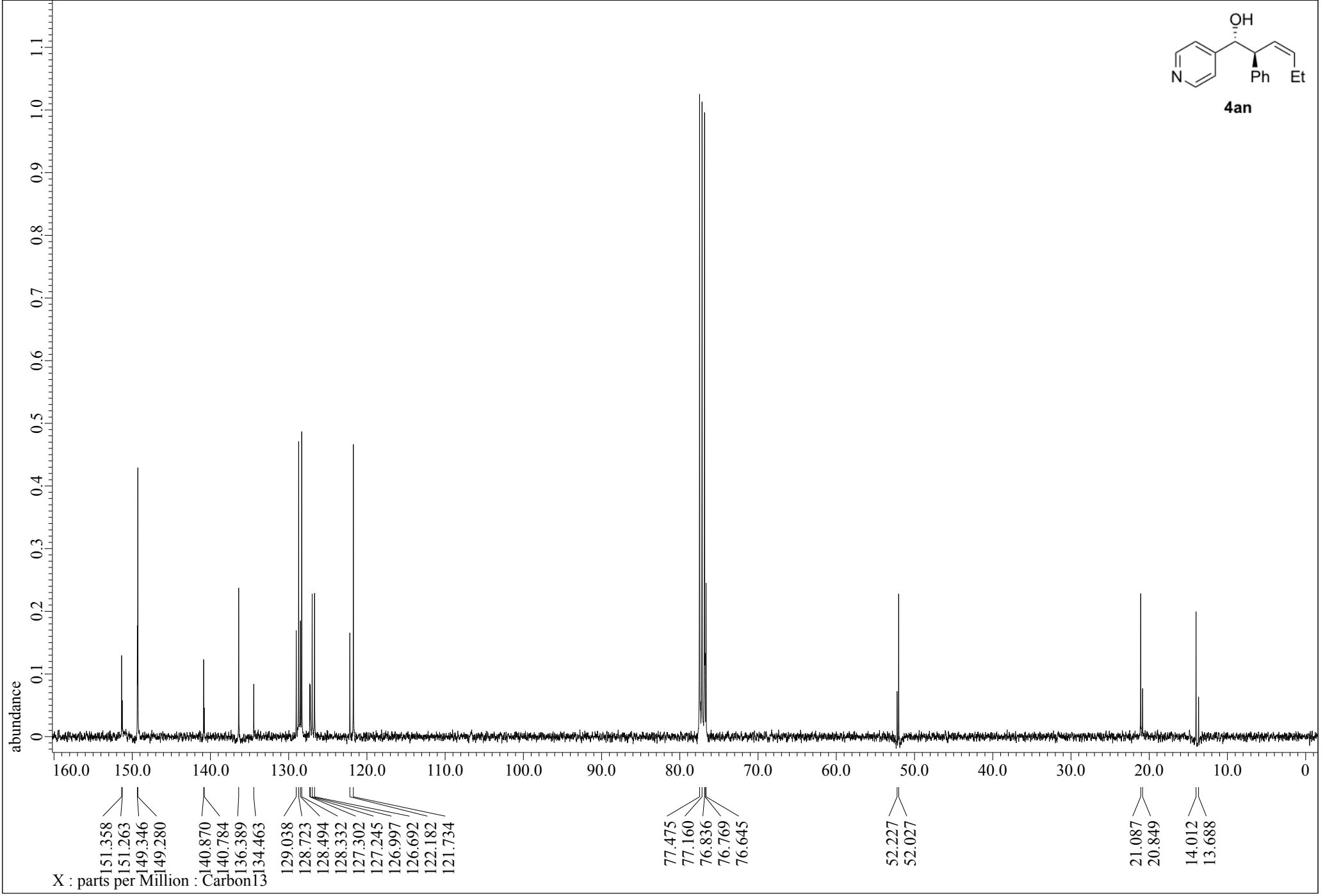

OH
HO
Ph
Et
4al
1.94
0.93
1.97
2.03
1.84
1.00
0.98
0.89
1.03
0.98
0.95
2.02
3.04
52.53m
abundance
X : parts per Million : Proton

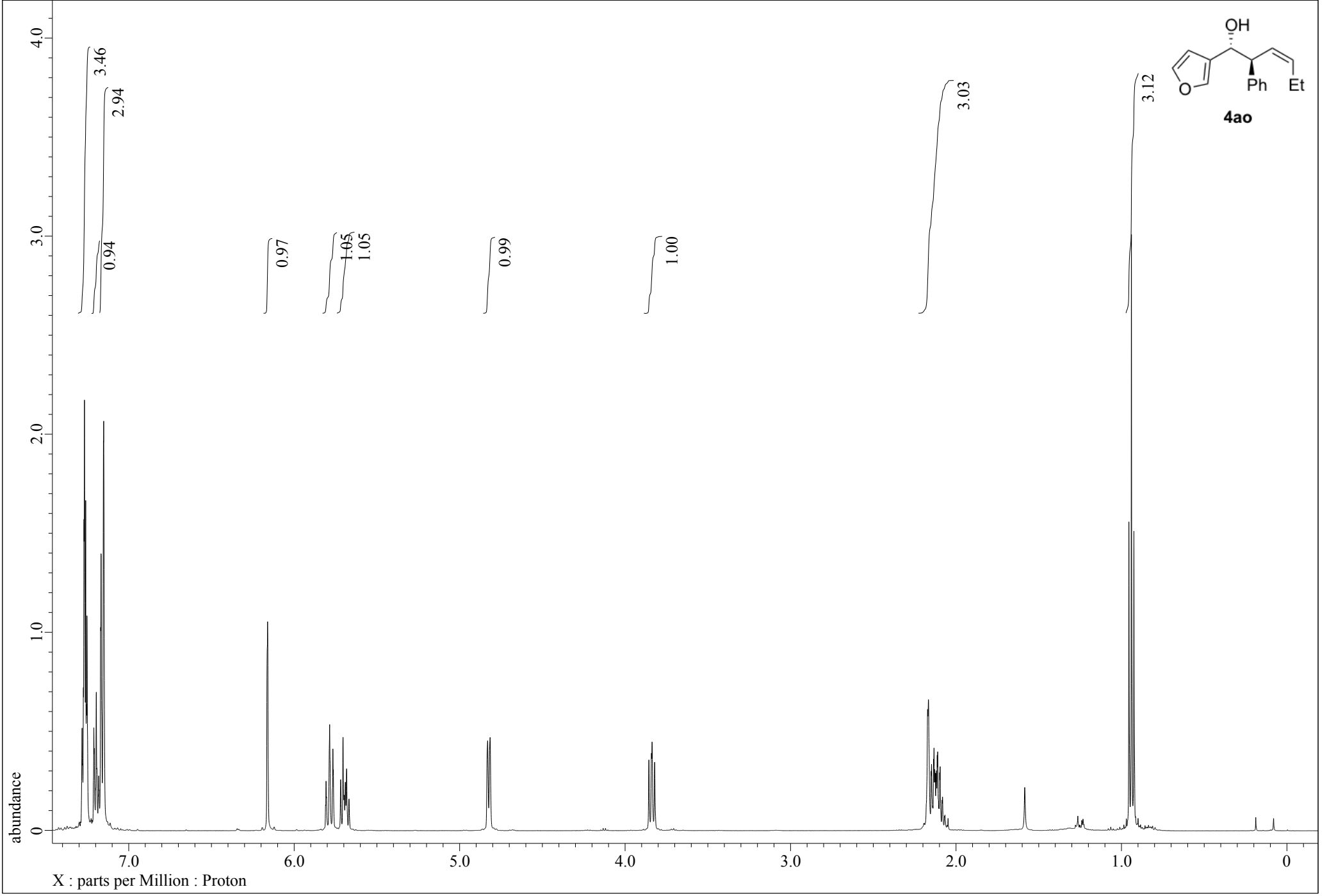

OH
HO
Ph
Et
4al
abundance
0.3
0.2
0.1
0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
154.924
141.596
135.879
134.256
128.471
128.403
128.141
126.537
114.900
77.743
77.413
77.160
76.907
52.642
21.134
14.134
X : parts per Million : Carbon13

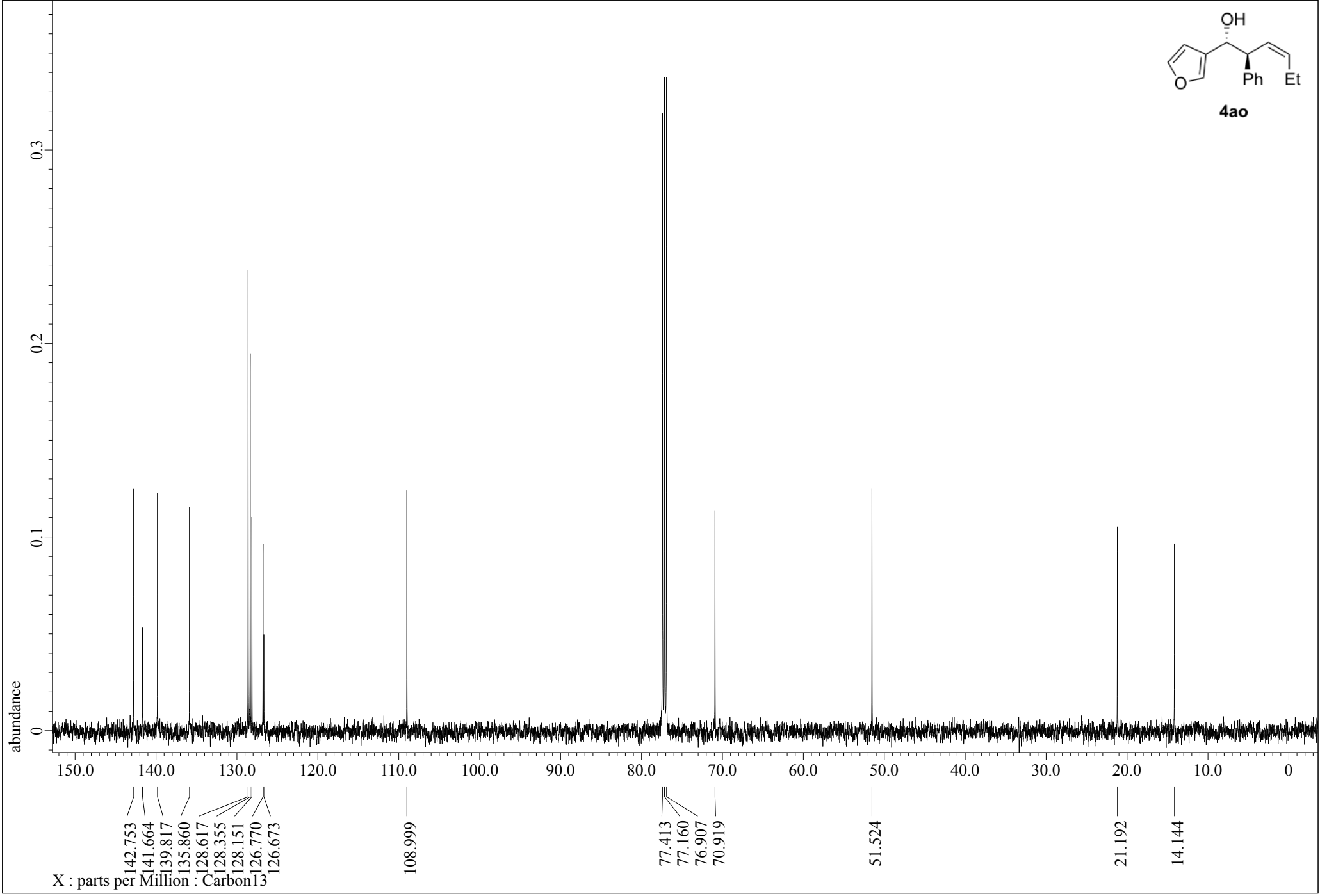

OH
N
Ph
Et
4am
2.87
1.91
0.99
0.99
1.01
2.00
2.04
2.04
1.00
0.99
0.96
0.97
28.32m
abundance
X : parts per Million : Proton

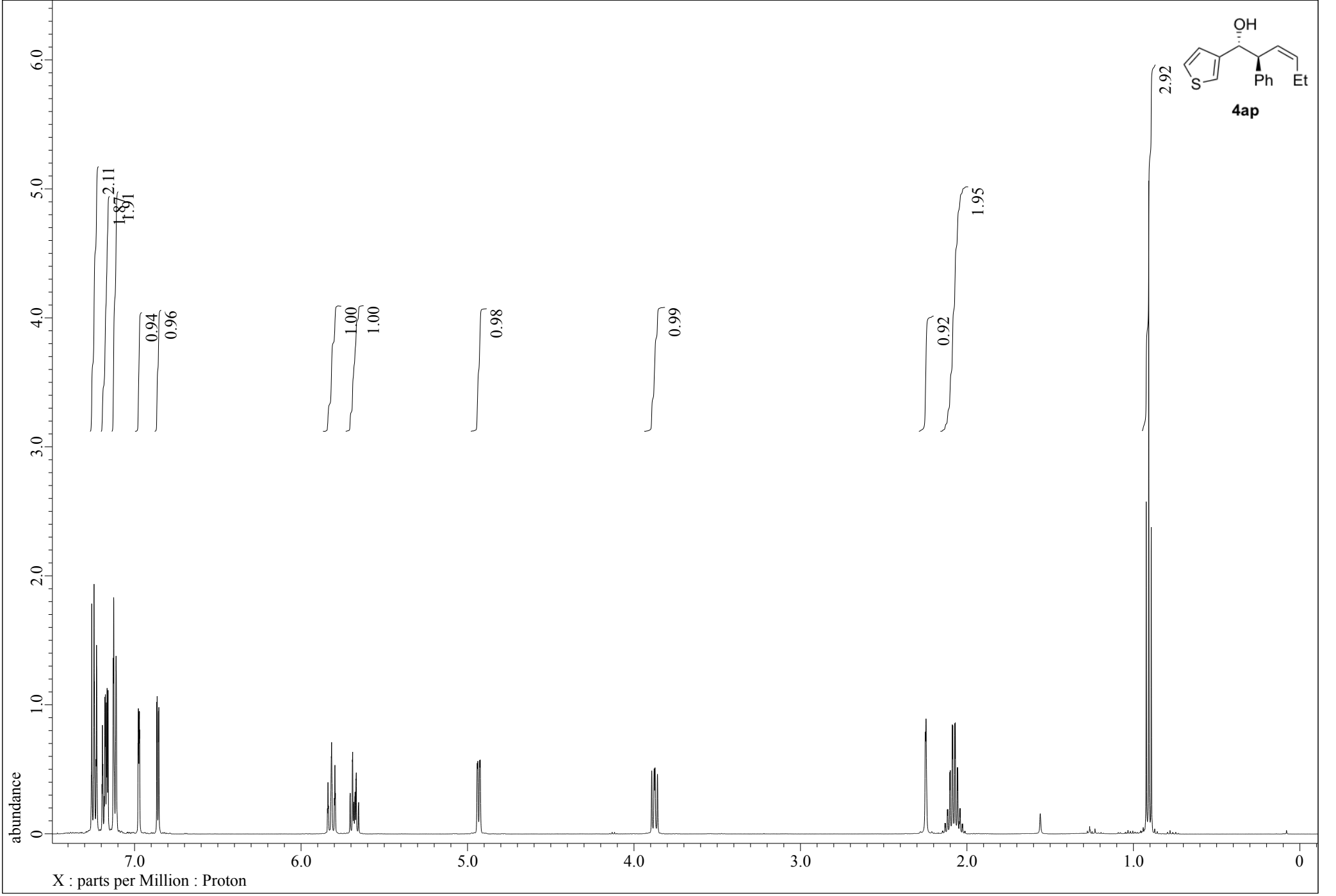

OH
N
Ph
Et
4am
abundance
148.631
148.412
140.899
137.705
136.341
134.387
128.713
128.332
127.188
126.940
123.002
77.484
77.160
76.845
75.854
52.504
21.097
14.041
X : parts per Million : Carbon13

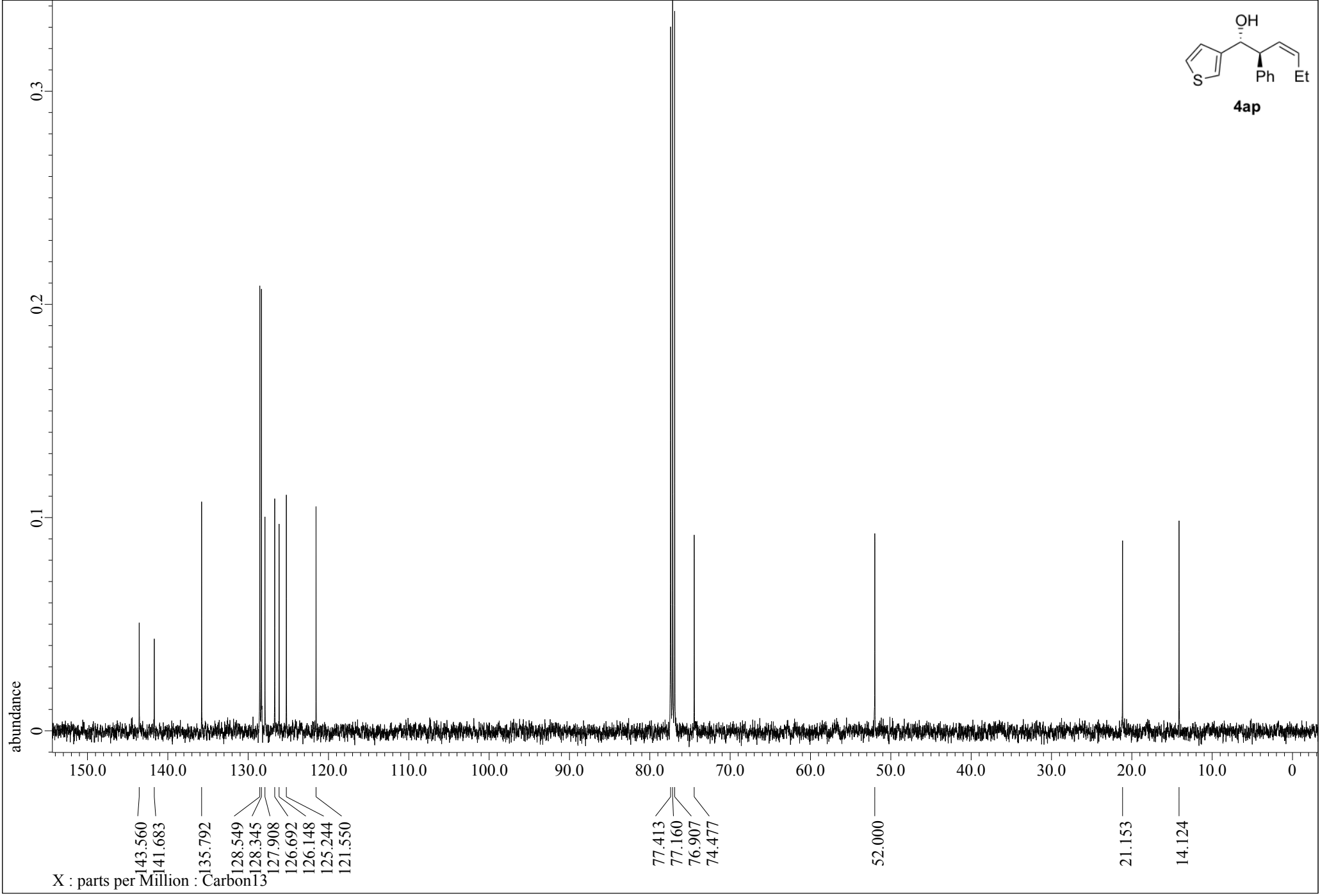

OH
N
Ph
Et
4an
7.03
4.16
2.00
0.70
0.70
1.00
1.00
0.35
0.35
1.36
1.34
1.95
1.80
2.93
0.97
abundance
X : parts per Million : Proton

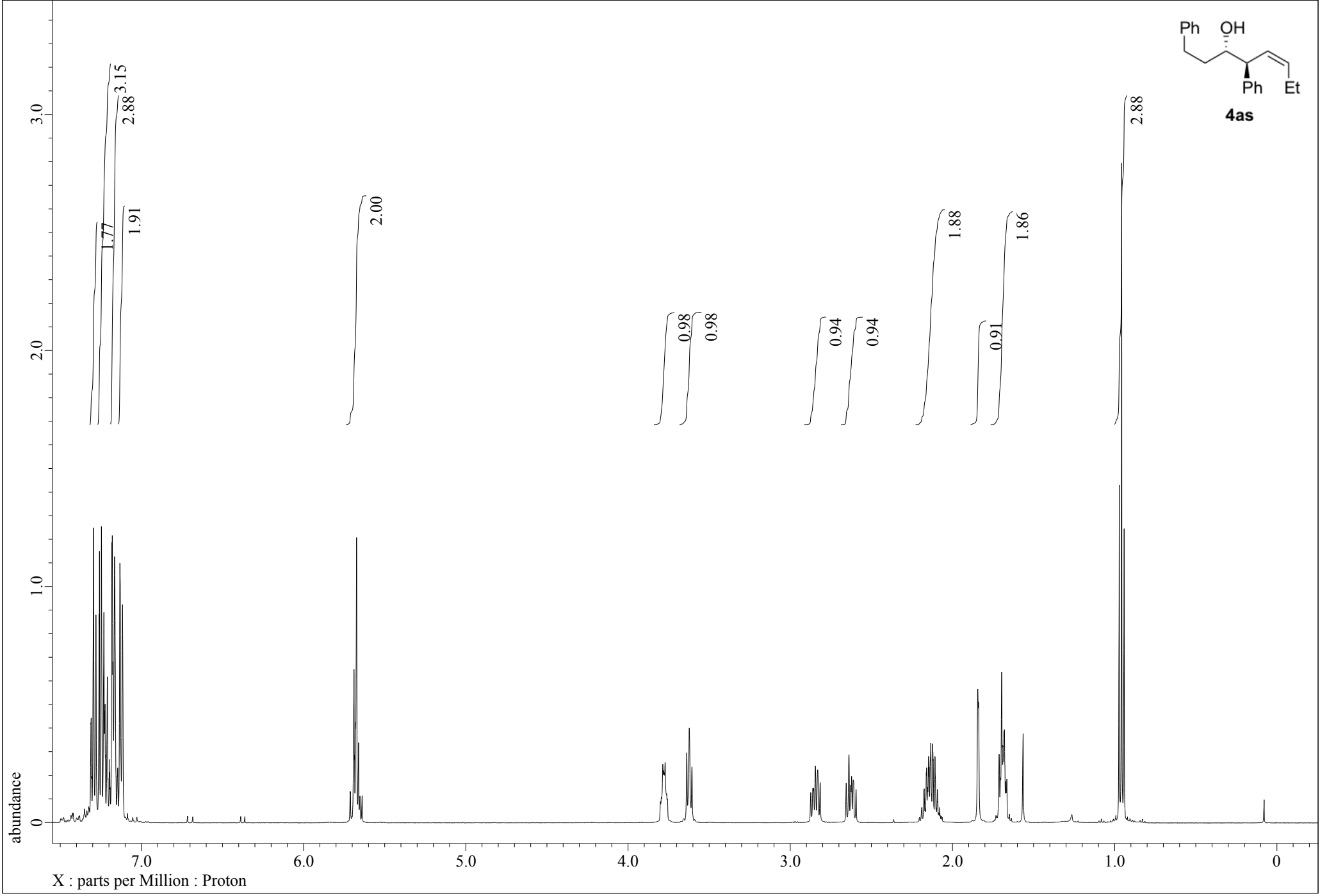

OH
N
Ph
Et
4an
abundance
151.358
151.263
149.346
149.280
140.870
140.784
136.389
134.463
129.038
128.723
128.494
128.332
127.302
127.245
126.997
126.692
122.182
121.734
77.475
77.160
76.836
76.769
76.645
52.227
52.027
21.087
20.849
14.012
13.688
X : parts per Million : Carbon13

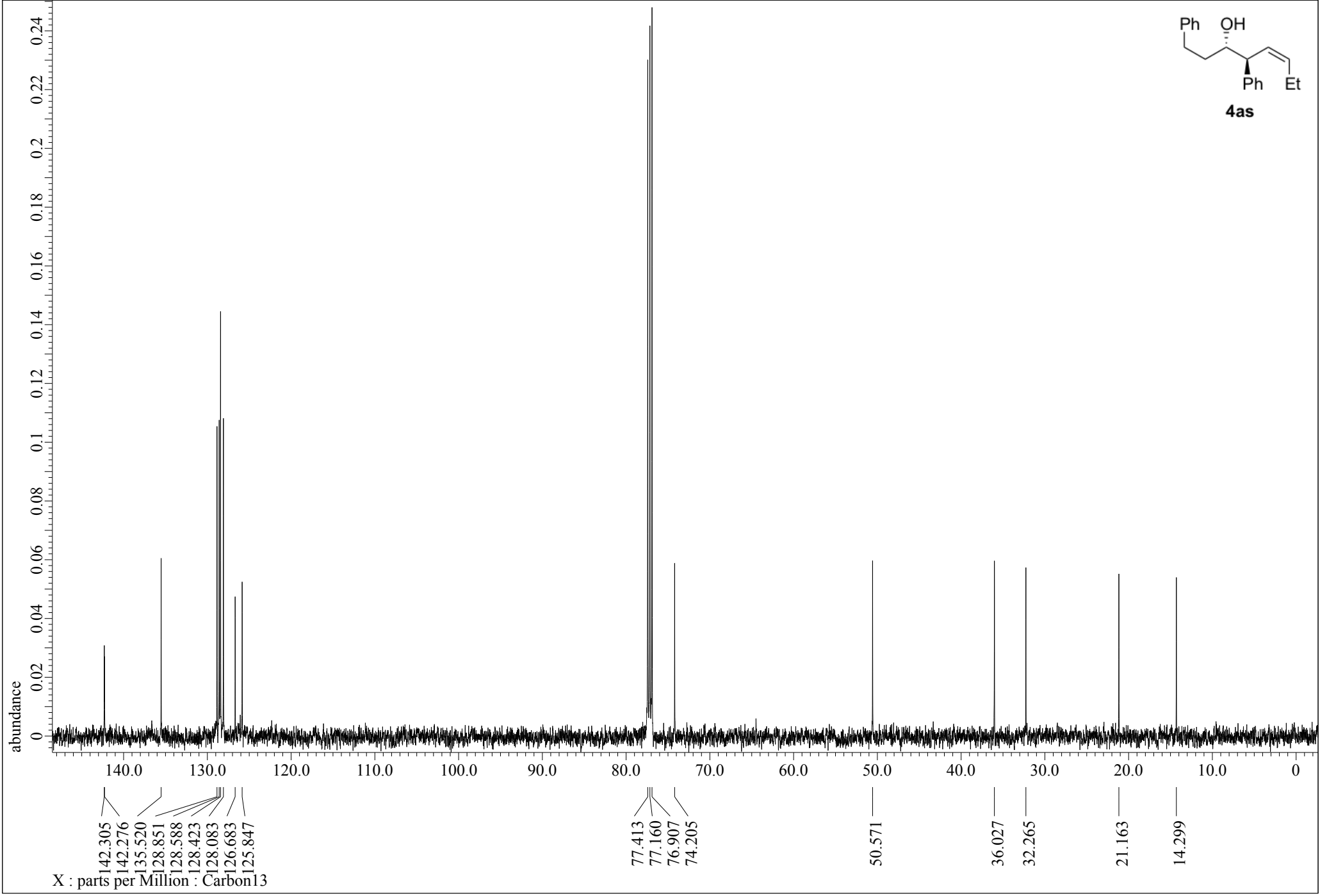

OH
O
Ph
Et
4ao
3.46
2.94
0.94
0.97
1.05
1.05
0.99
1.00
3.03
3.12
4.0
3.0
2.0
1.0
0
abundance
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : Proton

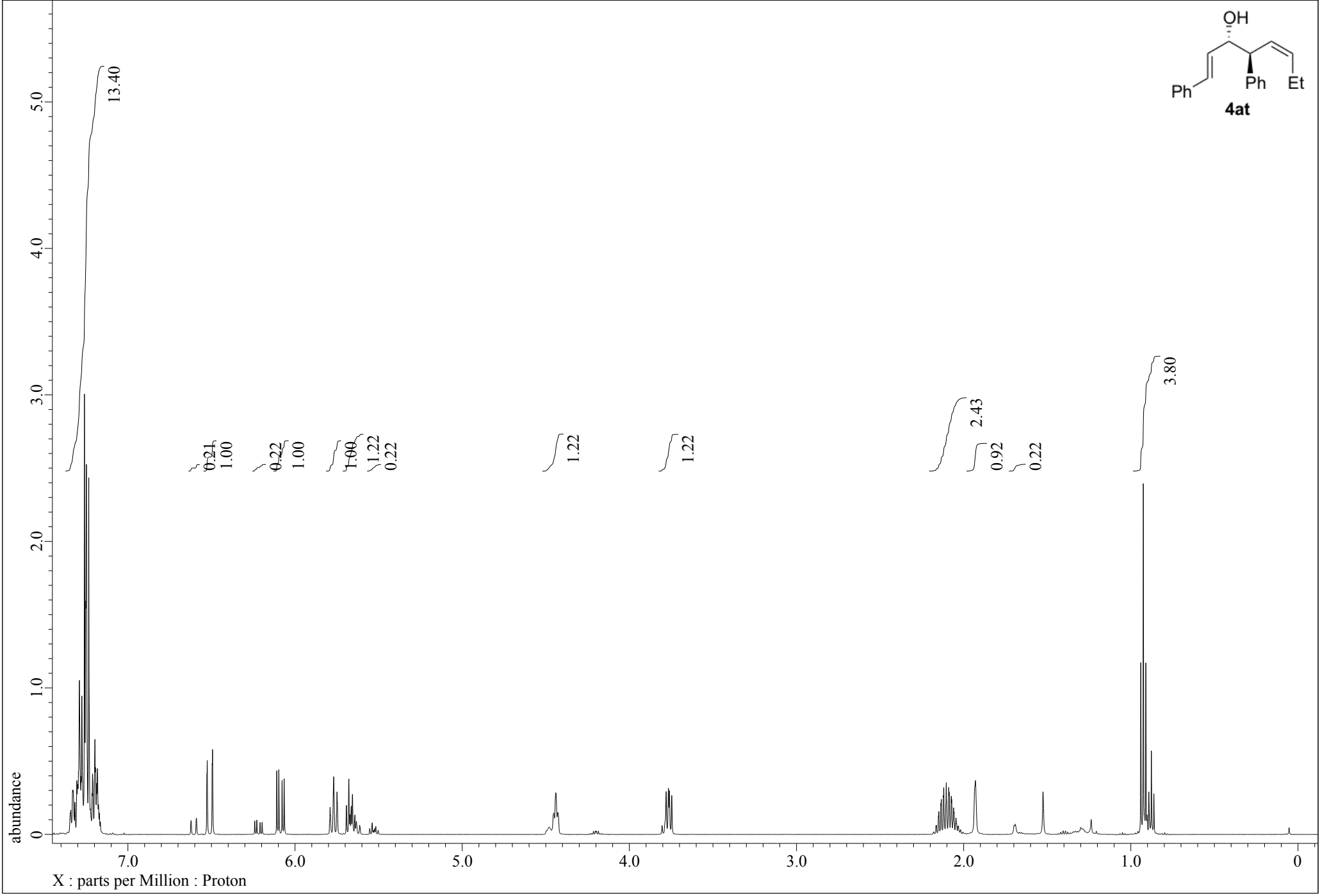

OH
Ph
Et
O
4ao
abundance
0.3
0.2
0.1
0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
142.753
141.664
139.817
135.860
128.617
128.355
128.151
126.770
126.673
108.999
77.413
77.160
76.907
70.919
51.524
21.192
14.144
X : parts per Million : Carbon13

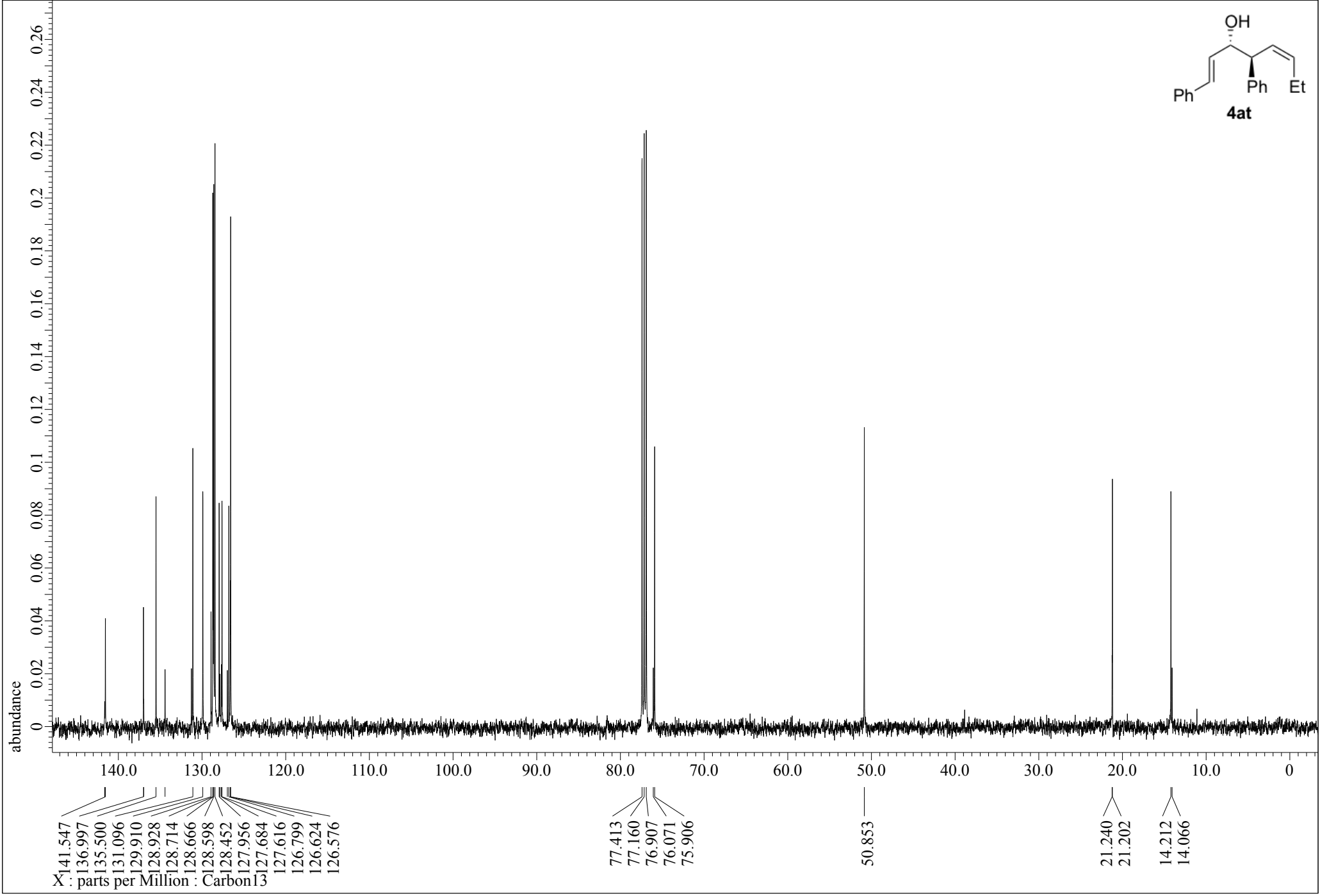

OH
S
Ph
Et
4ap
2.92
2.11
1.87
1.91
0.94
0.96
1.00
1.00
0.98
0.99
0.92
1.95
abundance
X : parts per Million : Proton

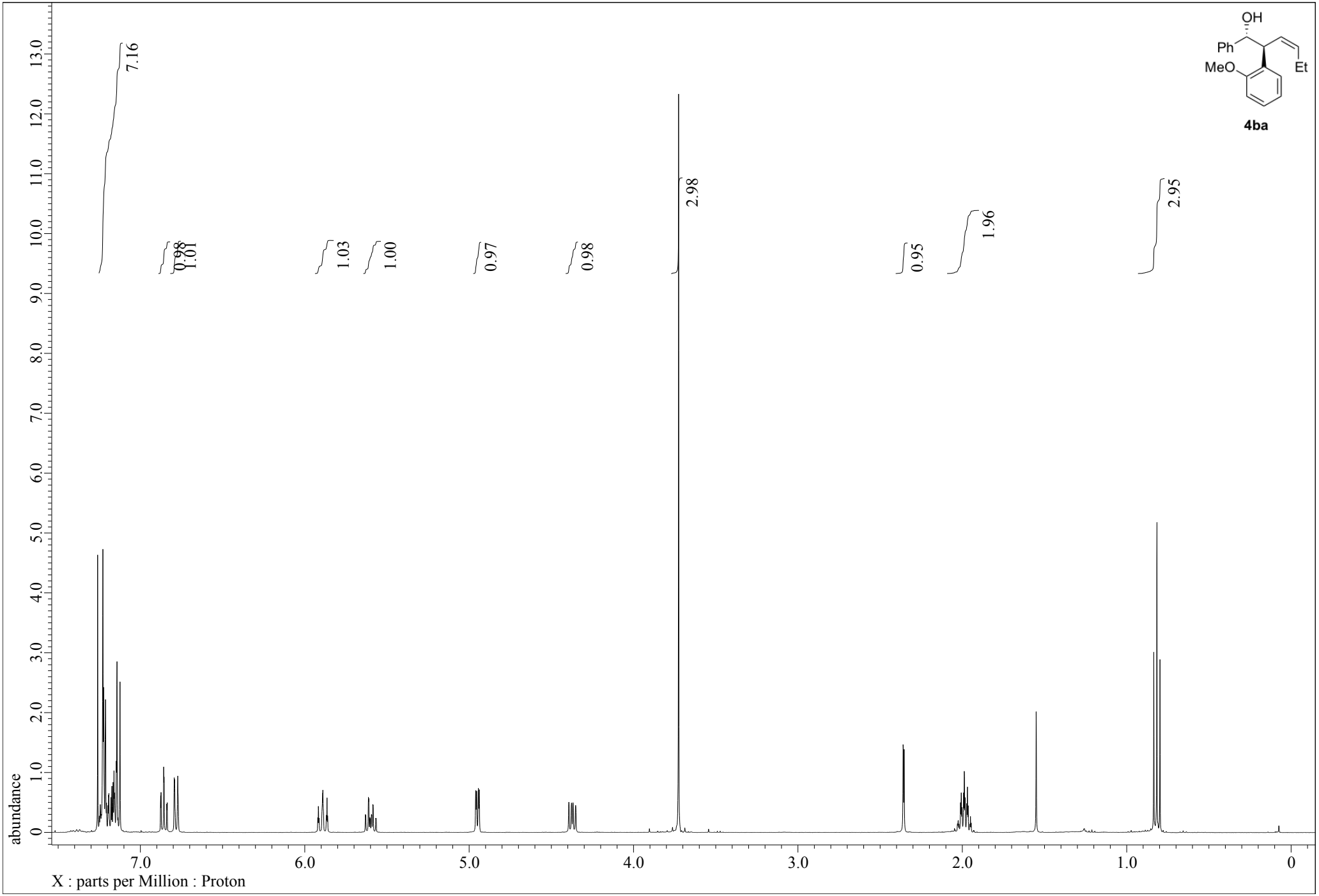

OH
S
Ph
Et
4ap
abundance
0.3
0.2
0.1
0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
143.560
141.683
135.792
128.549
128.345
127.908
126.692
126.148
125.244
121.550
77.413
77.160
76.907
74.477
52.000
21.153
14.124
X : parts per Million : Carbon13

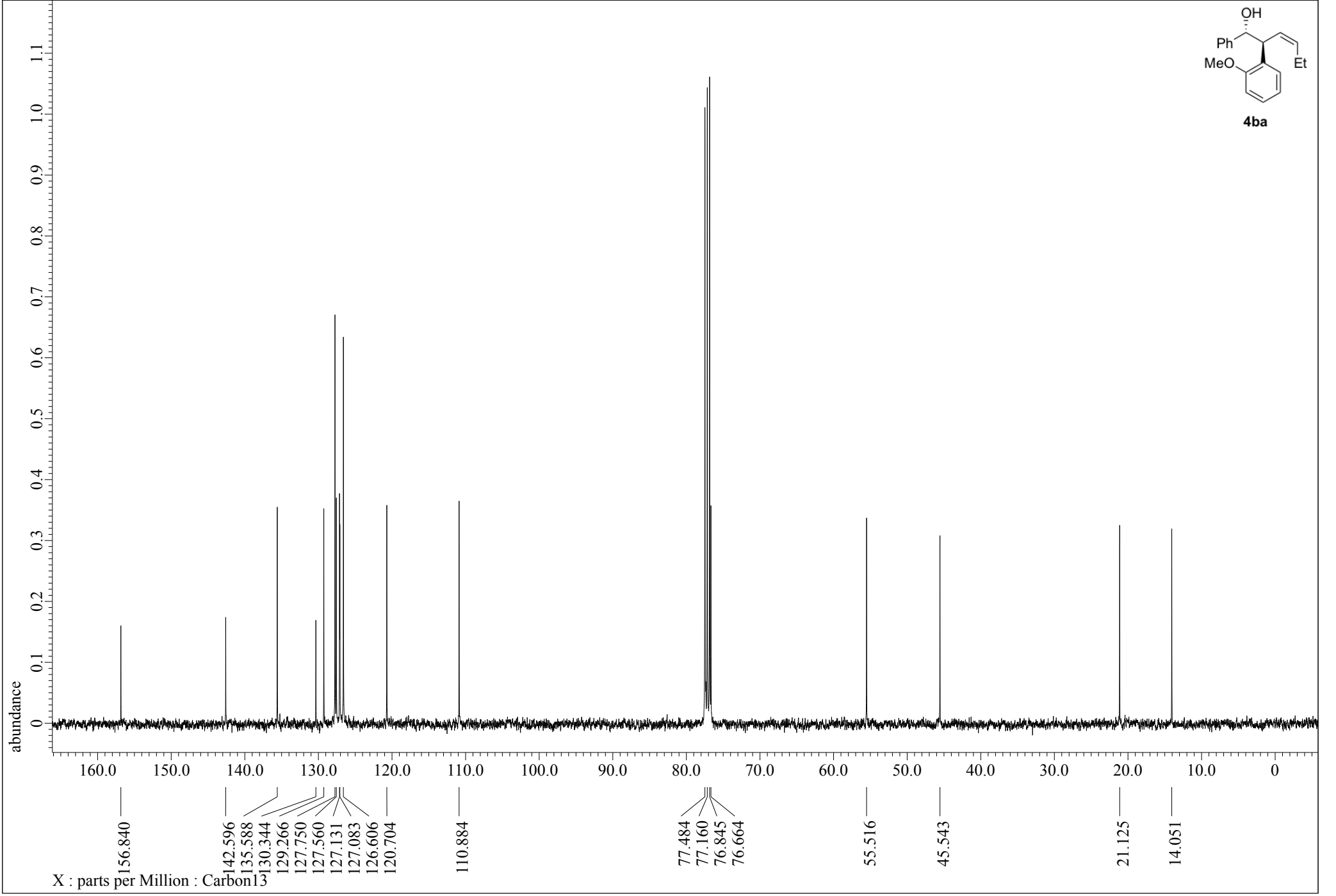

Ph
OH
Ph
Et
4as
3.15
2.88
1.77
1.91
2.00
0.98
0.98
0.94
0.94
1.88
0.91
1.86
2.88
3.0
2.0
1.0
0
abundance
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : Proton

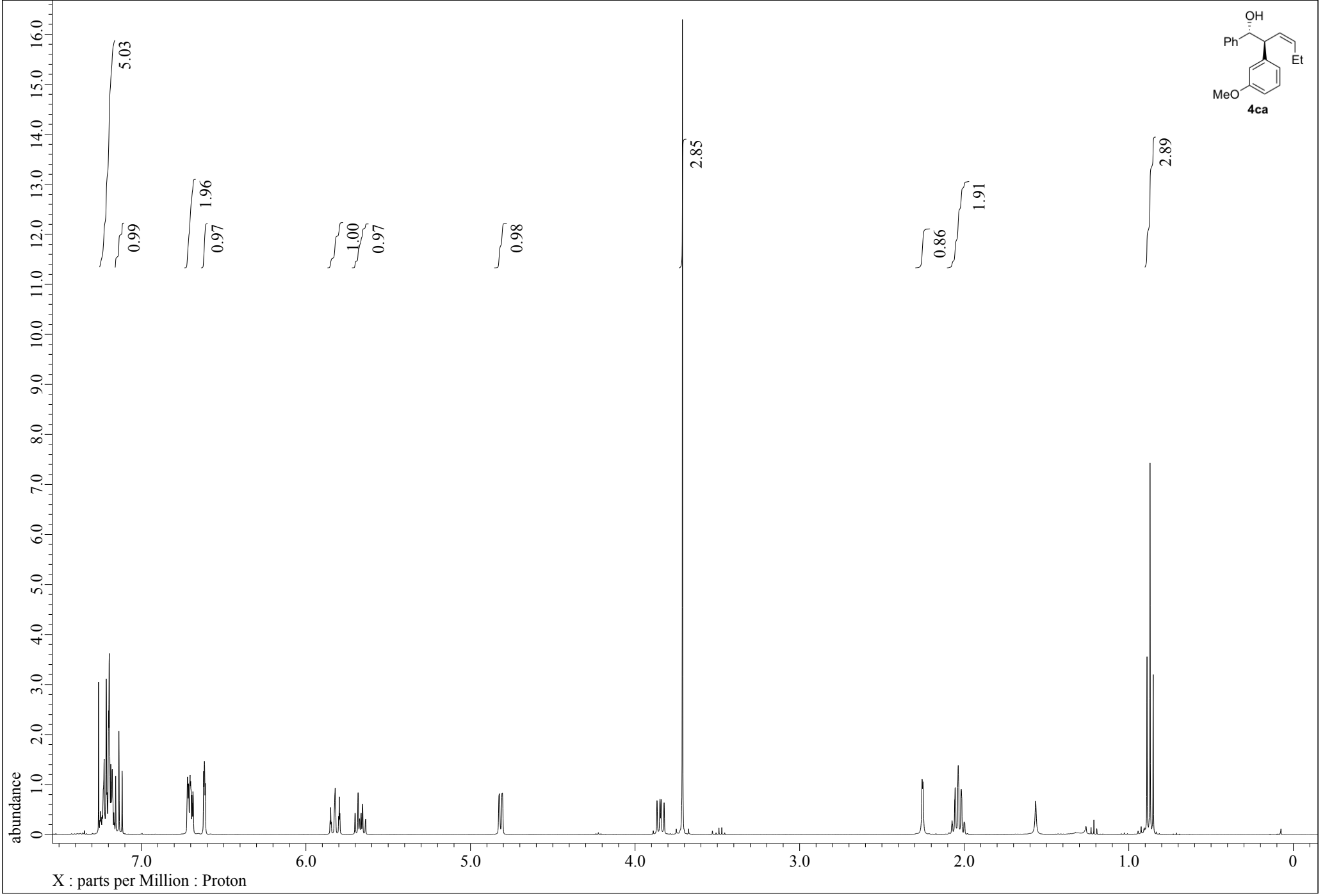

Ph
OH
Ph
Et
4as
abundance
0
0.02
0.04
0.06
0.08
0.1
0.12
0.14
0.16
0.18
0.2
0.22
0.24
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
142.305
142.276
135.520
128.851
128.588
128.423
128.083
126.683
125.847
77.413
77.160
76.907
74.205
50.571
36.027
32.265
21.163
14.299
X : parts per Million : Carbon13

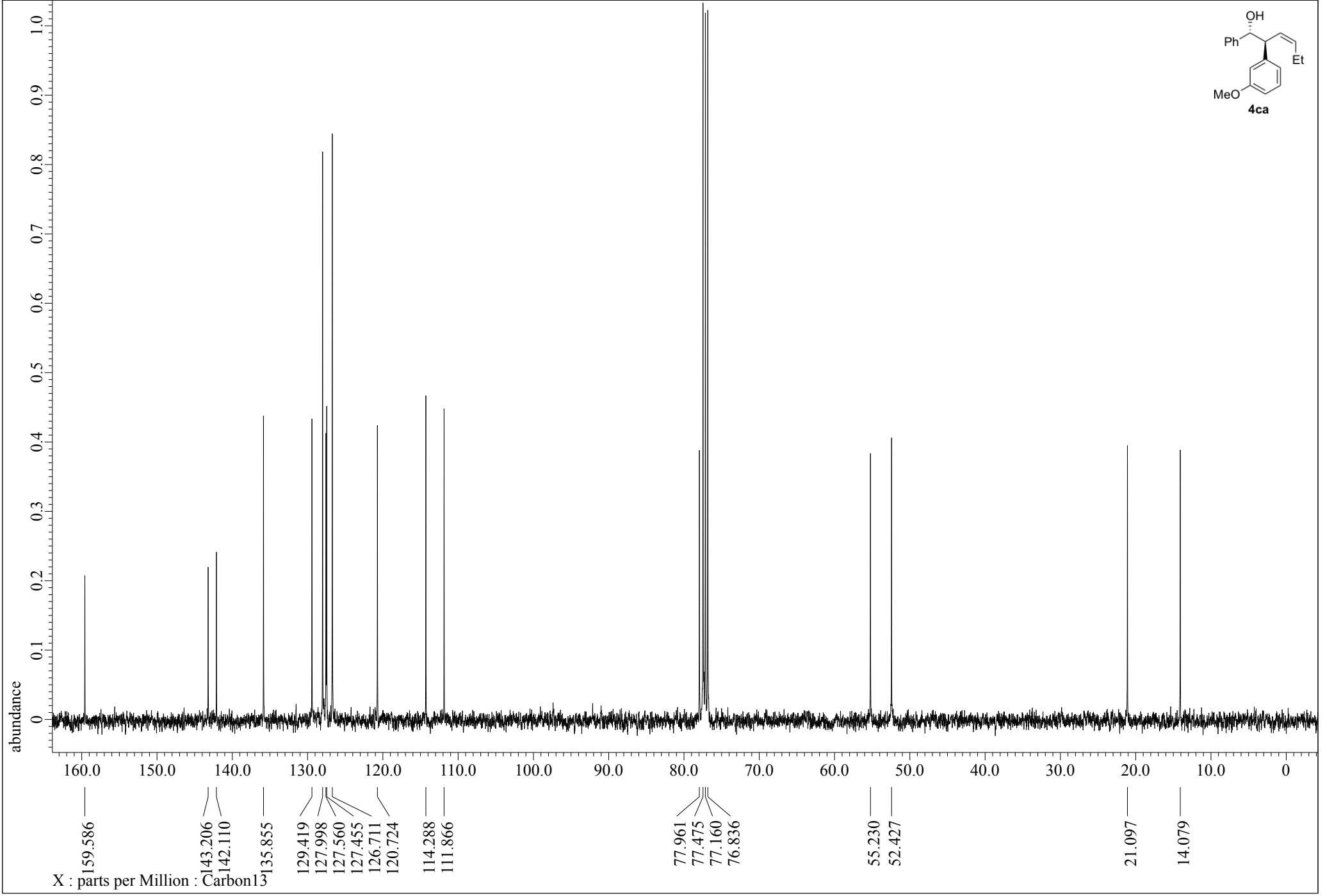

OH
Ph
Ph
Et
4at
13.40
0.21
1.00
0.22
1.00
1.00
1.22
0.22
1.22
1.22
2.43
0.92
0.22
3.80
abundance
X : parts per Million : Proton

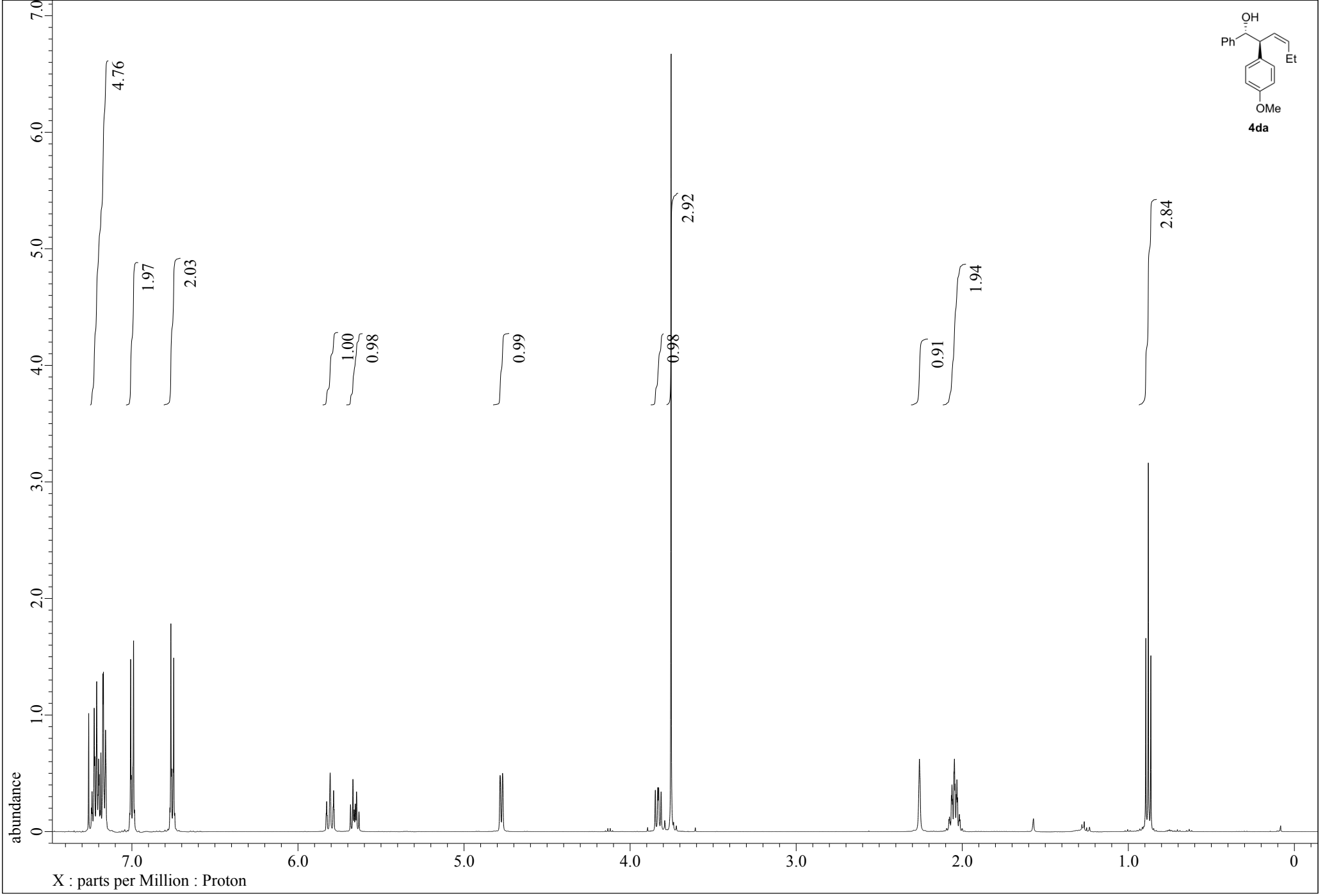

OH
Ph
Ph
Et
4at
abundance
0.26
0.24
0.22
0.2
0.18
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
141.547
136.997
135.500
131.096
129.910
128.928
128.714
128.666
128.598
128.452
127.956
127.684
127.616
126.799
126.624
126.576
77.413
77.160
76.907
76.071
75.906
50.853
21.240
21.202
14.212
14.066
X : parts per Million : Carbon13

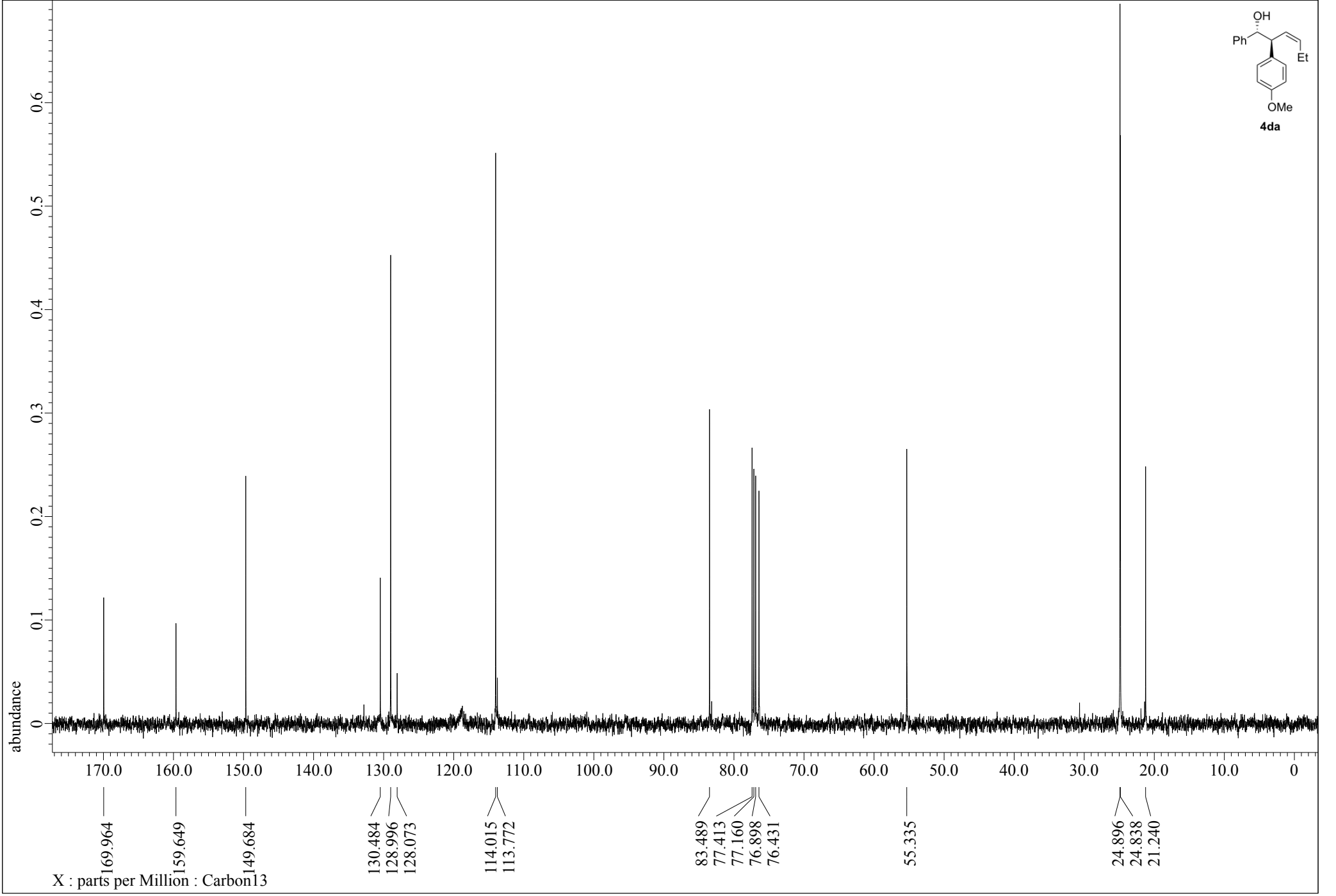

OH
Ph
MeO
Et
4ba
7.16
0.98
1.01
1.03
1.00
0.97
0.98
2.98
0.95
1.96
2.95
abundance
X : parts per Million : Proton

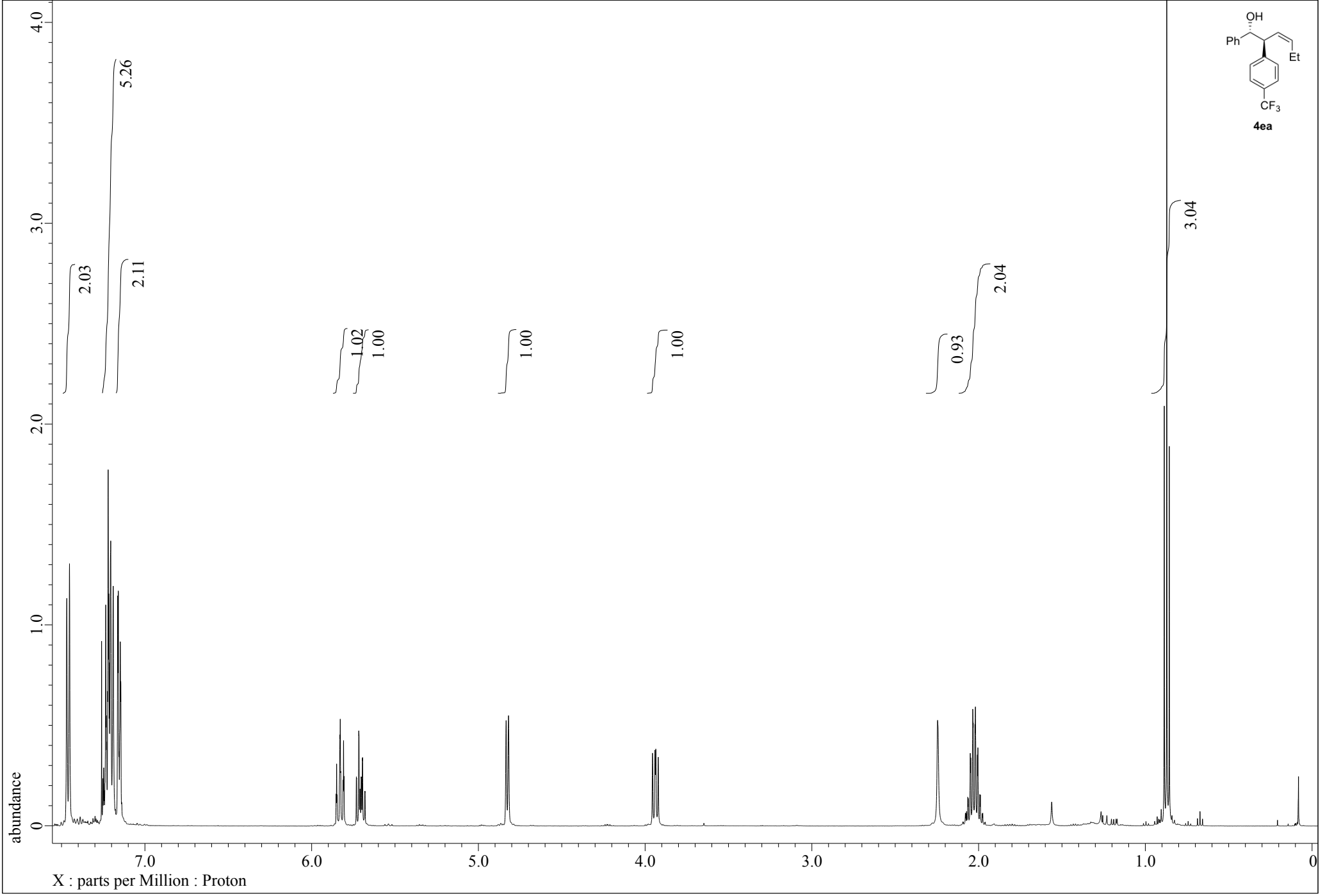

OH
Ph
MeO
Et
4ba
abundance
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
156.840
142.596
135.588
130.344
129.266
127.750
127.560
127.131
127.083
126.606
120.704
110.884
77.484
77.160
76.845
76.664
55.516
45.543
21.125
14.051
X : parts per Million : Carbon13

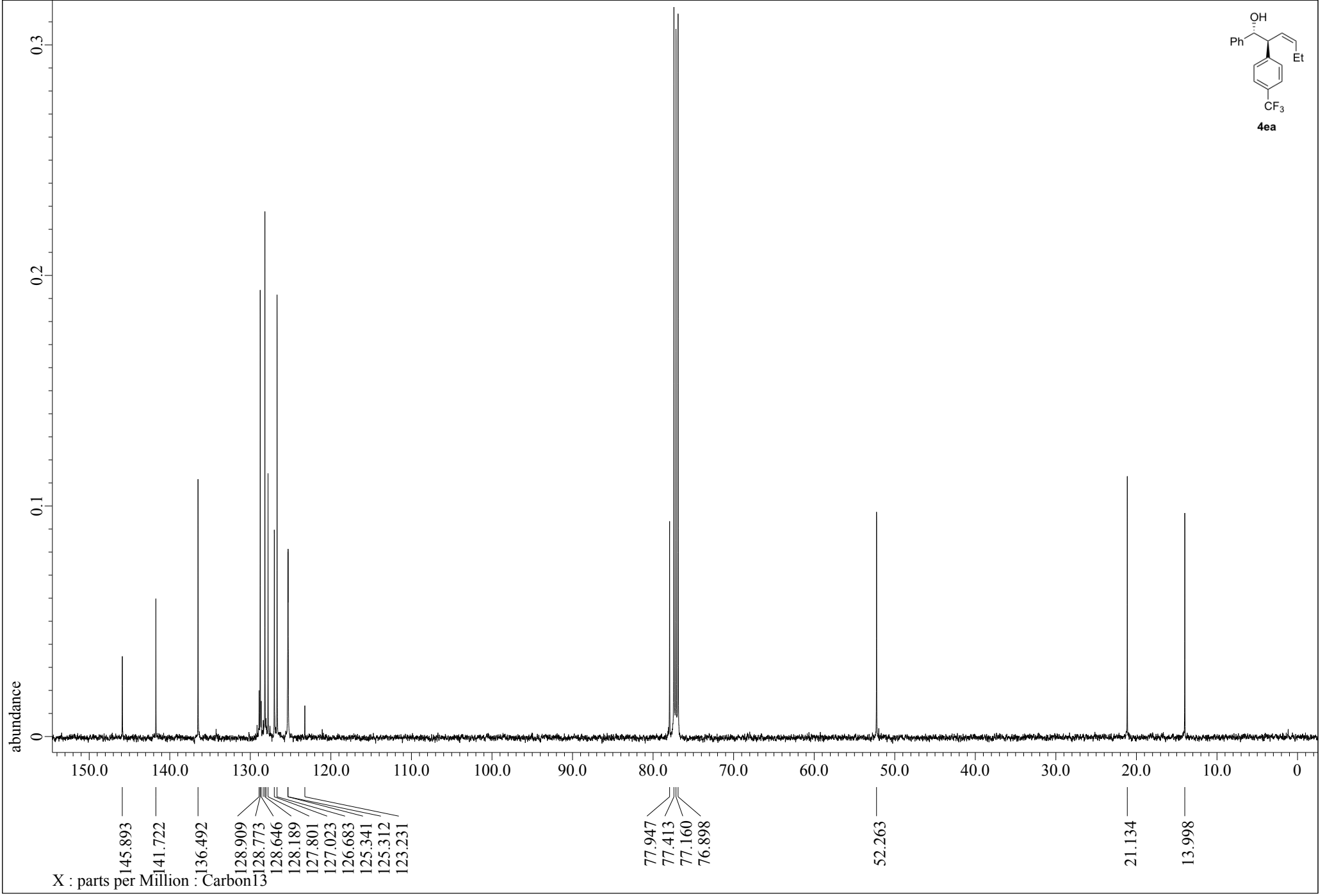

OH
Ph
Et
MeO
4ca
5.03
0.99
1.96
0.97
1.00
0.97
0.98
2.85
0.86
1.91
2.89
abundance
X : parts per Million : Proton

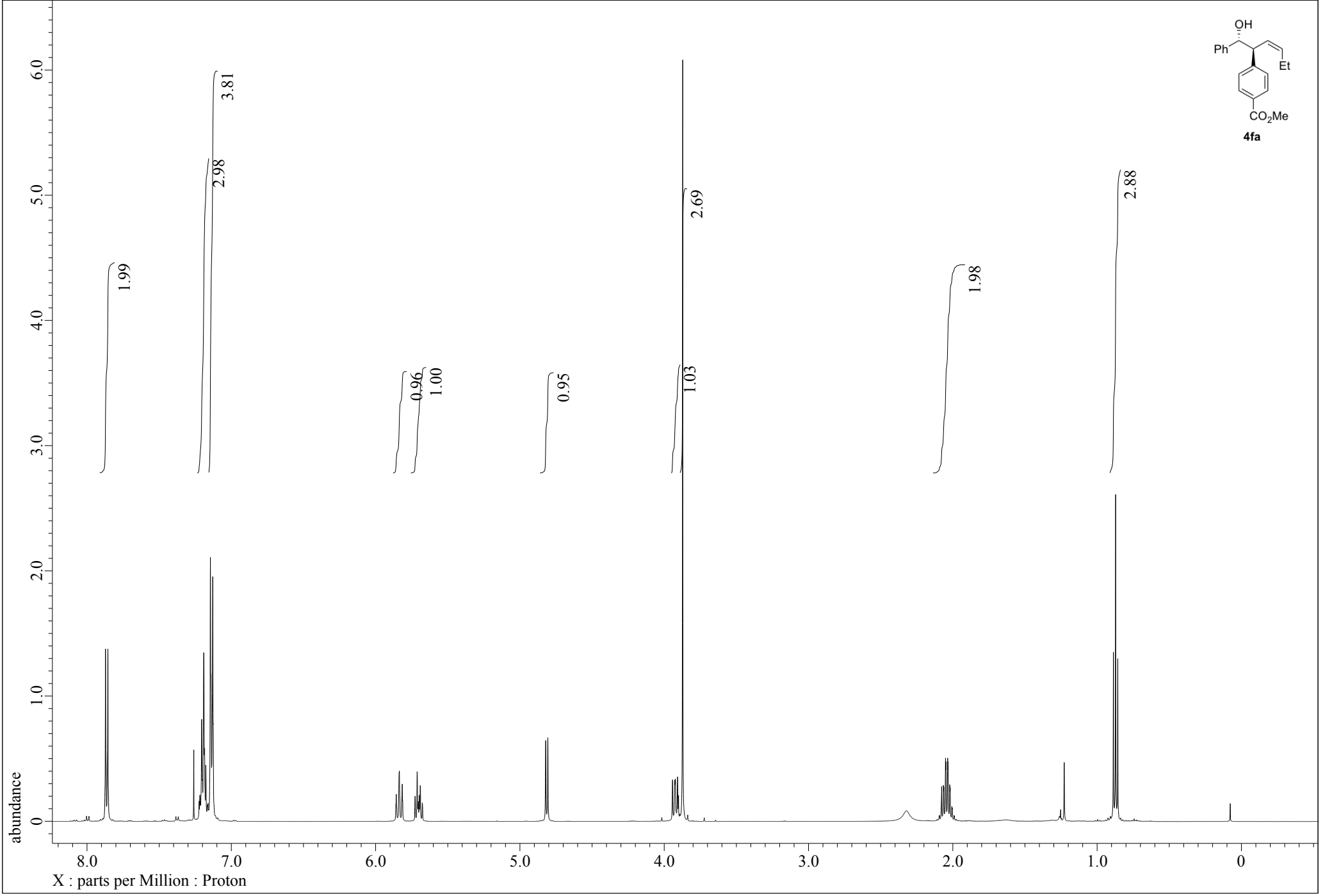

OH
Ph
Et
MeO
4ca
abundance
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
159.586
143.206
142.110
135.855
129.419
127.998
127.560
127.455
126.711
120.724
114.288
111.866
77.961
77.475
77.160
76.836
55.230
52.427
21.097
14.079
X : parts per Million : Carbon13

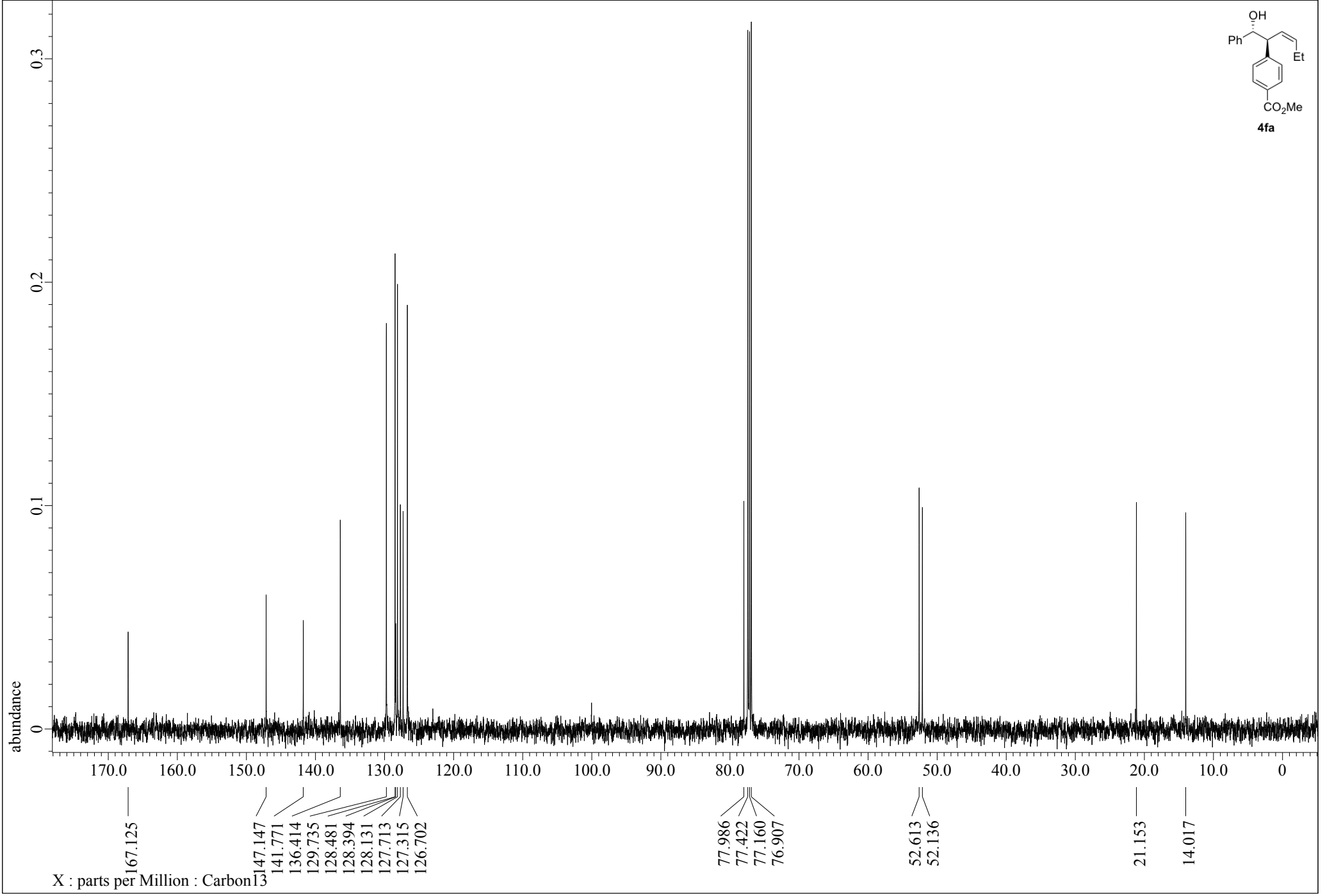

OH
Ph
Et
OMe
4da
4.76
1.97
2.03
1.00
0.98
0.99
0.98
2.92
0.91
1.94
2.84
abundance
X : parts per Million : Proton

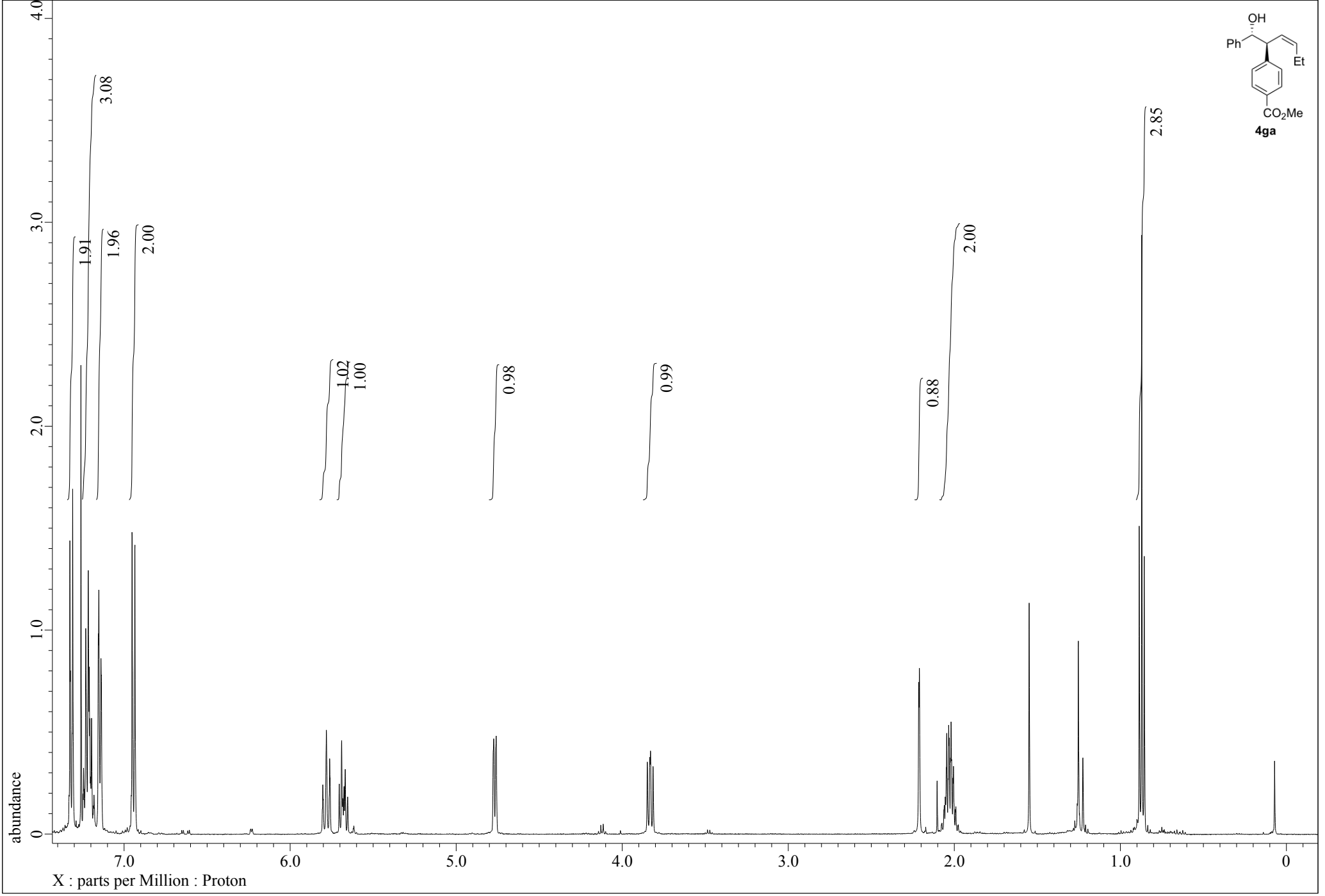

OH
Ph
Et
OMe
4da
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
169.964
159.649
149.684
130.484
128.996
128.073
114.015
113.772
83.489
77.413
77.160
76.898
76.431
55.335
24.896
24.838
21.240
X : parts per Million : Carbon13

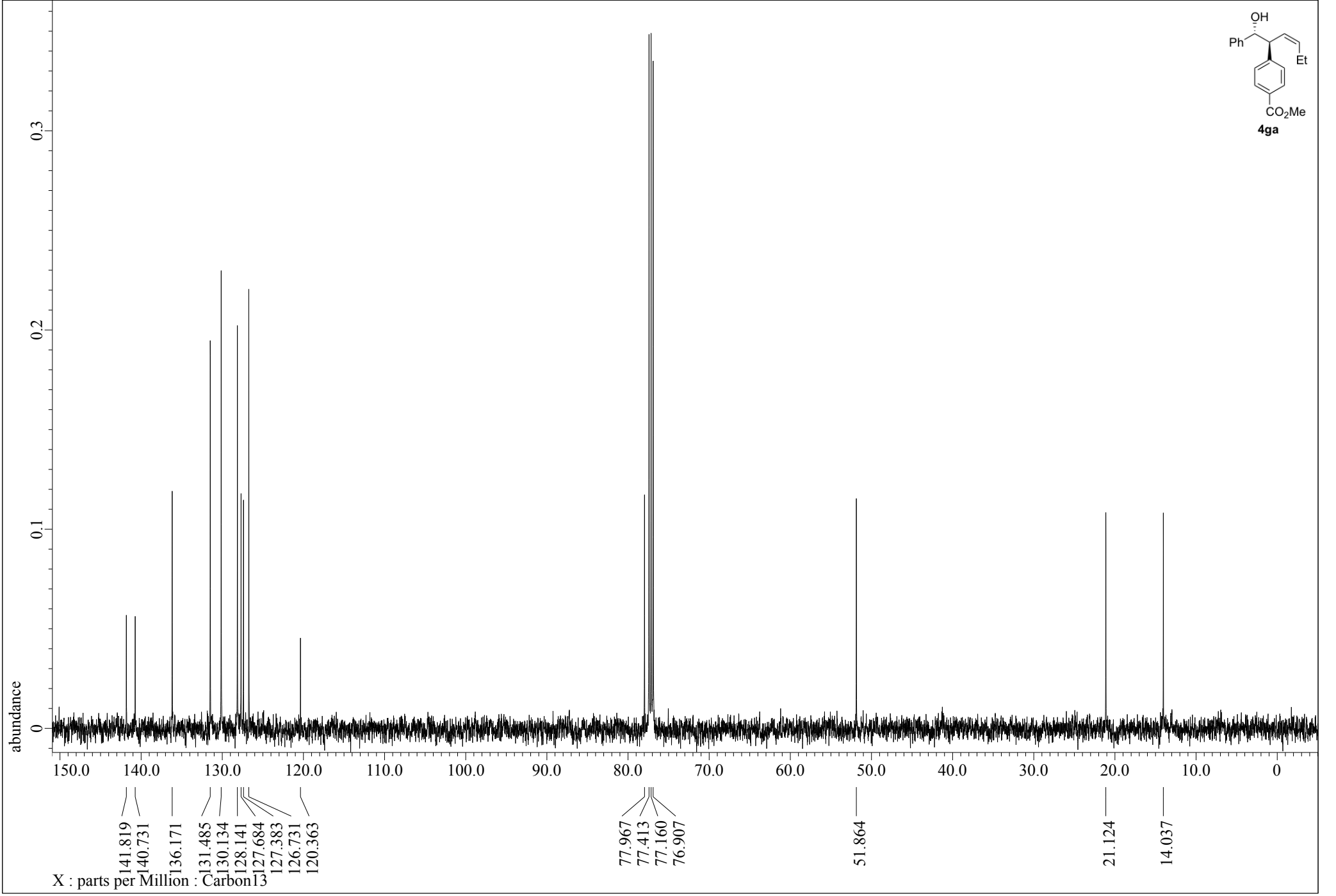

OH
Ph
Et
CF3
4ea
5.26
2.03
2.11
1.02
1.00
1.00
1.00
0.93
2.04
3.04
4.0
3.0
2.0
1.0
0
abundance
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : Proton

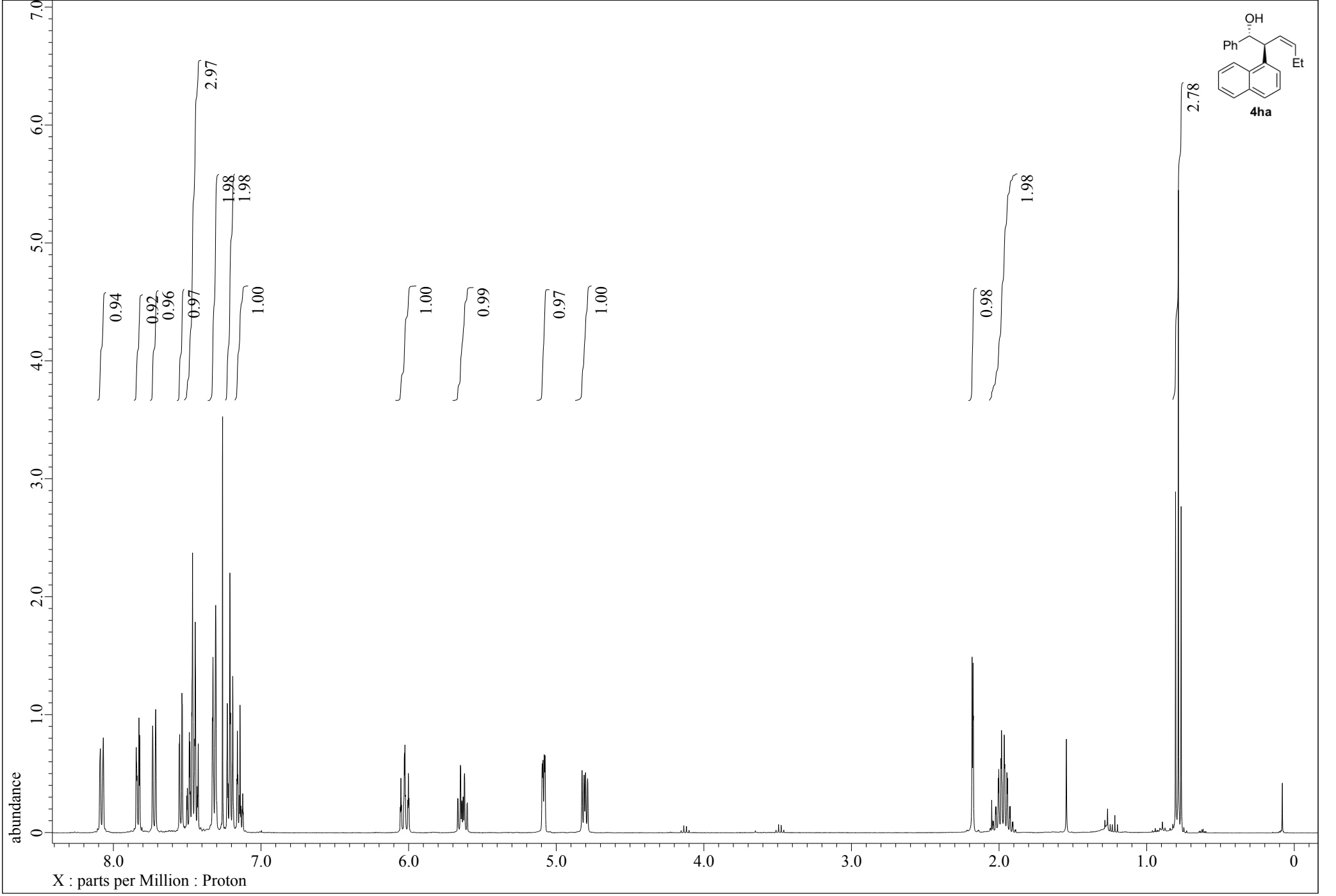

OH
Ph
Et
CF3
4ea
abundance
0.3
0.2
0.1
0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
145.893
141.722
136.492
128.909
128.773
128.646
128.189
127.801
127.023
126.683
125.341
125.312
123.231
77.947
77.413
77.160
76.898
52.263
21.134
13.998
X : parts per Million : Carbon13

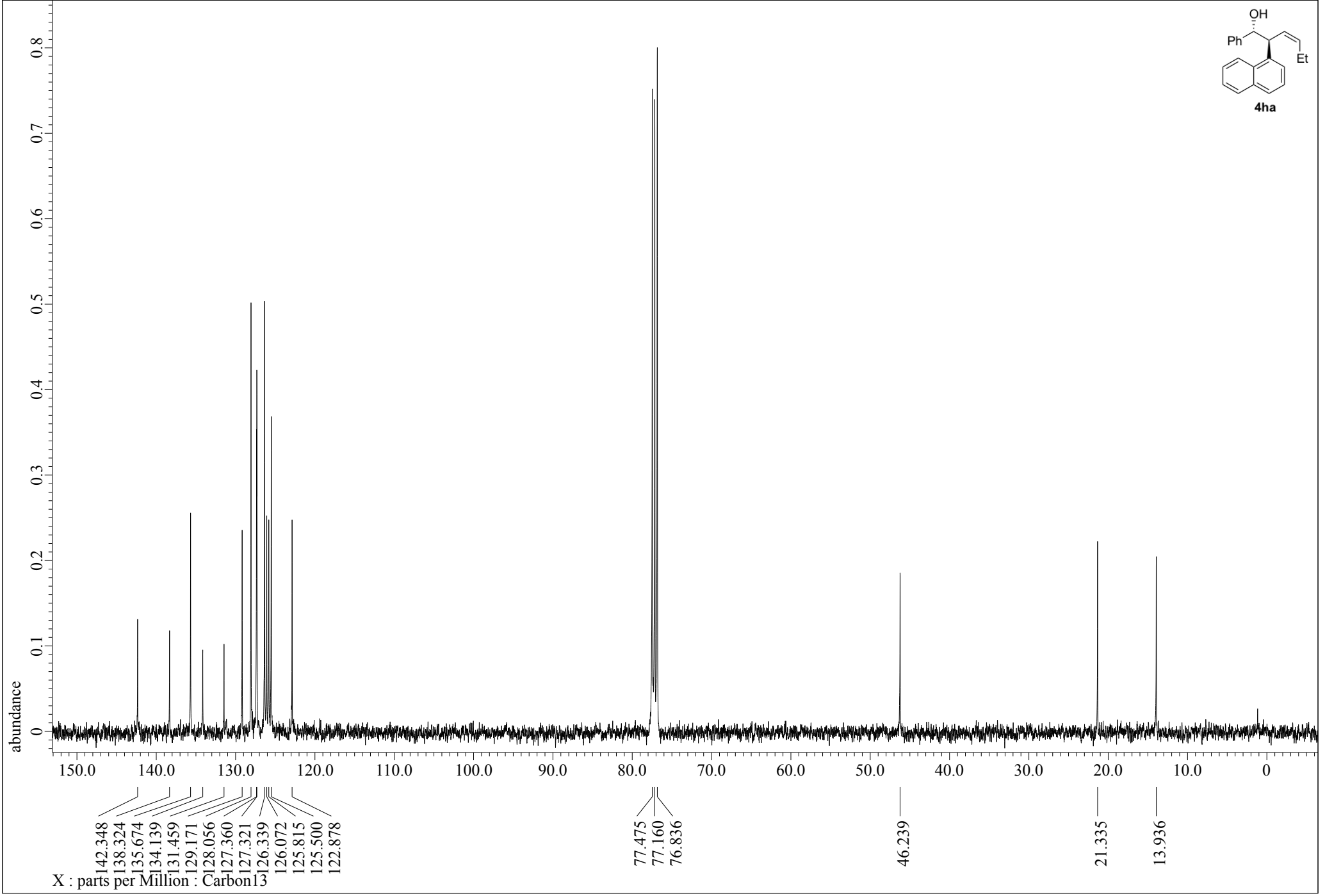

OH
Ph
Et
CO2Me
4fa
1.99
2.98
3.81
0.96
1.00
0.95
2.69
1.03
1.98
2.88
abundance
X : parts per Million : Proton

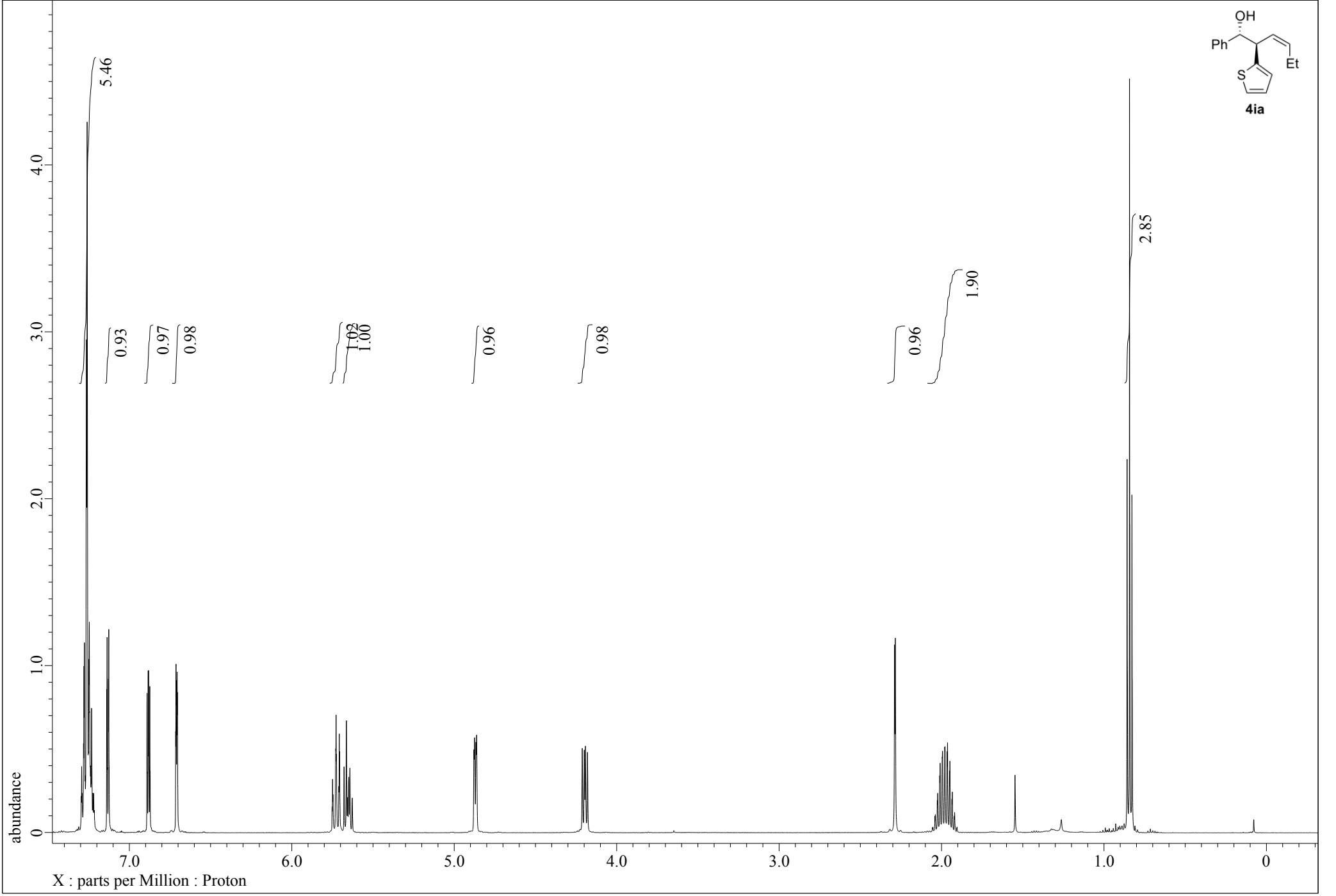

OH
Ph
Et
CO2Me
4fa
abundance
0.3
0.2
0.1
0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
167.125
147.147
141.771
136.414
129.735
128.481
128.394
128.131
127.713
127.315
126.702
77.986
77.422
77.160
76.907
52.613
52.136
21.153
14.017
X : parts per Million : Carbon13

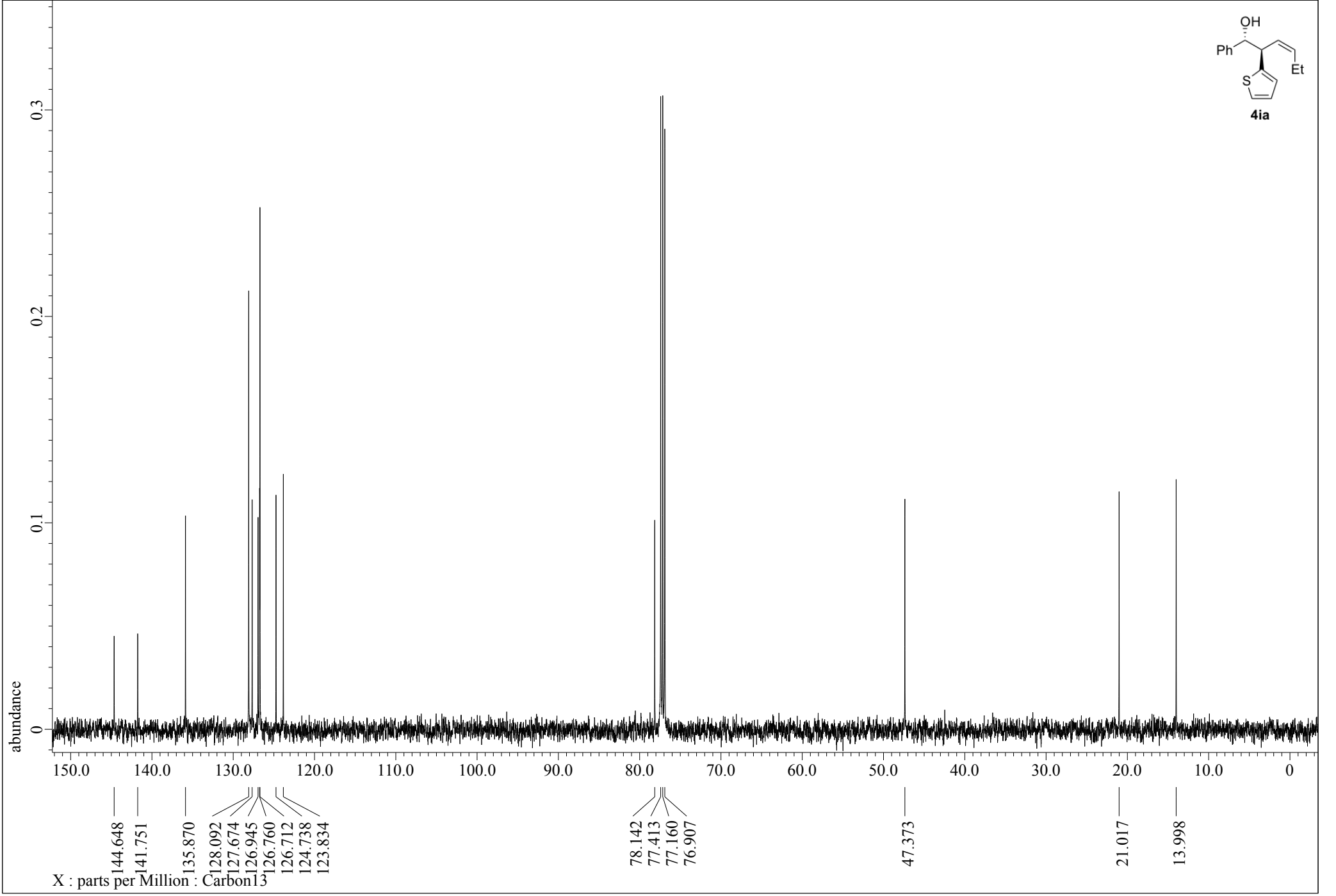

OH
Ph
Et
CO2Me
4ga
3.08
1.91
1.96
2.00
1.02
1.00
0.98
0.99
0.88
2.00
2.85
abundance
X : parts per Million : Proton

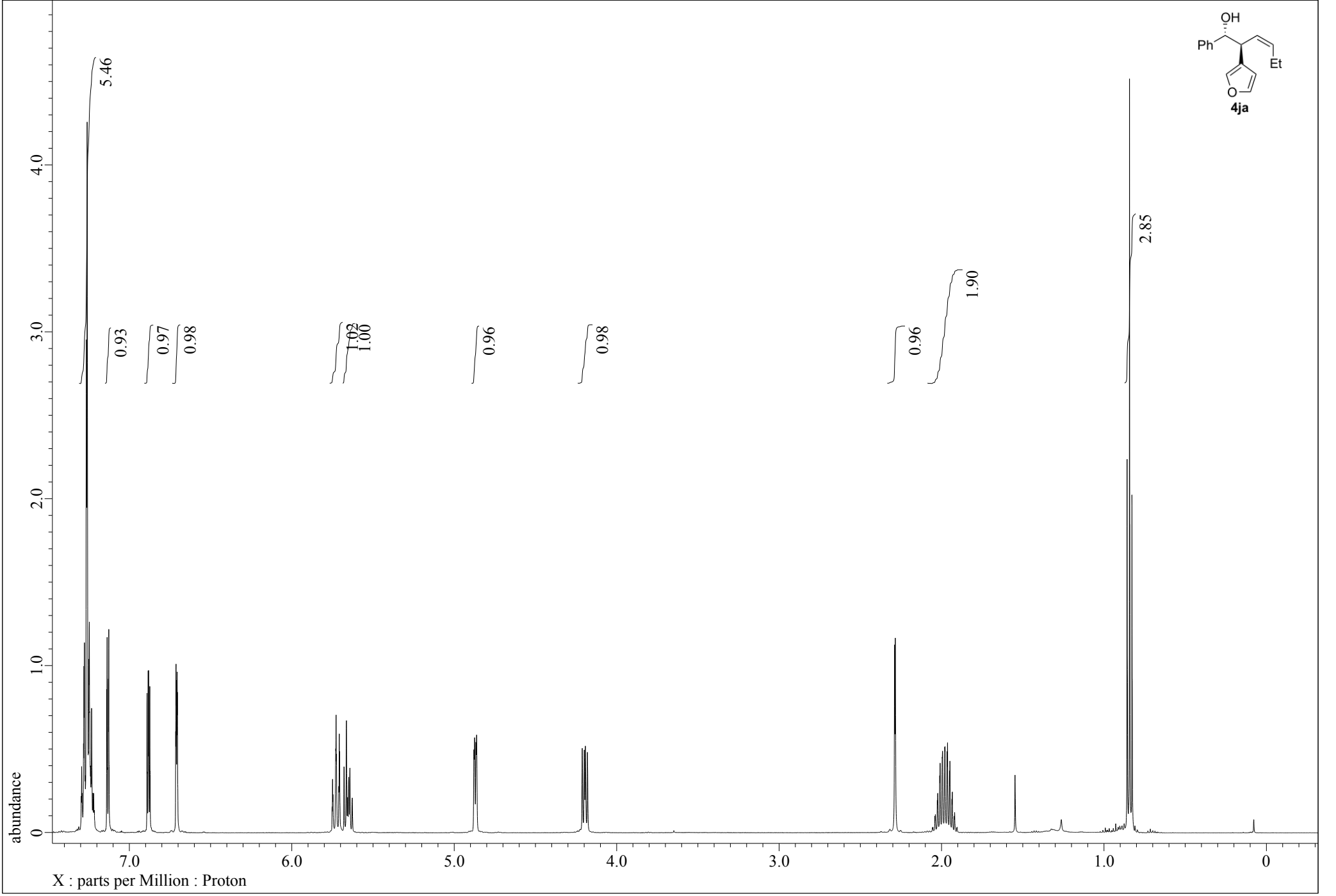

OH
Ph
Et
CO2Me
4ga
abundance
0.3
0.2
0.1
0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
141.819
140.731
136.171
131.485
130.134
128.141
127.684
127.383
126.731
120.363
77.967
77.413
77.160
76.907
51.864
21.124
14.037
X : parts per Million : Carbon13

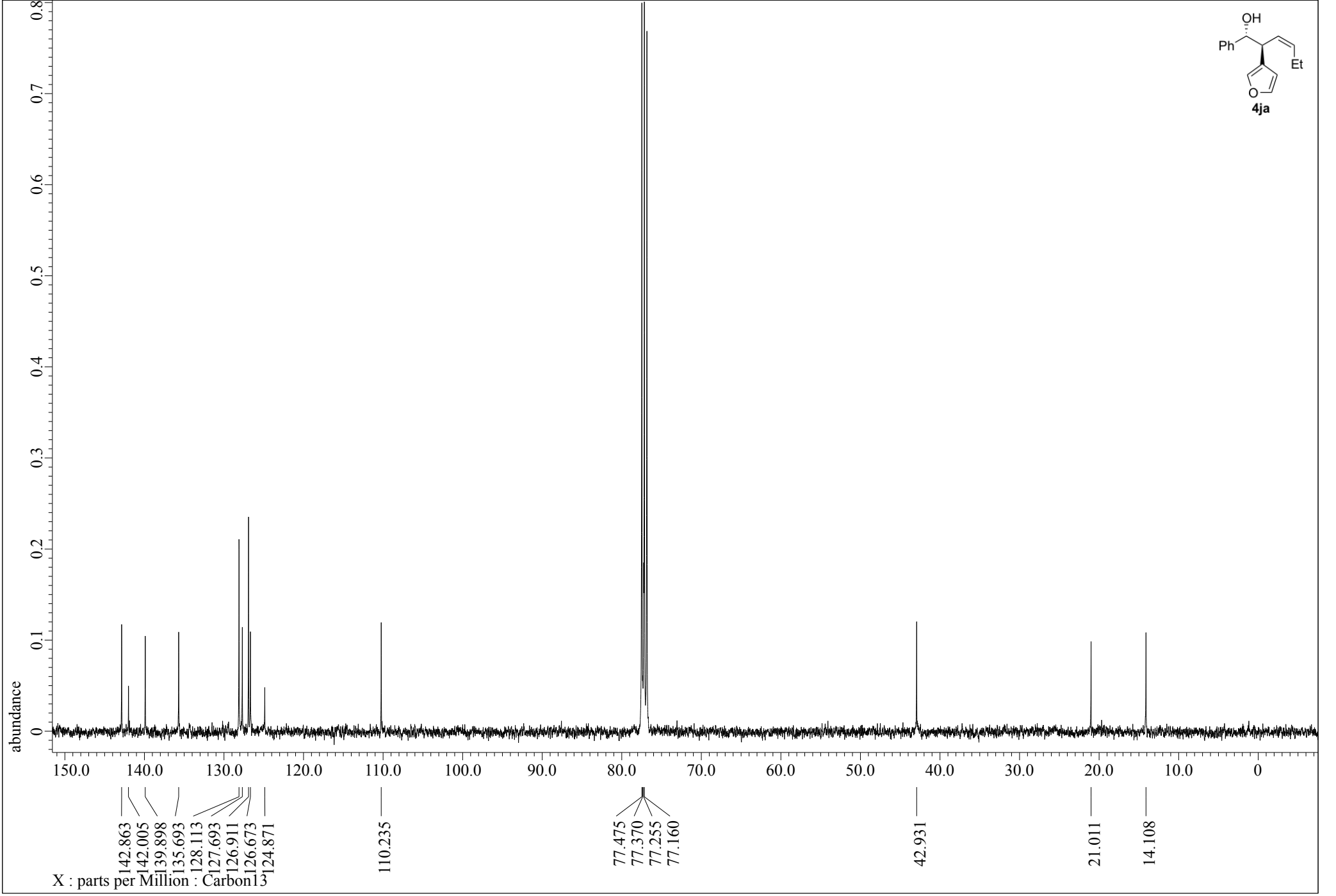

OH
Ph
Et
4ha
0.94
0.92
0.96
0.97
2.97
1.98
1.98
1.00
1.00
0.99
0.97
1.00
0.98
1.98
2.78
abundance
X : parts per Million : Proton

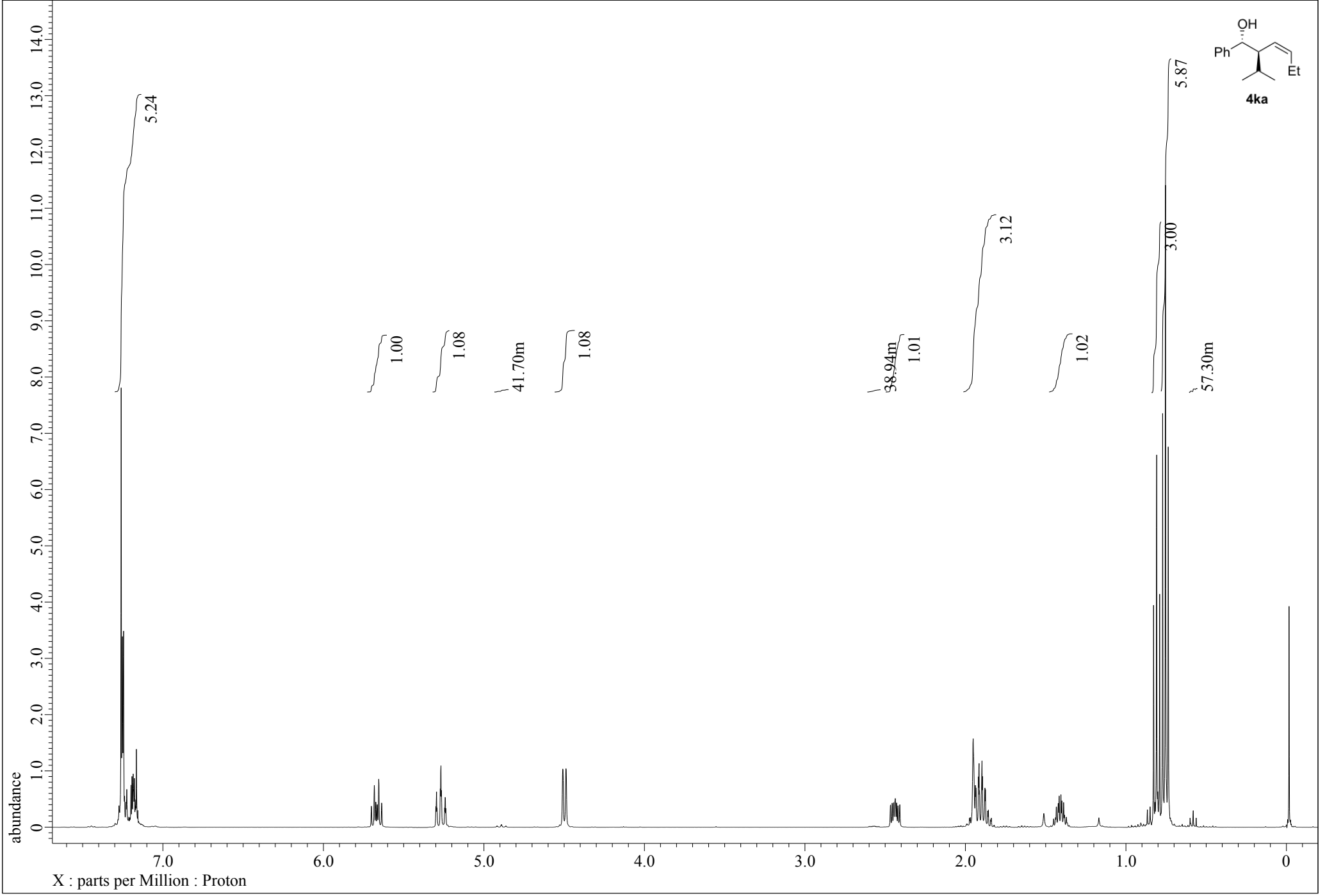

OH
Ph
Et
4ha
abundance
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
142.348
138.324
135.674
134.139
131.459
129.171
128.056
127.360
127.321
126.339
126.072
125.815
125.500
122.878
77.475
77.160
76.836
46.239
21.335
13.936
X : parts per Million : Carbon13

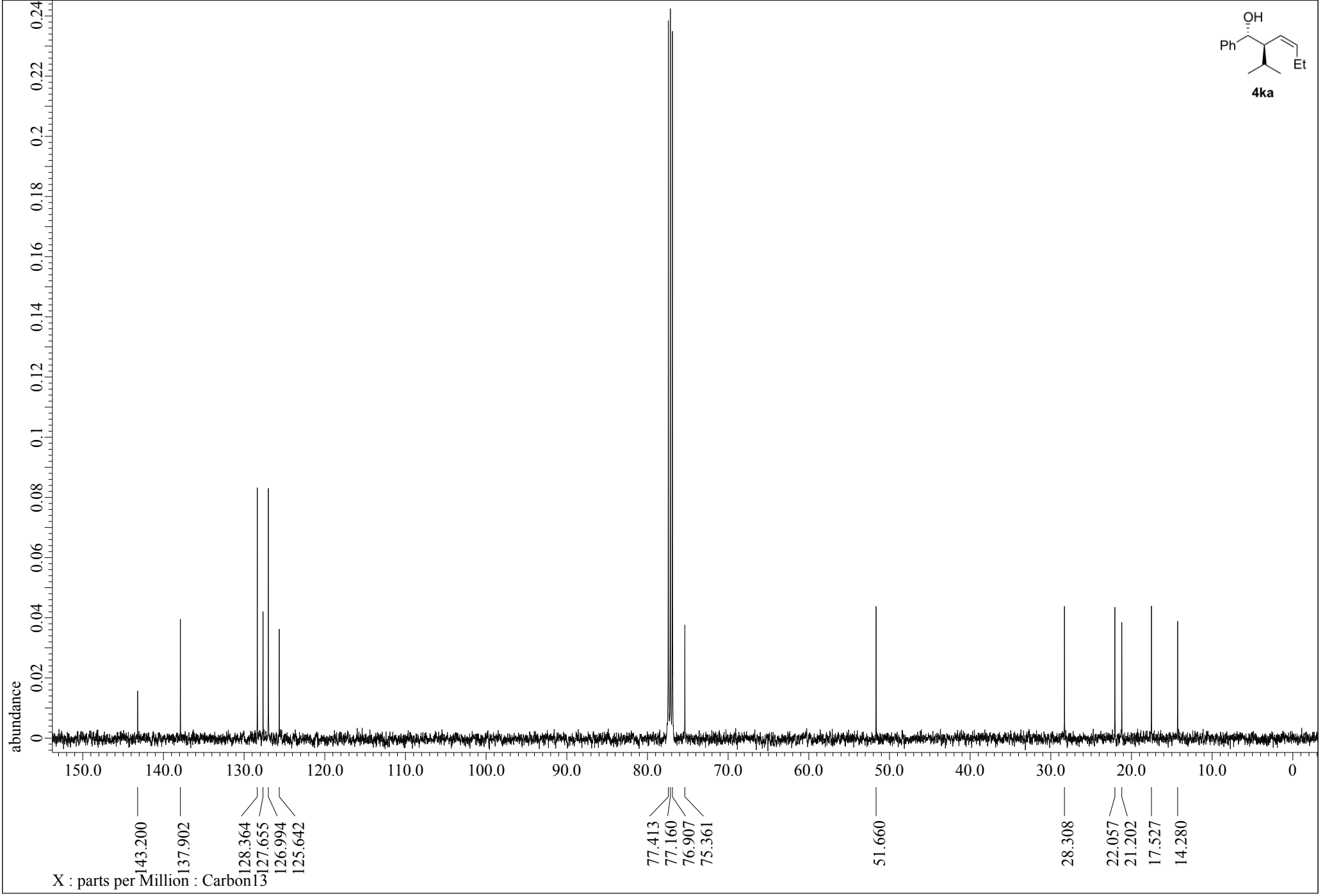

OH
Ph
Et
S
4ia
5.46
0.93
0.97
0.98
1.03
1.00
0.96
0.98
0.96
1.90
2.85
abundance
0
1.0
2.0
3.0
4.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : Proton

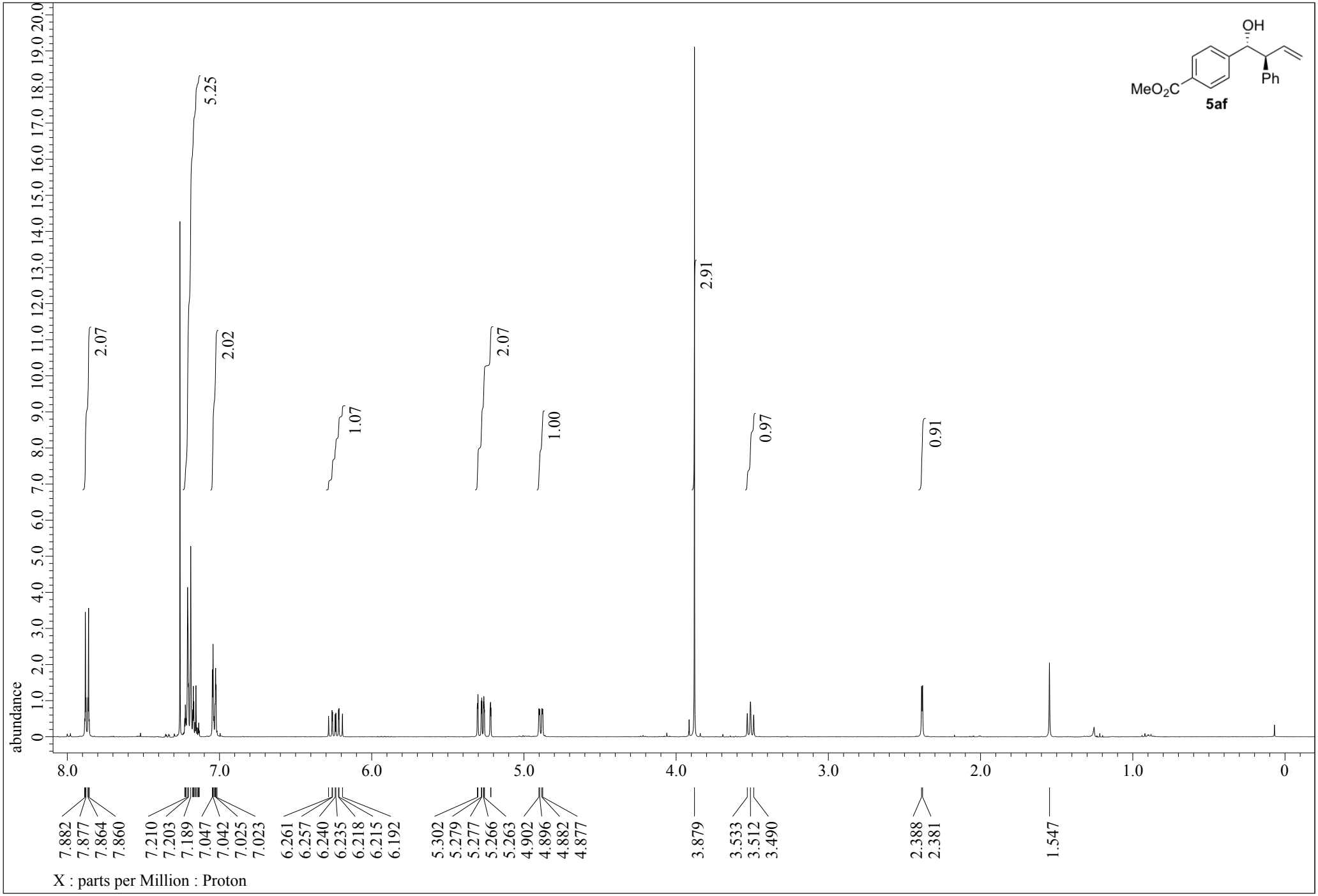

OH
Ph
Et
S
4ia
abundance
0.3
0.2
0.1
0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
144.648
141.751
135.870
128.092
127.674
126.945
126.760
126.712
124.738
123.834
78.142
77.413
77.160
76.907
47.373
21.017
13.998
X : parts per Million : Carbon13

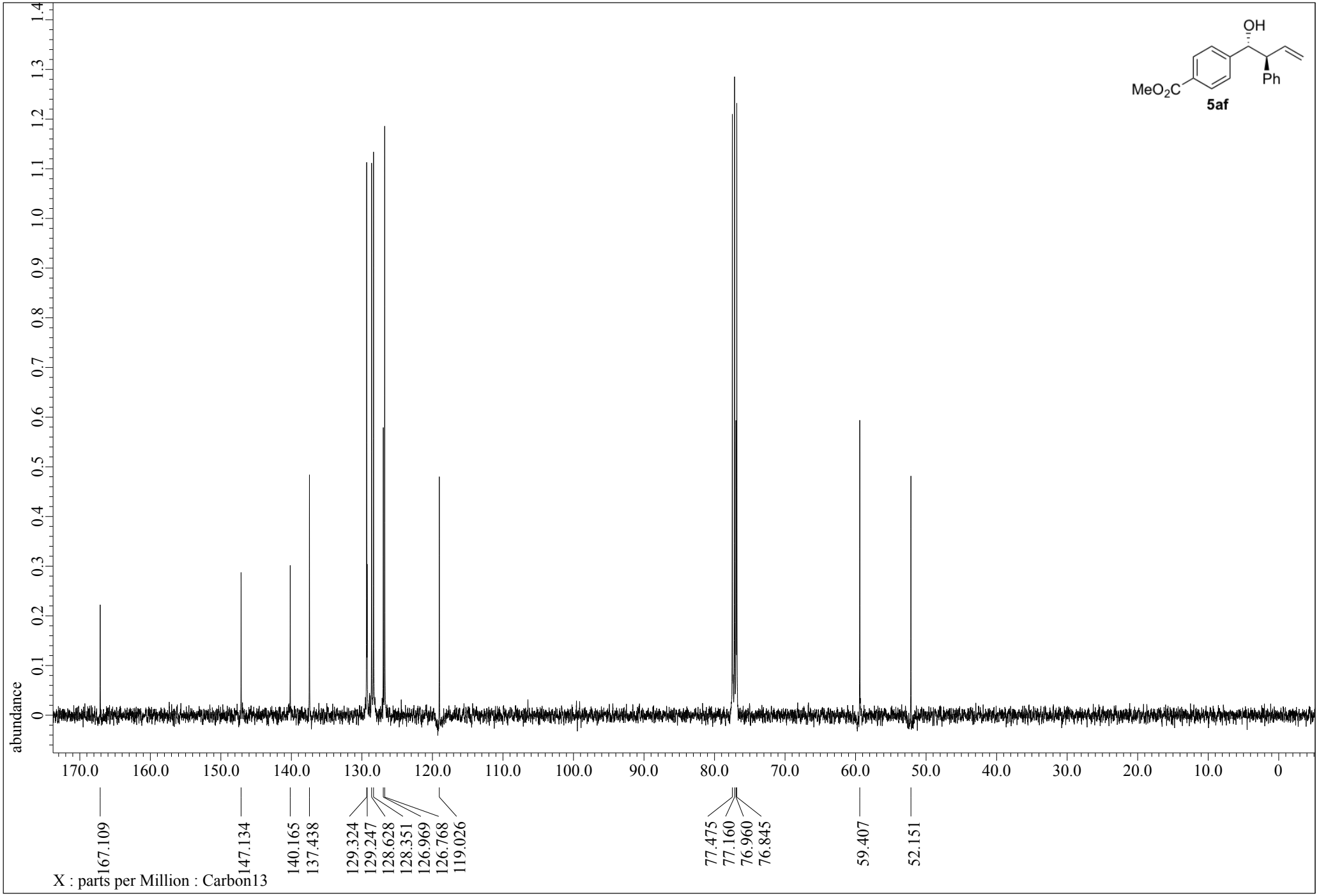

OH
Ph
Et
O
4ja
5.46
0.93
0.97
0.98
1.03
1.00
0.96
0.98
0.96
1.90
2.85
abundance
X : parts per Million : Proton

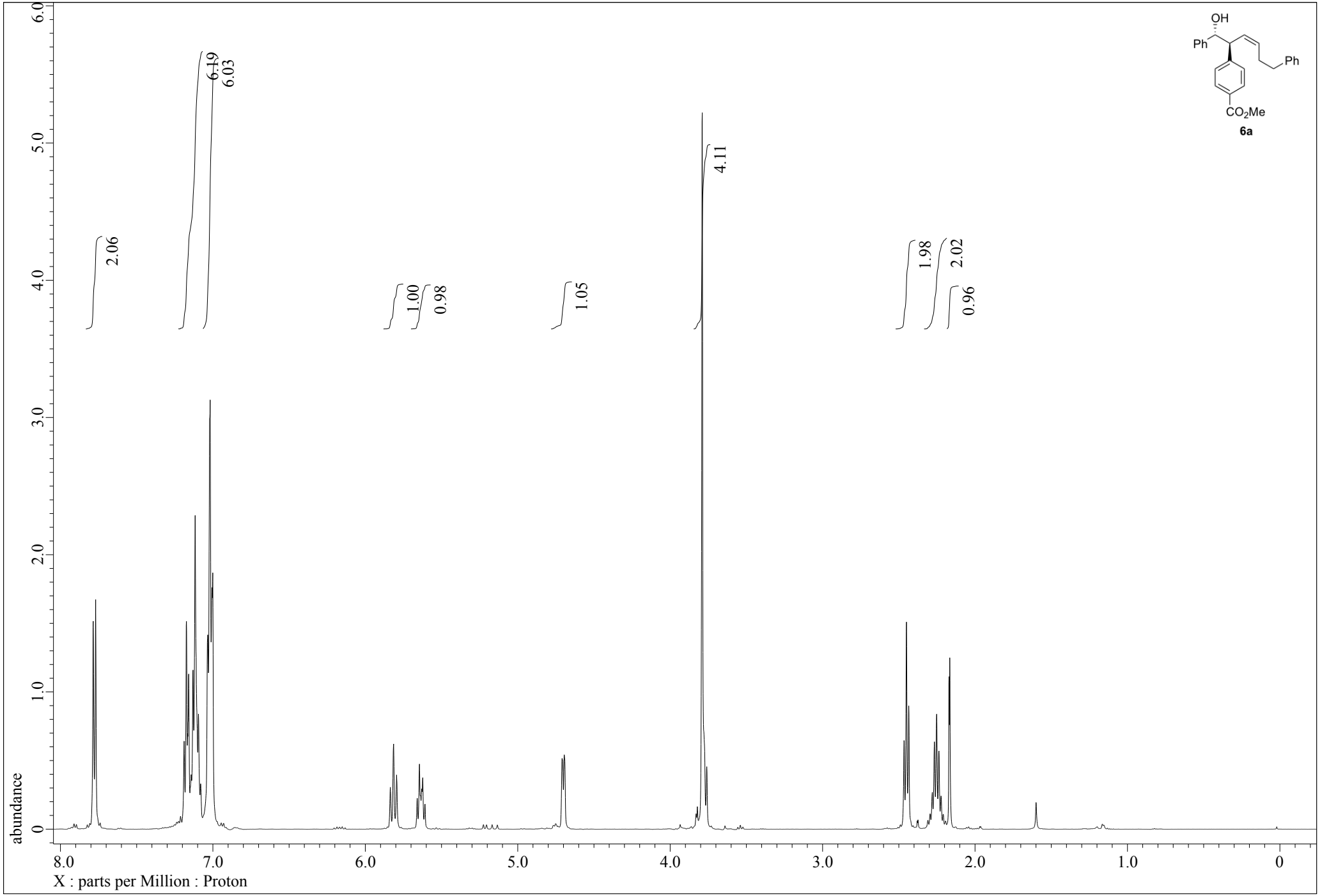

OH
Ph
Et
O
4ja
abundance
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
142.863
142.005
139.898
135.693
128.113
127.693
126.911
126.673
124.871
110.235
77.475
77.370
77.255
77.160
42.931
21.011
14.108
X : parts per Million : Carbon13

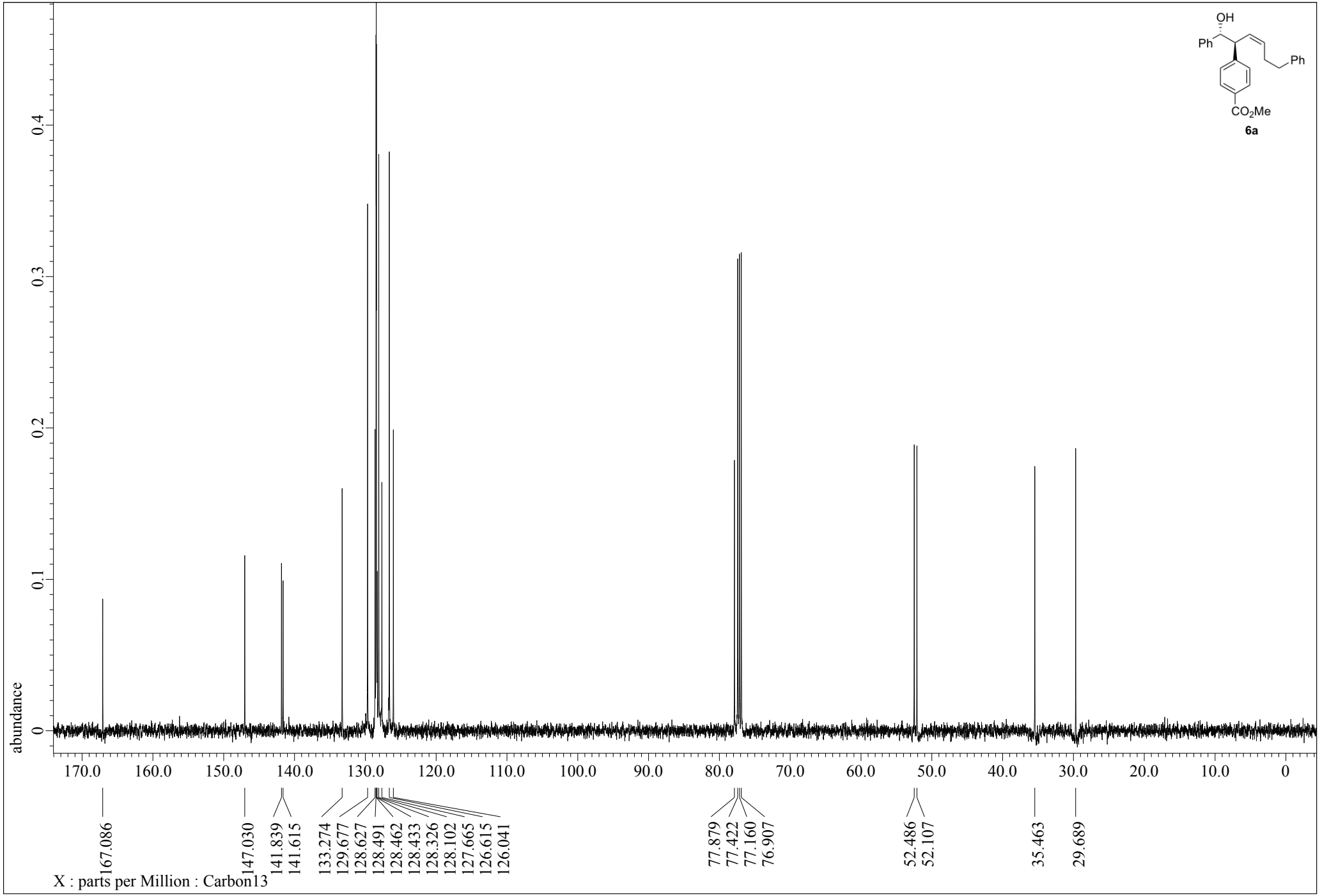

OH
Ph
Et
4ka
5.24
1.00
1.08
41.70m
1.08
38.94m
1.01
3.12
1.02
5.87
3.00
57.30m
abundance
X : parts per Million : Proton

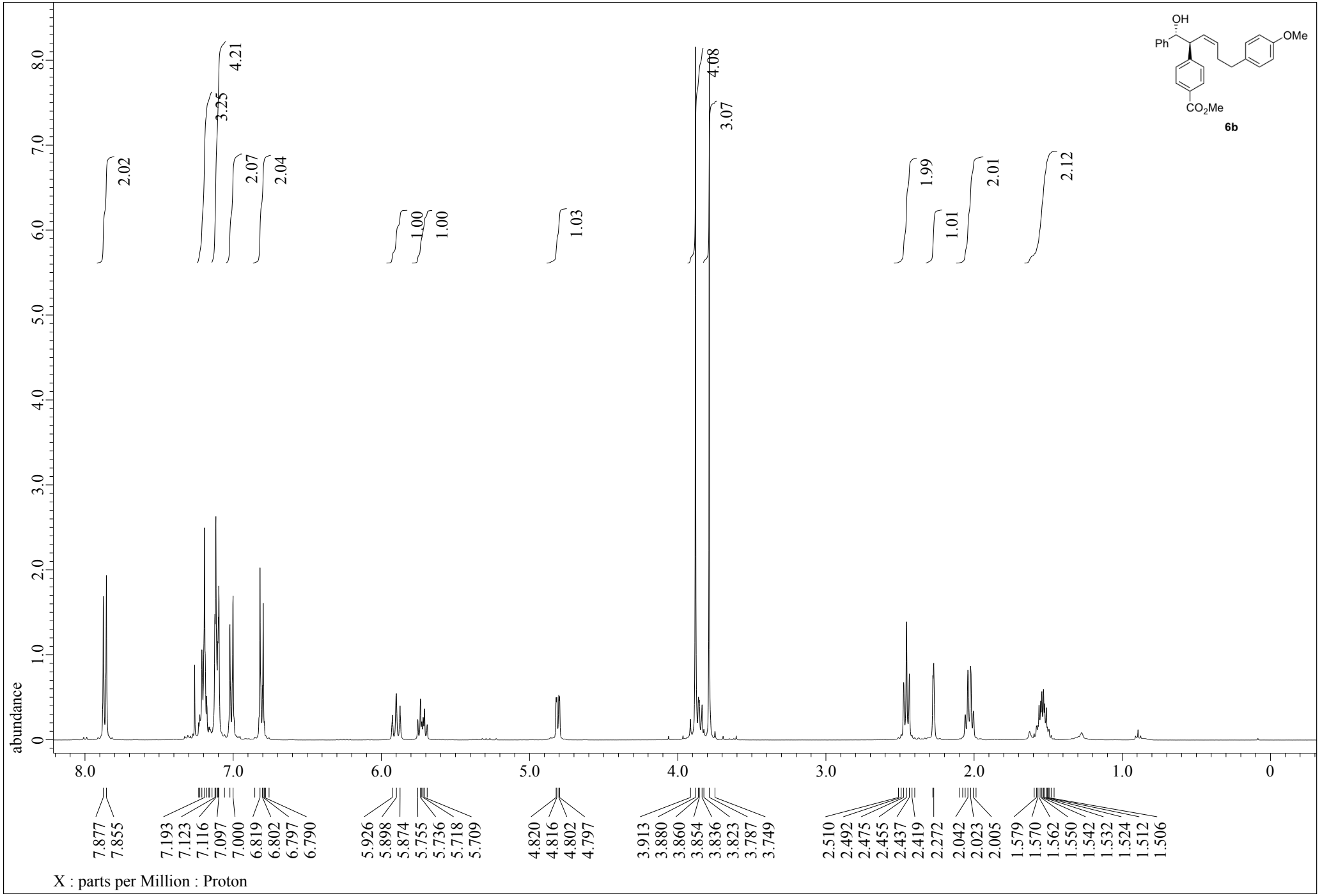

OH
Ph
Et
4ka
abundance
0
0.02
0.04
0.06
0.08
0.1
0.12
0.14
0.16
0.18
0.2
0.22
0.24
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
143.200
137.902
128.364
127.655
126.994
125.642
77.413
77.160
76.907
75.361
51.660
28.308
22.057
21.202
17.527
14.280
X : parts per Million : Carbon13

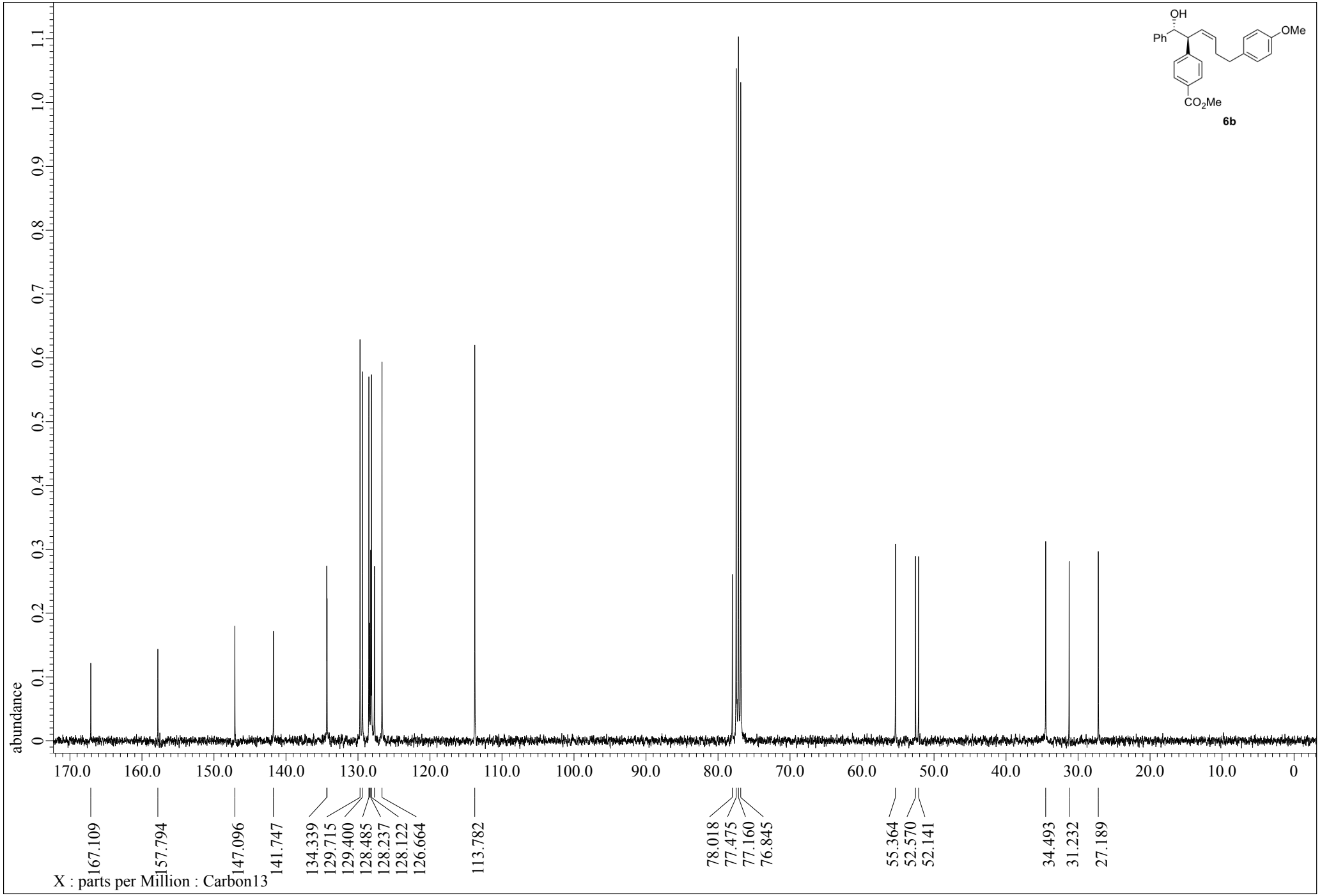

OH
Ph
MeO2C
5af
abundance
2.07
5.25
2.02
1.07
2.07
1.00
2.91
0.97
0.91
7.882
7.877
7.864
7.860
7.210
7.203
7.189
7.047
7.042
7.025
7.023
6.261
6.257
6.240
6.235
6.218
6.215
6.192
5.302
5.279
5.277
5.266
5.263
4.902
4.896
4.882
4.877
3.879
3.533
3.512
3.490
2.388
2.381
1.547
X : parts per Million : Proton

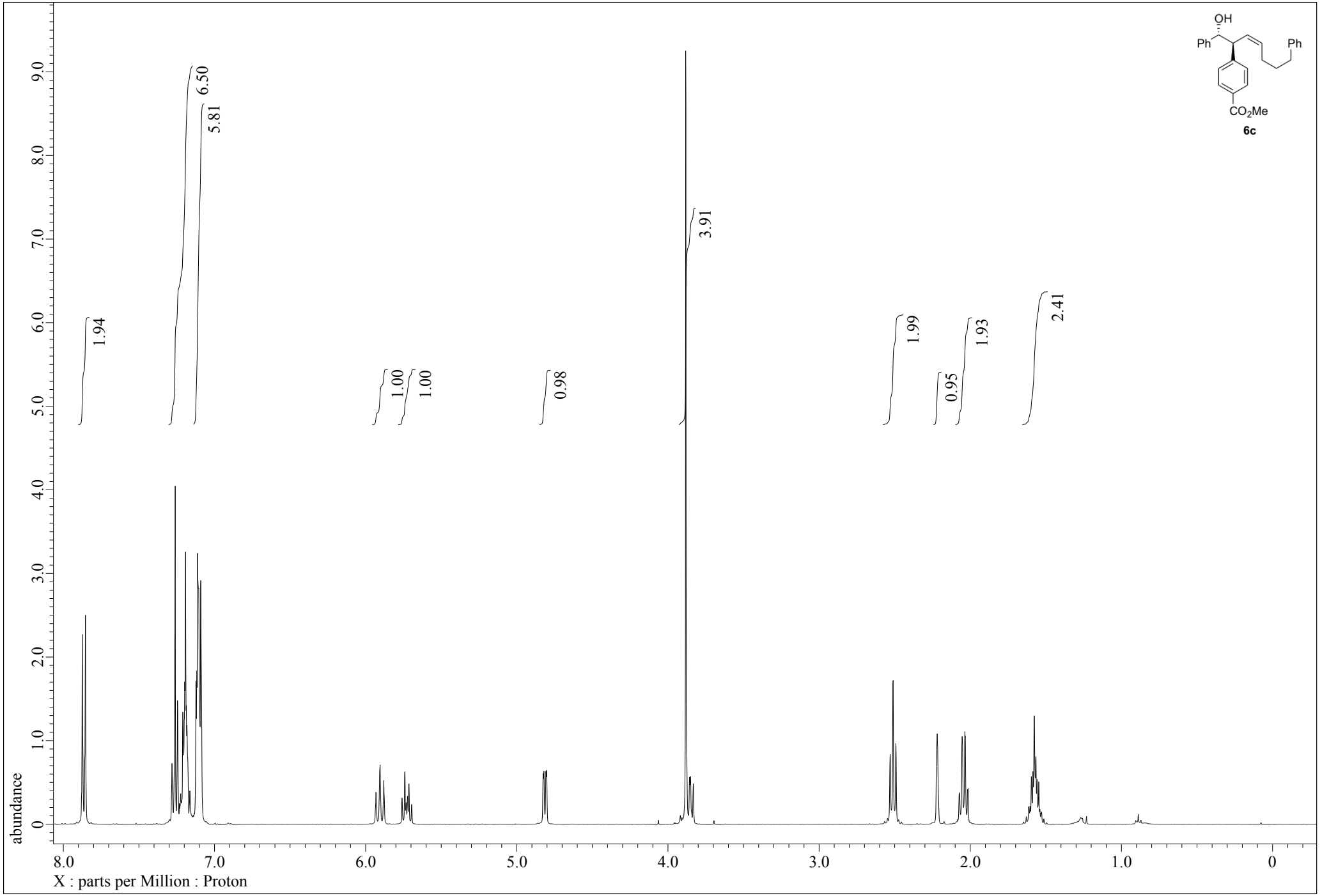

OH
Ph
MeO2C
5af
abundance
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
167.109
147.134
140.165
137.438
129.324
129.247
128.628
128.351
126.969
126.768
119.026
77.475
77.160
76.960
76.845
59.407
52.151
X : parts per Million : Carbon13

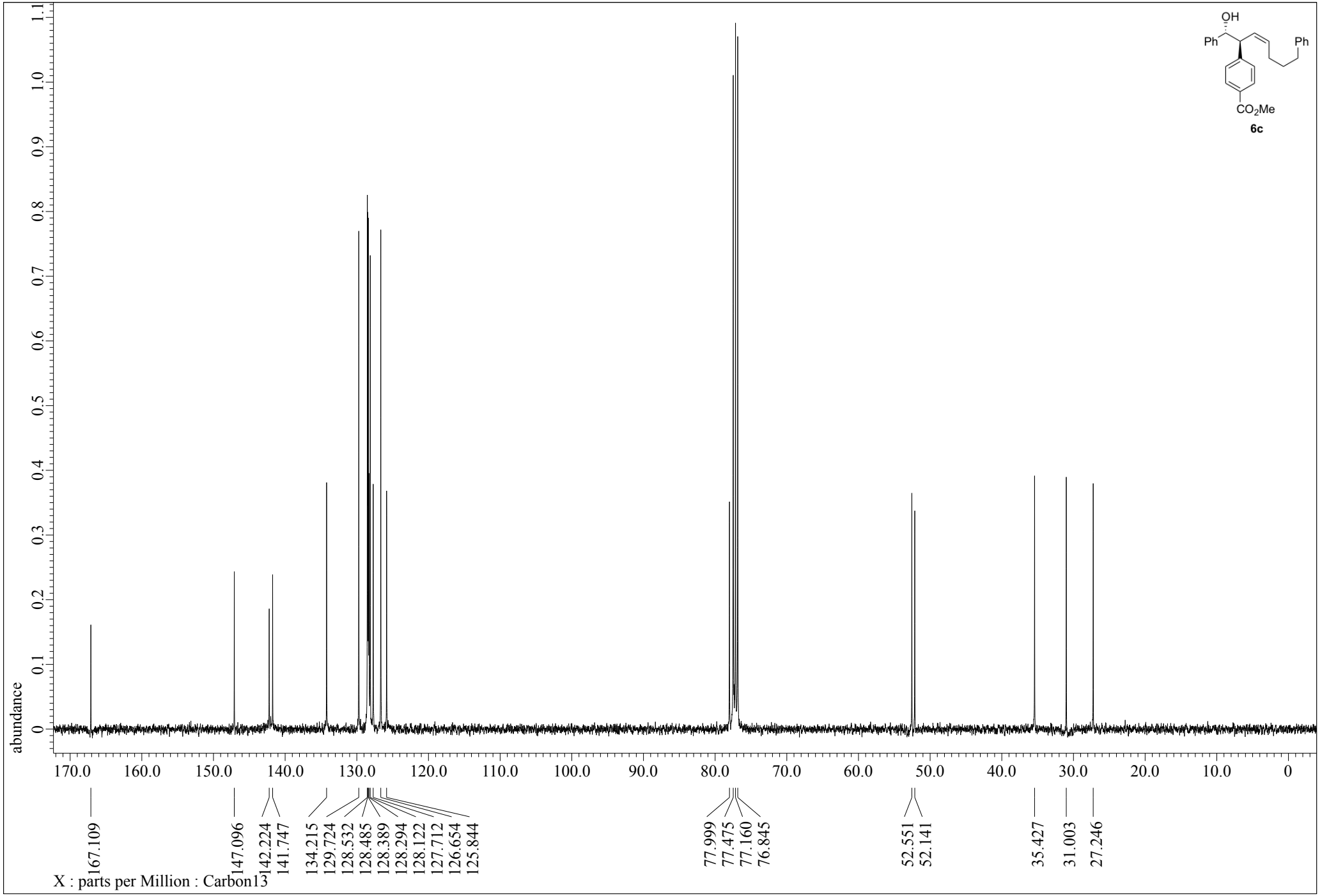

OH
Ph
Ph
CO2Me
6a
2.06
6.19
6.03
1.00
0.98
1.05
4.11
1.98
2.02
0.96
abundance
X : parts per Million : Proton

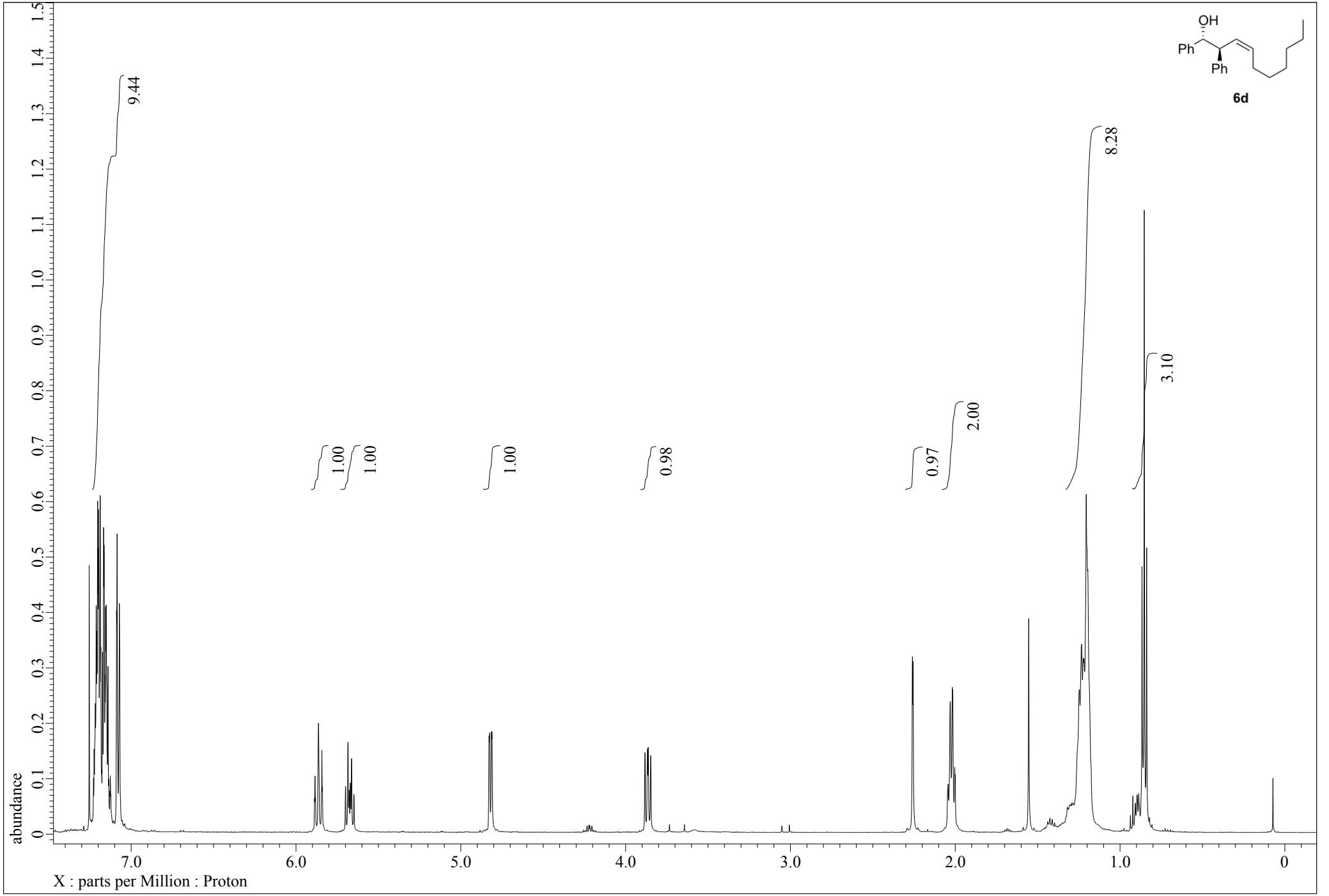

OH
Ph
Ph
CO2Me
6a
abundance
0
0.1
0.2
0.3
0.4
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
167.086
147.030
141.839
141.615
133.274
129.677
128.627
128.491
128.462
128.433
128.326
128.102
127.665
126.615
126.041
77.879
77.422
77.160
76.907
52.486
52.107
35.463
29.689
X : parts per Million : Carbon13

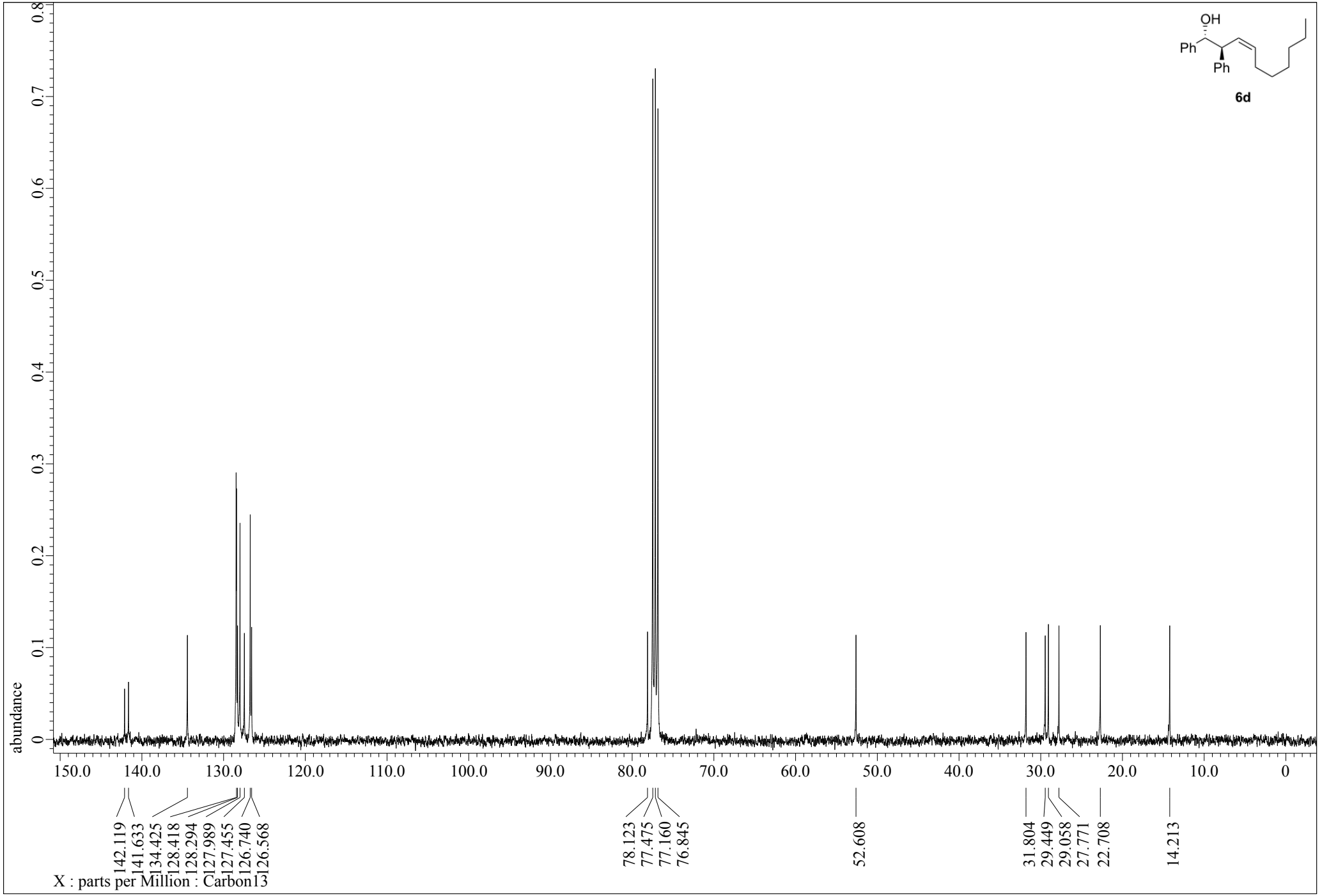

OH
Ph
OMe
CO2Me
6b
abundance
2.02
3.25
4.21
2.07
2.04
1.00
1.00
1.03
4.08
3.07
1.99
1.01
2.01
2.12
7.877
7.855
7.193
7.123
7.116
7.097
7.000
6.819
6.802
6.797
6.790
5.926
5.898
5.874
5.755
5.736
5.718
5.709
4.820
4.816
4.802
4.797
3.913
3.880
3.860
3.854
3.836
3.823
3.787
3.749
2.510
2.492
2.475
2.455
2.437
2.419
2.272
2.042
2.023
2.005
1.579
1.570
1.562
1.550
1.542
1.532
1.524
1.512
1.506
X : parts per Million : Proton

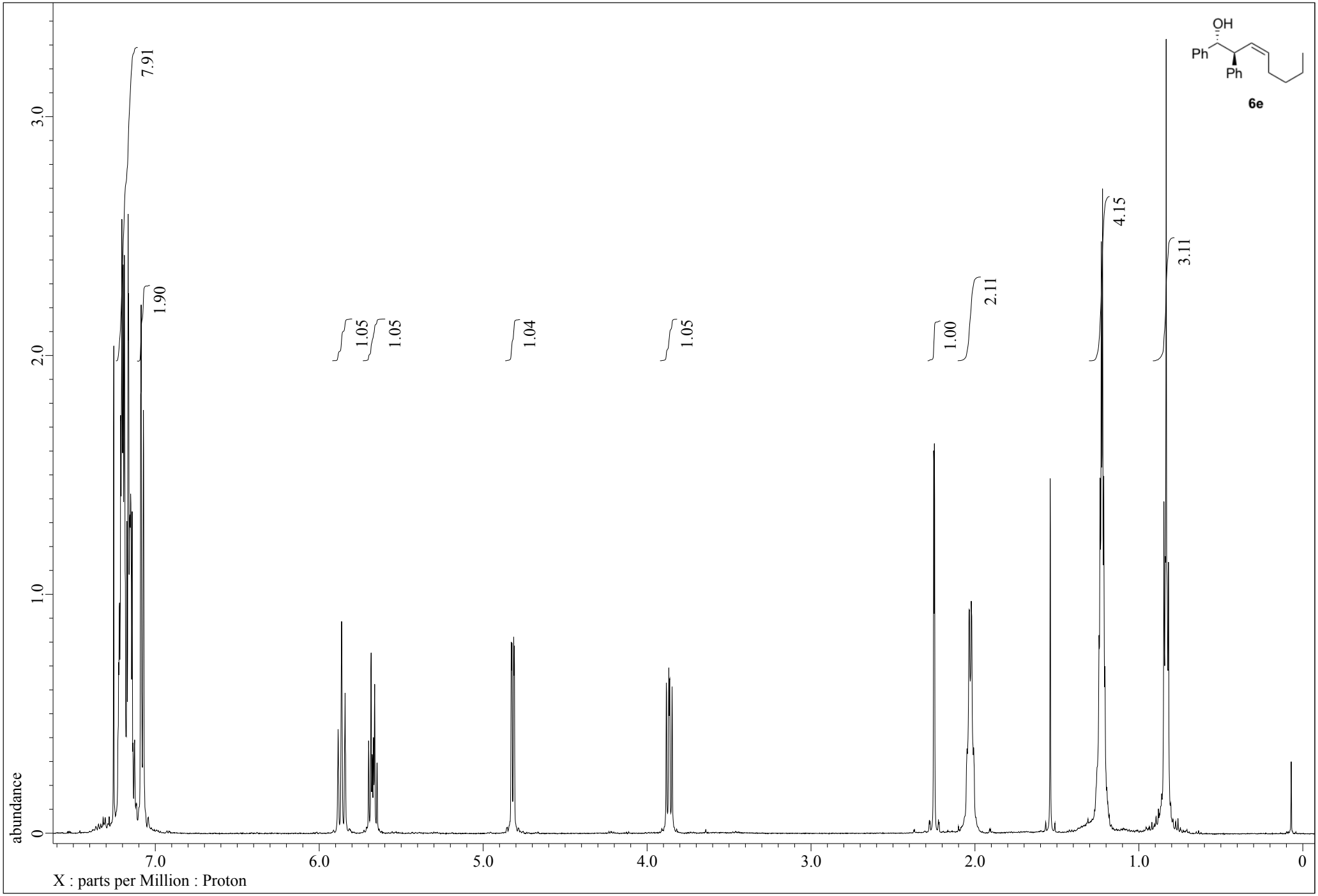

OH
Ph
OMe
CO2Me
6b
abundance
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
167.109
157.794
147.096
141.747
134.339
129.715
129.400
128.485
128.237
128.122
126.664
113.782
78.018
77.475
77.160
76.845
55.364
52.570
52.141
34.493
31.232
27.189
X : parts per Million : Carbon13

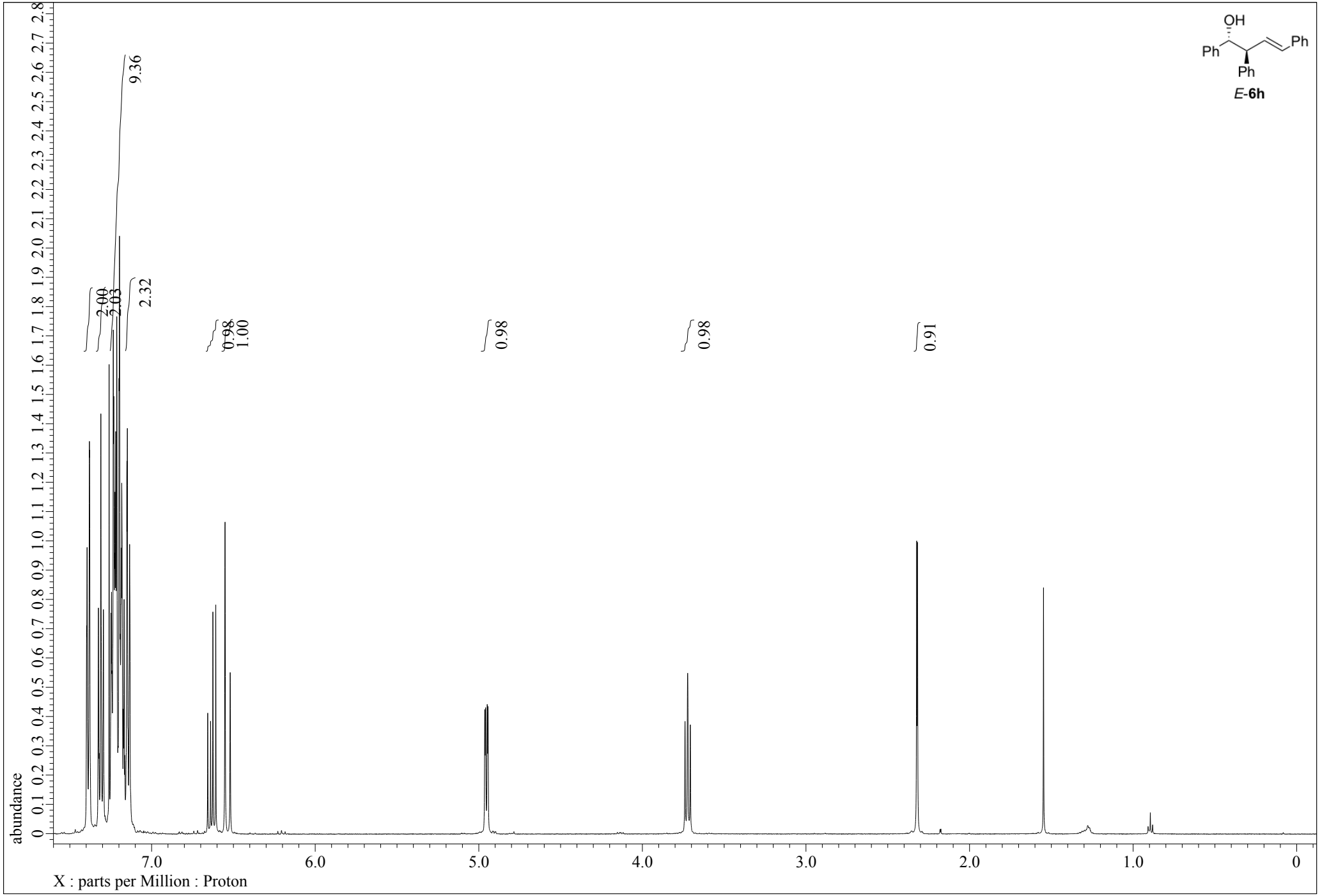

OH
Ph
Ph
CO2Me
6c
1.94
6.50
5.81
1.00
1.00
0.98
3.91
1.99
0.95
1.93
2.41
abundance
X : parts per Million : Proton

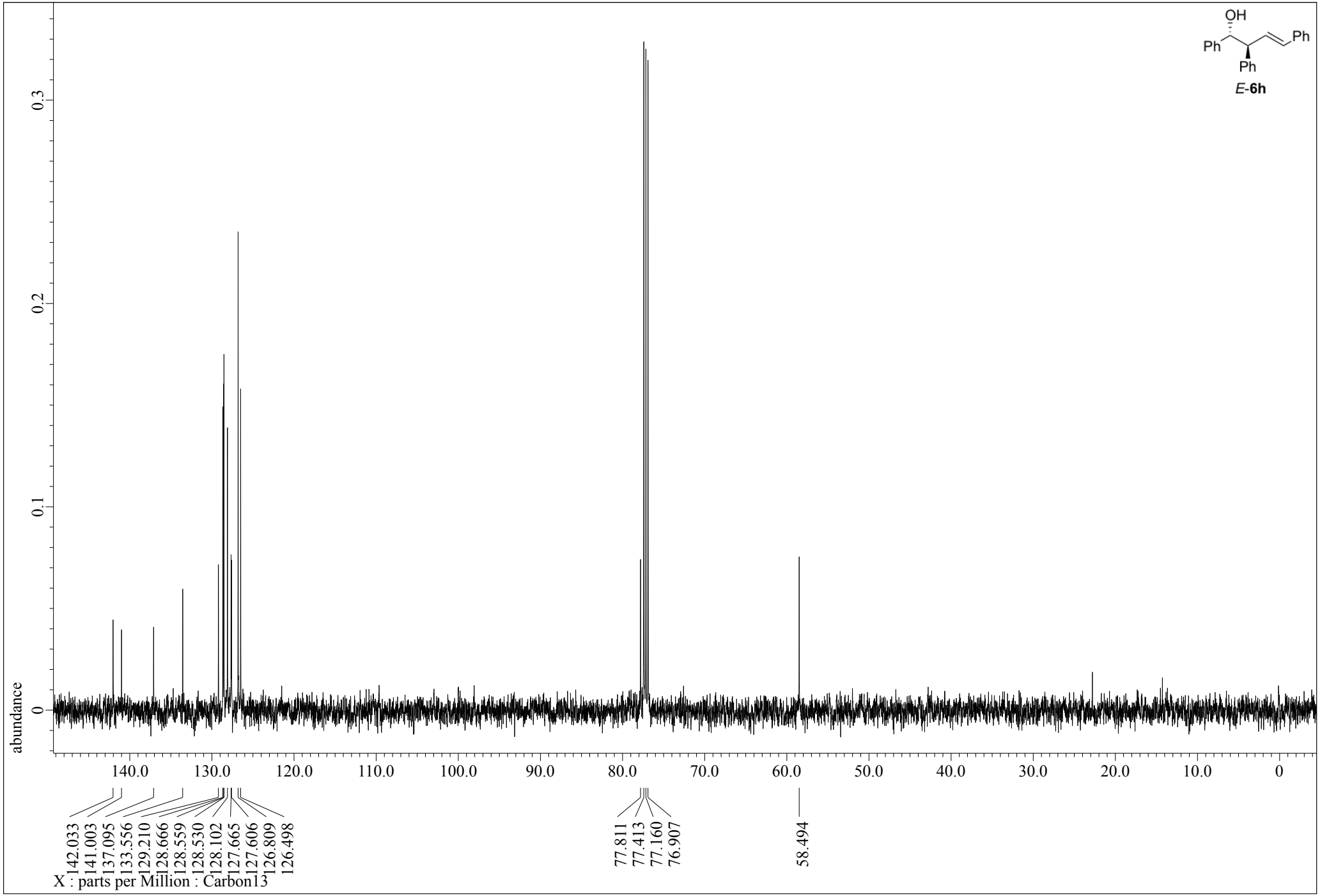

OH
Ph
Ph
CO2Me
6c
abundance
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
167.109
147.096
142.224
141.747
134.215
129.724
128.532
128.485
128.389
128.294
128.122
127.712
126.654
125.844
77.999
77.475
77.160
76.845
52.551
52.141
35.427
31.003
27.246
X : parts per Million : Carbon13

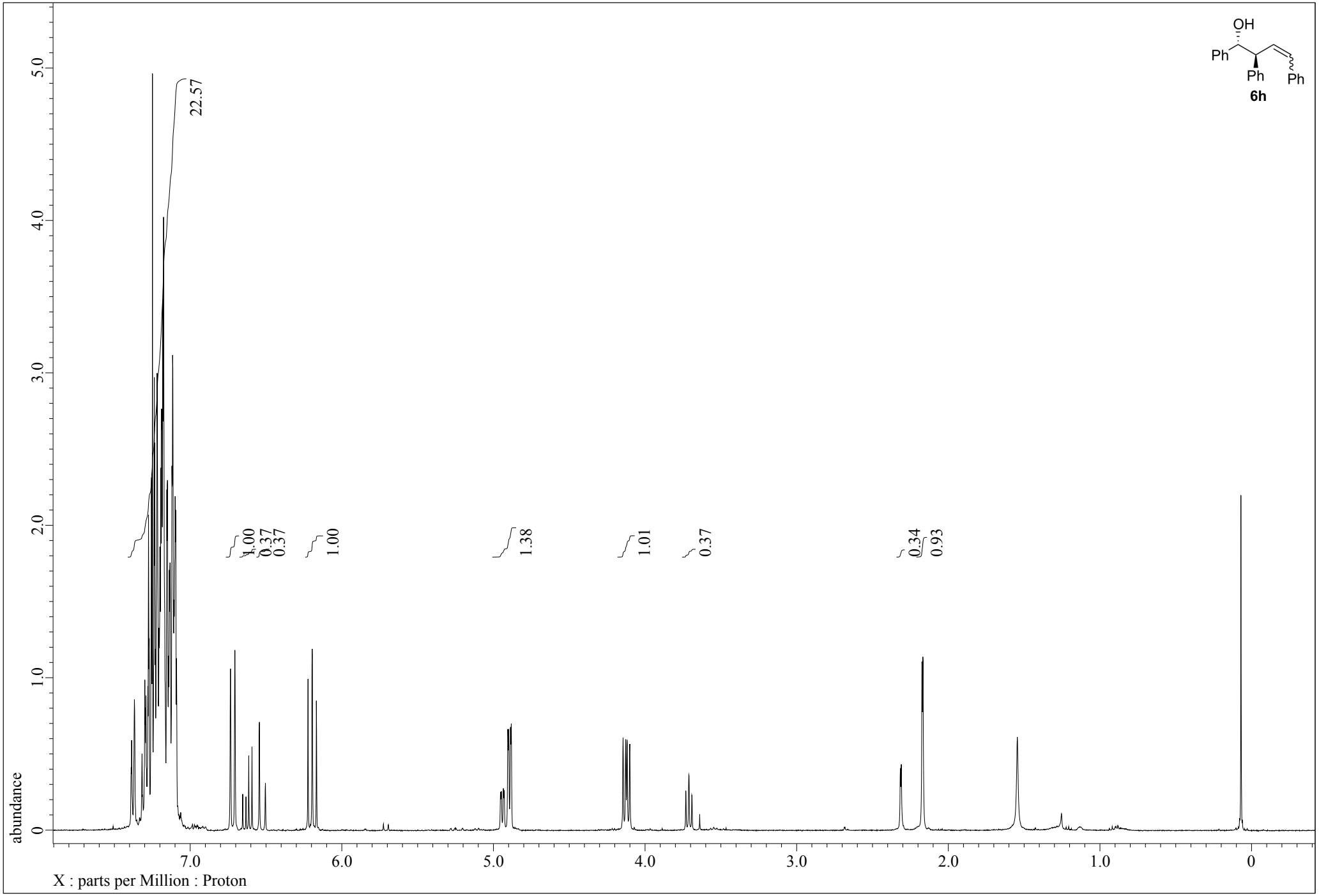

OH
Ph
Ph
6d
9.44
1.00
1.00
1.00
0.98
0.97
2.00
8.28
3.10
abundance
X : parts per Million : Proton

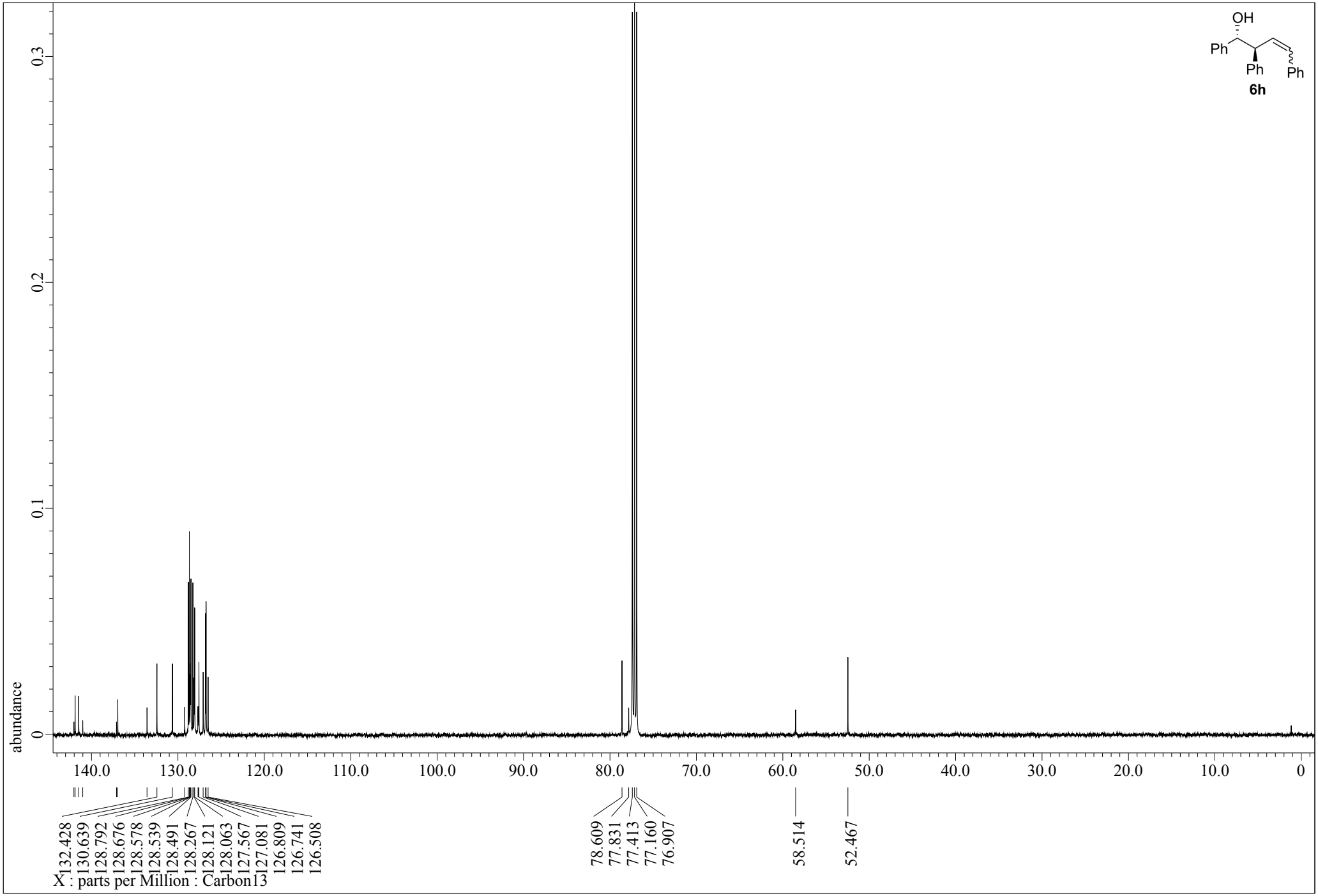

OH
Ph
Ph
6d
abundance
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
142.119
141.633
134.425
128.418
128.294
127.989
127.455
126.740
126.568
78.123
77.475
77.160
76.845
52.608
31.804
29.449
29.058
27.771
22.708
14.213
X : parts per Million : Carbon13


OH
Ph
Ph
6e
7.91
1.90
1.05
1.05
1.04
1.05
1.00
2.11
4.15
3.11
3.0
2.0
1.0
0
abundance
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : Proton


OH
Ph
Ph
Ph
Ph
E-6h
9.36
2.00
2.03
2.32
0.98
1.00
0.98
0.98
0.91
abundance
X : parts per Million : Proton


OH
Ph
Ph
Ph
Ph
E-6h
abundance
0.3
0.2
0.1
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
142.033
141.003
137.095
133.556
129.210
128.666
128.559
128.530
128.102
127.665
127.606
126.809
126.498
77.811
77.413
77.160
76.907
58.494
X : parts per Million : Carbon13


OH
Ph
Ph
Ph
6h
22.57
1.00
0.37
0.37
1.00
1.38
1.01
0.37
0.34
0.93
abundance
5.0
4.0
3.0
2.0
1.0
0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : Proton


OH
Ph
Ph
Ph
6h
abundance
0.3
0.2
0.1
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
132.428
130.639
128.792
128.676
128.578
128.539
128.491
128.267
128.121
128.063
127.567
127.081
126.809
126.741
126.508
78.609
77.831
77.413
77.160
76.907
58.514
52.467
X : parts per Million : Carbon13