Supporting Information

Heavy-metal-free desulfonylative Giese-type reaction of benzothiazole sulfones under visible-light conditions

Tetsuya Sengoku,*[a] Daichi Ogawa,[a] Haruka Iwama,[a] Toshiyasu Inuzuka[b] and Hidemi Yoda*[a]

[a] *Department of Applied Chemistry, Faculty of Engineering, Shizuoka University, 3-5-1 Johoku, Naka-ku, Hamamatsu 432-8561, Japan*
[b] *Division of Instrumental Analysis, Life Science Research Center, Gifu University, 1-1 Yanagido, Gifu 501-1193, Japan.*

E–mail: sengoku.tetsuya@shizuoka.ac.jp, yoda.hidemi@shizuoka.ac.jp

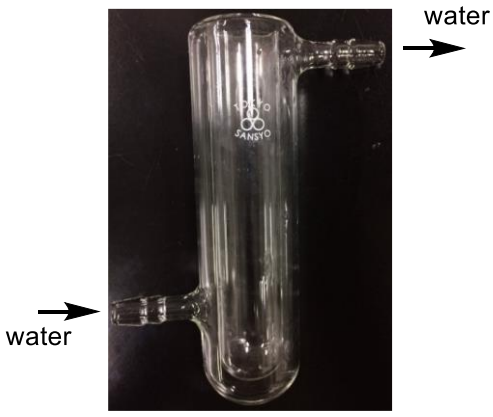
The following data are included in this material:

General methods:

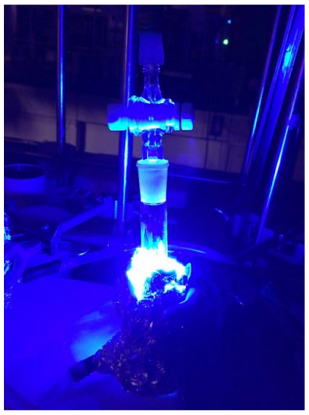
All solvents and reagents were of reagent grade quality and used without further purification unless otherwise stated. Dimethylsulfoxide (DMSO) and dichloromethane were dried over MS 4 Å under a nitrogen atmosphere. Tetrahydrofuran (THF) was dried over Na wire under a nitrogen atmosphere. Photochemical reactions were performed in a 20 mL test tube which was set into a glass vessel cooled with water (15–20 °C). The cooling vessel was wrapped with a 4.8 W Blue LED strip (the absorption maximum is around 460 nm). The reaction temperature was kept around 25 °C. Reactions were monitored by thin layer chromatography using 0.25 mm Merck silica gel 60–F254 precoated silica gel plates by irradiation with UV light and/or by treatment with a solution of phosphomolybdic acid in EtOH followed by heating. Column chromatography was performed using silica gel 60N from Kanto Chemical Co. and eluting with the indicated solvent system. All new compounds were characterized by NMR, IR, and elemental analysis. The ^{1}H NMR spectra operating at the frequency of 300 MHz on a JEOL JNM–AL300 spectrometer were recorded in chloroform–*d* ($CDCl_3$) unless otherwise noted. The ^{13}C NMR spectra operating at the frequencies of 75 or 200MHz on a JEOL JNM–AL300 or a Bruker AVANCE III spectrometer, respectively, were recorded in chloroform–*d* ($CDCl_3$) unless otherwise noted. Chemical shifts are reported in parts per million (ppm) relative to TMS and the solvent used as internal standards, and the coupling constants are reported in hertz (Hz). Fourier transform infrared (FTIR) spectra were recorded on a JASCO FT/IR–4100 spectrometer. Elemental analyses were performed by JSL Model JM 10 instruments. UV-vis spectra were recorded on a JASCO V-630 spectrophotometer. Melting points were measured with a Yanaco MP–S3 micro melting point apparatus. Mass spectra were recorded on a Waters UPLC-MS. Redox potentials were measured by cyclic voltammetry on a Hokuto Denko potentiostat/galvanostat HAB-151A. Compounds **1a**,[1] **1b**,[2] **1c**,[3] **1d**, [4] **1h**,[5] **1i**,[6] **1j**,[7] and **1k**[8] were synthesized according to the literature.

Reaction apparatus for photochemical reactions:

(a) cooling vessel

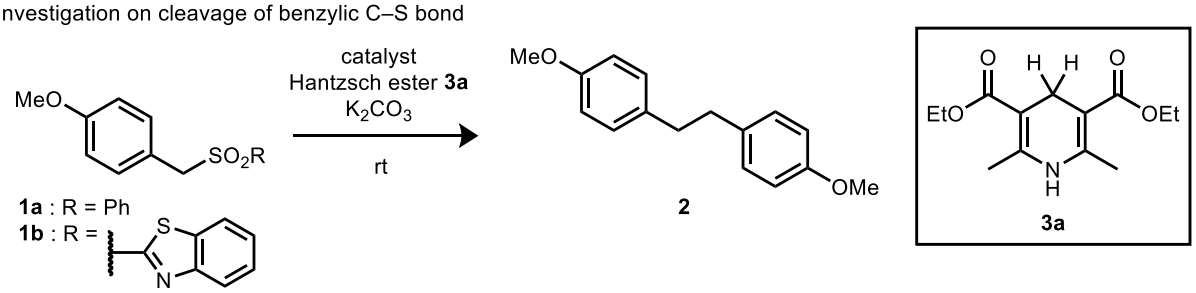


(b) exemplary reaction setup



Preliminary investigations on desulfonylative carbon–carbon bond formation:

(a) Investigation on cleavage of benzylic C–S bond



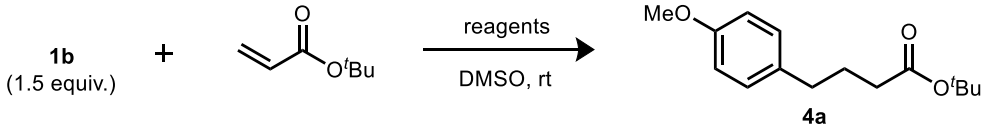
for **1a**

$Ru(bpy)_3Cl_2$ (1 mol %), **3a** (1.5 equiv.), pyridine, blue LEDs, 12 h	: >95% (recovery of **1a**)
Eosin Y (1 mol %), **3a** (1.5 equiv.), MeCN, blue LEDs, 12 h	: >95% (recovery of **1a**)
$Ir(ppy)_3$ (1 mol %), **3a** (1.5 equiv.), K_2CO_3 (1.8 equiv.), DMSO, blue LEDs, 12 h	: trace (**2**), 46% (recovery of **1a**)

for **1b**

$Ir(ppy)_3$ (1 mol %), **3a** (1.5 equiv.), K_2CO_3 (1.8 equiv.), DMSO, blue LEDs, 6 h	: 54% (**2**)
$Ir(ppy)_3$ (1 mol %), **3a** (1.5 equiv.), K_2CO_3 (1.8 equiv.), DMSO, in the dark, 22 h	: >95% (recovery of **1b**)

(b) Preliminary investigation on visible–light–induced desulfonylative Giese-type reaction



$Ir(ppy)_3$ (1 mol %), **3a** (1.5 equiv.), K_2CO_3 (1.8 equiv.), blue LEDs, 4.5 h	: 28%
$Ir(ppy)_3$ (none), **3a** (1.5 equiv.), K_2CO_3 (1.8 equiv.), blue LEDs, 7 h	: 45%
$Ir(ppy)_3$ (none), **3a** (1.5 equiv.), K_2CO_3 (1.8 equiv.), in the dark, 24 h	: 0%
$Ir(ppy)_3$ (none), **3a** (none), K_2CO_3 (1.8 equiv.), blue LEDs, 24 h	: 0%
$Ir(ppy)_3$ (none), **3a** (0.3 equiv.), K_2CO_3 (1.8 equiv.), blue LEDs, 7 h	: 23%

Scheme S1. Reactions of **1** under visible-light conditions. (a) Desulfonylative dimerization of **1a**,**b**. (b) Desulfonylative Giese-type reaction of **1b** with *tert*-butyl acrylate. Product **4a** was obtained as an inseparable mixture with **2**. The yields were determined by ^1H NMR analysis.

Optimization of reaction conditions for desulfonylative Giese-type reaction using 1b:

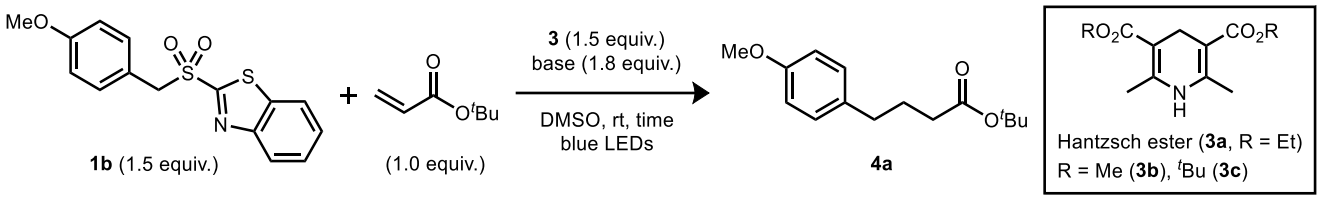


Table S1. Screening of additives for desulfonylative Giese-type reaction of **1b**.[a]

entry	**3**	base	time (h)[b]	**4a** (%)[c]
1	**3a**	K_2CO_3	7	45
2	**3a**	–	24	0
3	**3a**	Cs_2CO_3	12	0
4	**3a**	Na_2CO_3	24	40
5	**3a**	K_3PO_4	17	45
6	**3a**	K_2HPO_4	30	37
7	**3a**	K_2CO_3[d]	9	46
8	**3a**	TMG	15	37
9	**3a**	DBU	10	35
10	**3a**	DABCO	24	7
11	**3a**	pyridine	24	0
12	**3a**	Et_3N	24	0
13	**3b**	K_2CO_3	14	44
14	**3c**	K_2CO_3	24	44

[a] Reactions were carried out with **1b** (0.300 mmol), *tert*-butyl acrylate (0.200 mmol), **3a** (0.300 mmol), and K_2CO_3 (0.360 mmol) in DMSO (2.0 mL) at room temperature under blue LED irradiation. [b] The reaction mixture was allowed to stir until **1b** or **3** was completely consumed. [c] Product **4a** was obtained as an inseparable mixture with **2**. The yield was determined by ^{1}H NMR analysis. [d] 18-Crown-6 (0.1 equiv.) was added.

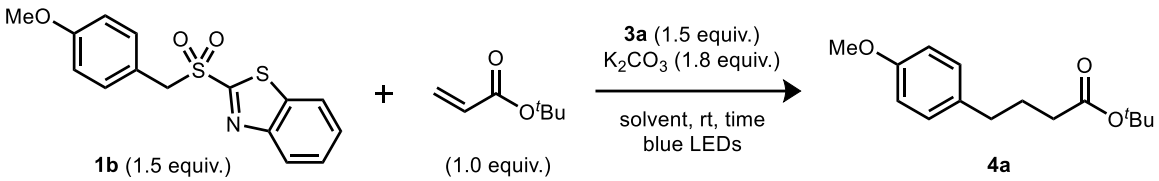


Table S2. Screening of solvents for desulfonylative Giese-type reaction of **1b**.[a]

entry	solvent	time (h)[b]	**4a** (%)[c]
1	DMSO	7	45
2	DMF	30	10
3	DMAA	30	27
4	DMI	30	19
5	CH_2Cl_2	24	0
6	THF	24	0
7	toluene	24	0
8	MeCN	24	0
9	DMSO/2-PrOH (10/1)	15	21
10	DMSO/*t*-BuOH (10/1)	12	29

[a] Reactions were carried out with **1b** (0.300 mmol), *tert*-butyl acrylate (0.200 mmol), **3a** (0.300 mmol), and K_2CO_3 (0.360 mmol) in DMSO (2.0 mL) at room temperature under blue LED irradiation. [b] The reaction mixture was allowed to stir until **1b** or **3a** was completely consumed. [c] Product **4a** was obtained as an inseparable mixture with **2**. The yield was determined by ^{1}H NMR analysis.

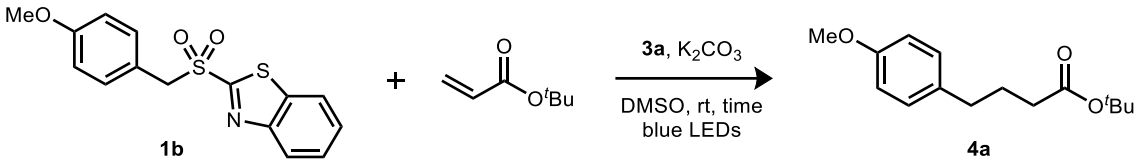


Table S3. Screening of reagent quantities for desulfonylative Giese-type reaction of **1b**.[a]

entry	**1b** (eq)	acrylate (eq)	**3a** (eq)	K_2CO_3 (eq)	DMSO (M of **1b**)	time (h)[b]	**4a** (%)[c]	**2** (%)
1	1.5	1.0	0.30	1.8	0.15	7	23	40
2	1.5	1.0	1.5	1.8	0.15	7	45	18
3	1.5	1.0	1.5	3.6	0.15	9	29	21
4	1.5	1.0	3.0	1.8	0.15	18	59	21
5	1.0	3.0	3.0	1.8	0.10	10	44	2
6	1.0	3.0	3.0	3.0	0.03	7	50	2
7	1.0	1.5	2.0	2.0	0.03	8	40	8
8	1.0	3.0	5.0	5.0	0.03	5	71	3

[a] Reactions were carried out with **1b** (0.300 mmol), *tert*-butyl acrylate (0.200 mmol), **3a** (0.300 mmol), and K_2CO_3 (0.360 mmol) in DMSO (2.0 mL) at room temperature under blue LED irradiation. [b] The reaction mixture was allowed to stir until **1b** or **3a** was completely consumed. [c] Product **4a** was obtained as an inseparable mixture with **2**. The yield was determined by ^{1}H NMR analysis.

Optimization of reagent quantities for desulfonylative Giese-type reaction using 1p:

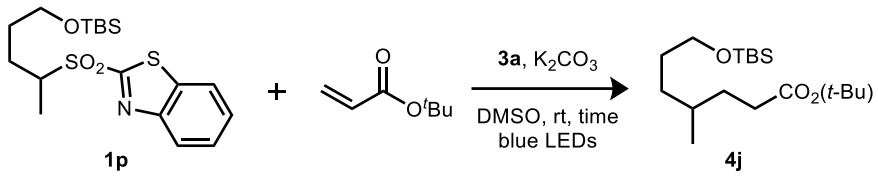


Table S4. Screening of reagent quantities for desulfonylative Giese-type reaction of **1p**.

entry	acrylate (eq)	**3a** (eq)	K_2CO_3 (eq)	DMSO (M of **1p**)	time (h)[a]	**4j** (%)
1	3.0	5.0	5.0	0.03	7	68
2	2.0	5.0	5.0	0.03	6	70
3	2.0	2.0	2.0	0.03	24	60
4	2.0	2.0	2.0	0.10	24	49
5	2.0	2.0	3.0	0.10	24	50
6	1.5	2.0	2.0	0.03	5	80
7	1.2	2.0	2.0	0.03	5	78

[a] The reaction mixture was allowed to stir until **1p** or **3** was completely consumed.

Cyclic voltammetry:

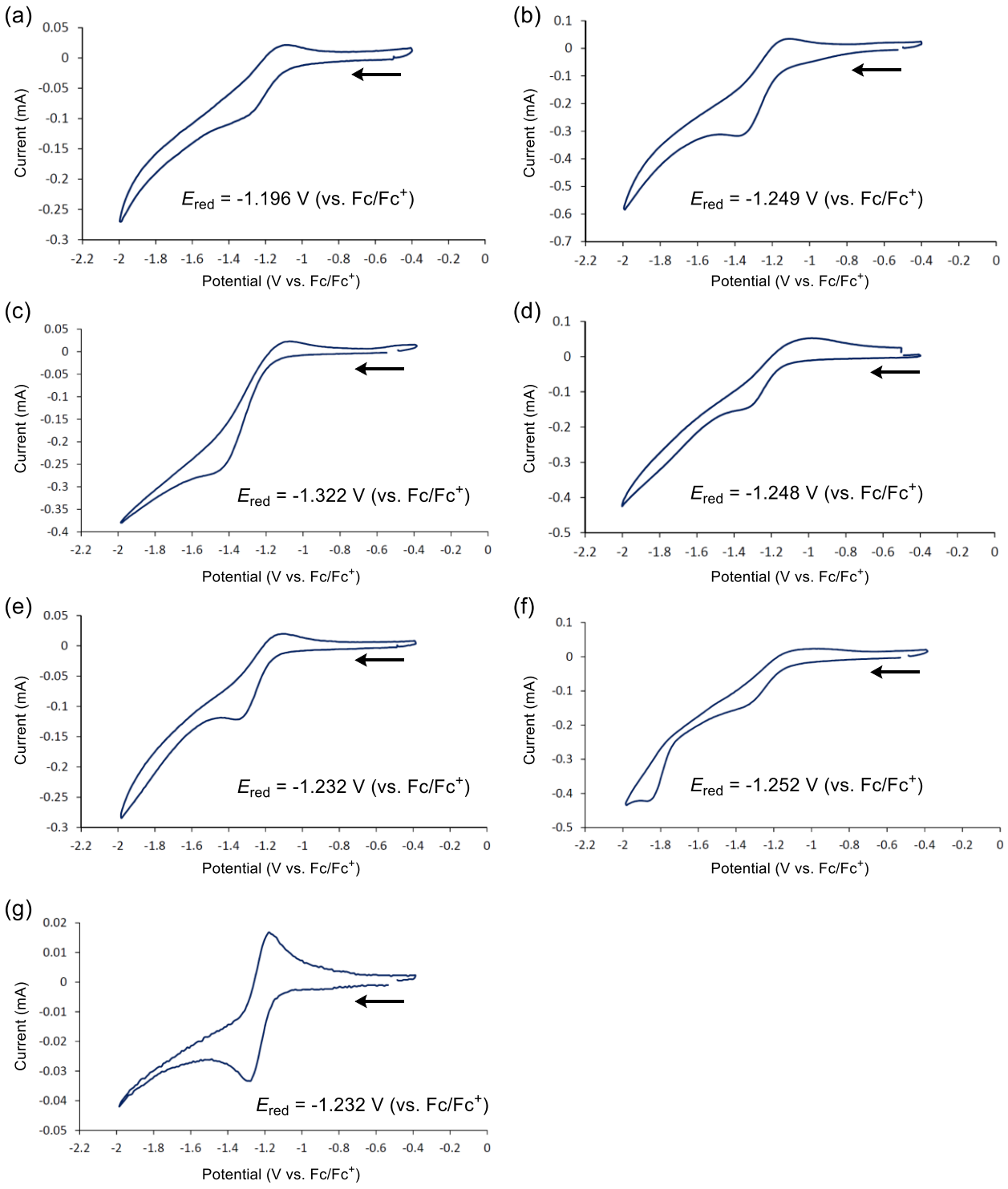


Figure S1. Cyclic voltammograms of (a) **1a**, (b) **1b**, (c) **1c**, (d) **1d**, (e) **1e**, (f) **1f**, and (g) **1g** in DMSO with a 0.1 M *n*-Bu_4NPF_6 as a supporting electrolyte. Working electrode: Pt wire; Counter electrode: Pt wire; Reference electrode: Ag/AgCl; Scan rate: 0.05 V/s. Ferrocene/ferrocenium ion redox couple was used as an external reference.

Radical inhibition experiment:

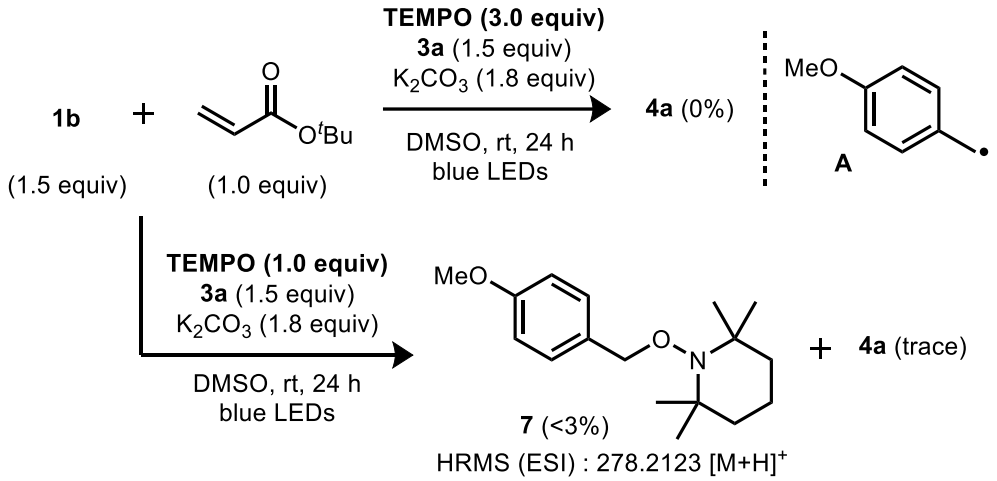


Figure S2. Radical inhibition experiment using TEMPO.

UV–Vis spectra:

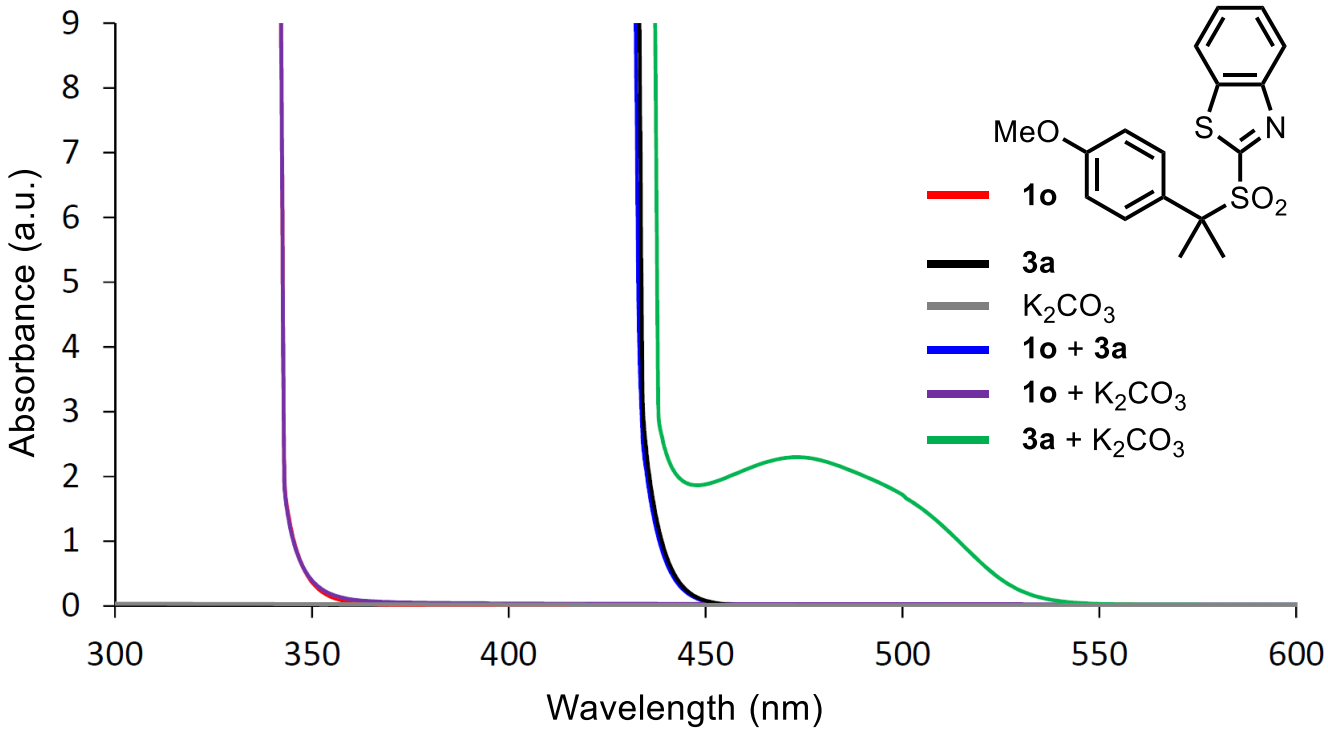


Figure S3. UV-vis absorption spectra of **1o** (red line, 0.03 M in DMSO), **3a** (black line, 0.1 M in DMSO), K_2CO_3 (gray line, 0.05 M in DMSO), a 1:3 mixture of **1o** and **3a** (blue line, 0.03 M in DMSO), a 1:3 mixture of **1o** and K_2CO_3 (purple line, 0.03 M in DMSO), and a 1:1 mixture of **3a** and K_2CO_3 (green line, 0.1 M in DMSO).

Light on-off experiments:

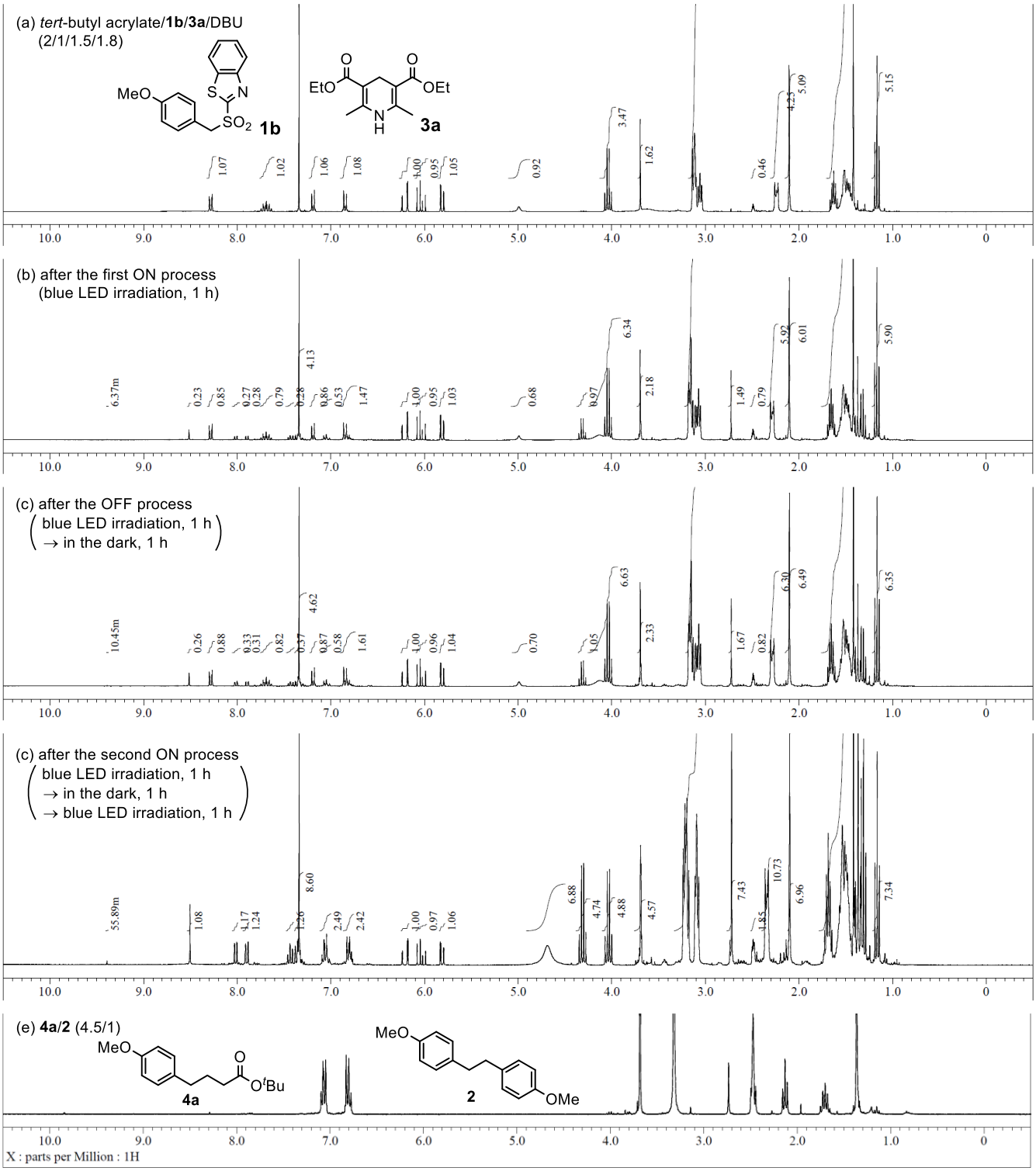


Figure S4. ^{1}H NMR spectra (300 MHz, DMSO-d_6 with benzene as an internal standard) (a) *tert*-butyl acrylate/**1b**/**3a**/DBU (2/1/1.5/1.8, 0.1 M for **1b**), (b) after the first irradiation of blue LEDs for 1h (ON), (c) after standing in the dark for 1h (ON-OFF), (d) after the second irradiation of blue LEDs for 1h (ON-OFF-ON), (e) the mixture of **4a**/**2** (4.5/1).

NMR experiments:

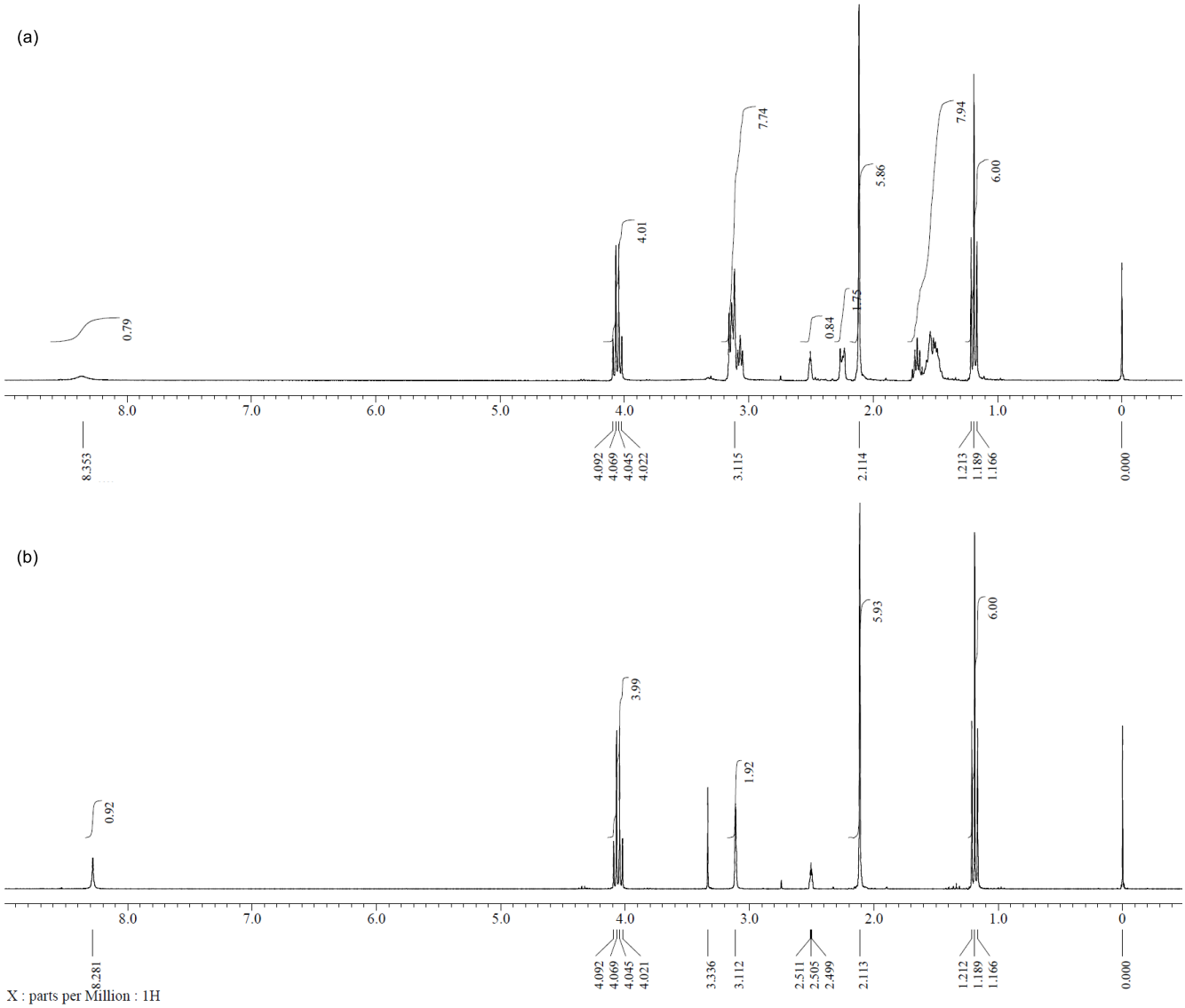
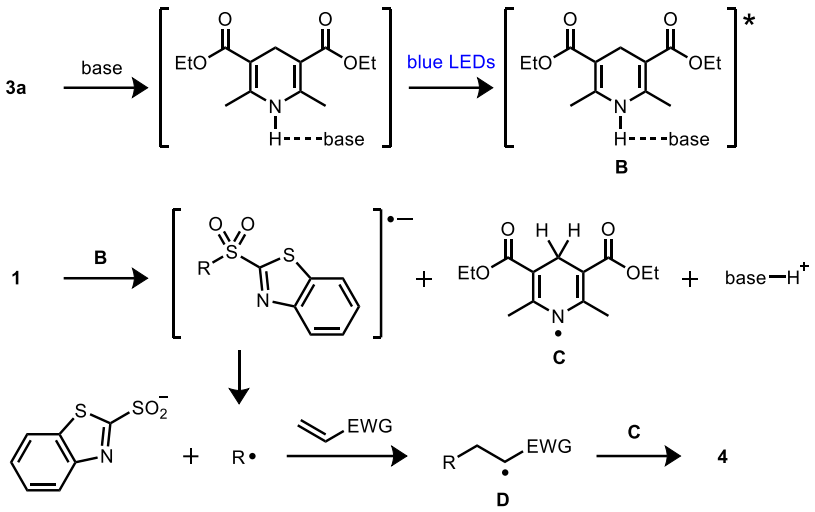


Figure S5. ^{1}H NMR spectra (300 MHz, DMSO-d_6) (a) the mixture of **3a**/DBU (1/1/, 0.1 M), (b) **3a** (0.1 M).

Proposed reaction mechanism:



Scheme S2. Proposed mechanism of desulfonylative Giese-type reaction of **1**.

Experimental procedures and characterization data:

Synthesis and characterization of thiazole sulfone 1e

To a solution of 4-methoxybenzyl clorode (314 mg, 2.00 mmol) in water (4.0 mL) was added 2-thiazolethiol (234 g, 2.00 mmol) and triethylamine (216 mg, 2.14 mmol). After stirring the solution for 3 hours at the same temperature, the reaction mixture was extracted with EtOAc (10 mL). The organic extract was dried over Na_2SO_4, filtered, and concentrated in vacuo to give a crude material. This material was roughly purified by column chromatography (silica gel, hexane/EtOAc = 15/1 to 10/1 to 8/1 to 6/1) to give a crude material (324 mg) including a sulfide as a white solid, which was used in the following reaction without further purification: R_f = 0.53 (silica gel, hexane/EtOAc = 3/1).

To a solution of the crude material (324 mg) in dichloromethane (6.0 mL) was added *m*-chloroperbenzoic acid (65%, 669 mg, 2.52 mmol) at 0 °C under a nitrogen atmosphere. The resulting suspension was warmed to room temperature and stirred for 18 h. The reaction was then quenched by addition of saturated aqueous $Na_2S_2O_3$ (10 mL), and the resulting mixture was extracted with EtOAc (15 mL). The combined organic extract was washed with saturated aqueous $NaHCO_3$ (2×10 mL) and brine (10 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo to give a crude material. This material was purified by column chromatography (silica gel, hexane/EtOAc = 5/1 to 3/1 to 1/1) to give **1e** (327 mg, 61%) as a white solid: R_f = 0.15 (silica gel, hexane/EtOAc = 3/1); m.p. 99–101 °C; IR (KBr) 3127, 3010, 2987, 2968, 2935, 2839, 1610, 1514, 1471 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.08 (d, J = 3.0 Hz, 1H), 7.67 (d, J = 3.0 Hz, 1H), 7.10 (m, 2H), 6.80 (m, 2H), 4.60 (s, 2H), 3.78 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.5, 160.2, 145.0, 132.1, 126.6, 118.5, 114.2, 60.6, 55.2. Anal. Calcd for $C_{11}H_{11}NO_3S_2$: C, 49.05; H, 4.12; N, 5.20. Found: C, 48.95; H, 5.39; N, 4.20.

Synthesis and characterization of pyridothiazole sulfone 1f

To a solution of 4-methoxybenzyl alcohol (476 mg, 3.44 mmol) in tetrahydrofuran (34 mL) were added

thiazolo[5,4-*b*]pyridine-2(1*H*)-thione (579 mg, 3.44 mmol), triphenylphosphine (1.26 g, 4.82 mmol), and diisopropyl azodicarboxylate (1.0 mL, 5.16 mmol) at 0 °C under a nitrogen atmosphere. The resulting solution was warmed to room temperature and stirred for 12 h. The reaction was then quenched by addition of water (20 mL), and the resulting mixture was extracted with EtOAc (20 mL). The organic extract was washed with brine (30 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo to give a crude material. This material was roughly purified by column chromatography (silica gel, hexane/EtOAc = 3/1 to 2/1) to give a crude material (755 mg) including a sulfide as a white solid, which was used in the following reaction without further purification: R_f = 0.30 (silica gel, hexane/EtOAc = 4/1).

To a solution of the crude material (755 mg) in dichloromethane (8.7 mL) was added added *m*-chloroperbenzoic acid (65%, 1.39 g, 5.23 mmol) at 0 °C under a nitrogen atmosphere. The resulting suspension was warmed to room temperature and stirred for 4 h. The reaction was then quenched by addition of saturated aqueous $Na_2S_2O_3$ (15 mL), and the resulting mixture was extracted with EtOAc (2×20 mL). The combined organic extract was washed with saturated aqueous $NaHCO_3$ (3×20 mL) and brine (20 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo to give a crude material. This material was purified by column chromatography (silica gel, hexane/EtOAc = 2/1 to 1/1) to give **1f** (549 mg, 50% in 2 steps) as a white solid: R_f = 0.50 (silica gel, hexane/EtOAc = 1/1); m.p. 148–150 °C; IR (KBr) 3068, 2983, 2935, 2844, 1606, 1512, 1464 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.77 (dd, *J* = 4.5, 1.5 Hz, 1H), 8.51 (dd, *J* = 8.4, 1.5 Hz, 1H), 7.61 (dd, J = 8.4, 4.5 Hz, 1H), 7.19 (m, 2H), 6.80 (m, 2H), 4.70 (s, 2H), 3.77 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.5, 160.4, 159.2, 150.2, 145.8, 132.8, 132.3, 122.7, 117.6, 114.5, 60.2, 55.2. Anal. Calcd for $C_{14}H_{12}N_2O_3S_2$: C, 52.49; H, 3.78; N, 8.74. Found: C, 52.10; H, 4.15; N, 8.97.

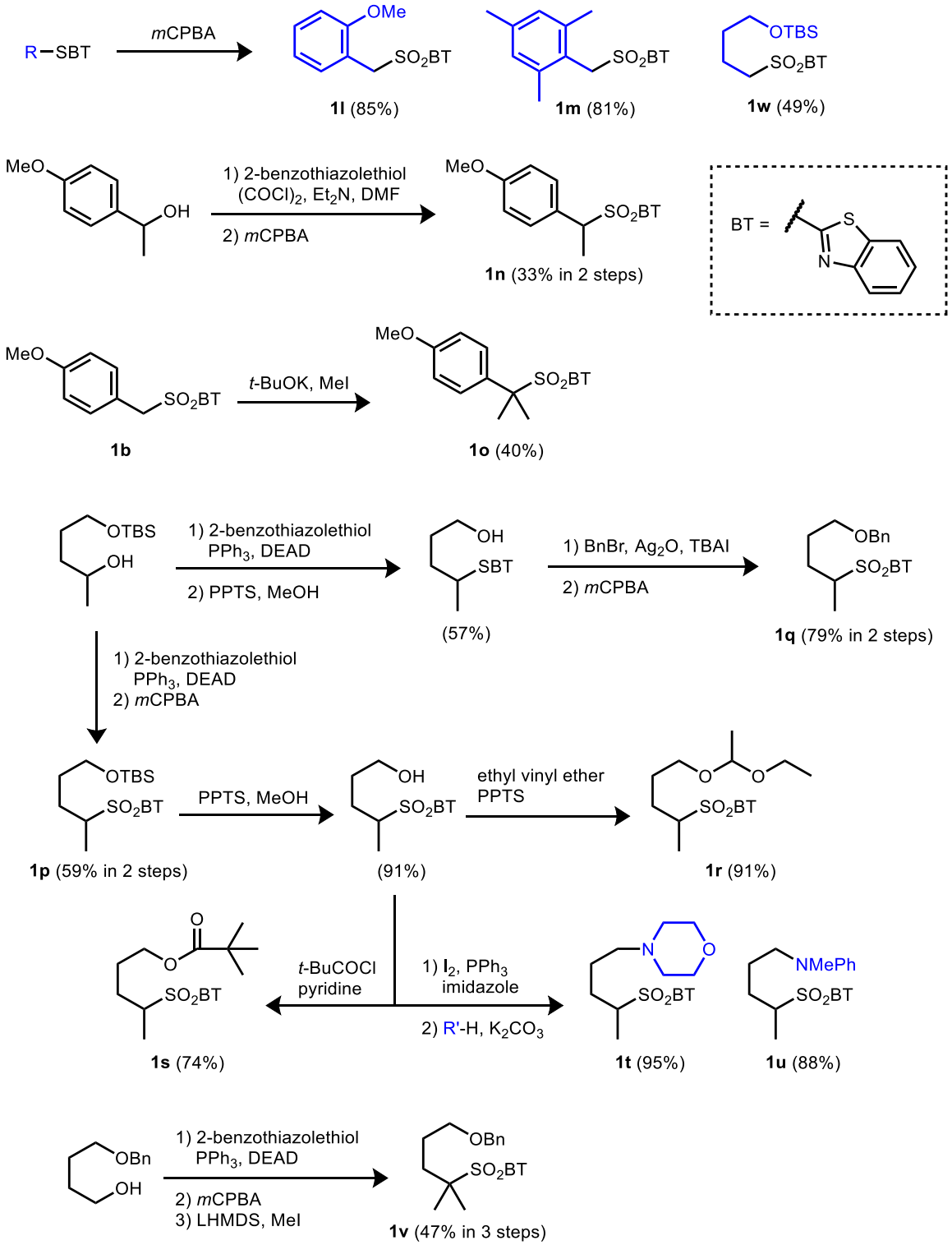
Synthesis and characterization of 4-nitrophenyl sulfone 1g

To a solution of (4-methoxybenzyl)(4-nitrophenyl)sulfane[9] (614 mg, 2.23 mmol) in dichloromethane

(11 mL) was added added *m*-chloroperbenzoic acid (65%, 1.24 g, 4.68 mmol) at 0 °C under a nitrogen atmosphere. The resulting suspension was warmed to room temperature and stirred for 7 h. The reaction was then quenched by addition of saturated aqueous $Na_2S_2O_3$ (10 mL), and the resulting mixture was extracted with EtOAc (20 mL). The combined organic extract was washed with saturated aqueous $NaHCO_3$ (2×20 mL) and brine (20 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo to give a crude material. This material was purified by column chromatography (silica gel, hexane/EtOAc = 7/1 to 5/1 to 3/1 to 2/1) to give **1f** (140 mg, 20%) as a white solid: R_f = 0.43 (silica gel, hexane/EtOAc = 2/1); m.p. 137–140 °C; IR (KBr) 3112, 3064, 3037, 2949, 2910, 2833, 1608, 1537, 1512 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.28 (d, *J* = 9.0 Hz, 2H), 7.80 (d, *J* = 9.0 Hz, 2H), 7.00 (d, *J* = 9.0 Hz, 2H), 6.80 (d, *J* = 9.0 Hz, 2H), 4.32 (s, 2H), 3.80 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.3, 150.7, 143.5, 132.0, 130.2, 123.9, 118.9, 114.3, 62.2, 55.3. Anal. Calcd for $C_{14}H_{13}NO_5S$: C, 54.72; H, 4.26; N, 4.56. Found: C, 54.43; H, 3.97; N, 4.17.

Syntheses of benzothiazole sulfones 1l–w

Synthetic methods for benzothiazole sulfones **1l**–**w** are summarized in the following scheme.



Synthesis and characterization of 1l

To a solution of 2-((2-methoxybenzyl)thio)benzo[*d*]thiazole[10] (1.21 g, 4.23 mmol) in dichloromethane (14 mL) was added *m*-chloroperbenzoic acid (65%, 2.36 g, 8.88 mmol) at 0 °C under a nitrogen atmosphere. The resulting suspension was warmed to room temperature and stirred for 18 h. The reaction was then quenched by addition of saturated aqueous $Na_2S_2O_3$ (20 mL), and the resulting mixture was extracted with EtOAc (2×20 mL). The combined organic extract was washed with saturated aqueous $NaHCO_3$ (3×20 mL) and brine (20 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo to give a crude material. This material was purified by recrystallization from EtOAc-hexane to give **1l** (1.16 g, 85%) as a white solid: R_f = 0.33 (silica gel, hexane/EtOAc = 2/1); m.p. 137–140 °C; IR (KBr) 3070, 3012, 2978, 2937, 2843, 1601, 1495, 1463 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.25 (m, 1H), 7.95 (m, 1H), 7.66–7.55 (m, 2H), 7.33–7.27 (m, 2H), 6.91 (td, *J* = 7.5, 0.9 Hz, 1H), 6.72 (d, *J* = 8.1 Hz, 1H), 4.83 (s, 2H), 3.39 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.4, 157.9, 152.6, 137.3, 132.6, 130.9, 127.8, 127.5, 125.4, 122.1, 120.8, 115.2, 110.6, 55.7, 55.2. Anal. Calcd for $C_{15}H_{13}NO_3S_2$: C, 56.41; H, 4.10; N, 4.39. Found: C, 56.07; H, 4.39; N, 4.15.

Synthesis and characterization of 1m

According to the synthetic procedure for **1l**, a solution of 2-((2,4,6-trimethylbenzyl)thio)benzo[*d*]thiazole[11] (581 mg, 1.94 mmol) and *m*-chloroperbenzoic acid (65%, 1.08 g, 4.07 mmol) was stirred at room temperature for 5 h. The crude product was purified by recrystallization from EtOAc-hexane to give **1m** (524 mg, 81%) as a pale yellow solid: R_f = 0.050 (silica gel, hexane/EtOAc = 1/1); m.p. 142–144 °C; IR (KBr) 3068, 3014, 2985, 2951, 2858, 1608, 1495, 1468 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.26 (dd, *J* = 7.8, 1.2 Hz, 1H), 8.01 (dd, J = 7.8, 1.5 Hz, 1H), 7.69–7.57 (m, 2H), 6.91 (s, 2H), 4.91 (s, 2H), 2.40 (s, 6H), 2.28 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.7, 152.7, 139.5, 139.1, 137.1, 129.6, 128.0, 127.6, 125.5, 122.3, 120.2, 55.7, 21.0, 20.5. Anal. Calcd for

$C_{17}H_{17}NO_2S_2$: C, 61.60; H, 5.17; N, 4.23. Found: C, 61.51; H, 5.05; N, 4.11.

Synthesis and characterization of 1n

To a solution of DMF (221 mg, 3.02 mmol) in tetrahydrofuran (8.0 mL) was added oxalyl chloride (525 mg, 3.02 mmol) at 0 °C under a nitrogen atmosphere. After stirring the solution for 30 min at the same temperature, 1-(4-methoxyphenyl)ethan-1-ol (609 mg, 4.00 mmol), triethylamine (838 mg, 8.28 mmol), and 2-benzothiazolethiol (796 mg, 2.77 mmol) were added. The resulting solution was warmed to room temperature and stirred for 24 h. The reaction was then quenched by addition of H_2O (10 mL), and the resulting mixture was extracted with EtOAc (10 mL). The combined organic extract was washed with brine (10 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The resultant mixture was roughly purified by column chromatography (silica gel, hexane/EtOAc = 15/1 to 10/1) to give a crude material (939 mg) including a sulfide as a yellow solid, which was used in the following reaction without further purification: R_f = 0.66 (silica gel, hexane/EtOAc = 3/1).

To a solution of the crude material (939 mg, <3.12 mmol) in dichloromethane (10 mL) was added *m*-chloroperbenzoic acid (65%, 1.74 g, 6.55 mmol) at -20 °C under a nitrogen atmosphere. The resulting suspension was warmed to room temperature and stirred for 5 h. The reaction was then quenched by addition of saturated aqueous $Na_2S_2O_3$ (15 mL), and the resulting mixture was extracted with EtOAc (10 mL). The combined organic extract was washed with saturated aqueous $NaHCO_3$ (15 mL) and brine (15 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo to give a crude material. This material was purified by column chromatography (silica gel, hexane/EtOAc = 10/1 to 6/1 to 3/1 to $CHCl_3$/MeOH = 10/1 to 5/1) and recrystallization from EtOAc-hexane to give **1n** (341 mg, 33% in 2 steps) as a white solid: R_f = 0.050 (silica gel, hexane/EtOAc = 3/1); m.p. 126–127 °C; IR (KBr) 3068, 3008, 2991, 2978, 2941, 2846, 1604, 1510, 1464 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.24 (m, 1H), 7.92 (m, 1H), 7.66–7.53 (m, 2H), 7.26–7.21 (m, 2H), 6.81–6.76 (m, 2H), 4.81 (q, J = 7.5 Hz, 1H), 3.76 (s, 3H), 1.86 (d, J =

7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.2, 160.2, 152.6, 137.1, 130.8, 127.8, 127.4, 125.4, 123.7, 122.2, 114.1, 64.7, 55.2, 14.1. Anal. Calcd for $C_{16}H_{15}NO_3S_2$: C, 57.64; H, 4.53; N, 4.20. Found: C, 57.53; H, 4.30; N, 4.14.

Synthesis and characterization of 1o

To a solution of **1b** (734 mg, 2.30 mmol) in *N*,*N*-dimethylformamide (7.7 mL) was added potassium *tert*-butoxide (386 mg, 3.45 mmol) at -40 °C under a nitrogen atmosphere. After stirring the mixture for 1 h at the same temperature, iodomethane (0.46 mL, 9.20 mmol) was added. The mixture was stirred for 3 h at the same temperature, and then potassium *tert*-butoxide (734 mg, 2.30 mmol) was added. The resulting mixture was stirred for additional 1 h, and iodomethane (0.46 mL, 9.20 mmol) was added to the resulting solution. After stirring the mixture for 20 h at the same temperature, potassium *tert*-butoxide (129 mg, 1.15 mmol) was added. The resulting mixture was stirred for additional 1 h, and iodomethane (0.23 mg, 4.60 mmol) was added to the resulting solution. After stirring the mixture for 14 h at the same temperature, the reaction was then quenched by addition of saturated aqueous NH_4Cl (15 mL), and the resulting mixture was extracted with EtOAc (2×15 mL). The combined organic extract was washed with saturated aqueous water (20 mL) and brine (20 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo to give a crude material. This material was purified by column chromatography (silica gel, hexane/EtOAc = 3/1) and recrystallization from EtOAc-hexane to give **1o** (321 mg, 40%) as a white solid: R_f = 0.40 (silica gel, hexane/EtOAc = 2/1); m.p. 131–133 °C; IR (KBr) 3082, 3066, 3051, 2992, 2968, 2935, 2834, 1604, 1511, 1468 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.23 (m, 1H), 7.87 (m, 1H), 7.63–7.50 (m, 2H), 7.39–7.34 (m, 2H), 6.79–6.74 (m, 2H), 3.76 (s, 3H), 2.02 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.2, 159.8, 152.5, 129.9, 127.64, 127.57, 127.3, 125.6, 121.9, 113.7, 67.4, 55.2, 22.7. Anal. Calcd for $C_{17}H_{17}NO_3S_2$: C, 58.77; H, 4.93; N, 4.03. Found: C, 58.56; H, 4.82; N, 4.06.

Synthesis and characterization of 1p

To a solution of 5-((*tert*-butyldimethylsilyl)oxy)pentan-2-ol[12] (2.02 g, 9.26 mmol) in tetrahydrofuran (23 mL) were added 2-benzothiazolethiol (2.47 g, 14.8 mmol), triphenylphosphine (3.88 g, 14.8 mmol), and diethyl azodicarboxylate (2.2 M in toluene, 4.2 mL, 9.24 mmol) at 0 °C under a nitrogen atmosphere. The resulting solution was warmed to room temperature and stirred for 42 h. The reaction was then quenched by addition of water (30 mL), and the resulting mixture was extracted with EtOAc (2×30 mL). The combined organic extract was washed with water (30 mL) and brine (30 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo to give a crude material. This material was purified by column chromatography (silica gel, hexane/EtOAc = 5/1, and silica gel, hexane/EtOAc = 20/1 to 10/1) to give a crude material (4.03 g) including a sulfide as a colorless oil, which was used in the following reaction without further purification: R_f = 0.30 (silica gel, hexane/EtOAc = 10/1).

To a solution of the crude material (4.03 g) in dichloromethane (22 mL) was added added *m*-chloroperbenzoic acid (65%, 6.13 g, 23.0 mmol) at 0 °C under a nitrogen atmosphere. The resulting suspension was warmed to room temperature and stirred for 12 h. The reaction was then quenched by addition of saturated aqueous $Na_2S_2O_3$ (30 mL), and the resulting mixture was extracted with EtOAc (2×30 mL). The combined organic extract was washed with saturated aqueous $NaHCO_3$ (4×30 mL) and brine (30 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo to give a crude material. This material was purified by column chromatography (silica gel, hexane/EtOAc = 10/1 to 5/1) to give **1p** (2.20 g, 59% in 2 steps) as a colorless oil: R_f = 0.36 (silica gel, hexane/EtOAc = 3/1); IR (NaCl) 2952, 2931, 2885, 2858, 1471 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.22 (m, 1H), 8.01 (m, 1H), 7.66–7.56 (m, 2H), 3.71–3.59 (m, 3H), 2.15 (m, 1H), 1.76–1.53 (m, 3H), 1.46 (d, J = 7.2 Hz, 3H), 0.80 (s, 9H), -0.011 (s, 3H), -0.014 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.1, 152.9, 136.9, 127.9, 127.5, 125.5, 122.2, 62.3, 59.7, 29.4, 25.83, 25.78, 18.1, 12.9, -5.5. Anal. Calcd for $C_{18}H_{29}NO_3S_2Si$: C, 54.10; H, 7.31; N, 3.50. Found: C, 53.97; H, 7.30; N, 3.67.

Synthesis and characterization of 1q via 4-(benzo[*d*]thiazol-2-ylthio)pentan-1-ol

To a solution of 5-((*tert*-butyldimethylsilyl)oxy)pentan-2-ol[12] (1.79 g, 8.20 mmol) in tetrahydrofuran (27 mL) were added 2-benzothiazolethiol (2.06 g, 12.3 mmol), triphenylphosphine (3.44 g, 13.1 mmol), and diethyl azodicarboxylate (2.2 M in toluene, 5.6 mL, 12.3 mmol) at 0 °C under a nitrogen atmosphere. The resulting solution was warmed to room temperature and stirred for 12 h. The reaction was then quenched by addition of water (30 mL), and the resulting mixture was extracted with EtOAc (30 mL). The organic extract was washed with water (35 mL) and brine (35 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo to give a crude material. This material was purified by column chromatography (silica gel, hexane/EtOAc = 50/1 to 30/1 to 10/1) to give a crude material (2.43 g) including a sulfide as a colorless oil, which was used in the following reaction without further purification: R_f = 0.30 (silica gel, hexane/EtOAc = 10/1).

To a solution of the sulfide (868 mg) in methanol (11 mL) was added pyridinium *p*-toluenesulfonate (PPTS, 119 mg, 0.472 mmol) at room temperature. After stirring the solution for 24 h, the reaction mixture was concentrated under reduced pressure. Then, water (30 mL) was added to the residue and the resulting solution was extracted with EtOAc (20 mL). The organic extract was washed with brine (30 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo to give a crude material. This material was purified by column chromatography (silica gel, hexane/EtOAc = 5/1 to 3/1 to 2/1 to 1/2) to give 4-(benzo[*d*]thiazol-2-ylthio)pentan-1-ol (478 mg, 57% in 2 steps) as a colorless oil: R_f = 0.47 (silica gel, hexane/EtOAc = 1/1); IR (NaCl) 3377, 2927, 2868, 1454 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.87 (dd, J = 8.1, 0.6 Hz, 1H), 7.73 (dt, J = 8.1, 0.6 Hz, 1H), 7.40 (m, 1H), 7.28 (m, 1H), 4.08 (m, 1H), 3.80–3.68 (m, 2H), 3.11 (brs, 1H), 2.01 (m, 1H), 1.86–1.69 (m, 3H), 1.48 (d, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.1, 152.9, 134.9, 126.0, 124.3, 121.2, 120.9, 61.8, 43.0, 33.5, 29.3, 20.5. Anal. Calcd for $C_{12}H_{15}NOS_2$: C, 56.88; H, 5.97; N, 5.53. Found: C, 56.50; H, 6.30; N, 5.62.

To a solution of 4-(benzo[*d*]thiazol-2-ylthio)pentan-1-ol (464 mg, 1.83 mmol) in dichloromethane (6.1 mL) were added Ag_2O (764 mg, 3.29 mmol), benzyl bromide (0.43 mL, 3.66 mmol), and tetra(*n*-butyl)ammonium iodide (169 mg, 0.458 mmol) at room temperature under a nitrogen atmosphere. After stirring the suspension for 24 h, the reaction mixture was filtered with a pad of Celite and the filtrate was concentrated in vacuo to give a crude material. This material was purified by column chromatography (silica gel, hexane/EtOAc = 15/1 to 10/1 to 5/1 to 3/1) to give the corresponding benzyl ether (569 mg) as a colorless oil: R_f = 0.40 (silica gel, hexane/EtOAc = 10/1).

To a solution of the benzyl ether (478 mg) in dichloromethane (4.6 mL) was added added *m*-chloroperbenzoic acid (65%, 738 mg, 2.78 mmol) at 0 °C under a nitrogen atmosphere. The resulting suspension was warmed to room temperature and stirred for 5 h. The reaction was then quenched by addition of saturated aqueous $Na_2S_2O_3$ (10 mL), and the resulting mixture was extracted with EtOAc (15 mL). The organic extract was washed with saturated aqueous $NaHCO_3$ (4×15 mL) and brine (15 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo to give a crude material. This material was purified by column chromatography (silica gel, hexane/EtOAc = 4/1 to 3/1) to give **1q** (452 mg, 79% in 2 steps) as a colorless oil: R_f = 0.42 (silica gel, hexane/EtOAc = 2/1); IR (NaCl) 3086, 3062, 3030, 2937, 2862, 1469 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.21 (m, 1H), .7.99 (m, 1H), 7.65–7.55 (m, 2H), 7.33–7.25 (m, 5H), 4.44 (s, 2H), 3.65 (m, 1H), 3.47 (t, *J* = 5.7 Hz, 2H), 2.21 (m, 1H), 1.88–1.63 (m, 3H), 1.45 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.9, 152.8, 138.1, 136.8, 128.2, 127.8, 127.5, 127.4, 125.4, 122.2, 72.8, 69.3, 59.5, 26.5, 26.0, 12.9. Anal. Calcd for $C_{19}H_{21}NO_3S_2$: C, 60.77; H, 5.64; N, 3.73. Found: C, 60.93; H, 5.71; N, 3.86.

Synthesis and characterization of 1r via 4-(benzo[*d*]thiazol-2-ylsulfonyl)pentan-1-ol

To a solution of **1p** (839 mg, 2.10 mmol) in methanol (11 mL) was added pyridinium *p*-toluenesulfonate (PPTS, 106 mg, 0.420 mmol) at room temperature. After stirring the solution for 70 h, the reaction

mixture was concentrated under reduced pressure. Then, water (10 mL) was added to the residue and the resulting solution was extracted with EtOAc (2×10 mL). The combined organic extract was washed with water (10 mL) and brine (10 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo to give a crude material. This material was purified by column chromatography (silica gel, hexane/EtOAc = 3/1 to 1/2) to give 4-(benzo[*d*]thiazol-2-ylsulfonyl)pentan-1-ol (545 mg, 91%) as a colorless oil: R_f = 0.33 (silica gel, hexane/EtOAc = 1/2); IR (NaCl) 3548, 3410, 2939, 2875, 1469 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.23 (m, 1H), 8.03 (m, 1H), 7.67–7.57 (m, 2H), 3.73–3.61 (m, 3H), 2.27–2.16 (m, 1H), 1.96 (s, 1H), 1.85–1.61 (m, 3H), 1.46 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.9, 152.8, 136.8, 127.9, 127.6, 125.4, 122.2, 61.9, 59.5, 29.2, 25.5, 13.1. Anal. Calcd for $C_{12}H_{15}NO_3S_2$: C, 50.51; H, 5.30; N, 4.91. Found: C, 50.14; H, 5.68; N, 5.22.

To a solution of 4-(benzo[*d*]thiazol-2-ylsulfonyl)pentan-1-ol (328 mg, 1.15 mmol) in dichloromethane (5.4 mL) were added ethyl vinyl ether (166 mg, 2.30 mmol) and PPTS (57.7 mg, 0.230 mmol) at room temperature under a nitrogen atmosphere. After stirring the solution for 3 h, the reaction mixture was concentrated under reduced pressure and water (10 mL) was added to the residue. The resulting material was extracted with EtOAc (2×10 mL). The combined organic extract was washed with water (10 mL) and brine (10 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo to give a crude material. This material was purified by column chromatography (silica gel, hexane/EtOAc = 3/1 to 1/1) to give **1r** (372 mg, 91%) as a colorless oil: R_f = 0.33 (silica gel, hexane/EtOAc = 2/1); IR (NaCl) 2979, 2935, 2875, 1469 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 1:1 mixture of diastereomers) δ 8.25–8.21 (m, 1H), 8.04–8.01 (m, 1H), 7.68–7.57 (m, 2H), 4.67–4.60 (m, 1H), 3.72–3.38 (m, 5H), 2.26–2.22 (m, 1H), 1.85–1.61 (m, 3H), 1.47 (d, *J* = 6.9 Hz, 3H), 1.25 (t, *J* = 5.4 Hz, 1.5H), 1.19 (d, *J* = 6.9 Hz, 1.5H), 1.16 (d, *J* = 7.2 Hz, 1.5H); ^{13}C NMR (75 MHz, $CDCl_3$, 1:1 mixture of diastereomers) δ 165.0, 152.9, 136.9, 127.9, 127.6, 125.5, 122.2, 99.6, 64.3, 64.2, 60.81, 60.77, 59.7, 59.6, 26.7, 26.09, 26.07, 19.72, 19.70, 15.3, 13.05, 13.03. Anal. Calcd for $C_{16}H_{23}NO_4S_2$: C, 53.76; H, 6.49; N, 3.92. Found: C, 54.03; H, 6.89; N, 3.87.

Synthesis and characterization of 1s

To a solution of 4-(benzo[*d*]thiazol-2-ylsulfonyl)pentan-1-ol (303 mg, 1.06 mmol) in dichloromethane (5.3 mL) were added pivaloyl chloride (257 mg, 2.13 mmol) and pyridine (168 mg, 2.13 mmol) at room temperature under a nitrogen atmosphere. After stirring the solution for 6 h, the reaction was quenched by addition of saturated aqueous $NaHCO_3$ (10 mL). The resulting mixture was extracted with EtOAc (2×50 mL). The combined organic extract was washed with saturated aqueous $NaHCO_3$ (4×10 mL), saturated aqueous Na_2CO_3 (4×10 mL) and brine (10 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo to give a crude material. This material was purified by column chromatography (silica gel, hexane/EtOAc = 5/1 to 3/1) to give **1s** (292 mg, 74%) as a colorless oil: R_f = 0.43 (silica gel, hexane/EtOAc = 2/1); IR (NaCl) 2974, 2939, 2898, 2875, 1712, 1471 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.23 (m, 1H), 8.03 (m, 1H), 7.68–7.57 (m, 2H), 4.07 (t, *J* = 6.0 Hz, 2H), 3.66 (m, 1H), 2.17 (m, 1H), 1.94-1.66 (m, 3H), 1.47 (d, *J* = 6.9 Hz, 3H), 1.12 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.3, 164.9, 152.9, 136.8, 128.0, 127.6, 125.5, 122.2, 63.3, 59.2, 38.6, 27.0, 25.8, 25.6, 12.9. Anal. Calcd for $C_{17}H_{23}NO_4S_2$: C, 55.26; H, 6.27; N, 3.79. Found: C, 55.21; H, 5.97; N, 3.82.

Synthesis and characterization of 1t

To a solution of 4-(benzo[*d*]thiazol-2-ylsulfonyl)pentan-1-ol (374 mg, 1.31 mmol) in acetonitrile/diethylether (4/1, 13 mL) were added triphenylphosphine (517 mg, 1.97 mmol), imidazole (250 mg, 3.67 mmol) and iodine (232 mg, 1.83 mmol) at 0 °C under a nitrogen atmosphere. The resulting solution was warmed to room temperature and stirred for 6 h. The reaction was then quenched by addition of saturated aqueous NH_4Cl (10 mL), and the resulting mixture was extracted with EtOAc (10 mL). The organic extract was washed with brine (10 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo to give a crude material. This material was purified by column chromatography (silica gel, hexane/EtOAc

= 7/1 to 4/1 to 1/1) to give the corresponding iodide (170 mg) as a colorless oil: R_f = 0.50 (silica gel, hexane/EtOAc = 2/1).

To a solution of the iodide (170 mg) in acetonitrile (4.8 mL) were added morpholine (50.2 mg, 0.576 mmol) and K_2CO_3 (79.6 mg, 0.576 mmol) at room temperature under a nitrogen atmosphere. The resulting solution was warmed to 60 °C and stirred for 24 h. The reaction was then quenched by addition of water (5 mL), and the resulting mixture was extracted with EtOAc (5 mL). The organic extract was washed with brine (5 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo to give a crude material. This material was purified by column chromatography (silica gel, hexane/EtOAc = 3/1 to 1/1 to $CHCl_3$/MeOH = 5/1) to give **1t** (162 mg, 95%) as a pale yellow oil: R_f = 0.27 (silica gel, $CHCl_3$/MeOH = 4/1); IR (NaCl) 2952, 2854, 2809, 1469 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.23 (m, 1H), 8.03 (m, 1H), 7.68–7.57 (m, 2H), 3.71–3.61 (m, 5H), 2.39–2.31 (m, 6H), 2.13 (m, 1H), 1.78–1.43 (m, 3H), 1.46 (d, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.1, 152.9, 136.9, 128.0, 127.6, 125.5, 122.3, 66.9, 59.5, 58.0, 53.6, 26.9, 23.3, 13.0. Anal. Calcd for $C_{16}H_{22}N_2O_3S_2$: C, 54.21; H, 6.26; N, 7.90. Found: C, 53.83; H, 6.28; N, 7.81.

Synthesis and characterization of 1u

According to the synthetic procedure for **1t**, a solution of 4-(benzo[*d*]thiazol-2-ylsulfonyl)pentan-1-ol (1.20 g, 4.21 mmol), triphenylphosphine (2.43 g, 9.26 mmol), imidazole (1.06 g, 15.6 mmol) and iodine (1.01 g, 7.99 mmol) in dichloromethane (14 mL) was stirred at room temperature for 24 h. The crude product was purified by column chromatography (silica gel, hexane/EtOAc = 5/1 to 3/1 to 2/1) to give the corresponding iodide (878 mg). A solution of the iodide (789 mg), *N*-methylaniline (321 mg, 3.00 mmol) and K_2CO_3 (414 mg, 3.00 mmol) in acetonitrile (6.7 mL) was stirred at 60 °C for 48 h. The crude product was purified by column chromatography (silica gel, hexane/EtOAc = 5/1 to 3/1 to 2/1) to give **1u** (664 mg, 88%) as a pale yellow solid: R_f = 0.33 (silica gel, hexane/EtOAc = 2/1); m.p. 67–69 °C; IR

(KBr) 3089, 3053, 2970, 2929, 2881, 2823, 2796, 1597, 1508, 1469 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.22 (m, 1H), 8.01 (m, 1H), 7.67–7.56 (m, 2H), 7.22–7.15 (m, 2H), 6.70–6.62 (m, 3H), 3.60 (m, 1H), 3.35–3.30 (m, 2H), 2.88 (s, 3H), 2.13 (m, 1H), 1.83–1.60 (m, 3H), 1.43 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.9, 152.9, 149.0, 136.9, 129.2, 127.9, 127.6, 125.5, 122.3, 116.4, 112.2, 59.7, 52.3, 38.4, 26.5, 23.8, 13.1. Anal. Calcd for $C_{19}H_{22}N_2O_2S_2$: C, 60.93; H, 5.92; N, 7.48. Found: C, 60.55; H, 5.61; N, 7.45.

Synthesis and characterization of 1v

To a solution of 4-(benzyloxy)butan-1-ol (798 mg, 4.24 mmol) in tetrahydrofuran (15 mL) were added 2-benzothiazolethiol (1.11 g, 6.64 mmol), triphenylphosphine (1.86 g, 7.08 mmol), and diethyl azodicarboxylate (2.2 M in toluene, 3.0 mL, 6.6 mmol) at 0 °C under a nitrogen atmosphere. The resulting solution was warmed to room temperature and stirred for 24 h. The reaction was then quenched by addition of water (20 mL), and the resulting mixture was extracted with EtOAc (2×20 mL). The combined organic extract was washed with water (20 mL) and brine (20 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo to give a crude material. This material was purified by column chromatography (silica gel, hexane/EtOAc = 8/1 to 5/1 to 3/1) to give the corresponding sulfide (1.10 g) as a colorless oil: R_f = 0.37 (silica gel, hexane/EtOAc = 12/1).

To a solution of the sulfide (1.10 g) in dichloromethane (11 mL) was added added *m*-chloroperbenzoic acid (65%, 1.59 g, 6.01 mmol) at 0 °C under a nitrogen atmosphere. The resulting suspension was warmed to room temperature and stirred for 5 h. The reaction was then quenched by addition of saturated aqueous $Na_2S_2O_3$ (20 mL), and the resulting mixture was extracted with EtOAc (2×20 mL). The combined organic extract was washed with saturated aqueous $NaHCO_3$ (4×20 mL) and brine (20 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo to give a crude material. This material was purified by column chromatography (silica gel, hexane/EtOAc = 5/1 to 3/1) to give the corresponding sulfone

(1.02 g) as a colorless oil: R_f = 0.50 (silica gel, hexane/EtOAc = 3/1).

To a solution of the sulfone (412 mg) in tetrahydrofuran (5.9 mL) was added lithium bis(trimethylsilyl)amide (0.31 M solution in tetrahydrofuran-hexane, 11 mL, 3.42 mmol) at -78 °C under a nitrogen atmosphere. After stirring the mixture for 30 min at the same temperature, iodomethane (0.28 mL, 4.56 mmol) was added. The mixture was warmed to room temperature and stirred for 5 h. Afterward, the reaction mixture was cooled to -78°C and lithium bis(trimethylsilyl)amide (0.31 M solution in tetrahydrofuran-hexane, 4.0 mL, 1.24 mmol) was added. The resulting mixture was stirred for additional 30 min at the same temperature and iodomethane (0.29 mL, 4.56 mmol) was added to the solution. The resulting solution was warmed to room temperature and stirred for 16 h. The reaction was quenched by addition of saturated aqueous NH_4Cl (15 mL), and the resulting mixture was extracted with EtOAc (20 mL). The organic extract was washed with saturated aqueous water (20 mL) and brine (20 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo to give a crude material. This material was purified by column chromatography (silica gel, hexane/EtOAc = 7/1 to 5/1 to 3/1) to give **1v** (311 mg, 47% in 3 steps) as a colorless oil: R_f = 0.38 (silica gel, hexane/EtOAc = 2/1); IR (NaCl) 3062, 3032, 2937, 2860, 1468 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.24 (m, 1H), 8.00 (m, 1H), 7.66–7.55 (m, 2H), 7.33–7.25 (m, 5H), 4.47 (s, 2H), 3.48 (t, J = 6.0 Hz, 2H), 2.03–1.97 (m, 2H), 1.79–1.71 (m, 2H), 1.51 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.9, 153.0, 138.2, 137.2, 128.3, 127.8, 127.5, 127.4, 125.6, 122.0, 72.9, 69.9, 65.0, 31.9, 24.2, 20.8. Anal. Calcd for $C_{20}H_{23}NO_3S_2$: C, 61.67; H, 5.95; N, 3.60. Found: C, 61.75; H, 5.75; N, 3.93.

Synthesis and characterization of 1w

According to the synthetic procedure for **1l**, a solution of 2-((4-((tert-butyldimethylsilyl)oxy)butyl)thio)benzo[*d*]thiazole[13] (1.21 g, 4.23 mmol) and *m*-chloroperbenzoic acid (65%, 899 mg, 3.38 mmol) was stirred at room temperature for 4 h. The crude product was purified by

column chromatography (silica gel, hexane/EtOAc = 10/1 to 5/1 to 3/1) to give **1w** (1.16 g, 85%) as a colorless oil: R_f = 0.47 (silica gel, hexane/EtOAc = 2/1); IR (NaCl) 2952, 2929, 2885, 2856, 1471 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.22 (m, 1H), 8.01 (m, 1H), 7.67–7.56 (m, 2H), 3.63–3.54 (m, 4H), 2.01–1.91 (m, 2H), 1.69–1.60 (m, 2H), 0.80 (s, 9H), 0.00 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.7, 152.7, 136.8, 128.0, 127.6, 125.5, 122.3, 62.0, 54.6, 31.0, 25.8, 19.4, 18.1, -5.5. Anal. Calcd for $C_{17}H_{27}NO_3S_2Si$: C, 52.95; H, 7.06; N, 3.63. Found: C, 53.02; H, 6.92; N, 3.70.

Desulfonylative dimerization

Benzothiazole sulfone **1b** (63.9 mg, 0.200 mmol), $Ir(ppy)_3$ (1.3 mg, 1 mol %), Hantzsch ester **3a** (76.0 mg, 0.300 mmol), and potassium carbonate (50.0 mg, 0.362 mmol) were dissolved in DMSO (2.0 mL). The mixture was degassed by three freeze-pump-thaw cycles. Afterward, the mixture was stirred and irradiated with blue LEDs at room temperature for 6 h. The reaction was then quenched by addition of water (20 mL), and the resulting mixture was extracted with EtOAc (3×20 mL). The combined organic extract was washed with water (20 mL) and brine (20 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo to give a crude material. This material was purified by column chromatography (silica gel, hexane/EtOAc = 50/1 to 25/1 to 15/1) to give **2**[14] (13.2 mg, 54%) as a white solid: R_f = 0.28 (silica gel, hexane/EtOAc = 10/1); m.p. 127–128°C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.09–7.07 (m, 4H), 6.83–6.80 (m, 4H), 3.79 (s, 6H), 2.83 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.8, 133.9, 129.3, 113.7, 55.2, 37.3.

General procedure for metal-free visible-light-induced desulfonylative Giese-type reaction

All the experiments for metal-free visible-light-induced desulfonylative Giese-type reaction were carried out as described in the following typical procedure. The synthesis of **5a** (via **4a**) was exemplified as follows.

Synthesis and characterization of 5a via 4a

Benzothiazole sulfone **1b** (63.1 mg, 0.198 mmol), *tert*-butyl acrylate (77.2 mg, 0.602 mmol), Hantzsch ester **3a** (252 mg, 0.995 mmol), and potassium carbonate (138 mg, 0.999 mmol) were dissolved in DMSO (6.0 mL). The mixture was degassed by three freeze-pump-thaw cycles. Afterward, the mixture was stirred and irradiated with blue LEDs at room temperature for 5 h. The reaction was then quenched by addition of water (90 mL), and the resulting mixture was extracted with EtOAc (90 mL). The combined organic extract was washed with brine (50 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo to give a crude material. This material was purified by column chromatography (silica gel, hexane/EtOAc = 50/1 to 25/1 to 15/1) to give a mixture of **4a**[15] and **2** (36.7 mg, **4a**/**2** = 100/4.75, 71% NMR yield of **4a**) as a colorless oil, which was used in the following reaction without further purification: R_f = 0.27 (silica gel, hexane/EtOAc = 15/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.10 (m, 2H, **4a**), 6.83 (m, 2H, **4a**), 3.79 (s, 3H, **4a**), 2.83 (s, 4H, **2**), 2.58 (t, J = 7.5 Hz, 2H, **4a**), 2.22 (t, J = 7.5 Hz, 2H, **4a**), 1.87 (quint, J = 7.5 Hz, 2H, **4a**), 1.44 (s, 9H, **4a**).

To a solution of the mixture of **4a** and **2** (25.4 mg, **4a**/**2** = 100/4.75) was added trifluoroacetic acid (878 mg, 7.70 mmol) at 0 °C. The resulting solution was warmed to room temperature and stirred for 5 h. The reaction mixture was concentrated under reduced pressure and purified by column chromatography (silica gel, hexane/EtOAc = 15/1 to 10/1 to 3/1 to 2/1) to give **5a**[16] (18.7 mg, 70% two-step yield from **1b**) as a white solid: R_f = 0.35 (silica gel, hexane/EtOAc = 1/1); m.p. 55–57 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.11–7.07 (m, 2H), 6.85–6.82 (m, 2H), 3.78 (s, 3H), 2.61 (t, J = 7.5 Hz, 2H), 2.36 (t, J = 7.5 Hz, 2H), 1.98-1.88 (quint, J = 7.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 179.8, 157.9, 133.2, 129.4, 113.8, 55.2, 34.1, 33.2, 26.4.

Synthesis and characterization of 4b

According to the synthetic procedure for **4a**, a suspension of **1h** (57.5 mg, 0.200 mmol), *tert*-butyl

acrylate (77.0 mg, 0.601 mmol), **3a** (254 mg, 1.00 mmol), and potassium carbonate (139 mg, 1.01 mmol) in DMSO (6.0 mL) was stirred at room temperature for 5 h. The crude product was purified by column chromatography (silica gel, hexane/EtOAc = 5/1, silica gel, hexane/EtOAc = 50/1 to 25/1 to 15/1 to 10/1) to give **4b**[15] (14.5 mg, 33%) as a colorless oil: R_f = 0.55 (silica gel, hexane/EtOAc = 7/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29–7.25 (m, 2H), 7.20–7.17 (m, 3H), 2.64 (t, J = 7.5 Hz, 2H), 2.24 (t, J = 7.5 Hz, 2H), 1.91 (quint, J = 7.5 Hz, 2H), 1.45 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.9, 141.6, 128.5, 128.3, 125.9, 80.1, 35.1, 34.9, 28.1, 26.7.

Synthesis and characterization of 5b via 4c

According to the synthetic procedure for **4a**, a solution of **1i** (64.2 mg, 0.198 mmol), *tert*-butyl acrylate (76.3 mg, 0.595 mmol), **3a** (254 mg, 1.00 mmol), and potassium carbonate (139 mg, 1.01 mmol) in DMSO (6.0 mL) was stirred at room temperature for 4 h. The crude product was purified by column chromatography (silica gel, hexane/EtOAc = 5/1, silica gel, hexane/EtOAc = 50/1 to 25/1 to 10/1 to 7/1) to give a crude material (111 mg) including **4c** as a yellow solid, which was used in the following reaction without further purification: R_f = 0.30 (silica gel, hexane/EtOAc = 15/1).

A solution of the mixture (111 mg) and trifluoroacetic acid (0.55 mL) in dichloromethane (0.55 mL) was stirred at room temperature for 5 h. The crude product was purified by column chromatography (silica gel, hexane/EtOAc = 9/2 to 3/1 to 2/3) to give **5b**[16] (13.5 mg, 34% in 2 steps) as a pale yellow solid: R_f = 0.47 (silica gel, hexane/EtOAc = 1/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 (m, 2H), 7.11 (m, 2H), 2.65 (t, J = 7.2 Hz, 2H), 2.37 (t, J = 7.2 Hz, 2H), 1.95 (quint, J = 7.2 Hz, 2H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 179.3, 139.6, 131.8, 129.8, 128.5, 34.3, 33.1, 26.1.

Synthesis and characterization of 4d

According to the synthetic procedure for **4a**, a solution of **1j** (60.5 mg, 0.199 mmol), *tert*-butyl acrylate

(76.3 mg, 0.595 mmol), **3a** (254 mg, 1.00 mmol), and potassium carbonate (138 mg, 0.999 mmol) in DMSO (6.0 mL) was stirred at room temperature for 5 h. The crude product was purified by column chromatography (silica gel, hexane/EtOAc = 5/1, silica gel, hexane/EtOAc = 100/1 to 50/1 to25/1 to 15/1) to give **4d**[15] (20.4 mg, 44%) as a colorless oil: R_f = 0.71 (silica gel, hexane/EtOAc = 7/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.11–7.04 (m, 4H), 2.59 (t, J = 7.5 Hz, 2H), 2.31 (s, 3H), 2.22 (t, J = 7.5 Hz, 2H), 1.88 (quint, J = 7.5 Hz, 2H), 1.44 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.9, 138.5, 135.3, 129.0, 128.4, 80.1, 34.9, 34.7, 28.1, 26.9, 21.0.

Synthesis and characterization of 5c via 4e

According to the synthetic procedure for **4a**, a solution of **1k** (63.5 mg, 0.199 mmol), *tert*-butyl acrylate (77.1 mg, 0.602 mmol), **3a** (254 mg, 1.00 mmol), and potassium carbonate (139 mg, 1.01 mmol) in DMSO (6.0 mL) was stirred at room temperature for 5 h. The crude product was purified by column chromatography (silica gel, hexane/EtOAc = 5/1, silica gel, hexane/EtOAc = 50/1 to 25/1 to 15/1 to 10/1) to give a mixture including **4e** (19.1 mg) as a colorless oil, which was used in the following reaction without further purification: R_f = 0.57 (silica gel, hexane/EtOAc = 7/1).

A solution of the mixture (19.1 mg) and trifluoroacetic acid (0.42 mL) in dichloromethane (0.42 mL) was stirred at room temperature for 4 h. The crude product was purified by column chromatography (silica gel, hexane/EtOAc = 10/1 to 5/1 to 3/1 to 1/1) to give **5c**[16] (12.5 mg, 32% in 2 steps) as a pale yellow solid: R_f = 0.57 (silica gel, hexane/EtOAc = 1/1); m.p. 42–44 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.21 (dt, J = 1.2, 7.5 Hz, 1H), 6.79–6.73 (m, 3H), 3.80 (s, 3H), 2.66 (t, J = 7.5 Hz, 2H), 2.38 (t, J = 7.5 Hz, 2H), 1.97 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 179.7, 159.6, 142.8, 129.4, 120.9, 114.2, 111.3, 55.1, 35.0, 33.2, 26.1

Synthesis and characterization of 5d via 4f

According to the synthetic procedure for **4a**, a solution of **1l** (63.5 mg, 0.199 mmol), *tert*-butyl acrylate (77.4 mg, 0.604 mmol), **3a** (253 mg, 0.999 mmol), and potassium carbonate (138 mg, 0.999 mmol) in DMSO (6.0 mL) was stirred at room temperature for 8 h. The crude product was purified by column chromatography (silica gel, hexane/EtOAc = 5/1, silica gel, hexane/EtOAc = 50/1 to 25/1 to 15/1 to 10/1) to give a mixture including **4f** (29.7 mg) as a colorless oil, which was used in the following reaction without further purification: R_f = 0.57 (silica gel, hexane/EtOAc = 2/1).

A solution of the mixture (29.7 mg) and trifluoroacetic acid (0.85 mL) in dichloromethane (0.85 mL) was stirred at room temperature for 4 h. The crude product was purified by column chromatography (silica gel, hexane/EtOAc = 9/1 to 6/1 to 3/1 to $CHCl_3$/MeOH = 10/1) to give **5d**[16] (16.9 mg, 44% in 2 steps) as a pale yellow solid: R_f = 0.57 (silica gel, hexane/EtOAc = 1/1); m.p. 37–38 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.21–7.10 (m, 2H), 6.90–6.83 (m, 2H), 3.81 (s, 3H), 2.68 (t, *J* = 7.8 Hz, 2H), 2.37 (t, J = 7.5 Hz, 2H), 1.94 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 179.9, 157.4, 130.0, 129.5, 127.3, 120.4, 110.2, 55.2, 33.5, 29.3, 24.7.

Synthesis and characterization of 4g

According to the synthetic procedure for **4a**, a solution of **1m** (62.2 mg, 0.188 mmol), *tert*-butyl acrylate (77.1 mg, 0.602 mmol), **3a** (238 mg, 0.940 mmol), and potassium carbonate (131 mg, 0.948 mmol) in DMSO (6.0 mL) was stirred at room temperature for 5 h. The crude product was purified by column chromatography (silica gel, hexane/EtOAc = 5/1, silica gel, hexane/EtOAc = 50/1 to 25/1 to 15/1 to 10/1) to give **4g** (27.1 mg, 55%) as a colorless oil: R_f = 0.47 (silica gel, hexane/EtOAc = 10/1); IR (NaCl) 3003, 2974, 2931, 1730, 1456 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.83 (s, 2H), 2.60 (m, 2H), 2.31 (t, *J* = 7.2 Hz, 2H), 2.29 (s, 6H), 2.24 (s, 3H), 1.78–1.68 (m, 2H), 1.46 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.8, 136.0, 135.5, 135.1, 128.9, 80.1, 35.9, 28.8, 28.1, 24.7, 20.8, 19.7. Anal. Calcd for $C_{17}H_{26}O_2$: C, 77.82; H, 9.99; N, 0.00. Found: C, 78.14; H, 9.59; N, 0.00.

Synthesis and characterization of 5e via 4h

According to the synthetic procedure for **4a**, a solution of **1n** (66.4 mg, 0.199 mmol), *tert*-butyl acrylate (77.5 mg, 0.605 mmol), **3a** (254 mg, 1.00 mmol), and potassium carbonate (139 mg, 1.01 mmol) in DMSO (6.0 mL) was stirred at room temperature for 7 h. The crude product was purified by column chromatography (silica gel, hexane/EtOAc = 5/1, silica gel, hexane/EtOAc = 50/1 to 25/1 to 15/1 to 10/1) to give a mixture including **4h** (39.1 mg) as a colorless oil, which was used in the following reaction without further purification: R_f = 0.37 (silica gel, hexane/EtOAc = 1/1).

A solution of the mixture (39.1 mg) and trifluoroacetic acid (0.80 mL) in dichloromethane (0.80 mL) was stirred at room temperature for 5 h. The crude product was purified by column chromatography (silica gel, hexane/EtOAc = 5/1 to 3/1 to 1/1) to give **5e**[17] (18.6 mg, 45% in 2 steps) as a pale yellow oil: R_f = 0.57 (silica gel, hexane/EtOAc = 1/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.09 (m, 2H), 6.83 (m, 2H), 3.78 (s, 3H), 2.69 (m, 1H), 2.25–2.20 (m, 2H), 1.98–1.77 (m, 2H), 1.25 (d, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 179.6, 158.0, 138.1, 127.9, 113.8, 55.2, 38.4, 33.1, 32.2, 22.3.

Synthesis and characterization of 5f via 4i

According to the synthetic procedure for **4a**, a solution of **1o** (69.3 mg, 0.199 mmol), *tert*-butyl acrylate (77.4 mg, 0.604 mmol), **3a** (254 mg, 1.00 mmol), and potassium carbonate (138 mg, 0.999 mmol) in DMSO (6.0 mL) was stirred at room temperature for 24 h. The crude product was purified by column chromatography (silica gel, hexane/EtOAc = 5/1, silica gel, hexane/EtOAc = 50/1 to 25/1 to 15/1 to 10/1) to give a mixture of **4i** and the corresponding dimer (41.6 mg, **4i**/dimer = 100/28, 57% NMR yield of **4i**) as a colorless oil: R_f = 0.50 (silica gel, hexane/EtOAc = 10/1), ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24 (m, 2H, **4i**), 6.96 (m, 4H, dimer), 6.84 (m, 2H, **4i**), 6.72 (m, 4H, dimer), 3.79 (s, 3H, **4i**), 2.00–1.85 (m, 4H, **4i**), 1.40 (s, 9H, **4i**), 1.29 (s, 6H, **4i**), 1.27 (s, 12H, dimer).

A solution of the mixture (39.8 mg) and trifluoroacetic acid (0.80 mL) in dichloromethane (0.80 mL) was stirred at room temperature for 5 h. The crude product was purified by column chromatography (silica gel, hexane/EtOAc = 10/1 to 7/1 to 5/1 to 3/1) to give **5f** (23.0 mg, 54% in 2 steps) as a pale yellow solid: R_f = 0.30 (silica gel, hexane/EtOAc = 2/1); m.p. 66–68 °C; IR (NaCl) 3010, 2964, 2875, 2072, 1707, 1612, 1514 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.23 (m, 2H), 6.84 (m, 2H), 3.78 (s, 3H), 2.12–2.06 (m, 2H), 1.96–1.90 (m, 2H), 1.30 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 180.3, 157.5, 139.8, 126.8, 113.5, 55.2, 38.8, 36.6, 30.0, 28.8. Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16; N, 0.00. Found: C, 70.63; H, 8.53; N, 0.00.

Synthesis and characterization of 4j

According to the synthetic procedure for **4a**, a solution of **1p** (79.8 mg, 0.200 mmol), *tert*-butyl acrylate (38.8 mg, 0.303 mmol), **3a** (101 mg, 0.399 mmol), and potassium carbonate (55.9 mg, 0.404 mmol) in DMSO (6.0 mL) was stirred at room temperature for 5 h. The crude product was purified by column chromatography (silica gel, hexane/EtOAc = 5/1, silica gel, hexane/EtOAc = 50/1 to 25/1 to 15/1 to 10/1) to give **4j** (52.8 mg, 80%) as a colorless oil: R_f = 0.59 (silica gel, hexane/EtOAc = 10/1); IR (NaCl) 2956, 2931, 2858, 1732 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.58 (t, J = 6.6 Hz, 2H), 2.25–2.18 (m, 2H), 1.64–1.13 (m, 16H), 0.89–0.87 (m, 12H), 0.05 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.5, 79.9, 63.5, 33.3, 32.7, 32.2, 32.0, 30.3, 28.1, 26.0, 19.3, 18.3, -5.3. Anal. Calcd for $C_{18}H_{38}O_3Si$: C, 65.40; H, 11.59; N, 0.00. Found: C, 65.76; H, 11.21; N, 0.00.

Synthesis and characterization of 4k

According to the synthetic procedure for **4a**, a solution of **1q** (71.5 mg, 0.190 mmol), *tert*-butyl acrylate (32.5 mg, 0.254 mmol), **3a** (101 mg, 0.399 mmol), and potassium carbonate (55.0 mg, 0.398 mmol) in DMSO (6.0 mL) was stirred at room temperature for 24 h. The crude product was purified by column

chromatography (silica gel, hexane/EtOAc = 50/1 to25/1 to 15/1) to give **4k** (37.8 mg, 65%) as a colorless oil: R_f = 0.40 (silica gel, hexane/EtOAc = 10/1); IR (NaCl) 2933, 2858, 1730, 1454 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.35–7.26 (m, 5H), 4.50 (s, 2H), 3.45 (t, *J* = 6.6 Hz, 2H), 2.30–2.12 (m, 2H), 1.71–1.32 (m, 15H), 1.21 (m, 1H), 0.88 (d, J = 5.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.4, 138.6, 128.3, 127.6, 127.4, 79.9, 72.8, 70.7, 33.3, 33.0, 32.2, 31.9, 28.1, 27.2, 19.2. Anal. Calcd for $C_{19}H_{30}O_3$: C, 74.47; H, 9.87; N, 0.00. Found: C, 74.87; H, 9.61; N, 0.00.

Synthesis and characterization of 4l

According to the synthetic procedure for **4a**, a solution of **1r** (71.5 mg, 0.200 mmol), *tert*-butyl acrylate (36.0 mg, 0.281 mmol), **3a** (101 mg, 0.399 mmol), and potassium carbonate (55.4 mg, 0.401 mmol) in DMSO (6.0 mL) was stirred at room temperature for 24 h. The crude product was purified by column chromatography (silica gel, hexane/EtOAc = 5/1, silica gel, hexane/EtOAc = 50/1 to 25/1 to 15/1 to 10/1) to give **4l** (29.1 mg, 50%) as a colorless oil: R_f = 0.30 (silica gel, hexane/EtOAc = 10/1); IR (NaCl) 2978, 2933, 2873, 1730 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.68 (q, *J* = 5.4 Hz, 1H), 3.70–3.35 (m, 4H), 2.30–2.13 (m, 2H), 1.72–1.14 (m, 7H), 1.44 (s, 9H), 1.30 (d, *J* = 5.4 Hz, 3H), 1.21 (t, *J* = 6.9 Hz, 3H), 0.89 (d, J = 6.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.4, 99.52, 99.50, 79.9, 65.52, 65.47, 60.66, 60.63, 33.3, 33.1, 32.3, 31.9, 28.1, 27.3, 19.9, 19.2, 15.3. Anal. Calcd for $C_{16}H_{32}O_4$: C, 66.63; H, 11.18; N, 0.00. Found: C, 66.47; H, 10.79; N, 0.00.

Synthesis and characterization of 4m

According to the synthetic procedure for **4a**, a solution of **1s** (73.0 mg, 0.198 mmol), *tert*-butyl acrylate (31.6 mg, 0.243 mmol), **3a** (101 mg, 0.399 mmol), and potassium carbonate (55.3 mg, 0.400 mmol) in DMSO (6.0 mL) was stirred at room temperature for 24 h. The crude product was purified by column chromatography (silica gel, hexane/EtOAc = 50/1 to 25/1 to 15/1 to 10/1 to 7/1) to give **4m** (34.2 mg,

57%) as a colorless oil: R_f = 0.37 (silica gel, hexane/EtOAc = 10/1); IR (NaCl) 2972, 2935, 2873, 1730 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.04 (t, *J* = 6.6 Hz, 2H), 2.28–2.15 (m, 2H), 1.73–1.13 (m, 7H), 1.44 (s, 9H), 1.20 (s, 9H), 0.89 (d, J = 6.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.5, 173.3, 80.0, 64.5, 38.7, 33.2, 32.8, 32.0, 31.8, 28.1, 27.2, 26.1, 19.2. Anal. Calcd for $C_{17}H_{32}O_4$: C, 67.96; H, 10.74; N, 0.00. Found: C, 68.11; H, 10.66; N, 0.00.

Synthesis and characterization of 4n

According to the synthetic procedure for **4a**, a solution of **1t** (70.9 mg, 0.200 mmol), *tert*-butyl acrylate (31.0 mg, 0.242 mmol), **3a** (101 mg, 0.399 mmol), and potassium carbonate (55.7 mg, 0.403 mmol) in DMSO (6.0 mL) was stirred at room temperature for 48 h. The crude product was purified by column chromatography (silica gel, hexane/EtOAc = 5/1 to 4/1 to 3/1 to 2/1 to 1/1) to give **4n** (42.5 mg, 74%) as a colorless oil: R_f = 0.50 (silica gel, EtOAc); IR (NaCl) 2956, 2870, 2808, 1728 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.72 (t, *J* = 4.5 Hz, 4H), 2.43 (t, *J* = 4.5 Hz, 4H), 2.33–2.15 (m, 4H), 1.75-1.08 (m, 7H), 1.44 (s, 9H), 0.88 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.4, 79.9, 66.9, 59.4, 53.8, 34.3, 33.3, 32.3, 31.9, 28.1, 23.9, 19.3. Anal. Calcd for $C_{16}H_{31}NO_3$: C, 67.33; H, 10.95; N, 4.91. Found: C, 66.97; H, 10.95; N, 4.86.

Synthesis and characterization of 4o

According to the synthetic procedure for **4a**, a solution of **1u** (75.1 mg, 0.201 mmol), *tert*-butyl acrylate (38.5 mg, 0.300 mmol), **3a** (101 mg, 0.399 mmol), and potassium carbonate (55.3 mg, 0.400 mmol) in DMSO (6.0 mL) was stirred at room temperature for 24 h. The crude product was purified by column chromatography (silica gel, hexane/EtOAc = 25/1 to 10/1 to 7/1 to 5/1) to give **4o** (41.5 mg, 68%) as a colorless oil: R_f = 0.33 (silica gel, hexane/EtOAc = 10/1); IR (NaCl) 2956, 2931, 2870, 1730, 1601, 1506, 1456 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.25–7.19 (m, 2H), 6.70–6.64 (m, 3H), 3.27 (t, *J* = 7.5 Hz,

2H), 2.91 (s, 3H), 2.28–2.14 (m, 2H), 1.67–1.13 (m, 16H), 0.88 (d, J = 6.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.4, 149.3, 129.1, 115.8, 112.1, 80.0, 53.0, 38.2, 34.1, 33.3, 32.4, 32.0, 28.1, 24.0, 19.3. Anal. Calcd for $C_{19}H_{31}NO_2$: C, 74.71; H, 10.23; N, 4.59. Found: C, 75.09; H, 10.28; N, 4.51.

Synthesis and characterization of 4p

According to the synthetic procedure for **4a**, a solution of **1v** (76.0 mg, 0.195 mmol), *tert*-butyl acrylate (38.8 mg, 0.303 mmol), **3a** (101 mg, 0.399 mmol), and potassium carbonate (55.6 mg, 0.402 mmol) in DMSO (6.0 mL) was stirred at room temperature for 24 h. The crude product was purified by column chromatography (silica gel, hexane/EtOAc = 50/1 to 25/1 to 15/1) to give **4p** (48.7 mg, 78%) as a colorless oil: R_f = 0.37 (silica gel, hexane/EtOAc = 10/1); IR (NaCl) 2956, 2866, 1730, 1456 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37–7.24 (m, 5H), 4.50 (s, 2H), 3.44 (t, J = 6.6 Hz, 2H), 2.19–2.14 (m, 2H), 1.65–1.37 (m, 13H), 1.26–1.20 (m, 2H), 0.86 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.7, 138.6, 128.3, 127.6, 127.4, 79.9, 72.8, 71.2, 37.9, 36.5, 32.2, 30.8, 28.1, 26.7, 24.4. Anal. Calcd for $C_{20}H_{32}O_3$: C, 74.96; H, 10.07; N, 0.00. Found: C, 74.63; H, 10.09; N, 0.00.

Synthesis and characterization of 4q

According to the synthetic procedure for **4a**, a solution of **1w** (73.9 mg, 0.199 mmol), *tert*-butyl acrylate (77.1 mg, 0.602 mmol), **3a** (254 mg, 1.00 mmol), and potassium carbonate (138 mg, 0.999 mmol) in DMSO (6.0 mL) was stirred at room temperature for 5 h. The crude product was purified by column chromatography (silica gel, hexane/EtOAc = 50/1 to 25/1 to 15/1 to 10/1 to 7/1 to 6/1) to give **4q** (8.3 mg, 14%) as a colorless oil: R_f = 0.50 (silica gel, hexane/EtOAc = 10/1); IR (NaCl) 2931, 2858, 1732 cm^{-1}; ^{1}H NMR (300 MHz, CD_3OD) δ 3.62 (t, J = 6.3 Hz, 2H), 2.21 (t, J = 7.5 Hz, 2H), 1.59–1.28 (m, 8H), 1.44 (s, 9H), 0.89 (s, 9H), 0.05 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.3, 79.9, 63.2, 35.6, 32.7, 28.9, 28.1, 26.0, 25.5, 25.1, 18.4, -5.3. Anal. Calcd for $C_{17}H_{36}O_3Si$: C, 64.50; H, 11.46; N, 0.00. Found:

C, 64.54; H, 11.09; N, 0.00.

Synthesis and characterization of 4r

According to the synthetic procedure for **4a**, a solution of **1p** (79.3 mg, 0.198 mmol), ethyl acrylate (29.2 mg, 0.292 mmol), **3a** (101 mg, 0.399 mmol), and potassium carbonate (55.4 mg, 0.399 mmol) in DMSO (6.0 mL) was stirred at room temperature for 24 h. The crude product was purified by column chromatography (silica gel, hexane/EtOAc = 50/1 to 25/1 to 15/1) to give **4r** (36.5 mg, 61%) as a colorless oil: R_f = 0.43 (silica gel, hexane/EtOAc = 10/1); IR (NaCl) 2954, 2933, 2858, 1739 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.12 (q, J = 7.2 Hz, 2H), 3.59 (t, J = 6.6 Hz, 2H), 2.38–2.21 (m, 2H), 1.71–1.10 (m, 7H), 1.25 (t, J = 7.2 Hz, 3H), 0.90–0.86 (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.1, 63.4, 60.2, 32.6, 32.2, 32.1, 31.9, 30.2, 26.0, 19.3, 18.3, 14.2, -5.3. Anal. Calcd for $C_{16}H_{34}O_3Si$: C, 63.52; H, 11.33; N, 0.00. Found: C, 63.13; H, 10.96; N, 0.00.

Synthesis and characterization of 4s

According to the synthetic procedure for **4a**, a solution of **1b** (63.5 mg, 0.199 mmol), acrylonitrile (31.6 mg, 0.596 mmol), **3a** (254 mg, 1.00 mmol), and potassium carbonate (139 mg, 1.01 mmol) in DMSO (6.0 mL) was stirred at room temperature for 7 h. The crude product was roughly purified by column chromatography (silica gel, hexane/EtOAc = 25/1 to 15/1 to 10/1). The resulting crude material was dissolved in EtOAc (50 mL). The organic solution was washed with 3% aqueous HCl (15×50 mL) and brine (50 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo to give a crude material. This material was purified by column chromatography (silica gel, hexane/EtOAc = 15/1 to 10/1 to 7/1 to 4/1) to give **4s**[18] (18.2 mg, 52%) as a colorless oil: R_f = 0.33 (silica gel, hexane/EtOAc = 3/1); ^1H NMR (300 MHz, $CDCl_3$) δ 7.11–7.09 (m, 2H), 6.87–6.84 (m, 2H), 3.80 (s, 3H), 2.72 (t, J = 7.2 Hz, 2H), 2.30 (t, J = 7.2 Hz, 2H), 1.95 (quint, J = 7.2 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.2, 131.7, 129.4, 119.5, 114.0,

55.2, 33.4, 27.1, 16.2.

Synthesis and characterization of 4t

According to the synthetic procedure for **4a**, a solution of **1p** (79.2 mg, 0.198 mmol), *N,N*-didecylacrylamide[19] (105 mg, 0.299 mmol), **3a** (101 mg, 0.399 mmol), and potassium carbonate (56.0 mg, 0.405 mmol) in DMSO (6.0 mL) was stirred at room temperature for 24 h. The crude product was purified by column chromatography (silica gel, hexane/EtOAc = 50/1 to 25/1 to 15/1) to give **4t** (50.3 mg, 46%) as a colorless oil: R_f = 0.50 (silica gel, hexane/EtOAc = 7/1); IR (NaCl) 2954, 2927, 2856, 1649 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.58 (t, J = 6.6 Hz, 2H), 3.29–3.16 (m, 4H), 2.30–2.23 (m, 2H), 1.70–1.15 (m, 39H), 0.90–0.84 (s, 18H), 0.03 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.8, 63.5, 48.0, 45.9, 32.8, 32.6, 32.5, 31.9, 31.8, 30.9, 30.3, 29.6, 29.5, 29.5, 29.4, 29.3, 29.3, 29.1, 27.8, 27.0, 26.9, 25.9, 22.6, 19.4, 18.3, 14.1, -5.3. Anal. Calcd for $C_{34}H_{71}NO_2Si$: C, 73.71; H, 12.92; N, 2.53. Found: C, 74.05; H, 12.84; N, 2.57.

Synthesis and characterization of 4u

According to the synthetic procedure for **4a**, a solution of **1p** (80.1 mg, 0.200 mmol), *tert*-butyl methacrylate (43.2 mg, 0.304 mmol), **3a** (102 mg, 0.403 mmol), and potassium carbonate (56.0 mg, 0.405 mmol) in DMSO (6.0 mL) was stirred at room temperature for 48 h. The crude product was purified by column chromatography (silica gel, hexane/EtOAc = 100/1 to 50/1 to 25/1 to 15/1) to give **4u** (35.6 mg, 52%, 3:2 mixture of diastereomers) as a colorless oil: R_f = 0.55 (silica gel, hexane/EtOAc = 15/1); IR (NaCl) 2956, 2933, 2858, 1730 cm^{-1}; ^1H NMR (300 MHz, CD_3OD) δ 3.613 (t, J = 6.3 Hz, 2H, minor isomer), 3.607 (t, J = 6.3 Hz, 2H, major isomer), 2.49–2.37 (m, 1H), 1.70–1.02 (m, 7H), 1.44 (s, 9H), 1.08 (d, J = 6.6 Hz, 3H, major isomer), 1.06 (d, J = 6.9 Hz, 3H, minor isomer), 0.91–0.84 (m, 3H), 0.898 (s, 9H, minor isomer), 0.895 (s, 9H, major isomer), 0.053 (s, 6H, minor isomer), 0.050 (s, 6H, major

isomer); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.7, 176.5, 79.7, 63.6, 63.5, 41.5, 41.1, 38.3, 38.2, 33.1, 32.9, 30.7, 30.5, 30.2, 28.1, 26.0, 19.53, 19.47, 18.4, 18.1, 17.3, -5.3. Anal. Calcd for $C_{19}H_{40}O_3Si$: C, 66.22; H, 11.70; N, 0.00. Found: C, 65.97; H, 12.05; N, 0.00.

Synthesis and characterization of 4v

According to the synthetic procedure for **4a**, a solution of **1p** (80.3 mg, 0.201 mmol), *tert*-butyl 2-(((tert-butyldimethylsilyl)oxy)methyl)acrylate (40.8 mg, 0.300 mmol), **3a** (101 mg, 0.400 mmol), and potassium carbonate (55.2 mg, 0.400 mmol) in DMSO (6.0 mL) was stirred at room temperature for 24 h. The crude product was purified by column chromatography (silica gel, hexane/EtOAc = 15/1 to 10/1 to 5/1) to give **4v** (47.8 mg, 50%) as a colorless oil: R_f = 0.33 (silica gel, hexane/EtOAc = 15/1); IR (NaCl) 2954, 2931, 2858, 1730 cm^{-1}; ^{1}H NMR (300 MHz, CD_3OD) δ 3.74–3.57 (m, 4H), 2.57–2.51 (m, 1H), 1.60–1.07 (m, 8H), 1.45 (s, 9H), 0.94–0.84 (m, 20H), 0.10–0.04 (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.5, 174.3, 80.0, 65.2, 64.8, 63.6, 63.5, 47.4, 47.3, 36.0, 35.9, 33.6, 32.4, 30.7, 30.6, 30.3, 30.1, 28.1, 26.0, 25.8, 20.0, 19.3, 18.3, 18.2, -5.3, -5.47, -5.53. Anal. Calcd for $C_{25}H_{54}O_4Si$: C, 63.23; H, 11.46; N, 0.00. Found: C, 62.88; H, 11.11; N, 0.00.

Synthesis and characterization of 4w

According to the synthetic procedure for **4a**, a solution of **1p** (79.3 mg, 0.198 mmol), 1-morpholinoprop-2-yn-1-one (41.3 mg, 0.297 mmol), **3a** (101 mg, 0.399 mmol), and potassium carbonate (54.8 mg, 0.397 mmol) in DMSO (6.0 mL) was stirred at room temperature for 30 h. The crude product was purified by column chromatography (silica gel, hexane/EtOAc = 7/1 to 5/1 to 3/1 to 5/2 to 2/1 to 1/1). The resulting material was dissolved with hexane/EtOAc (20/1) and filtered through filter paper. The filtrate was concentrated in vacuo to give **4w** (32.6 mg, 48%) as a pale yellow oil: R_f = 0.53, 0.47 (silica gel, hexane/EtOAc = 1/1); IR (NaCl) 3739, 3730, 2856, 1649, 1628 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.81

(dd, J = 7.8, 15.0 Hz, 1H, *E*-isomer), 6.15 (dd, J = 0.9, 15.0 Hz, 1H, *E*-isomer), 5.89 (d, J = 11.7 Hz, 1H, *Z*-isomer), 5.68 (dd, J = 10.2, 11.7 Hz, 1H, *Z*-isomer), 3.72–3.48 (m, 10H), 2.80 (m, 1H, *Z*-isomer), 2.31 (m, 1H, *E*-isomer), 1.59–1.23 (m, 4H), 1.06 (d, J = 6.6 Hz, 3H, *E*-isomer), 1.02 (d, J = 6.6 Hz, 3H, *Z*-isomer), 0.88 (m, 9H), 0.04 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.6, 165.7, 152.4, 147.2, 120.1, 117.6, 66.8, 66.7, 63.1, 63.1, 46.6, 41.5, 36.6, 33.6, 33.0, 32.3, 30.7, 30.4, 29.7, 25.9, 20.5, 19.7, 18.3, -5.3. Anal. Calcd for $C_{18}H_{35}NO_3Si$: C, 63.30; H, 10.33; N, 4.10. Found: C, 63.69; H, 10.28; N, 4.10.

Synthesis and characterization of 4x

According to the synthetic procedure for **4a**, a solution of **1p** (80.2 mg, 0.201 mmol), phenyl vinyl sulfone (50.0 mg, 0.300 mmol), **3a** (102 mg, 0.403 mmol), and potassium carbonate (55.6 mg, 0.402 mmol) in DMSO (6.0 mL) was stirred at room temperature for 30 h. The crude product was purified by column chromatography (silica gel, hexane/EtOAc = 25/1 to 15/1 to 10/1 to 7/1 to 5/1). The resulting crude material was dissolved in EtOAc (10 mL). The organic solution was washed with 3% aqueous HCl (15×10 mL) and brine (10 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo to give **4x**[20] (52.5 mg, 71%) as a pale yellow oil: R_f = 0.50 (silica gel, hexane/EtOAc = 3/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91–7.88 (m, 2H), 7.67–7.53 (m, 3H), 3.60–3.46 (m, 2H), 3.15–2.99 (m, 2H), 1.71 (m, 1H), 1.57–1.14 (m, 6H), 0.88–0.83 (m, 12H), 0.01 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.1, 133.6, 129.2, 128.0, 63.1, 54.4, 32.4, 31.7, 29.9, 29.1, 25.9, 19.1, 18.3, -5.3. Anal. Calcd for $C_{19}H_{34}O_3SSi$: C, 61.57; H, 9.25; N, 0.00. Found: C, 61.83; H, 8.85; N, 0.00.

Radical inhibit experiment

Benzothiazole sulfone **1b** (95.8 mg, 0.300 mmol), *tert*-butyl acrylate (26.2 mg, 0.204 mmol), Hantzsch ester **3a** (76.0 mg, 0.300 mmol), 2,2,6,6-tetramethylpiperidine-1-oxyl (31.2 mg, 0.200 mmol), and potassium carbonate (49.7 mg, 0.360 mmol) were dissolved in DMSO (2.0 mL). The mixture was

degassed by three freeze-pump-thaw cycles. Afterward, the mixture was stirred and irradiated with blue LEDs at room temperature for 24 h. The reaction was then quenched by addition of water (100 mL), and the resulting mixture was extracted with EtOAc (100 mL). The combined organic extract was washed with brine (80 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo to give a crude material. This material was purified by column chromatography (silica gel, hexane/EtOAc = 50/1 to 25/1) to give **7**[21] (2.9 mg, <3%, including a small amount of structure unidentified product) as a colorless oil: R_f = 0.47 (silica gel, hexane/EtOAc = 20/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29 (m, 2H) 6.88 (m, 2H), 4.74 (s, 2H), 3.81 (s, 3H), 1.61–1.31 (m, 6H), 1.26 (s, 6H), 1.13 (s, 6H). HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{17}H_{28}NO_2$ 278.2120; Found 278.2123.

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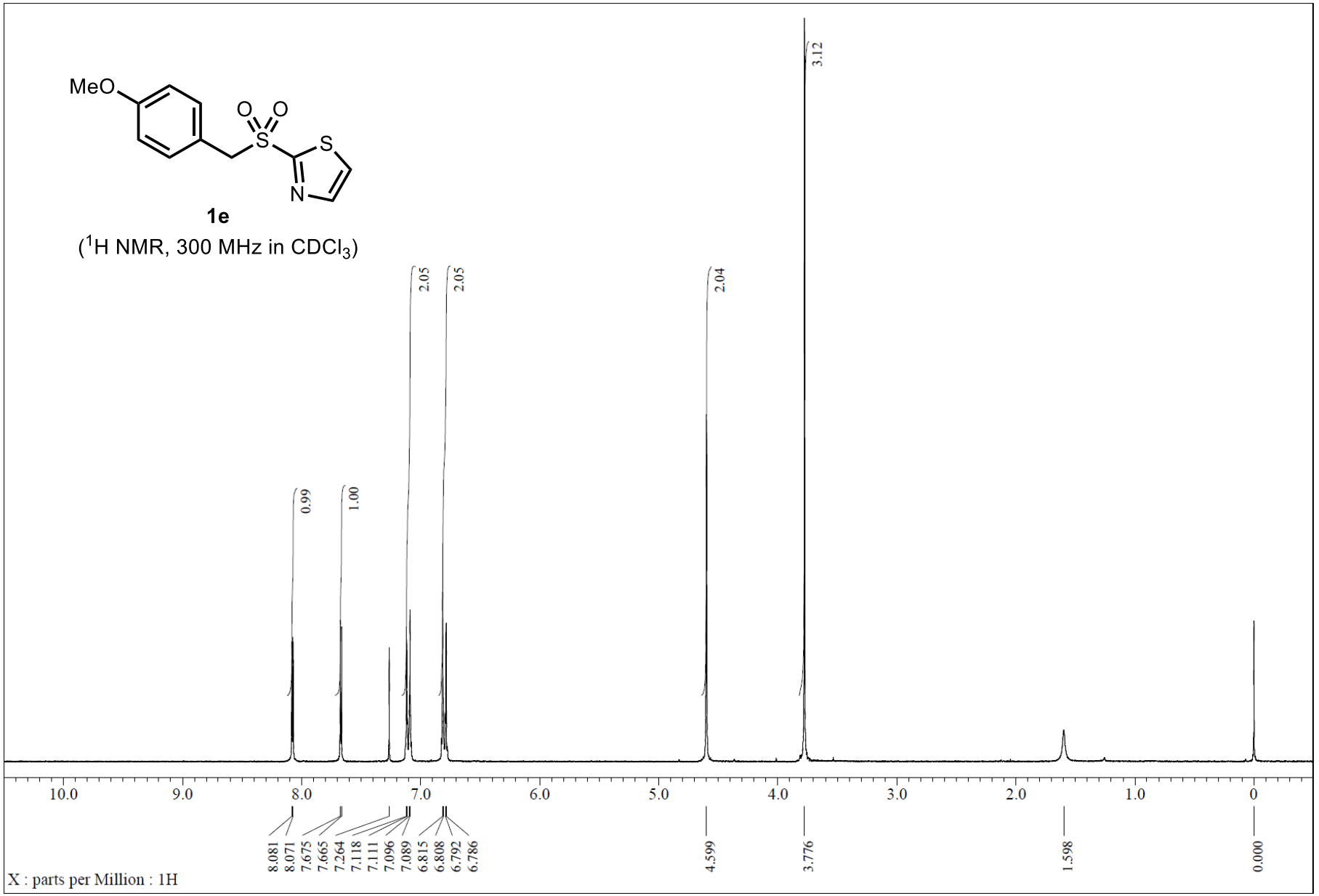
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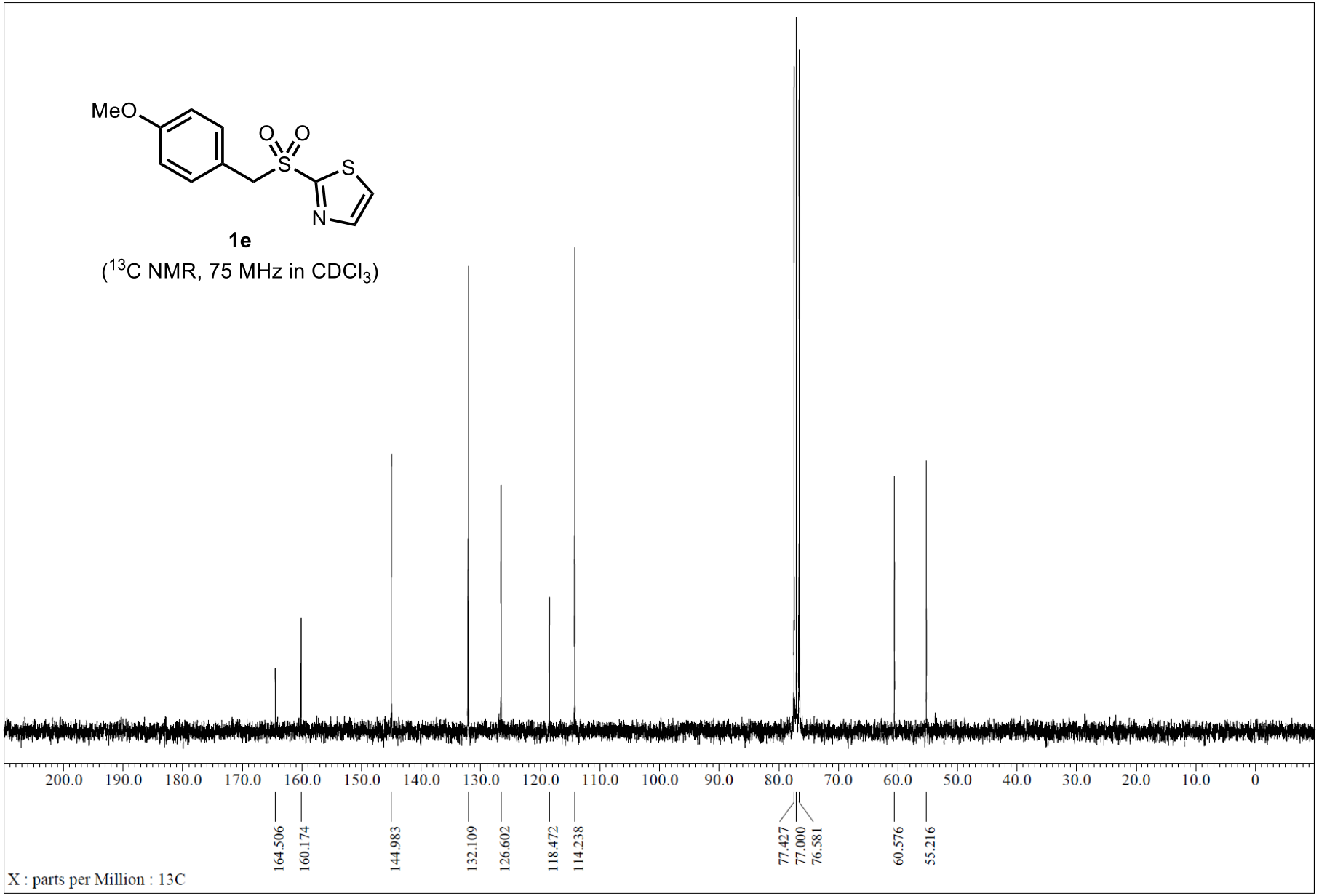
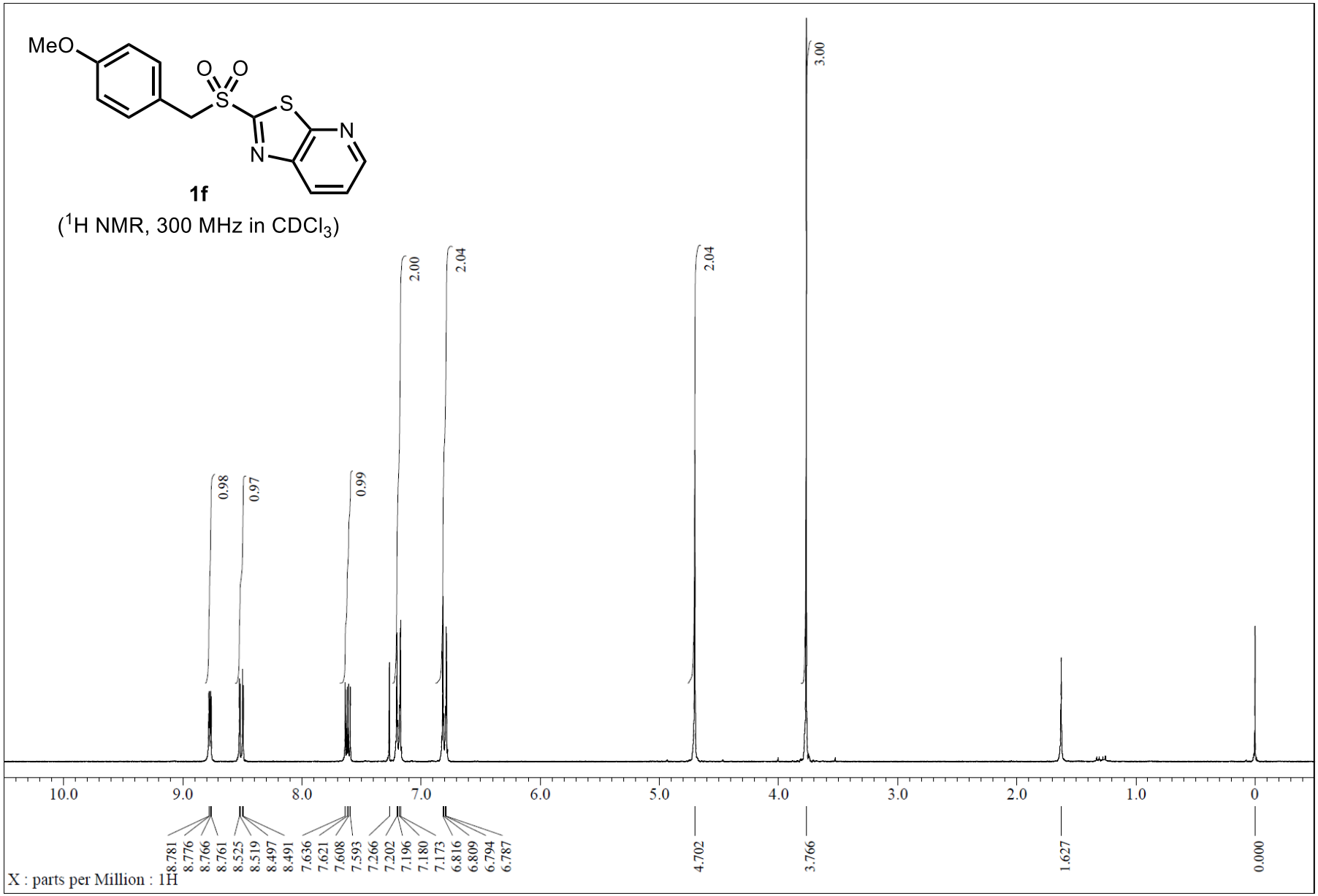
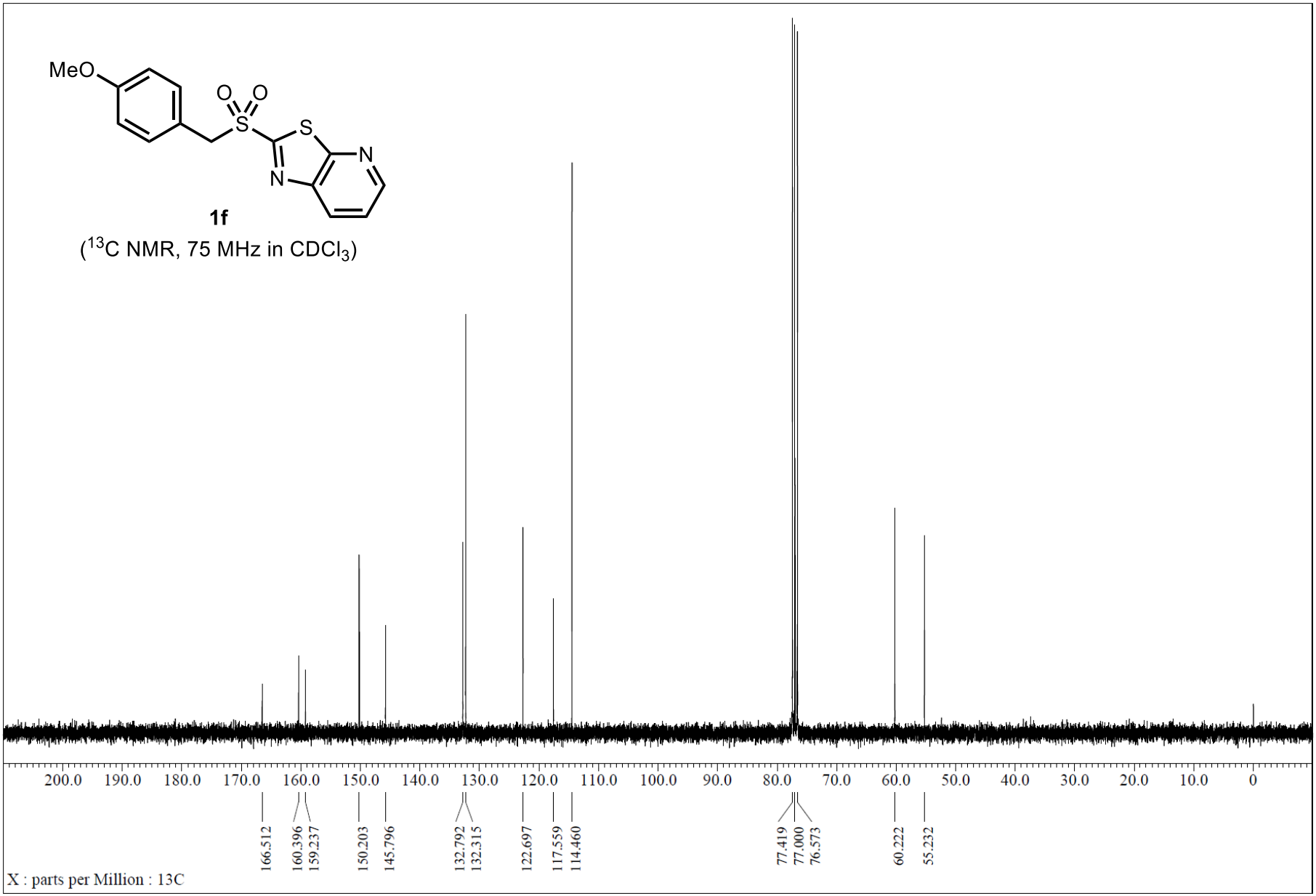
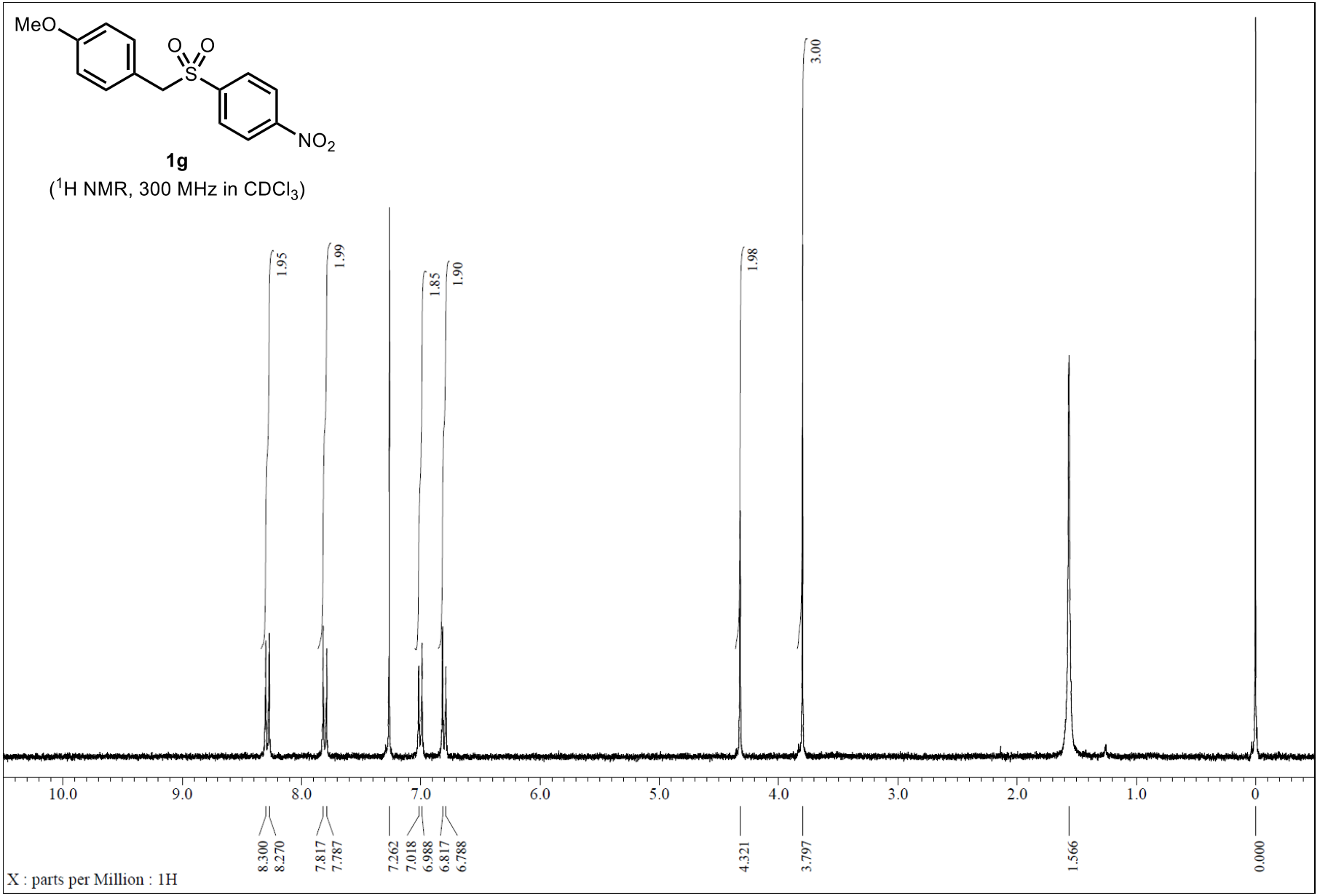
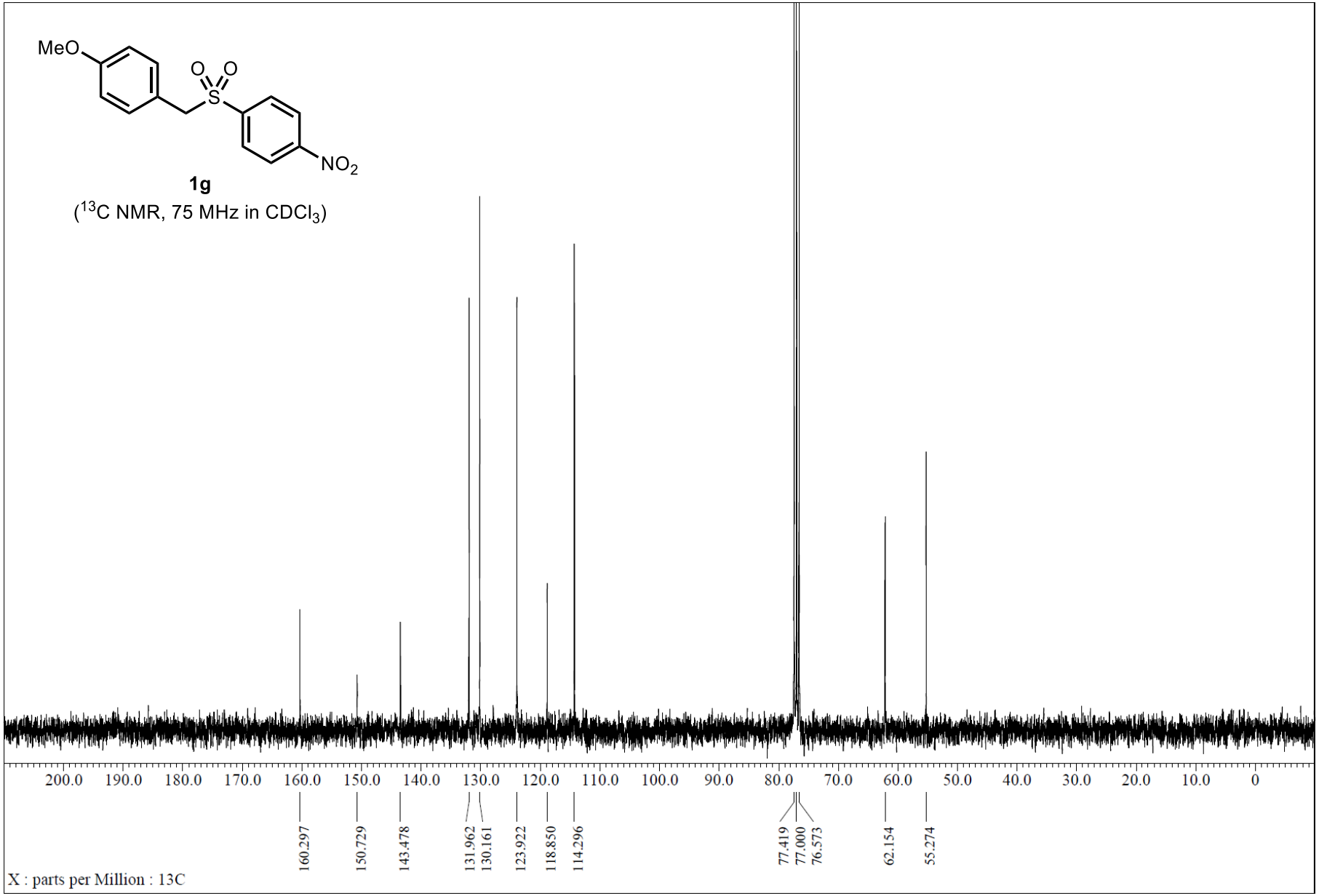
3.0
2.0
1.0
0
8.081
8.071
7.675
7.665
7.264
7.118
7.111
7.096
7.089
6.815
6.808
6.792
6.786
4.599
3.776
1.598
0.000
X : parts per Million : 1H

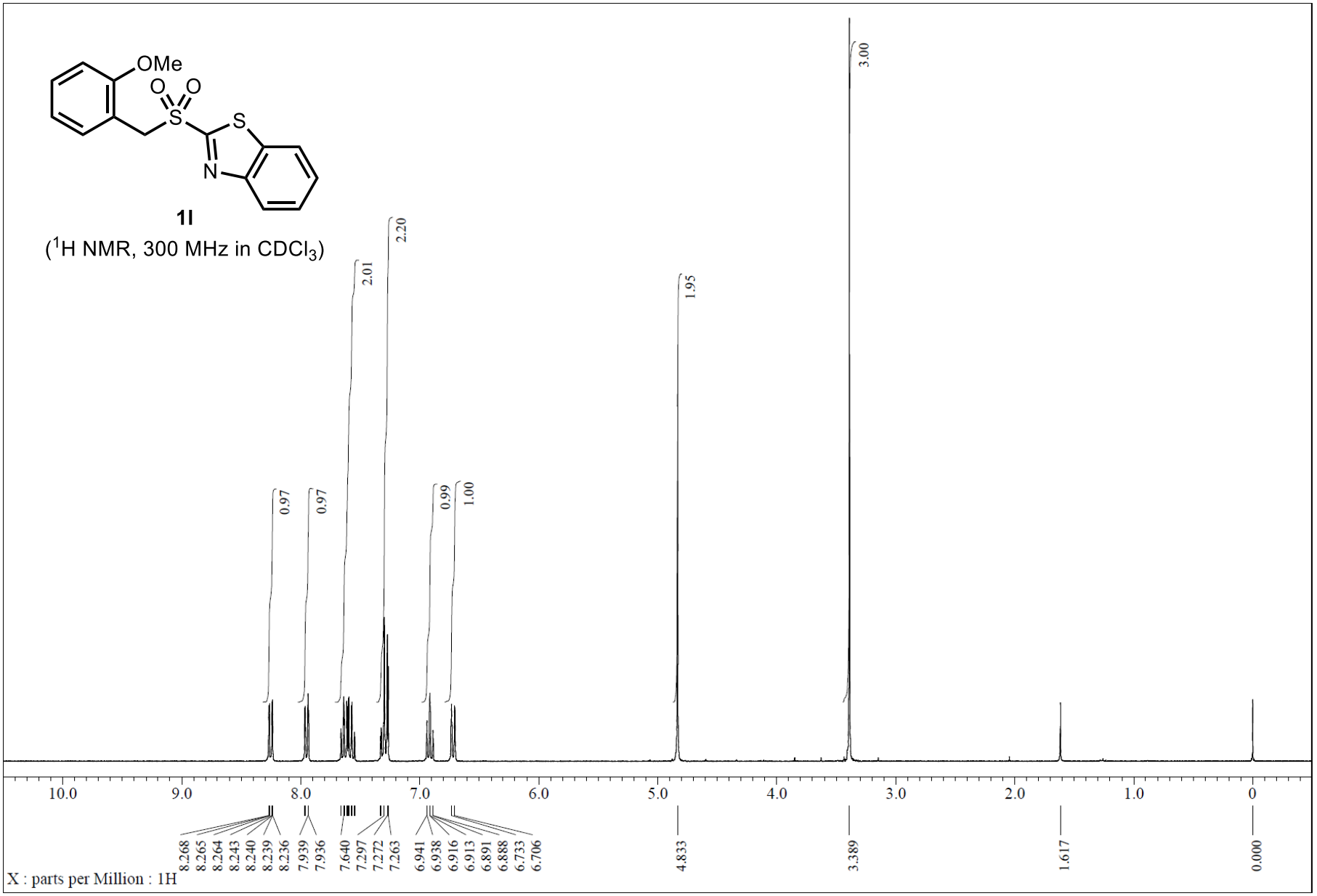

MeO
O
O
S
S
N
1e
(13C NMR, 75 MHz in CDCl3)
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
164.506
160.174
144.983
132.109
126.602
118.472
114.238
77.427
77.000
76.581
60.576
55.216
X : parts per Million : 13C

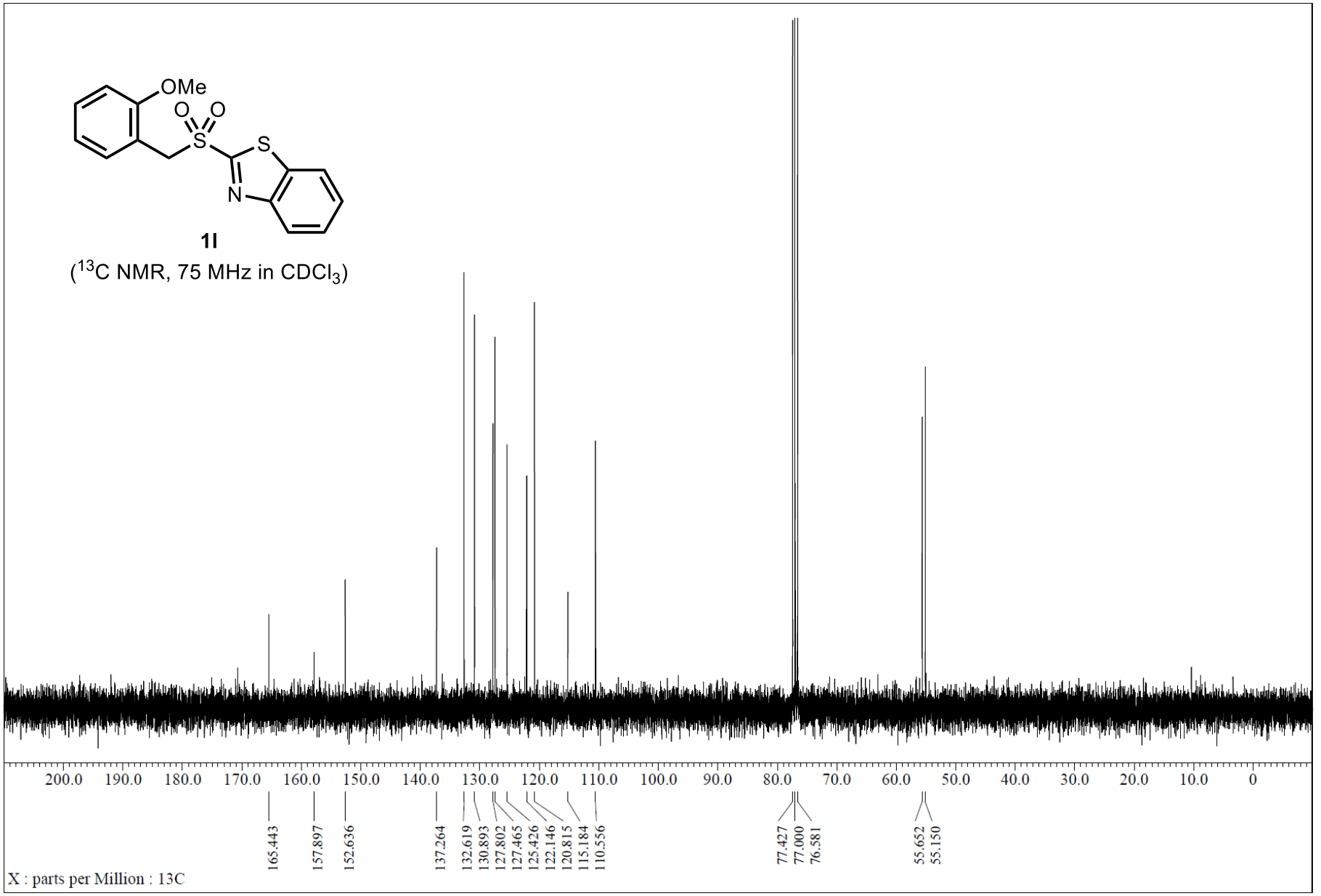

MeO
O
O
S
S
N
N
1f
(1H NMR, 300 MHz in CDCl3)
3.00
2.00
2.04
2.04
0.98
0.97
0.99
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.781
8.776
8.766
8.761
8.525
8.519
8.497
8.491
7.636
7.621
7.608
7.593
7.266
7.202
7.196
7.180
7.173
6.816
6.809
6.794
6.787
4.702
3.766
1.627
0.000
X : parts per Million : 1H


MeO
O
O
S
S
N
N
1f
(13C NMR, 75 MHz in CDCl3)
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
166.512
160.396
159.237
150.203
145.796
132.792
132.315
122.697
117.559
114.460
77.419
77.000
76.573
60.222
55.232
X : parts per Million : 13C


MeO
O
O
S
NO2
1g
(1H NMR, 300 MHz in CDCl3)
1.95
1.99
1.85
1.90
1.98
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.300
8.270
7.817
7.787
7.262
7.018
6.988
6.817
6.788
4.321
3.797
1.566
0.000
X : parts per Million : 1H

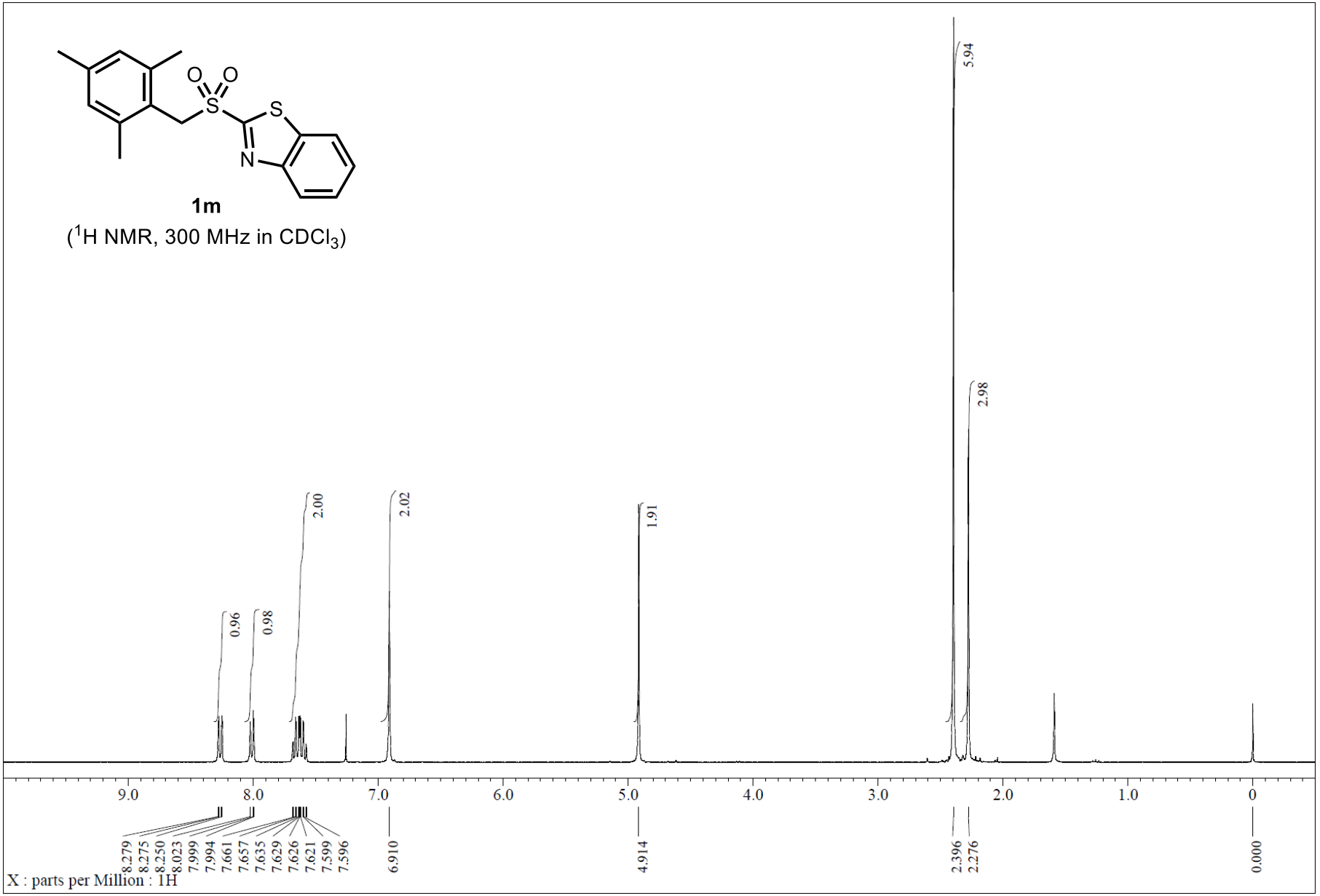

MeO
O
O
S
NO2
1g
(13C NMR, 75 MHz in CDCl3)
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
160.297
150.729
143.478
131.962
130.161
123.922
118.850
114.296
77.419
77.000
76.573
62.154
55.274
X : parts per Million : 13C

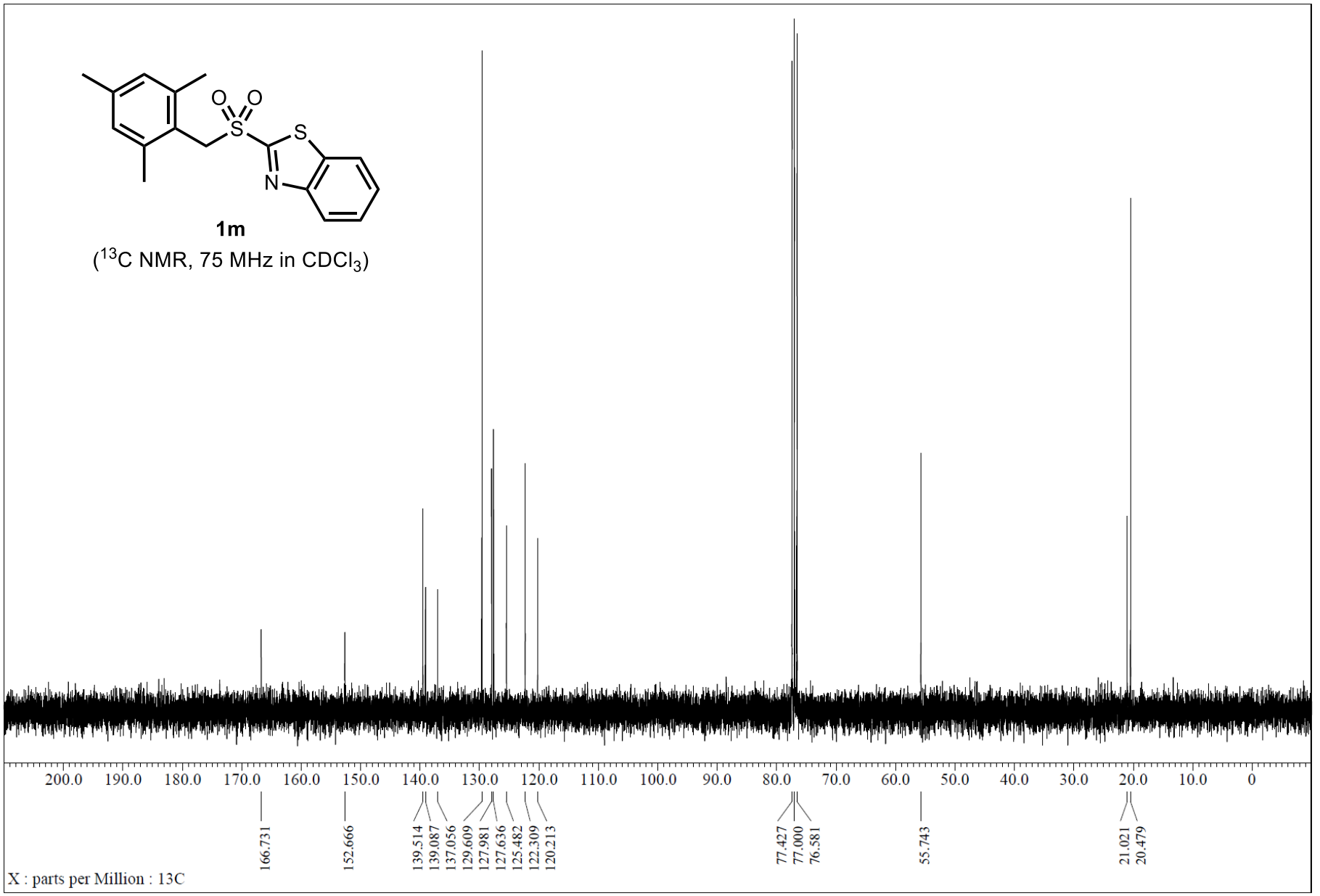

OMe
O
O
S
S
N
1l
(1H NMR, 300 MHz in CDCl3)
0.97
0.97
2.01
2.20
1.95
0.99
1.00
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.268
8.265
8.264
8.243
8.240
8.239
8.236
7.939
7.936
7.640
7.297
7.272
7.263
6.941
6.938
6.916
6.913
6.891
6.888
6.733
6.706
4.833
3.389
1.617
0.000
X : parts per Million : 1H

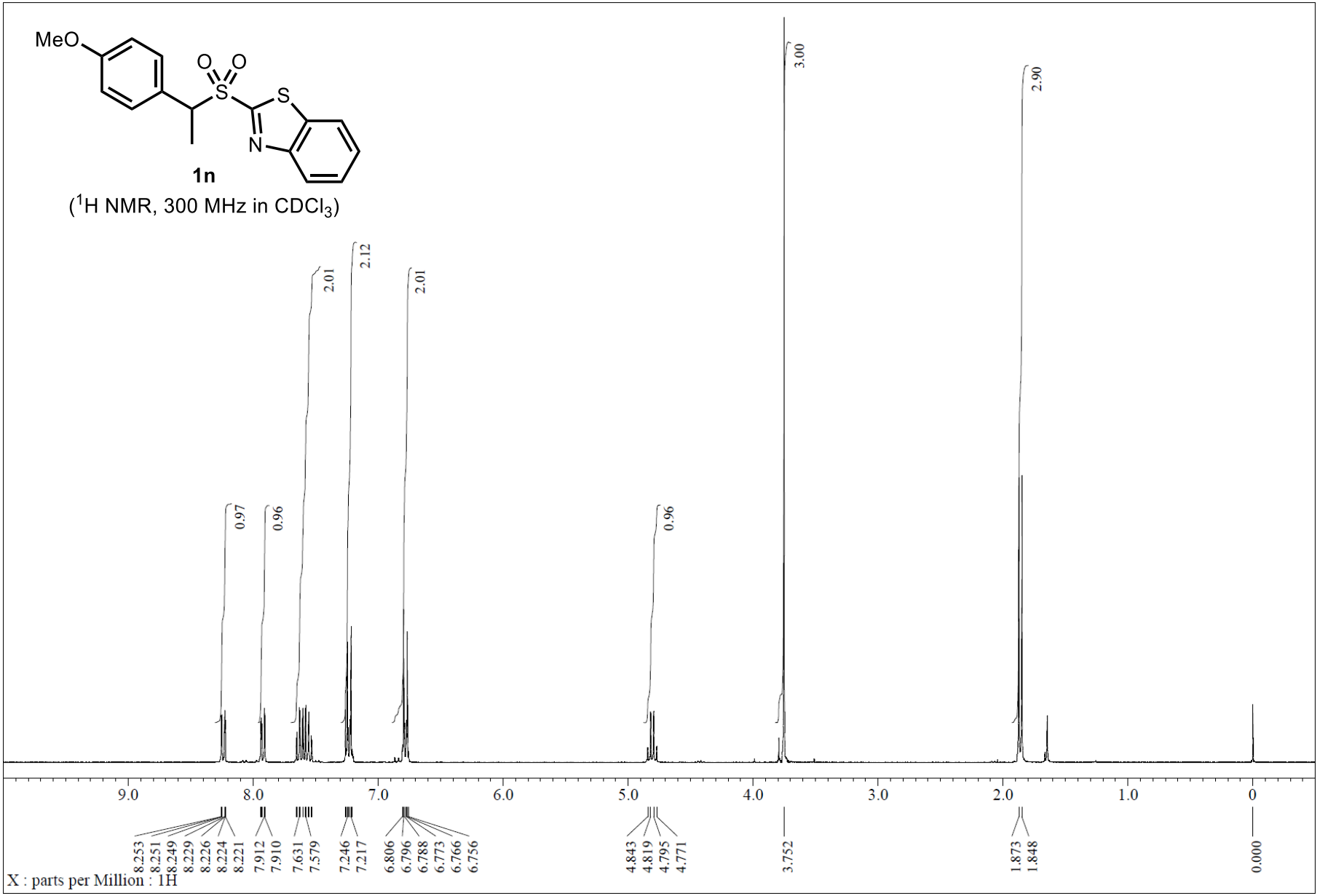


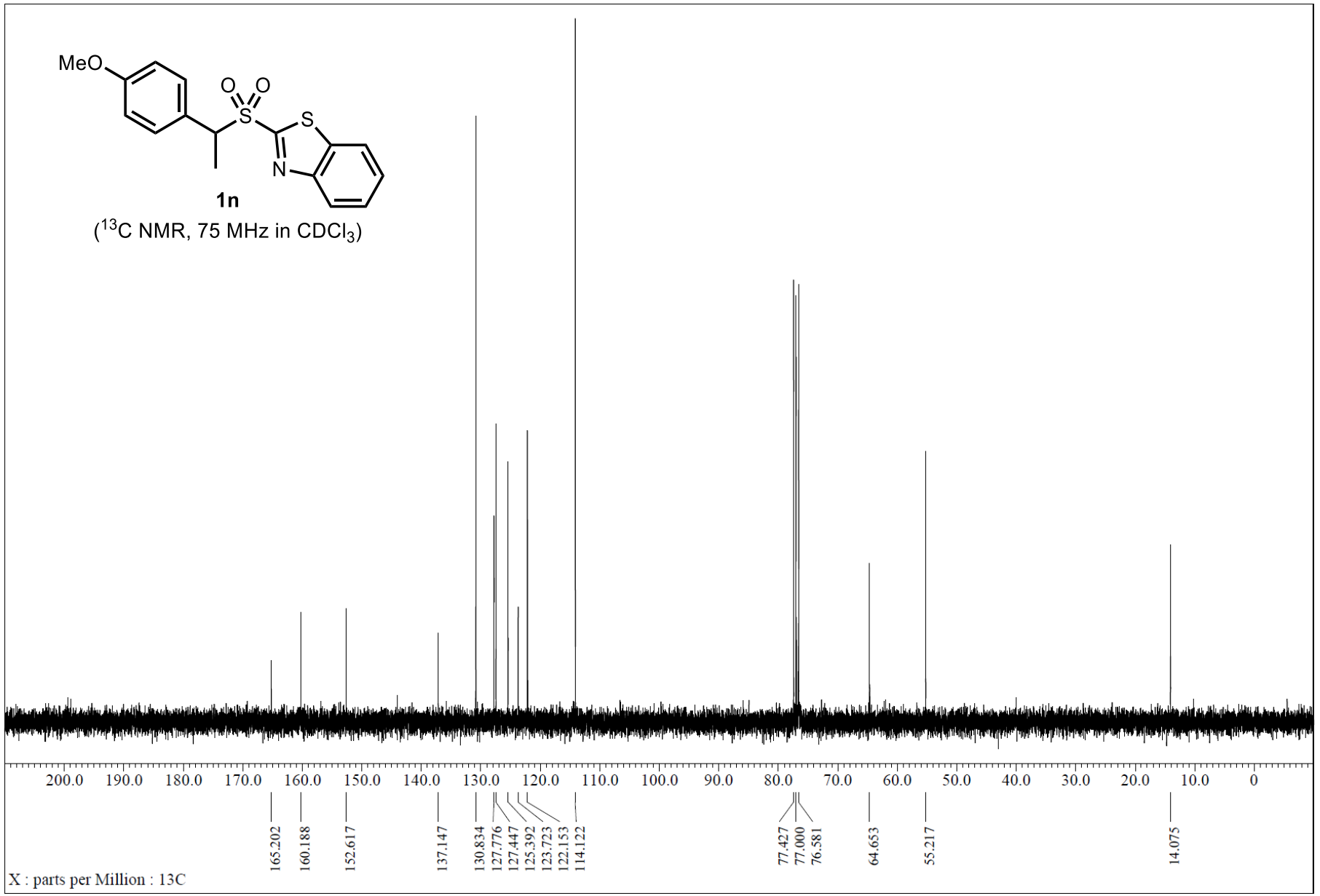
1l

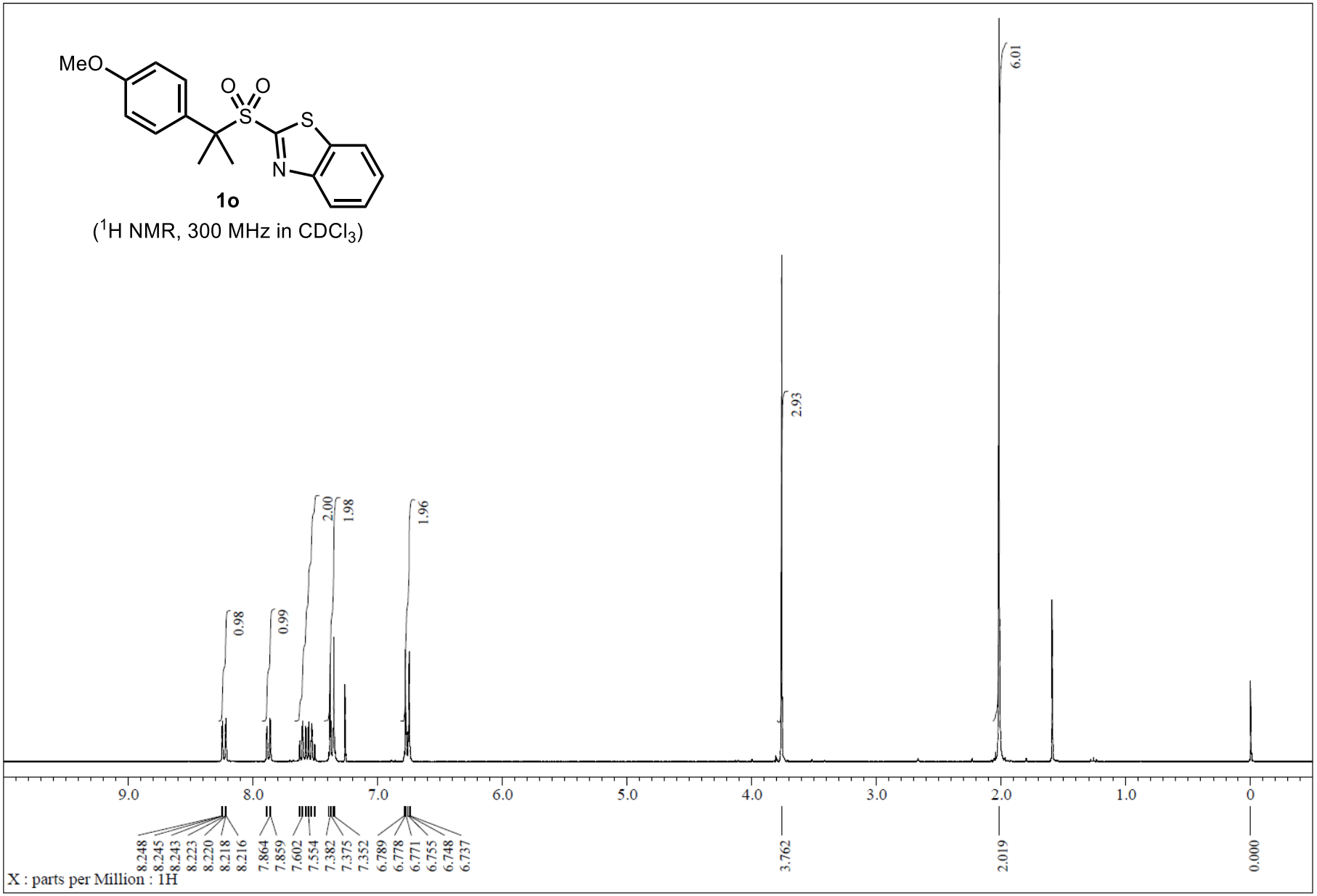
(^{13}C NMR, 75 MHz in $CDCl_3$)

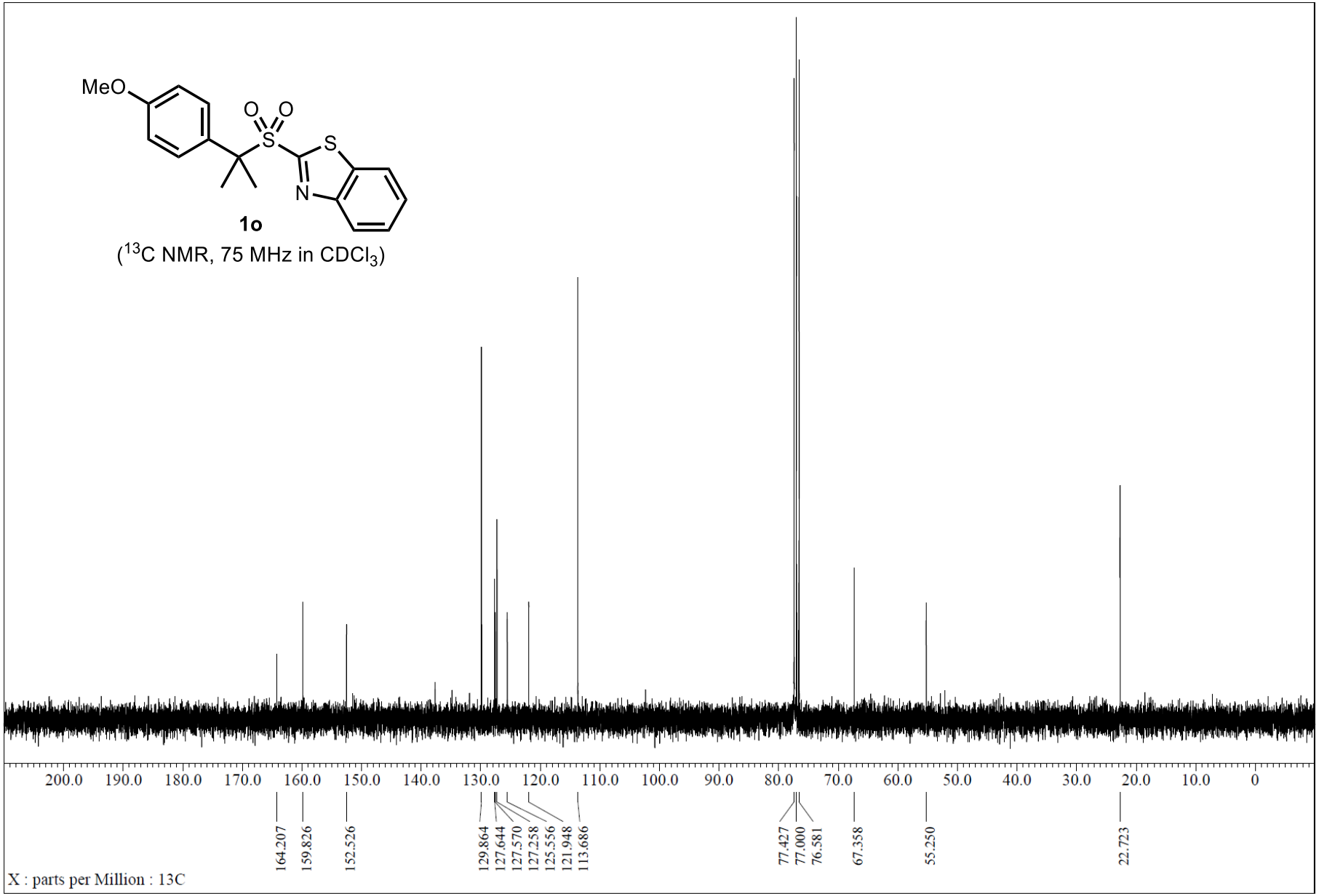

1m
(1H NMR, 300 MHz in CDCl3)
5.94
2.98
2.00
2.02
1.91
0.96
0.98
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.279
8.275
8.250
8.023
7.999
7.994
7.661
7.657
7.635
7.629
7.626
7.621
7.599
7.596
6.910
4.914
2.396
2.276
0.000
X : parts per Million : 1H

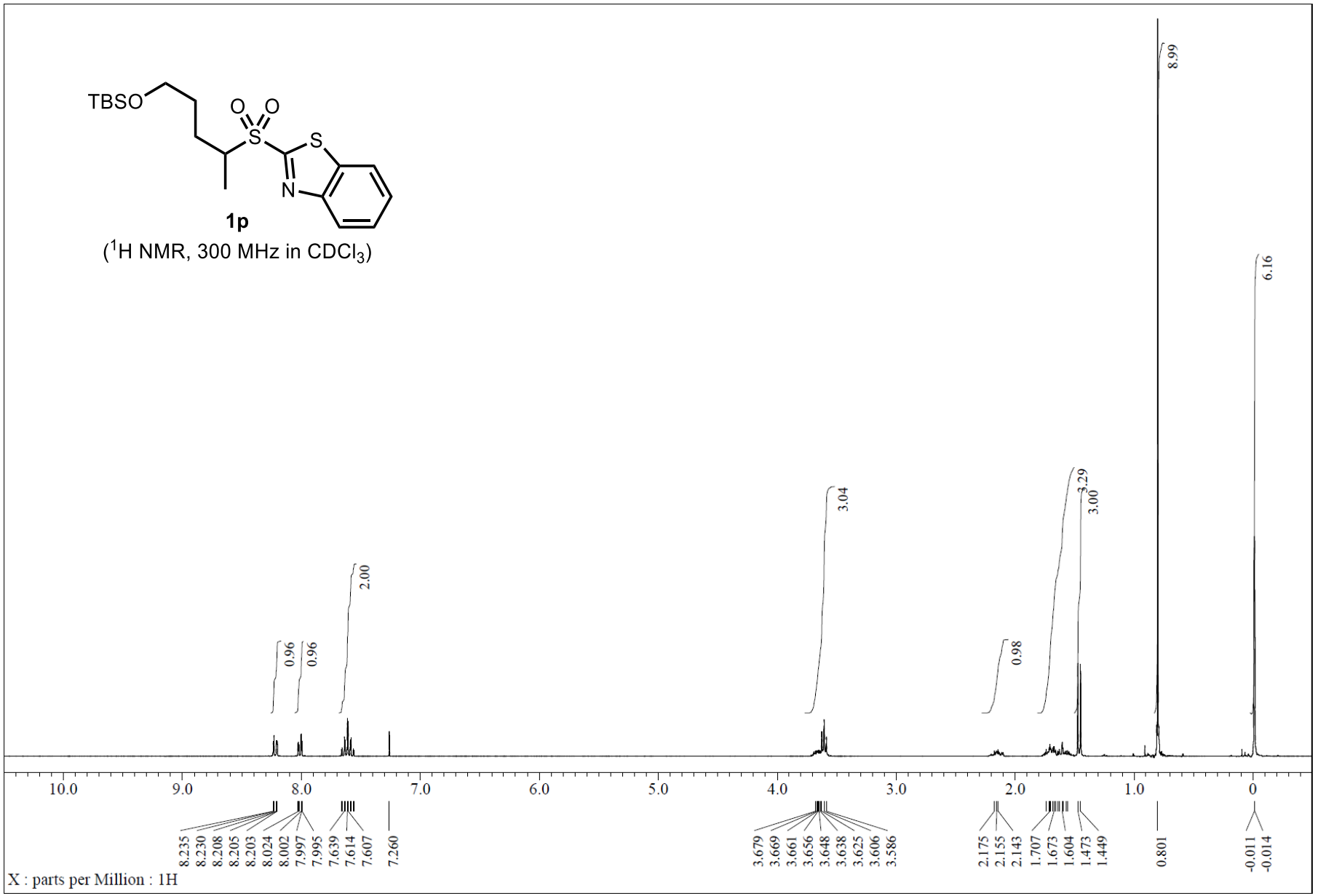

1m
(13C NMR, 75 MHz in CDCl3)
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
166.731
152.666
139.514
139.087
137.056
129.609
127.981
127.636
125.482
122.309
120.213
77.427
77.000
76.581
55.743
21.021
20.479
X : parts per Million : 13C

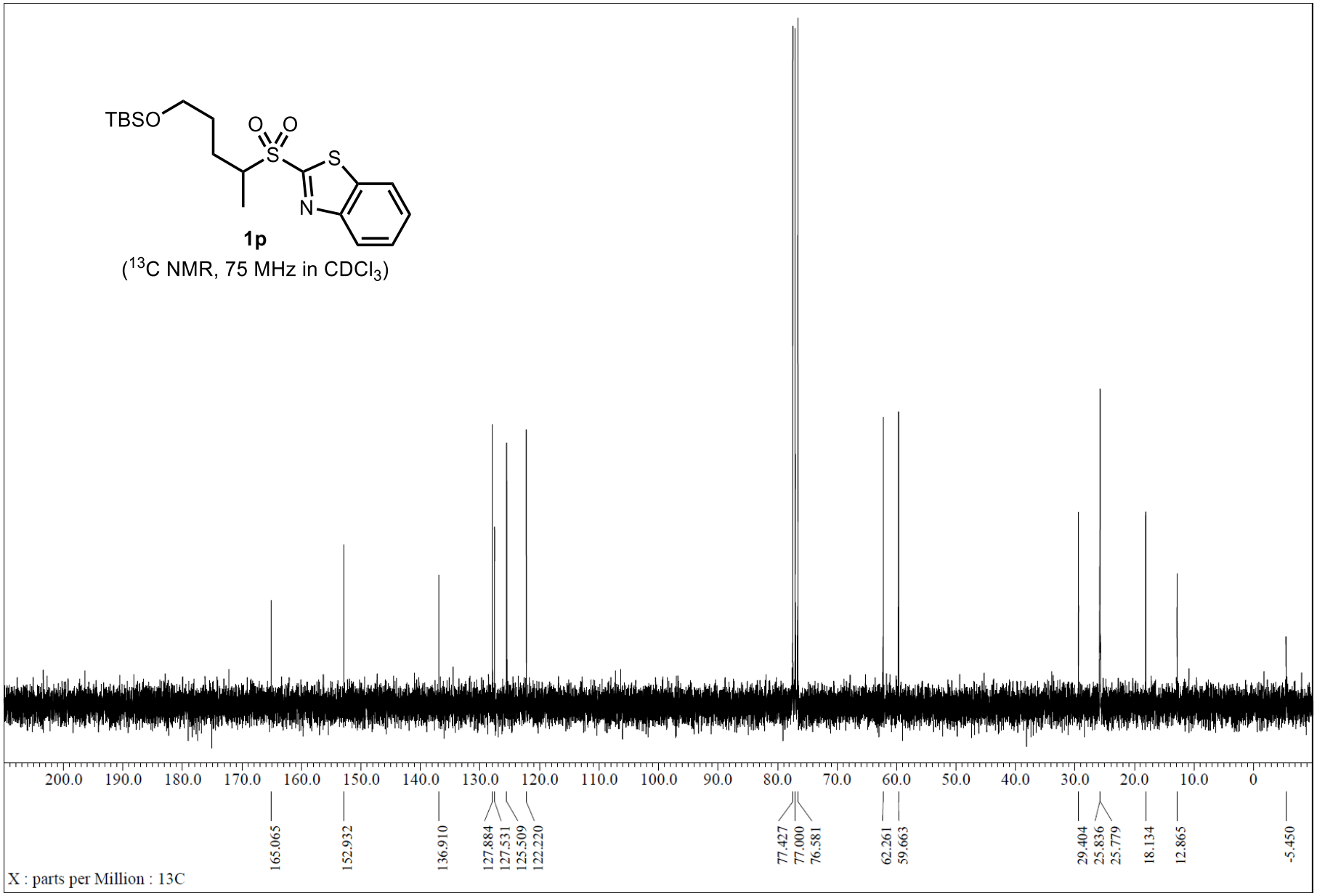

MeO
O
O
S
S
N
1n
(1H NMR, 300 MHz in CDCl3)
0.97
0.96
2.01
2.12
2.01
0.96
3.00
2.90
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.253
8.251
8.249
8.229
8.226
8.224
8.221
7.912
7.910
7.631
7.579
7.246
7.217
6.806
6.796
6.788
6.773
6.766
6.756
4.843
4.819
4.795
4.771
3.752
1.873
1.848
0.000
X : parts per Million : 1H

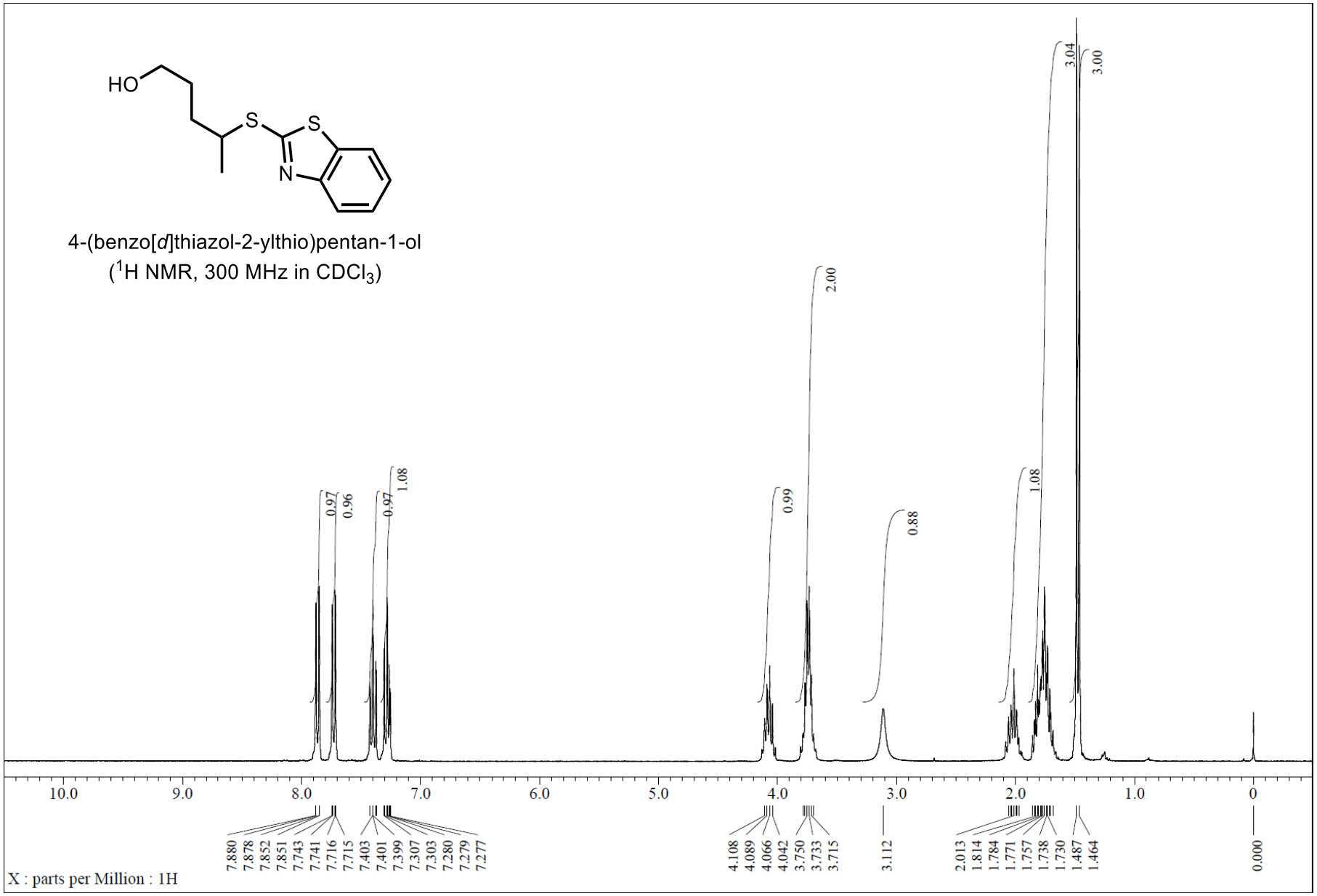

MeO
O
O
S
S
N
1n
(^{13}C NMR, 75 MHz in $CDCl_3$)
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
165.202
160.188
152.617
137.147
130.834
127.776
127.447
125.392
123.723
122.153
114.122
77.427
77.000
76.581
64.653
55.217
14.075
X : parts per Million : 13C

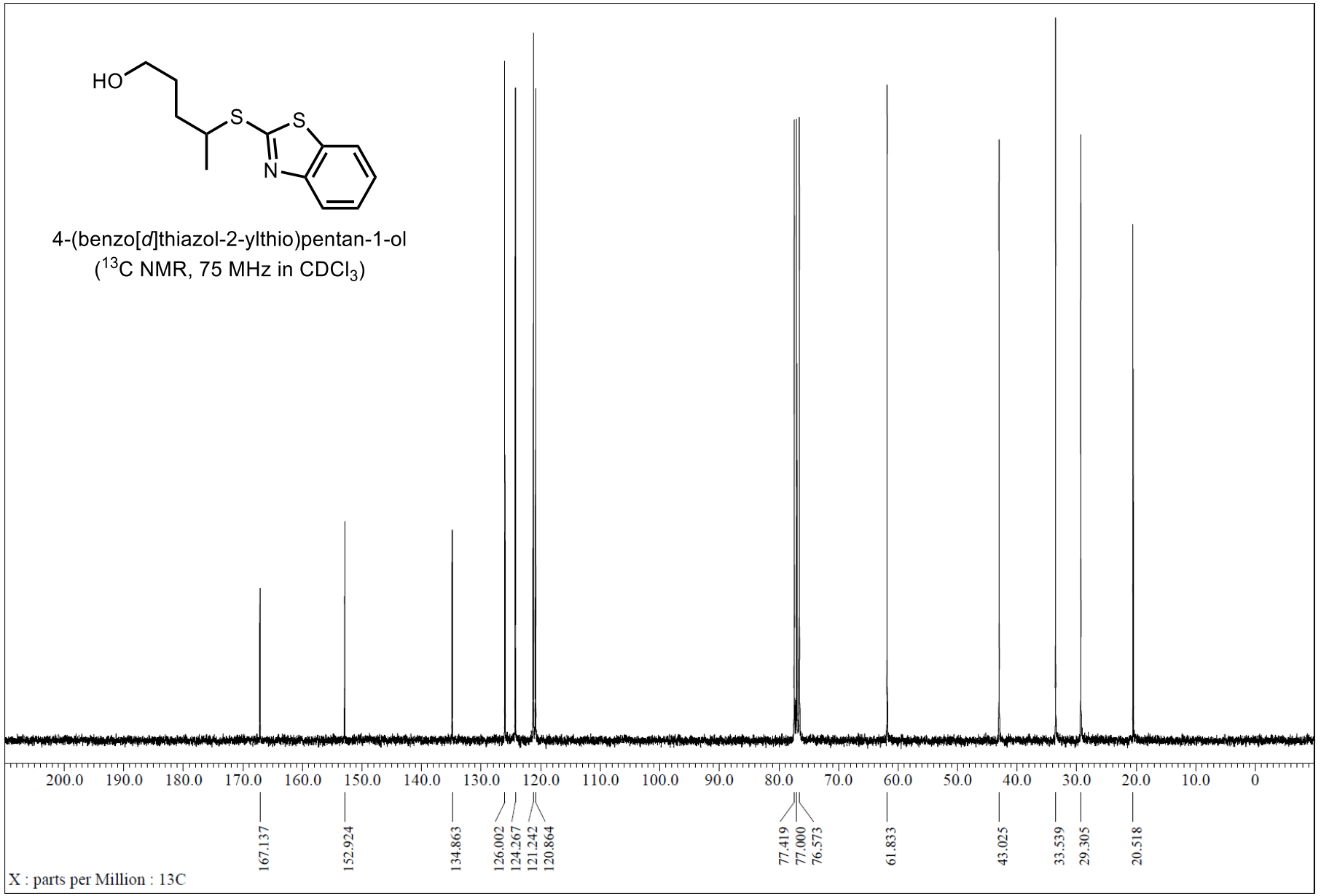

MeO
O
O
S
S
N
1o
(1H NMR, 300 MHz in CDCl3)
6.01
2.93
2.00
1.98
1.96
0.98
0.99
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.248
8.245
8.243
8.223
8.220
8.218
8.216
7.864
7.859
7.602
7.554
7.382
7.375
7.352
6.789
6.778
6.771
6.755
6.748
6.737
3.762
2.019
0.000
X : parts per Million : 1H

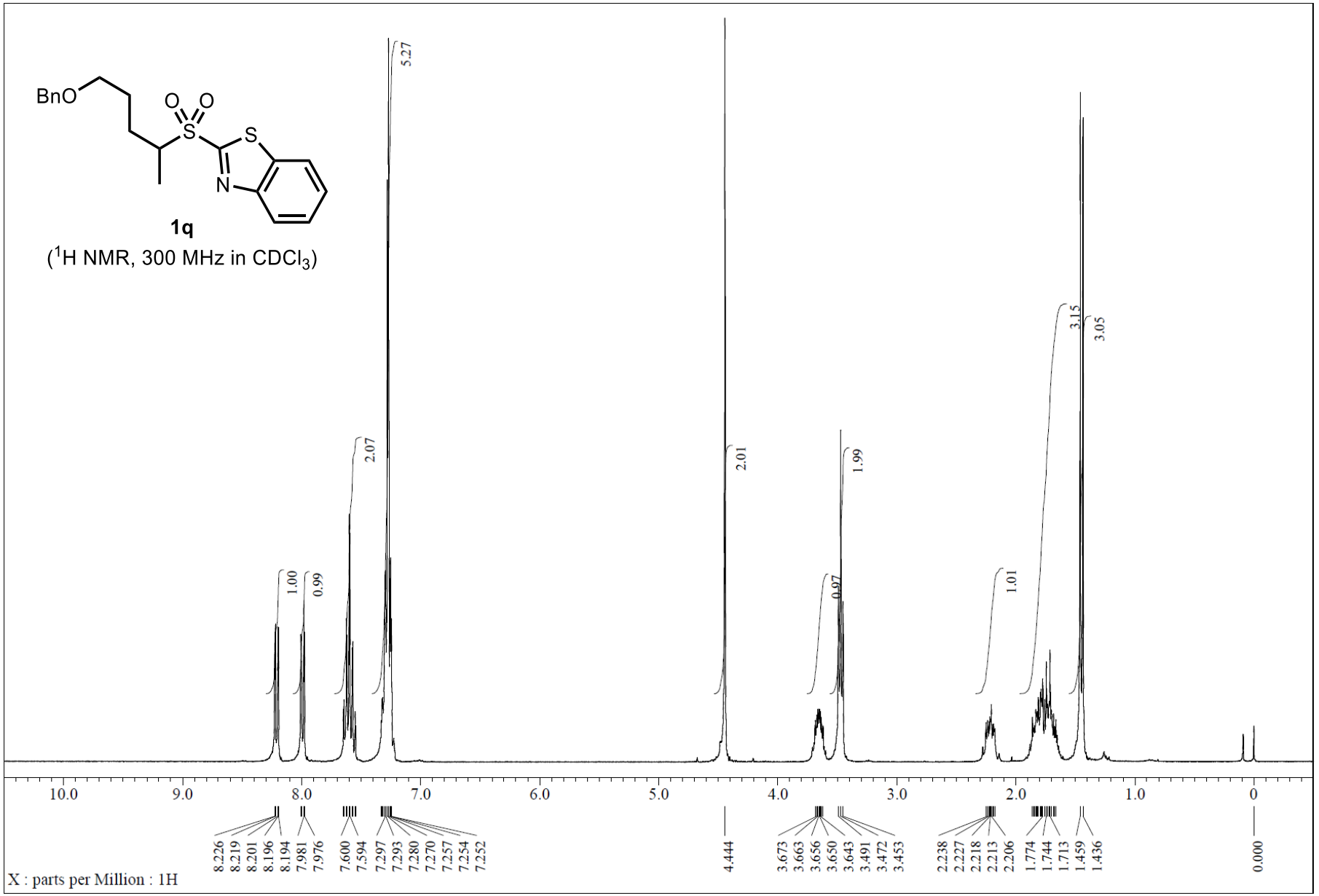

MeO
O
O
S
S
N
1o
(13C NMR, 75 MHz in CDCl3)
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
164.207
159.826
152.526
129.864
127.644
127.570
127.258
125.556
121.948
113.686
77.427
77.000
76.581
67.358
55.250
22.723
X : parts per Million : 13C

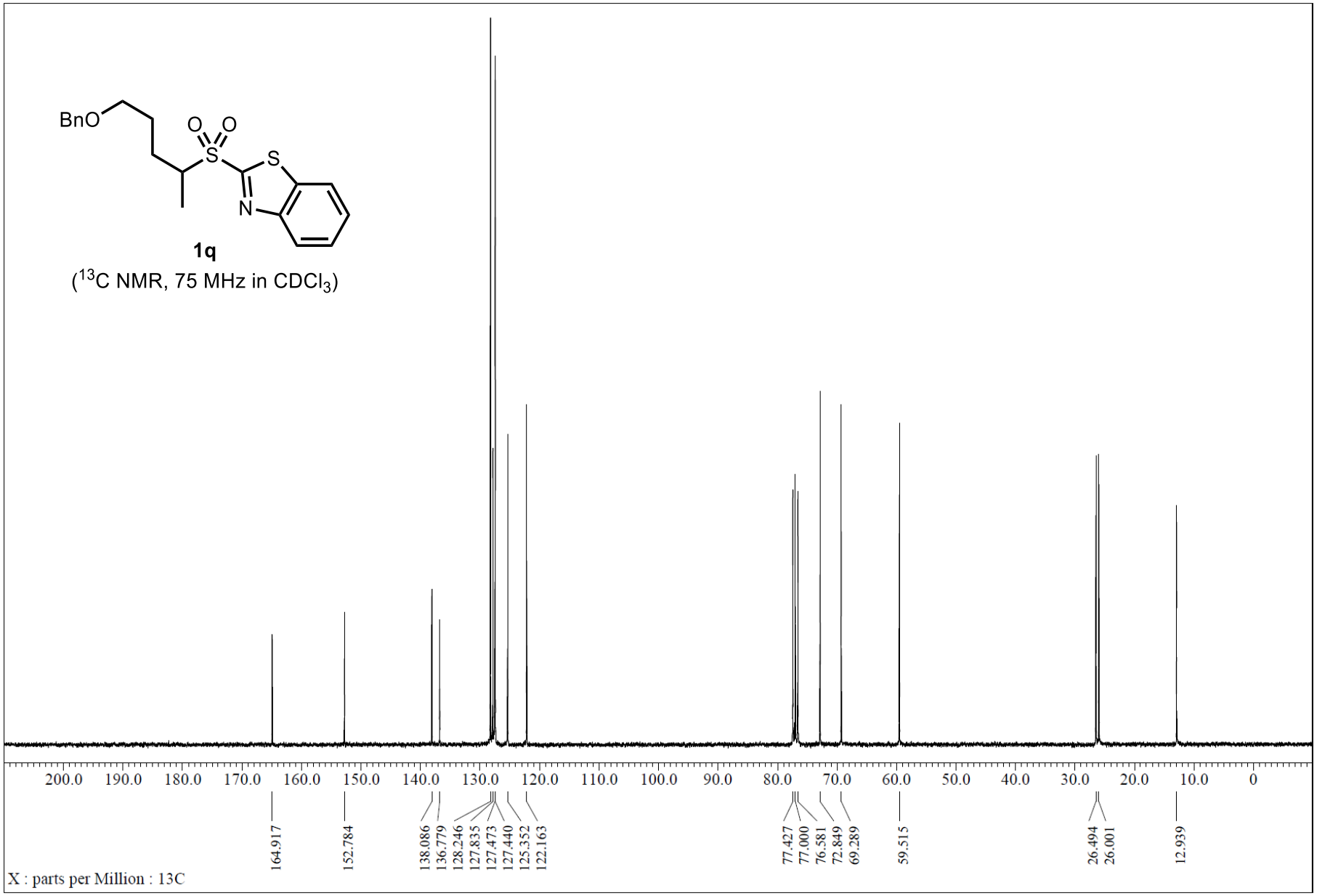

TBSO
O
O
S
S
N
1p
(1H NMR, 300 MHz in CDCl3)
8.99
6.16
3.04
3.29
3.00
2.00
0.96
0.96
0.98
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.235
8.230
8.208
8.205
8.203
8.024
8.002
7.997
7.995
7.639
7.614
7.607
7.260
3.679
3.669
3.661
3.656
3.648
3.638
3.625
3.606
3.586
2.175
2.155
2.143
1.707
1.673
1.604
1.473
1.449
0.801
-0.011
-0.014
X : parts per Million : 1H

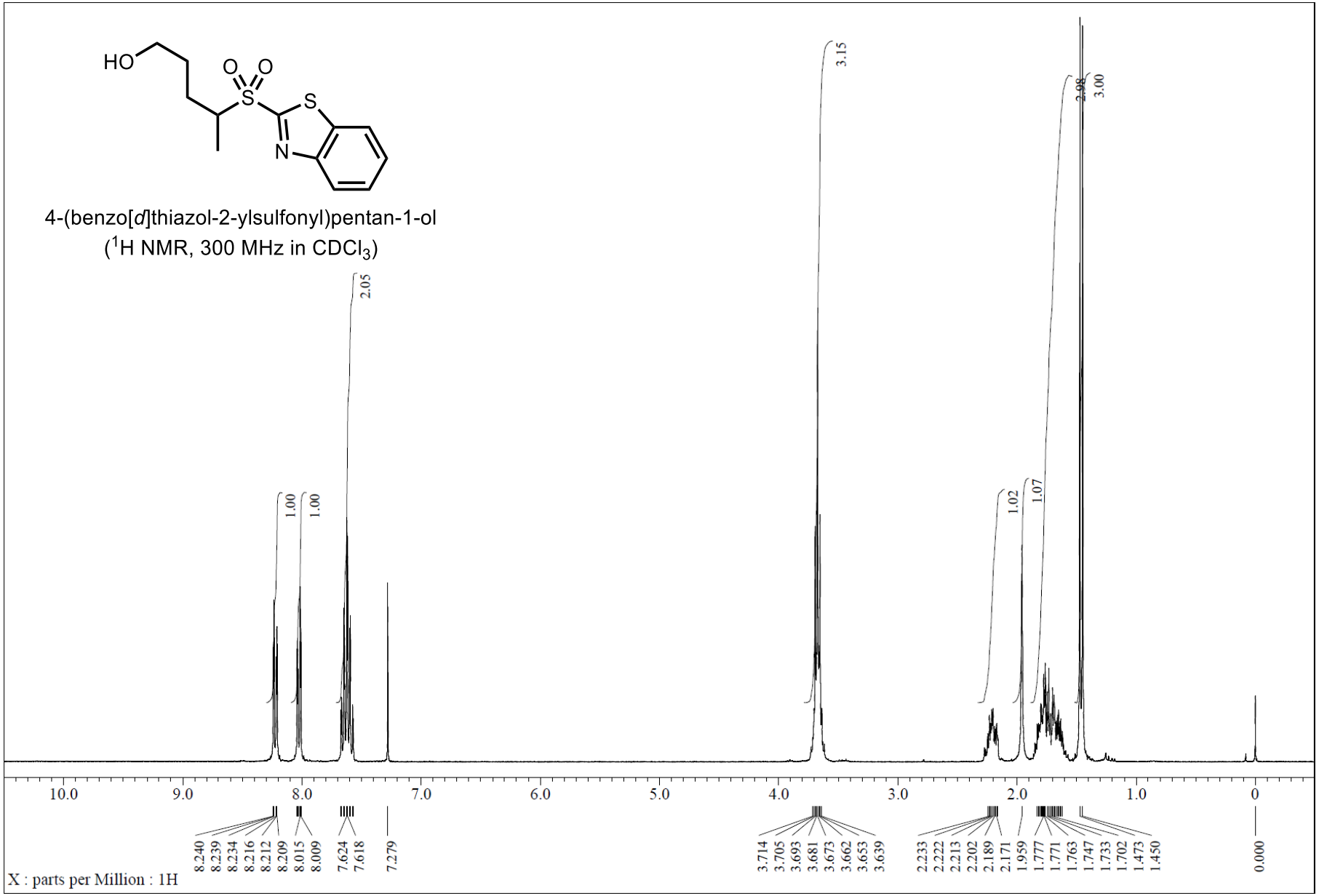

TBSO
O
O
S
S
N
1p
(13C NMR, 75 MHz in CDCl3)
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
165.065
152.932
136.910
127.884
127.531
125.509
122.220
77.427
77.000
76.581
62.261
59.663
29.404
25.836
25.779
18.134
12.865
-5.450
X : parts per Million : 13C

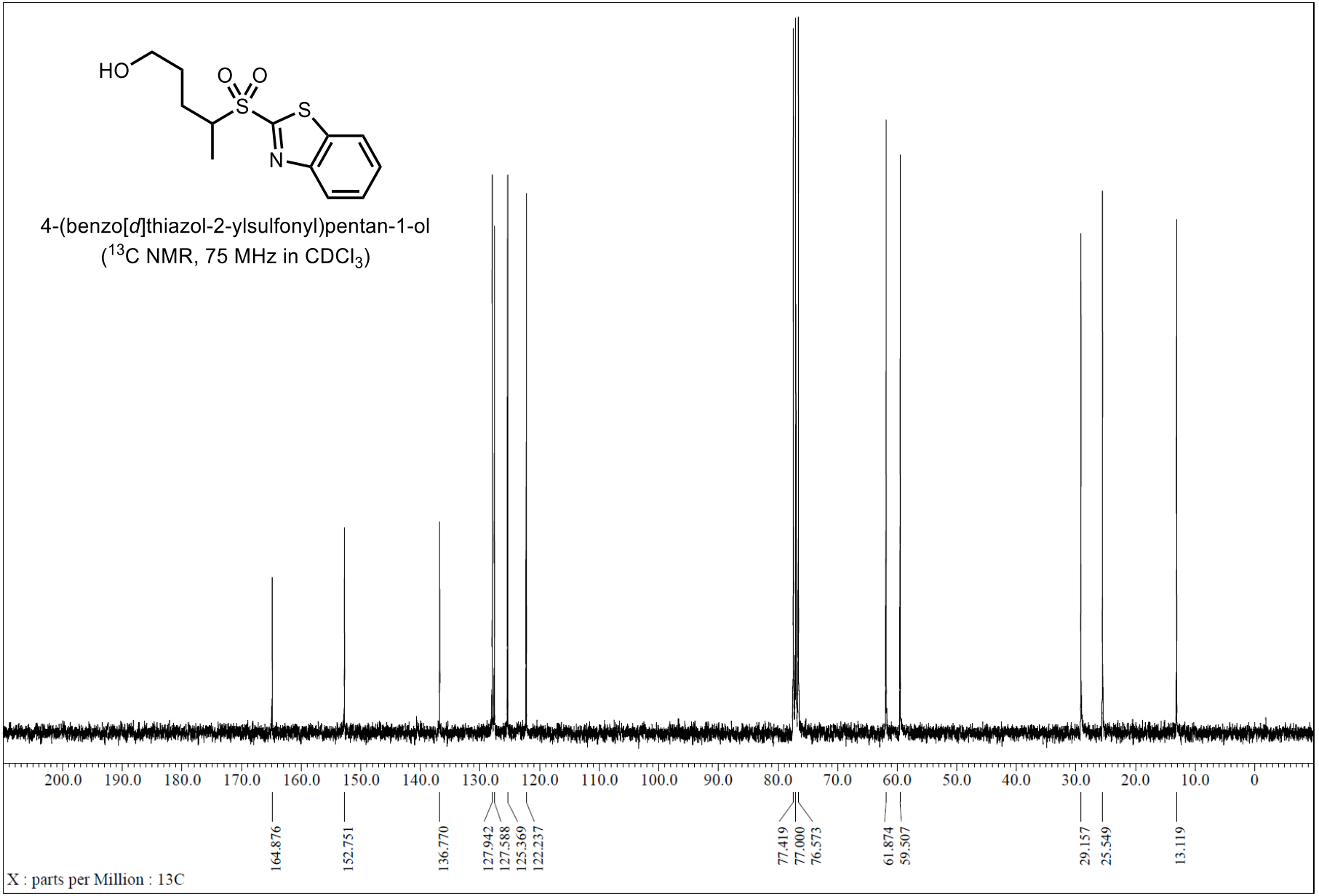

HO
S
S
N
4-(benzo[d]thiazol-2-ylthio)pentan-1-ol
(1H NMR, 300 MHz in CDCl3)
0.97
0.96
0.97
1.08
0.99
2.00
0.88
1.08
3.04
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.880
7.878
7.852
7.851
7.743
7.741
7.716
7.715
7.403
7.401
7.399
7.307
7.303
7.280
7.279
7.277
4.108
4.089
4.066
4.042
3.750
3.733
3.715
3.112
2.013
1.814
1.784
1.771
1.757
1.738
1.730
1.487
1.464
0.000
X : parts per Million : 1H

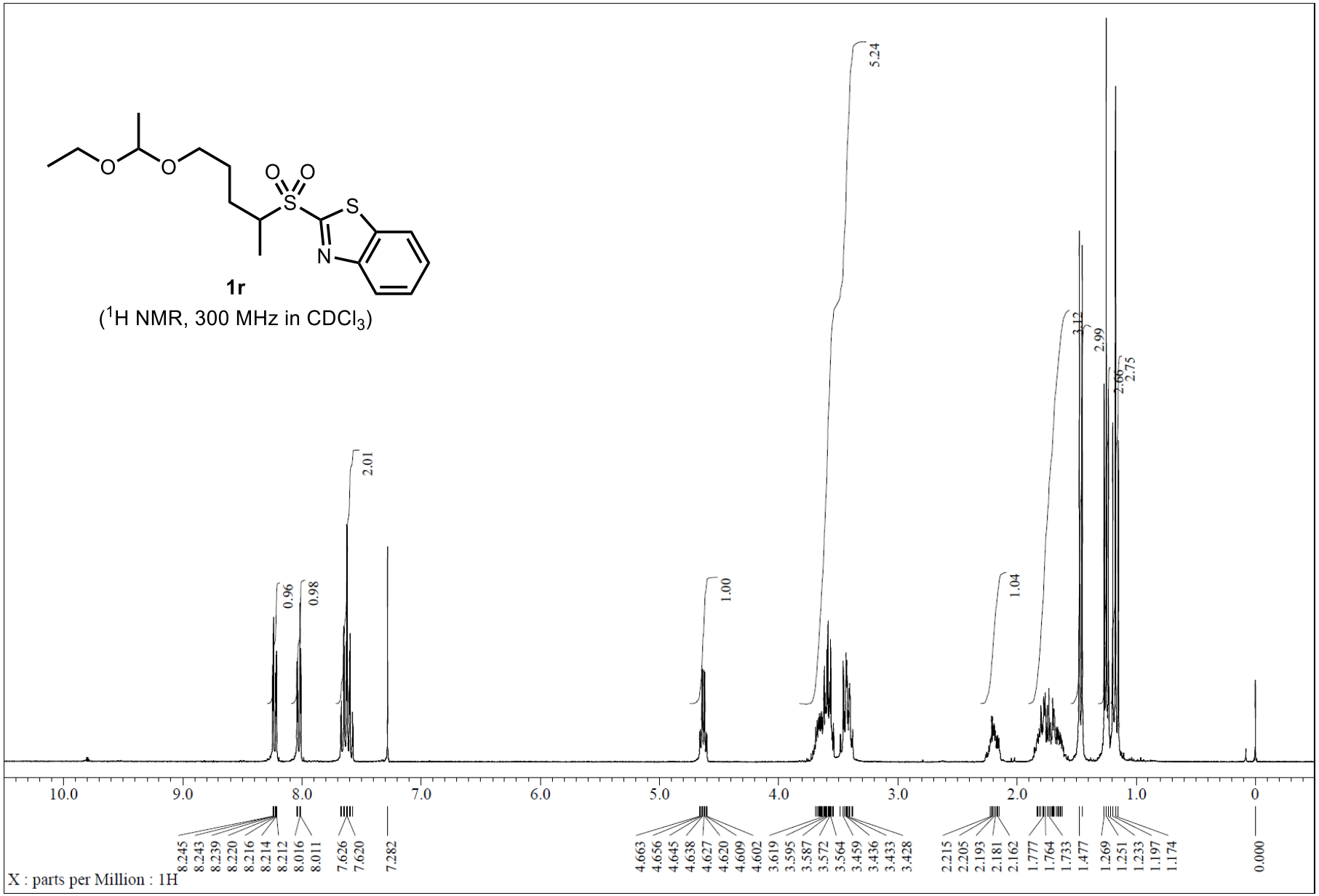

HO
S
S
N
4-(benzo[d]thiazol-2-ylthio)pentan-1-ol
(13C NMR, 75 MHz in CDCl3)
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
167.137
152.924
134.863
126.002
124.267
121.242
120.864
77.419
77.000
76.573
61.833
43.025
33.539
29.305
20.518
X : parts per Million : 13C

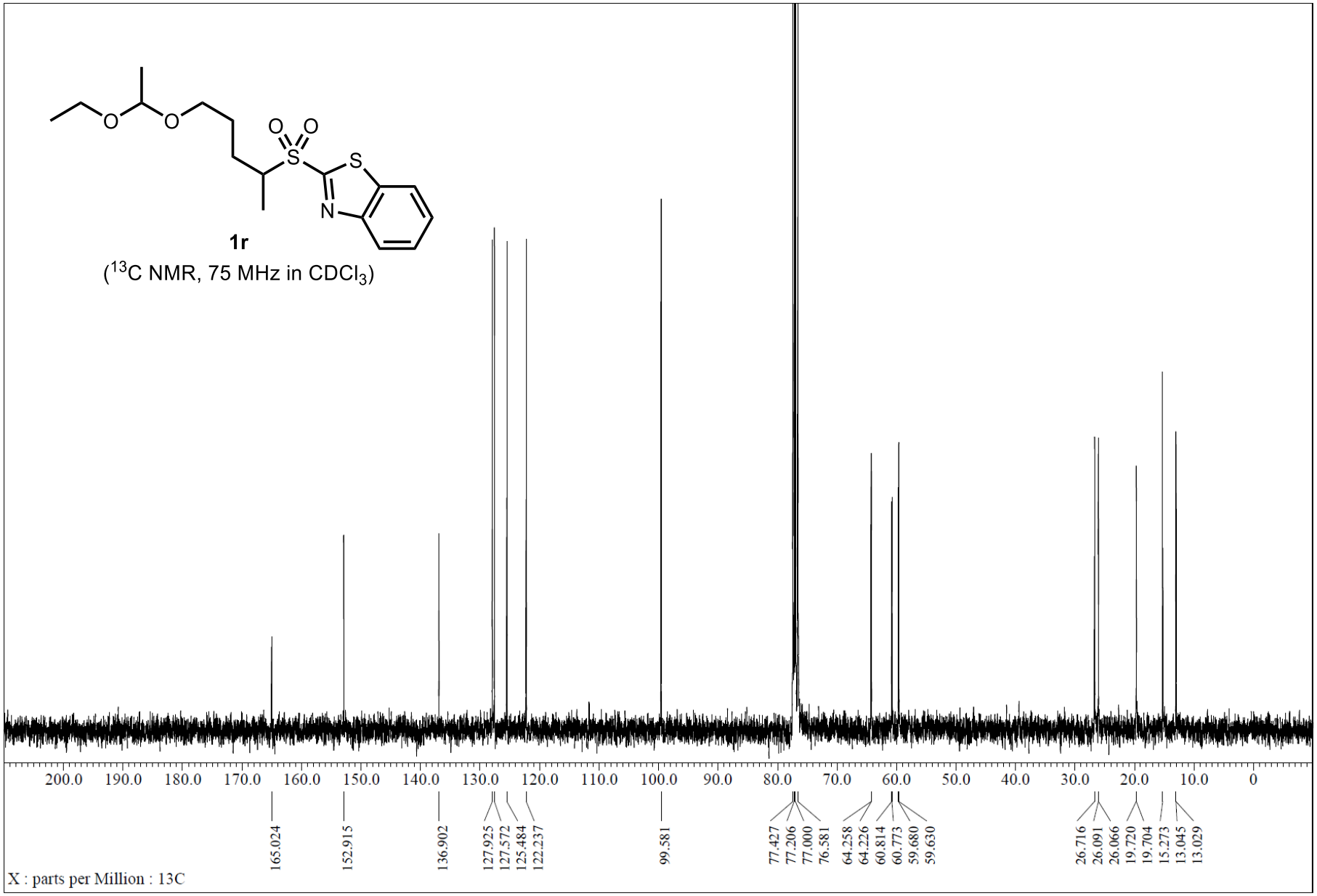

BnO
O
O
S
S
N
1q
(1H NMR, 300 MHz in CDCl3)
5.27
2.07
2.01
1.99
1.00
0.99
0.97
1.01
3.15
3.05
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.226
8.219
8.201
8.196
8.194
7.981
7.976
7.600
7.594
7.297
7.293
7.280
7.270
7.257
7.254
7.252
4.444
3.673
3.663
3.656
3.650
3.643
3.491
3.472
3.453
2.238
2.227
2.218
2.213
2.206
1.774
1.744
1.713
1.459
1.436
0.000
X : parts per Million : 1H

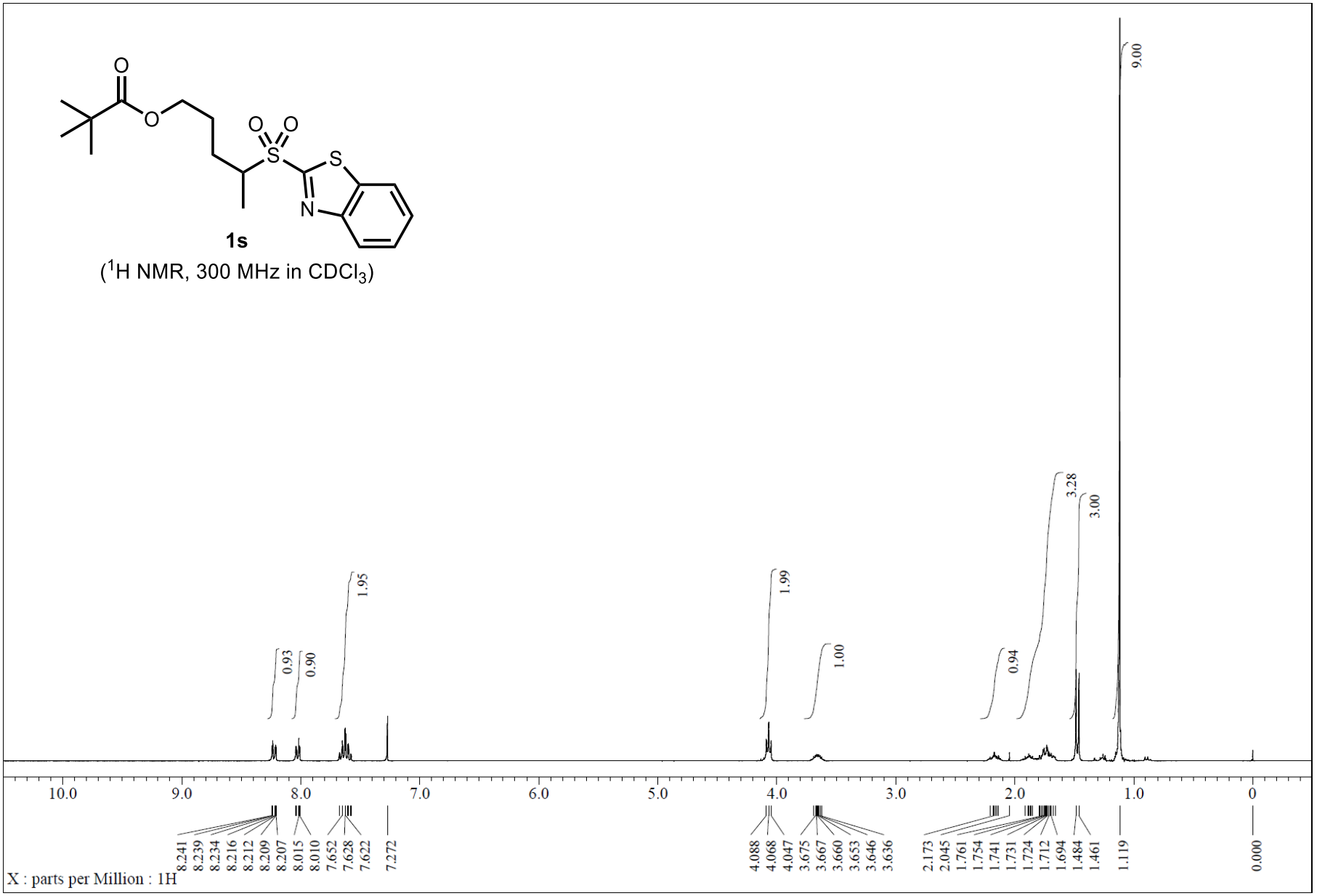

BnO
O
O
S
S
N
1q
(13C NMR, 75 MHz in CDCl3)
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
164.917
152.784
138.086
136.779
128.246
127.835
127.473
127.440
125.352
122.163
77.427
77.000
76.581
72.849
69.289
59.515
26.494
26.001
12.939
X : parts per Million : 13C

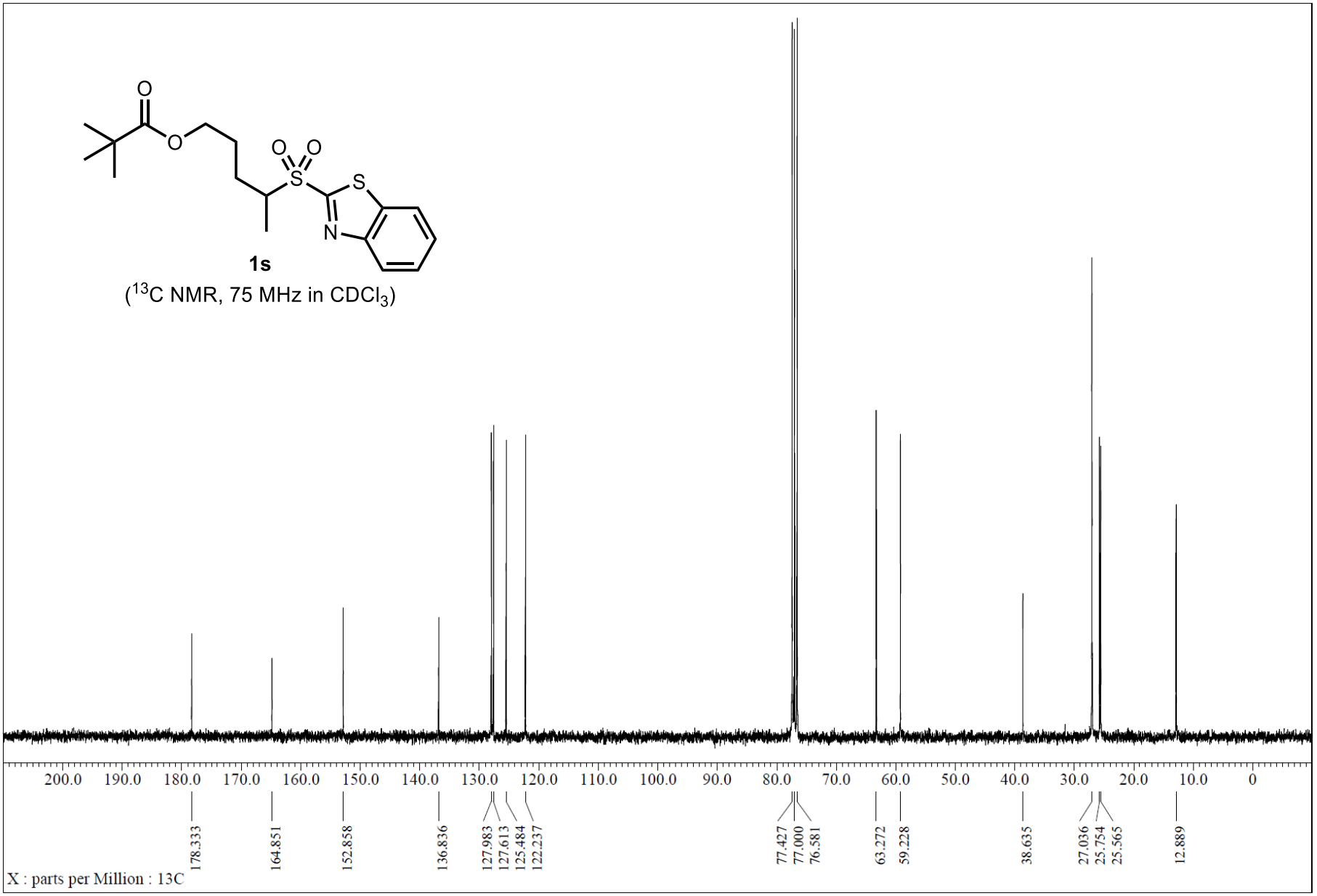

HO
O
O
S
S
N
4-(benzo[d]thiazol-2-ylsulfonyl)pentan-1-ol
(1H NMR, 300 MHz in CDCl3)
3.15
2.98
3.00
2.05
1.00
1.00
1.02
1.07
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.240
8.239
8.234
8.216
8.212
8.209
8.015
8.009
7.624
7.618
7.279
3.714
3.705
3.693
3.681
3.673
3.662
3.653
3.639
2.233
2.222
2.213
2.202
2.189
2.171
1.959
1.777
1.771
1.763
1.747
1.733
1.702
1.473
1.450
0.000
X : parts per Million : 1H

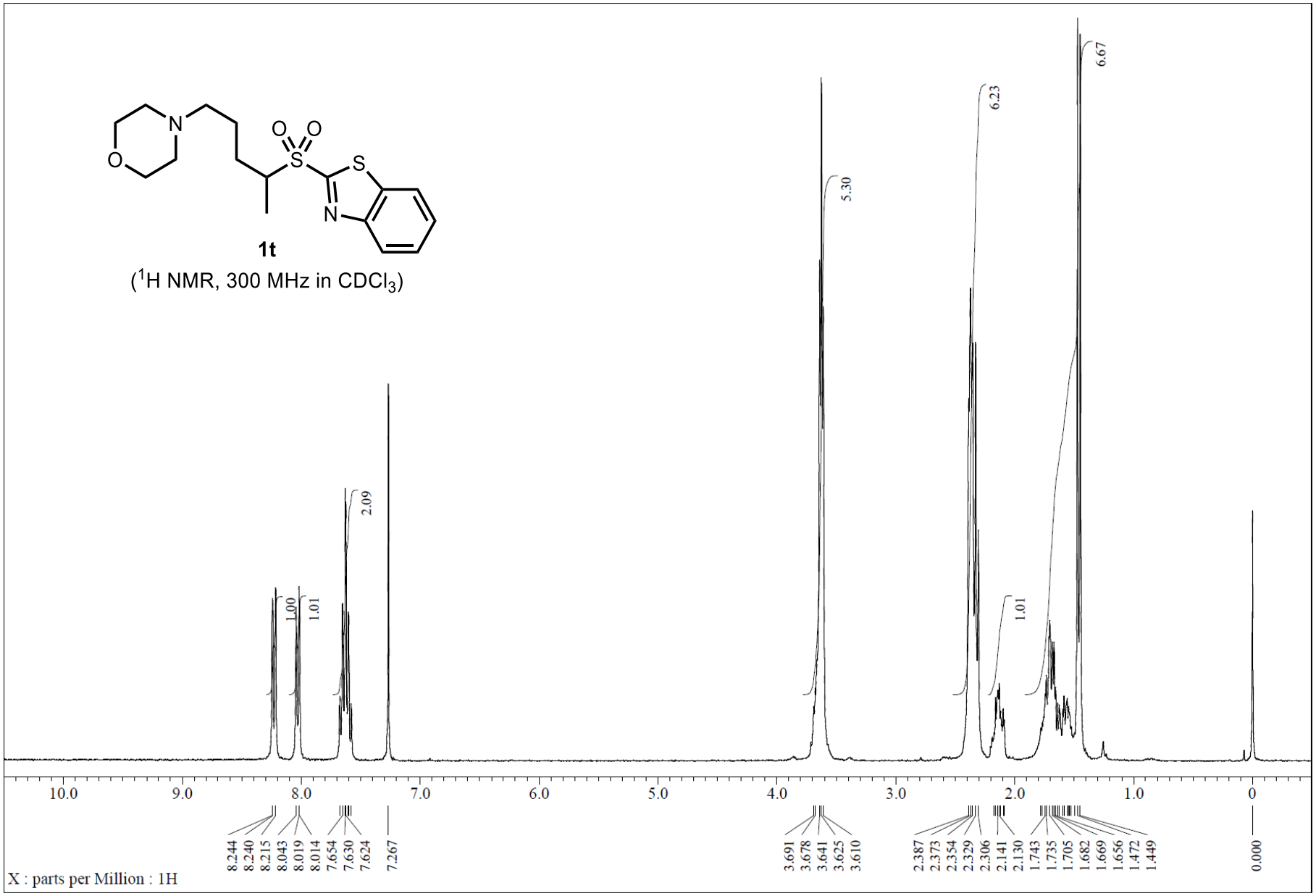

HO
O
O
S
S
N
4-(benzo[d]thiazol-2-ylsulfonyl)pentan-1-ol
(13C NMR, 75 MHz in CDCl3)
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
164.876
152.751
136.770
127.942
127.588
125.369
122.237
77.419
77.000
76.573
61.874
59.507
29.157
25.549
13.119
X : parts per Million : 13C

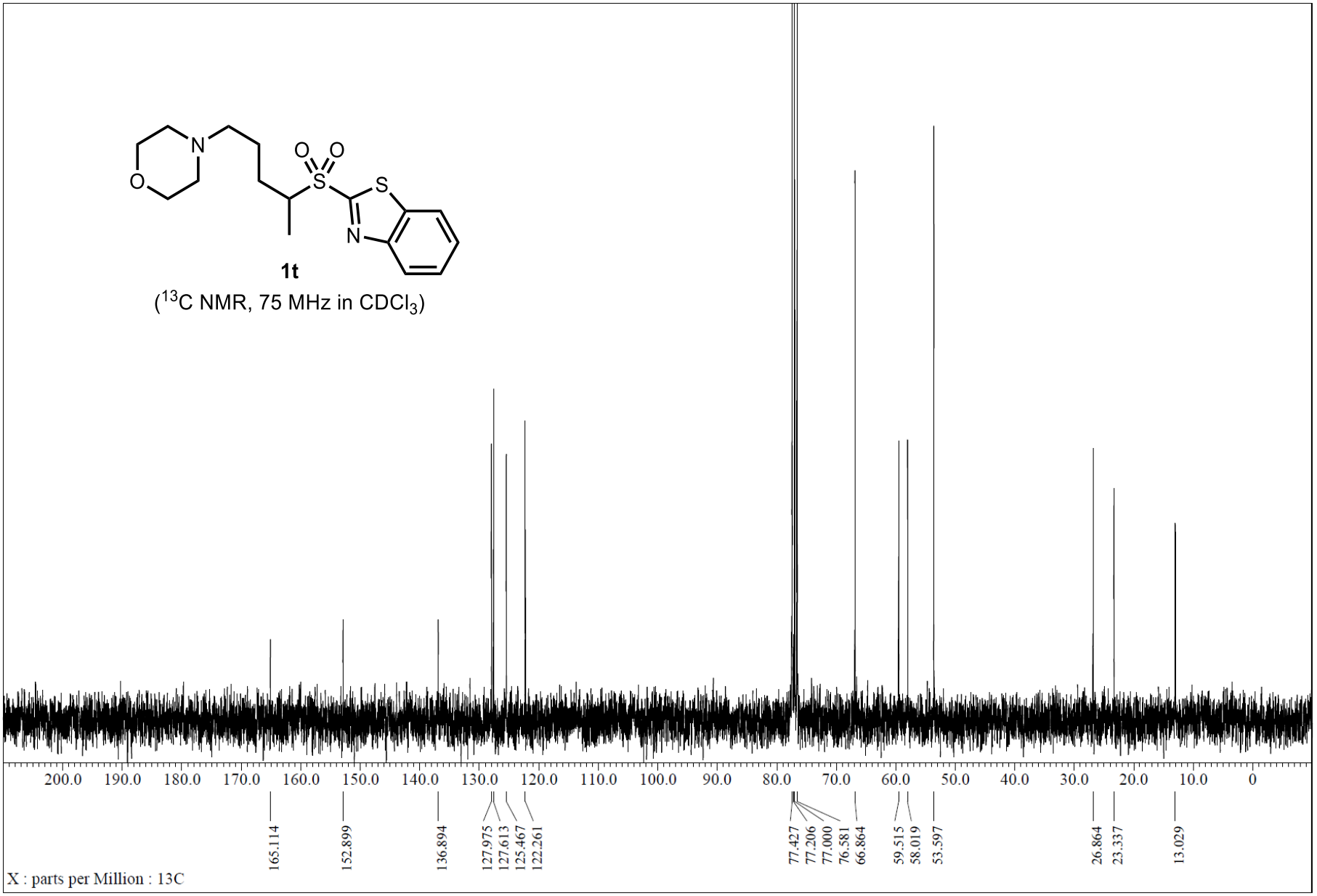

1r
(1H NMR, 300 MHz in CDCl3)
5.24
3.12
2.99
2.75
2.66
2.01
0.96
0.98
1.00
1.04
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.245
8.243
8.239
8.220
8.216
8.214
8.212
8.016
8.011
7.626
7.620
7.282
4.663
4.656
4.645
4.638
4.627
4.620
4.609
4.602
3.619
3.595
3.587
3.572
3.564
3.459
3.436
3.433
3.428
2.215
2.205
2.193
2.181
2.162
1.777
1.764
1.733
1.477
1.269
1.251
1.233
1.197
1.174
0.000
X : parts per Million : 1H

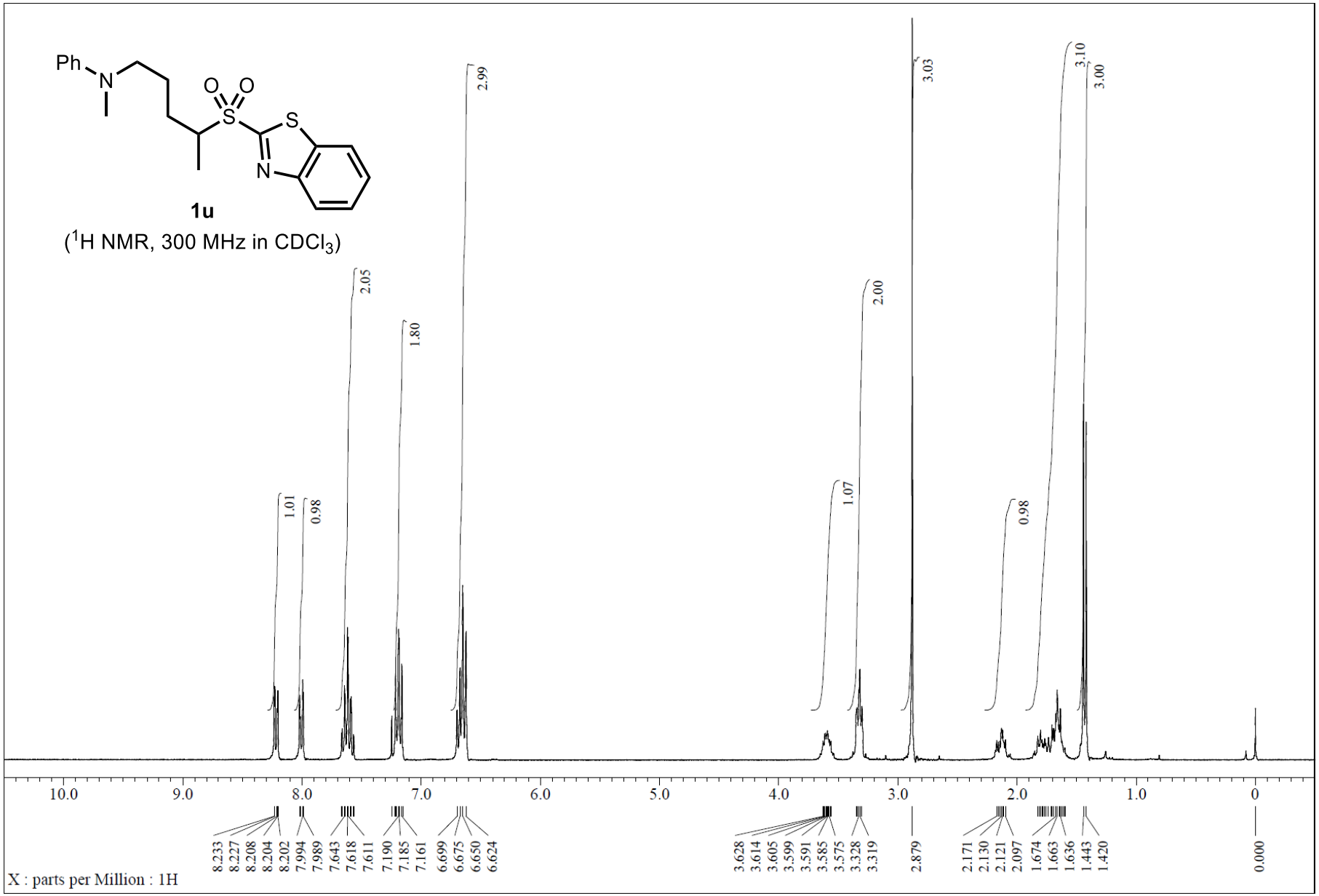

1r
(13C NMR, 75 MHz in CDCl3)
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
165.024
152.915
136.902
127.925
127.572
125.484
122.237
99.581
77.427
77.206
77.000
76.581
64.258
64.226
60.814
60.773
59.680
59.630
26.716
26.091
26.066
19.720
19.704
15.273
13.045
13.029
X : parts per Million : 13C

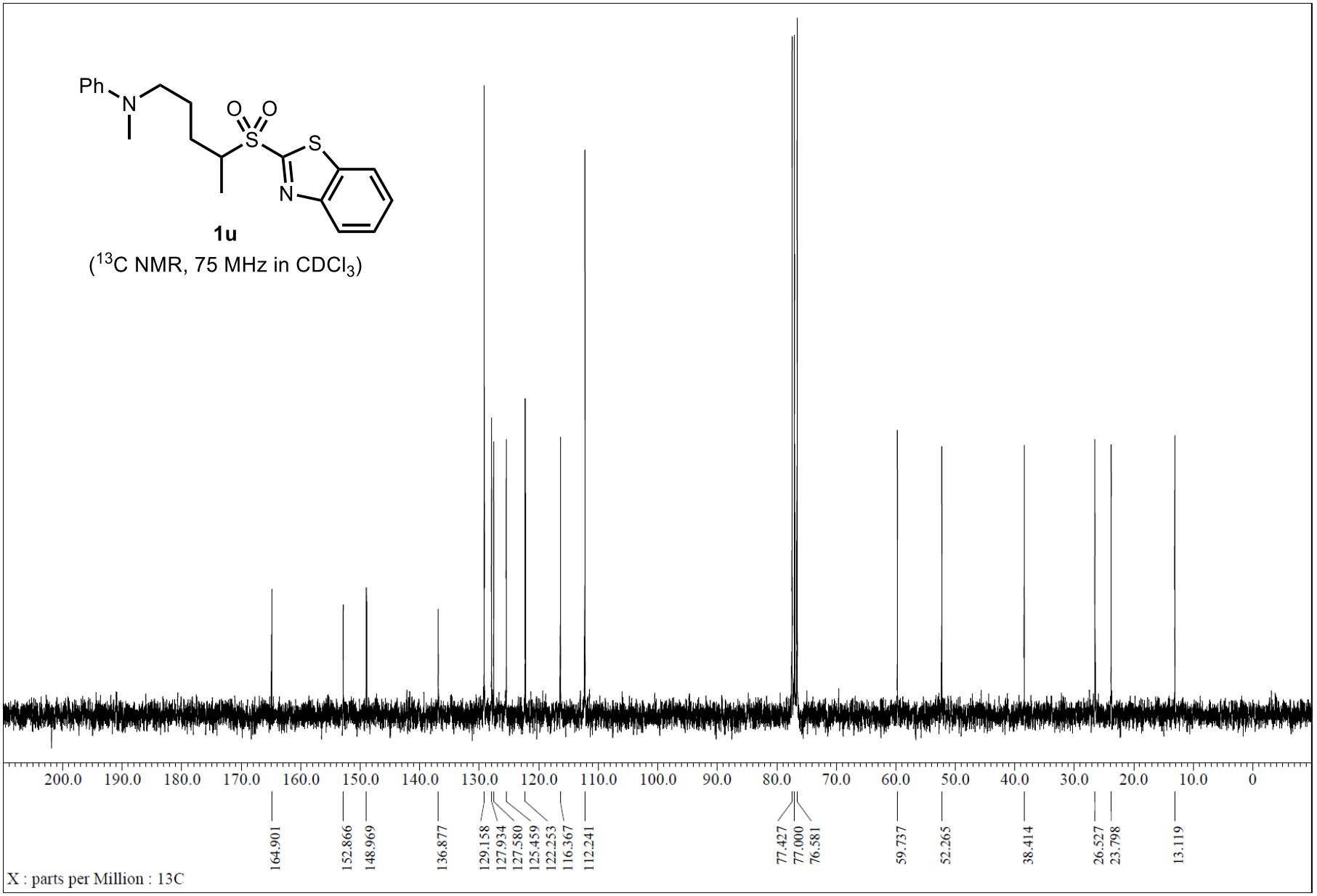

O
O
O
O
S
S
N
1s
(1H NMR, 300 MHz in CDCl3)
9.00
3.28
3.00
1.95
1.99
1.00
0.94
0.93
0.90
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.241
8.239
8.234
8.216
8.212
8.209
8.207
8.015
8.010
7.652
7.628
7.622
7.272
4.088
4.068
4.047
3.675
3.667
3.660
3.653
3.646
3.636
2.173
2.045
1.761
1.754
1.741
1.731
1.724
1.712
1.694
1.484
1.461
1.119
0.000
X : parts per Million : 1H

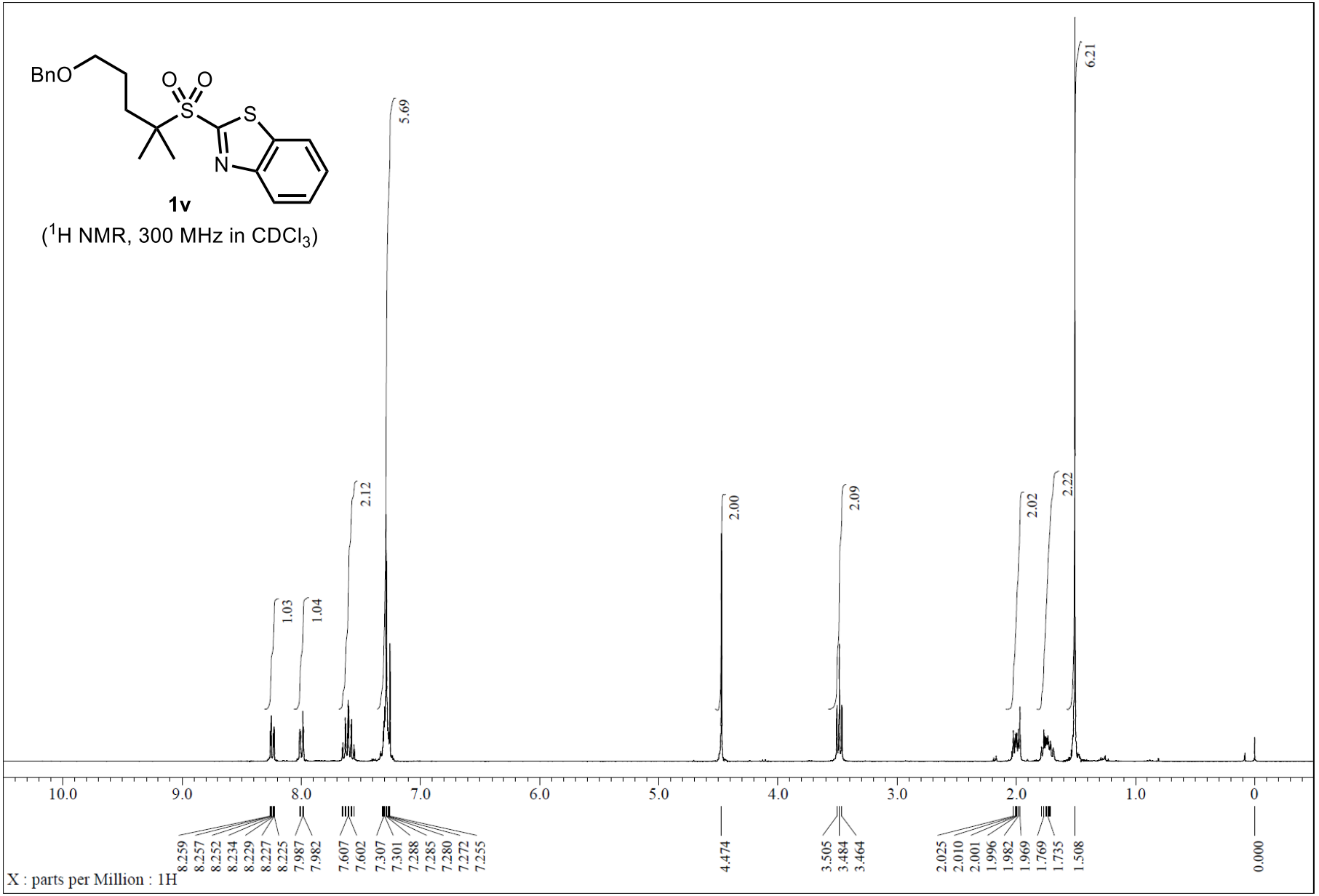

O
O
O
O
S
S
N
1s
(13C NMR, 75 MHz in CDCl3)
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
178.333
164.851
152.858
136.836
127.983
127.613
125.484
122.237
77.427
77.000
76.581
63.272
59.228
38.635
27.036
25.754
25.565
12.889
X : parts per Million : 13C

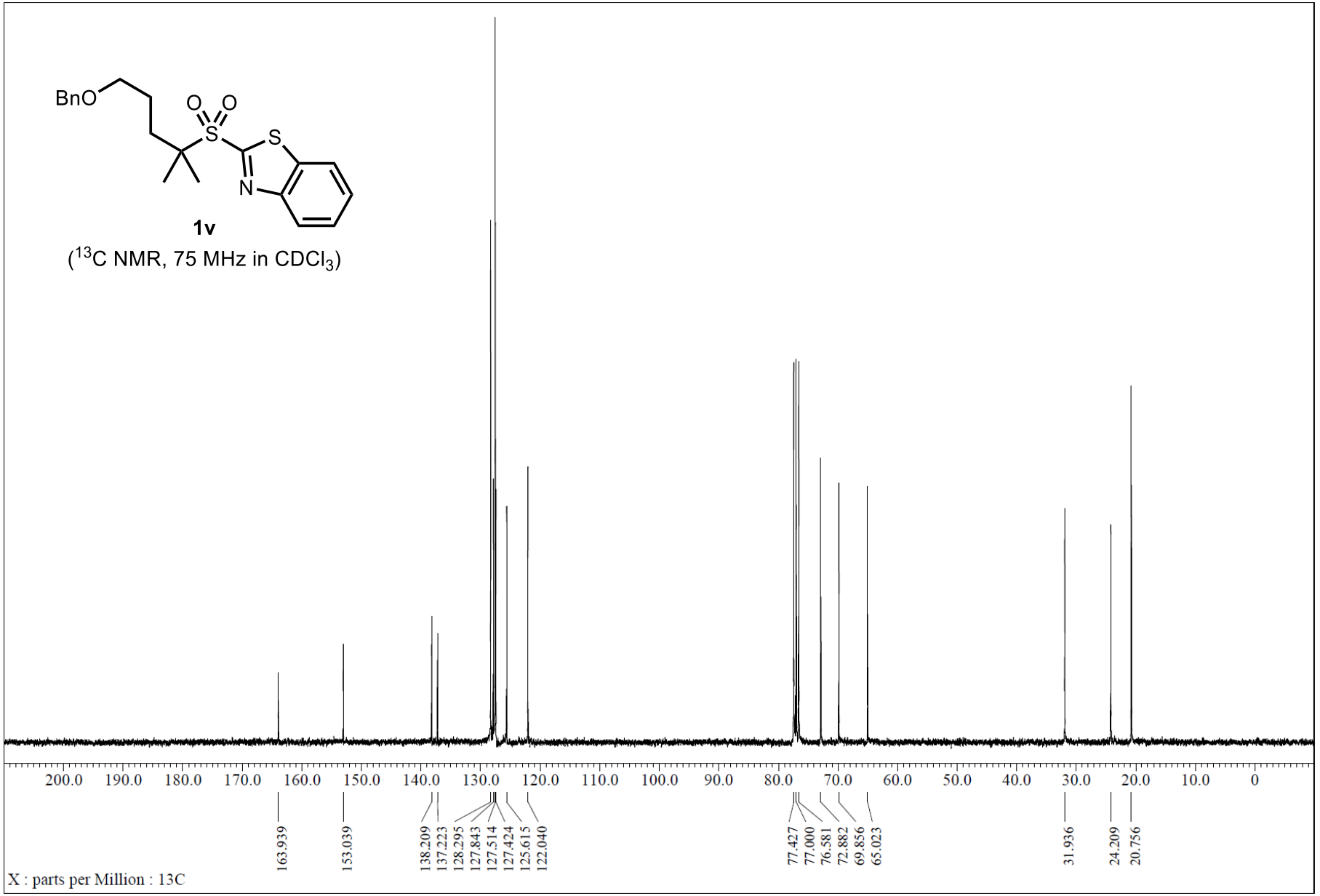

1t
(1H NMR, 300 MHz in CDCl3)
5.30
6.23
6.67
2.09
1.00
1.01
1.01
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.244
8.240
8.215
8.043
8.019
8.014
7.654
7.630
7.624
7.267
3.691
3.678
3.641
3.625
3.610
2.387
2.373
2.354
2.329
2.306
2.141
2.130
1.743
1.735
1.705
1.682
1.669
1.656
1.472
1.449
0.000
X : parts per Million : 1H

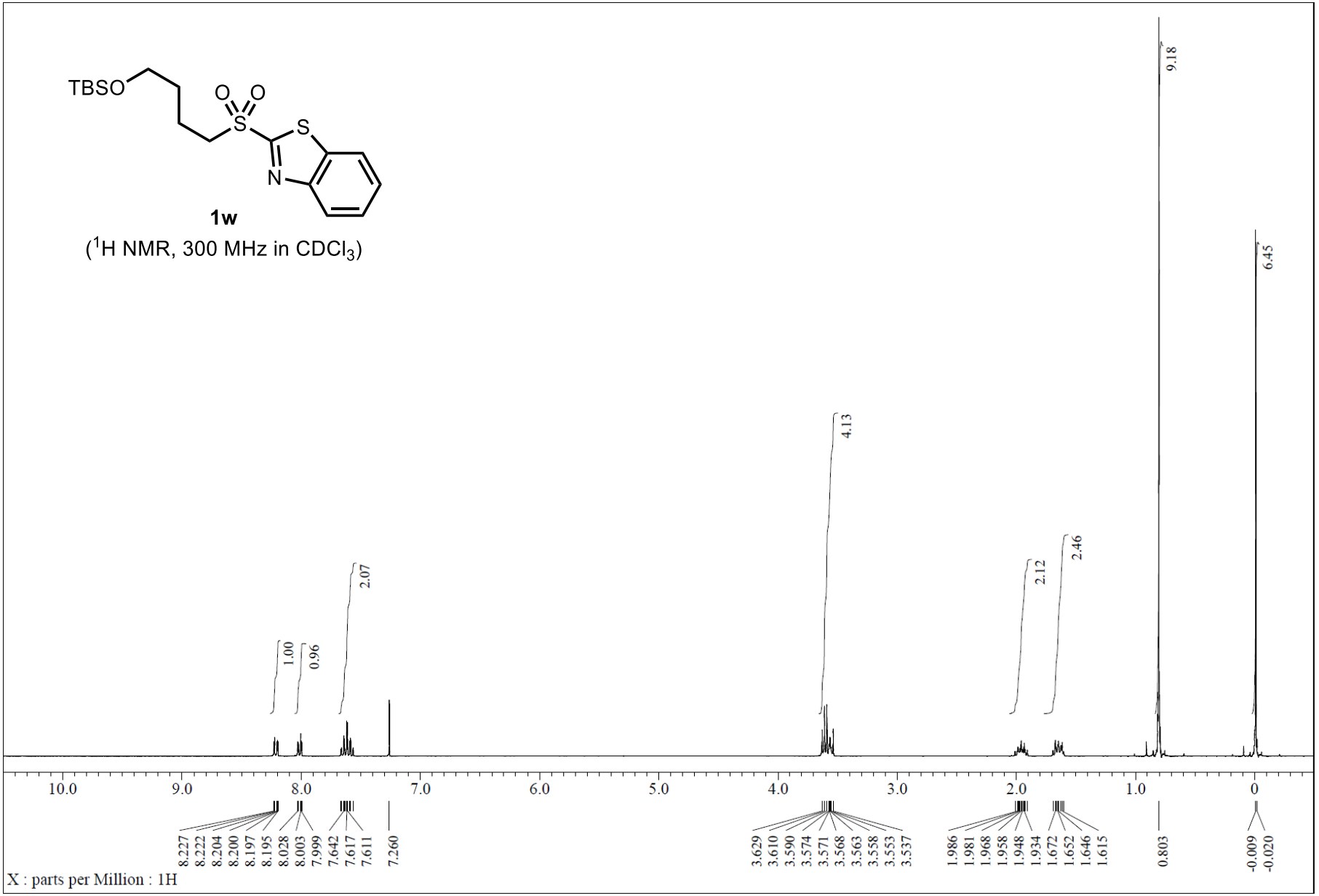

1t
(13C NMR, 75 MHz in CDCl3)
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
165.114
152.899
136.894
127.975
127.613
125.467
122.261
77.427
77.206
77.000
76.581
66.864
59.515
58.019
53.597
26.864
23.337
13.029
X : parts per Million : 13C

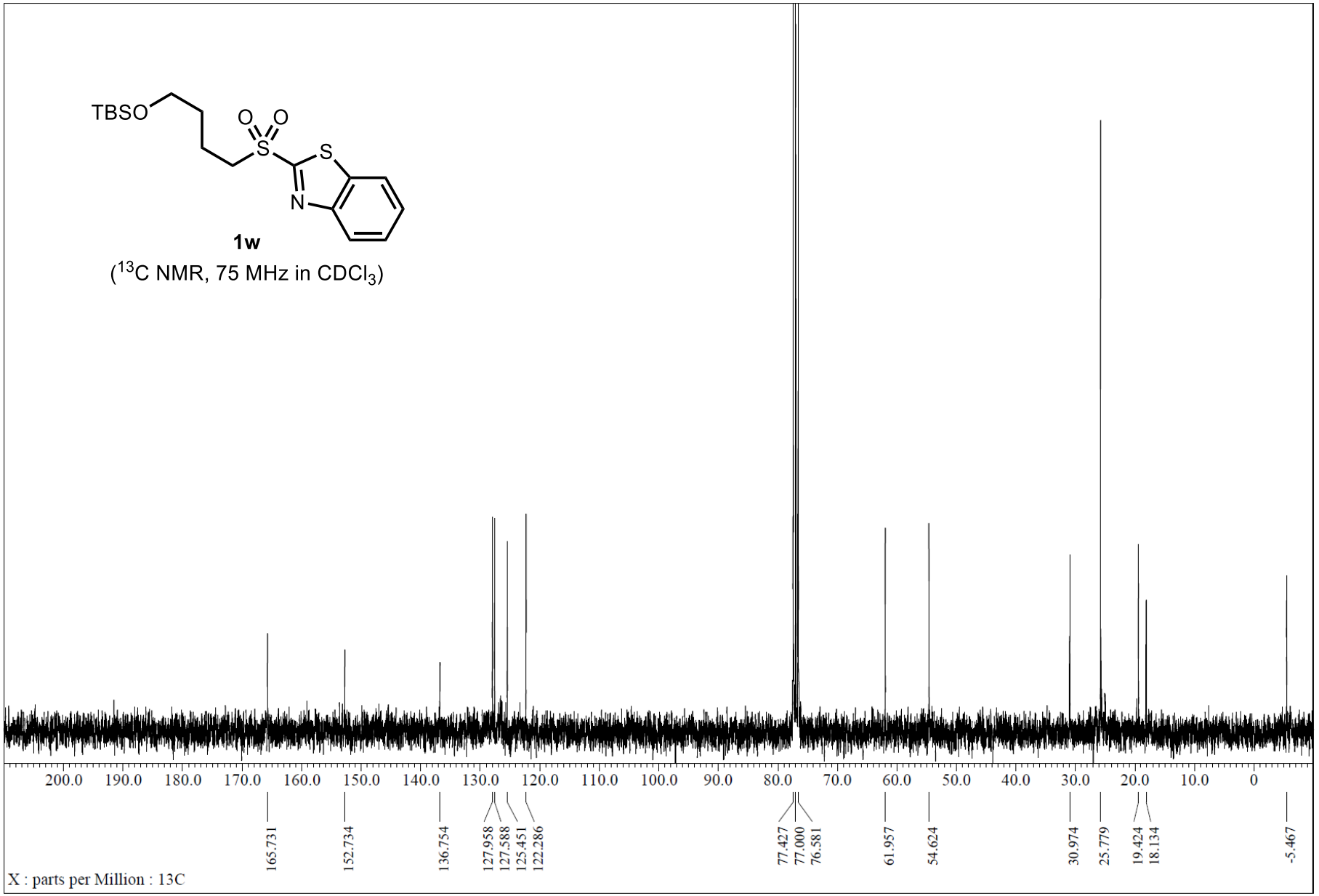

Ph
N
O
O
S
S
N
1u
(1H NMR, 300 MHz in CDCl3)
1.01
0.98
2.05
1.80
2.99
1.07
2.00
3.03
0.98
3.10
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.233
8.227
8.208
8.204
8.202
7.994
7.989
7.643
7.618
7.611
7.190
7.185
7.161
6.699
6.675
6.650
6.624
3.628
3.614
3.605
3.599
3.591
3.585
3.575
3.328
3.319
2.879
2.171
2.130
2.121
2.097
1.674
1.663
1.636
1.443
1.420
0.000
X : parts per Million : 1H

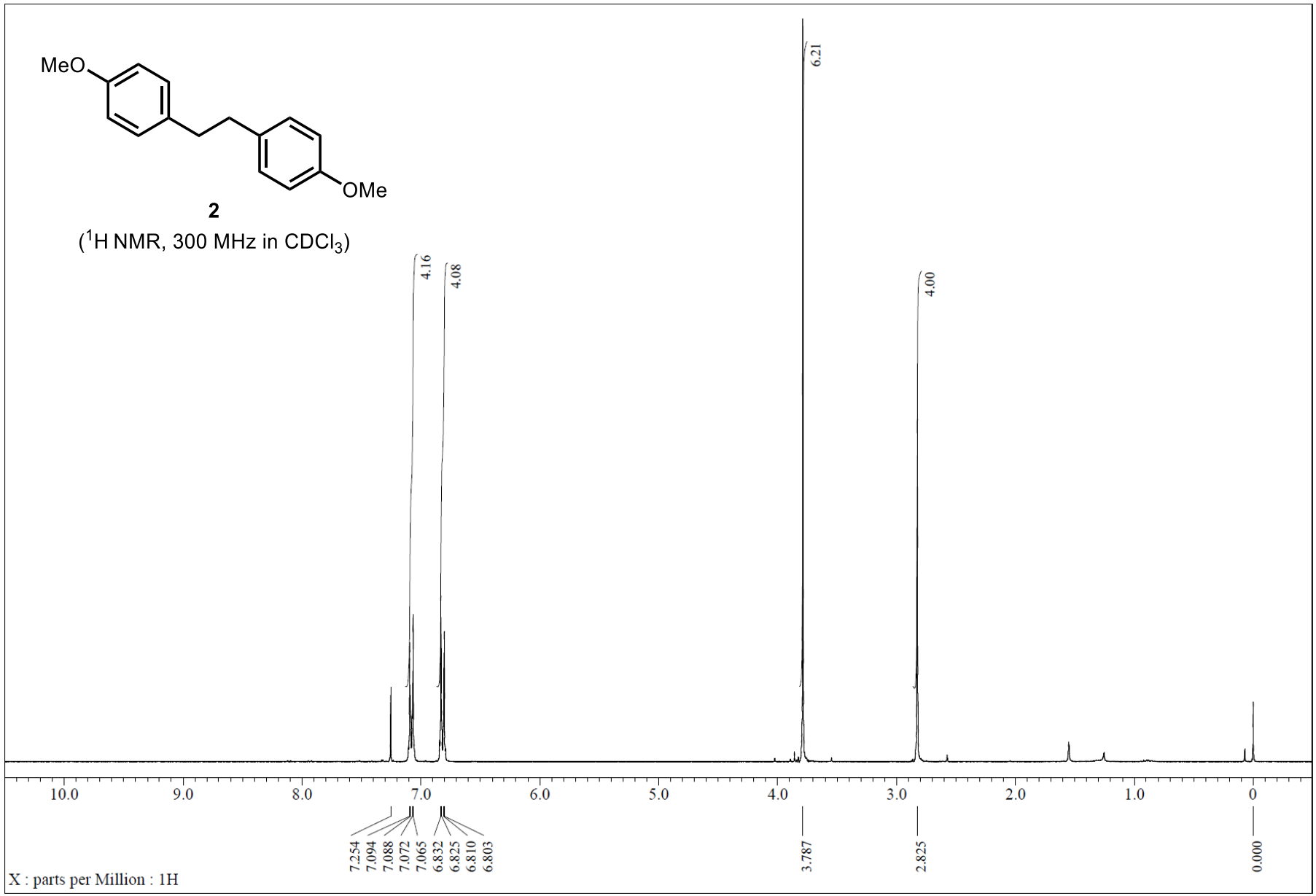

Ph
N
O
O
S
S
N
1u
(13C NMR, 75 MHz in CDCl3)
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
164.901
152.866
148.969
136.877
129.158
127.934
127.580
125.459
122.253
116.367
112.241
77.427
77.000
76.581
59.737
52.265
38.414
26.527
23.798
13.119
X : parts per Million : 13C

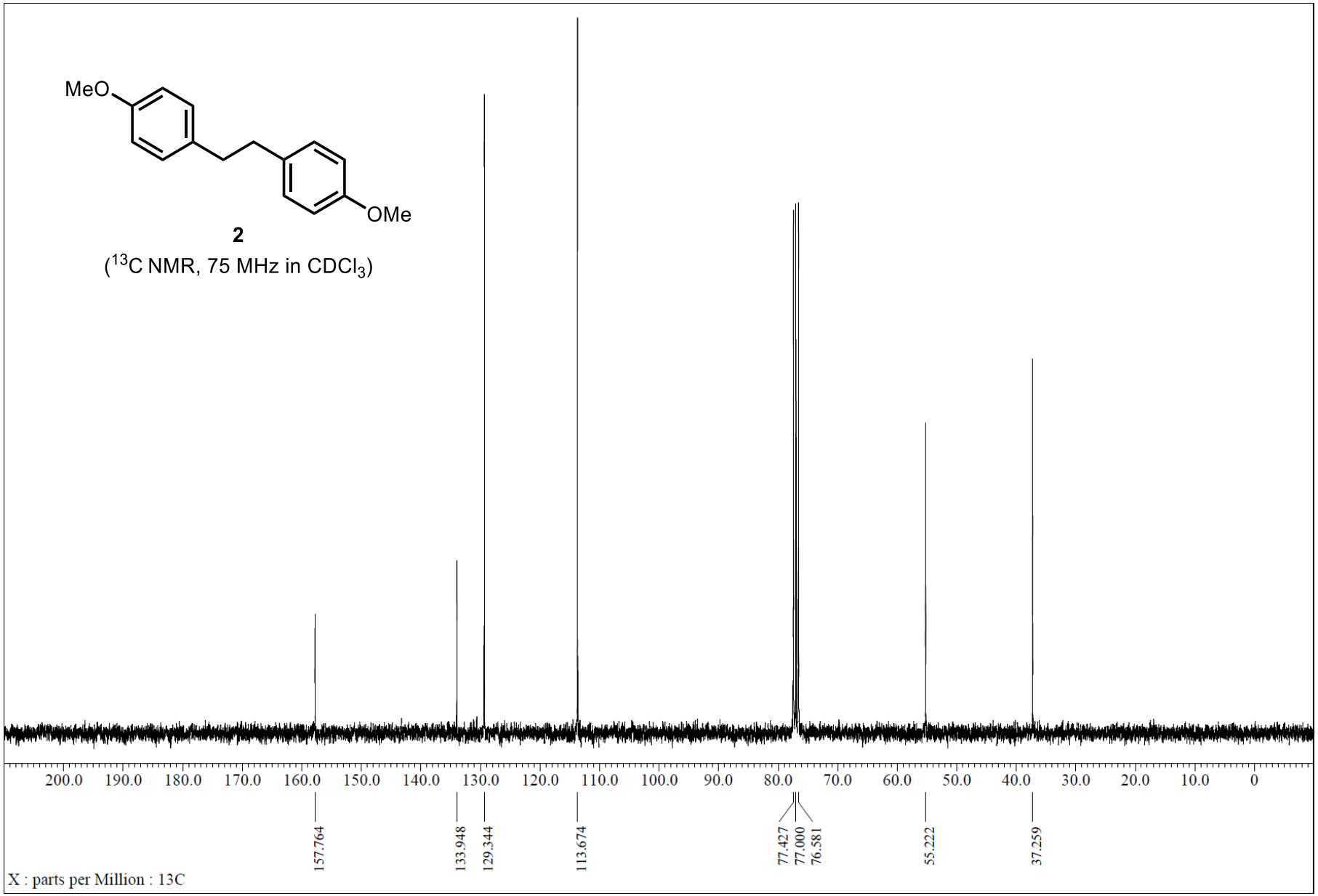

BnO
O
O
S
S
N
1v
(1H NMR, 300 MHz in CDCl3)
5.69
6.21
2.12
2.00
2.09
2.02
2.22
1.03
1.04
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.259
8.257
8.252
8.234
8.229
8.227
8.225
7.987
7.982
7.607
7.602
7.307
7.301
7.288
7.285
7.280
7.272
7.255
4.474
3.505
3.484
3.464
2.025
2.010
2.001
1.996
1.982
1.969
1.769
1.735
1.508
0.000
X : parts per Million : 1H

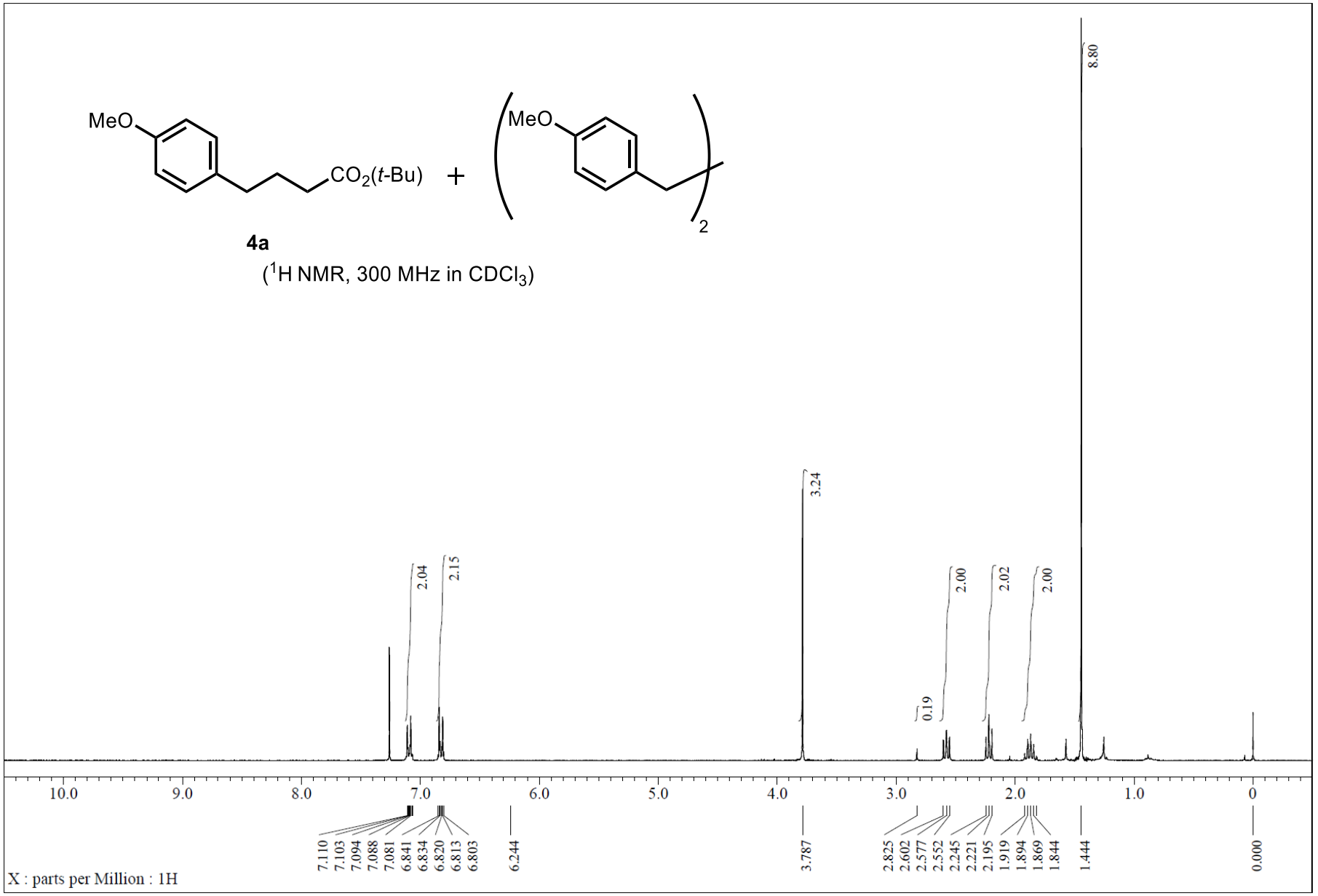

BnO
O
O
S
S
N
1v
(13C NMR, 75 MHz in CDCl3)
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
163.939
153.039
138.209
137.223
128.295
127.843
127.514
127.424
125.615
122.040
77.427
77.000
76.581
72.882
69.856
65.023
31.936
24.209
20.756
X : parts per Million : 13C

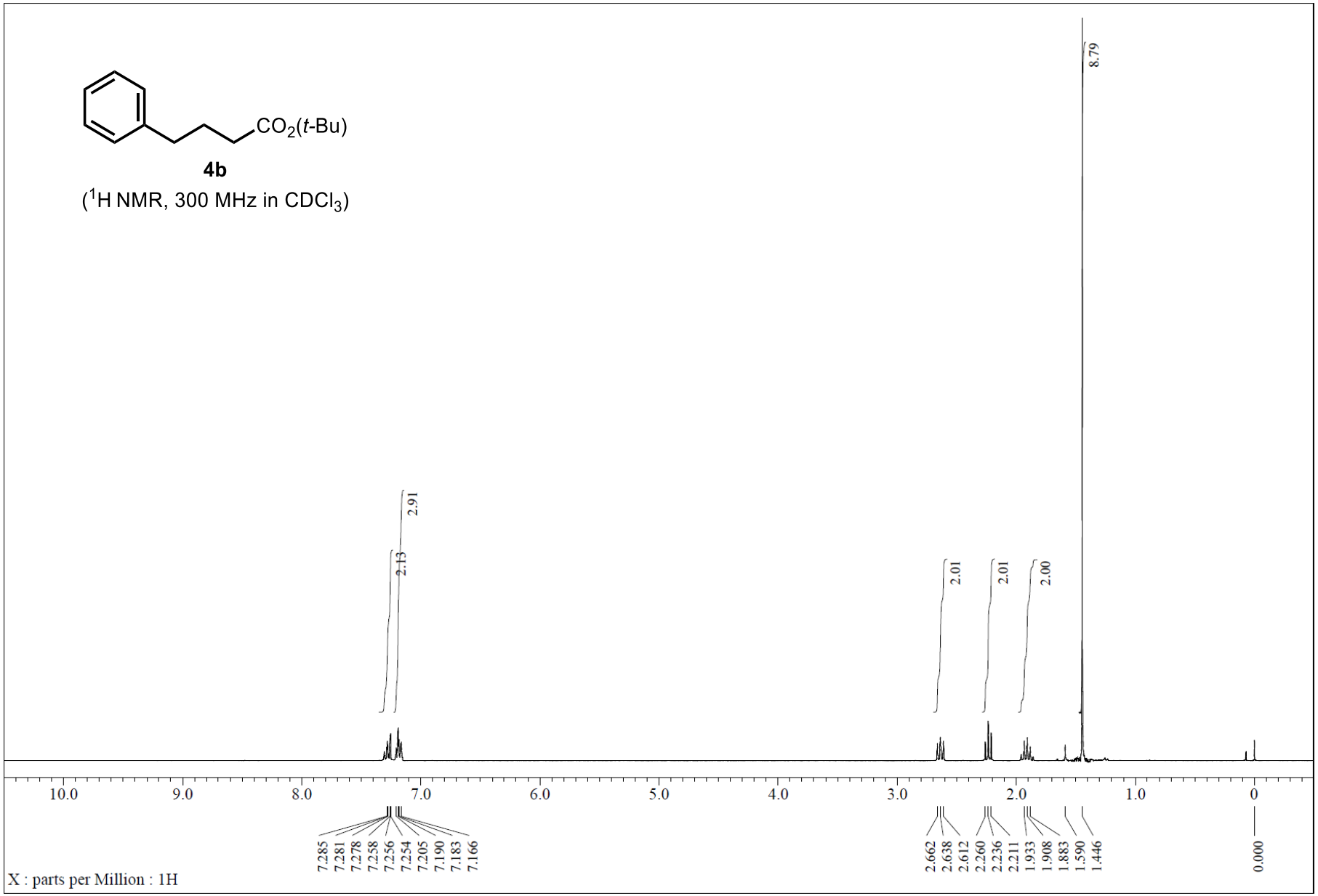

TBSO
O
O
S
S
N
1w
(1H NMR, 300 MHz in CDCl3)
9.18
6.45
4.13
2.07
2.12
2.46
1.00
0.96
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.227
8.222
8.204
8.200
8.197
8.195
8.028
8.003
7.999
7.642
7.617
7.611
7.260
3.629
3.610
3.590
3.574
3.571
3.568
3.563
3.558
3.553
3.537
1.986
1.981
1.968
1.958
1.948
1.934
1.672
1.652
1.646
1.615
0.803
-0.009
-0.020
X : parts per Million : 1H

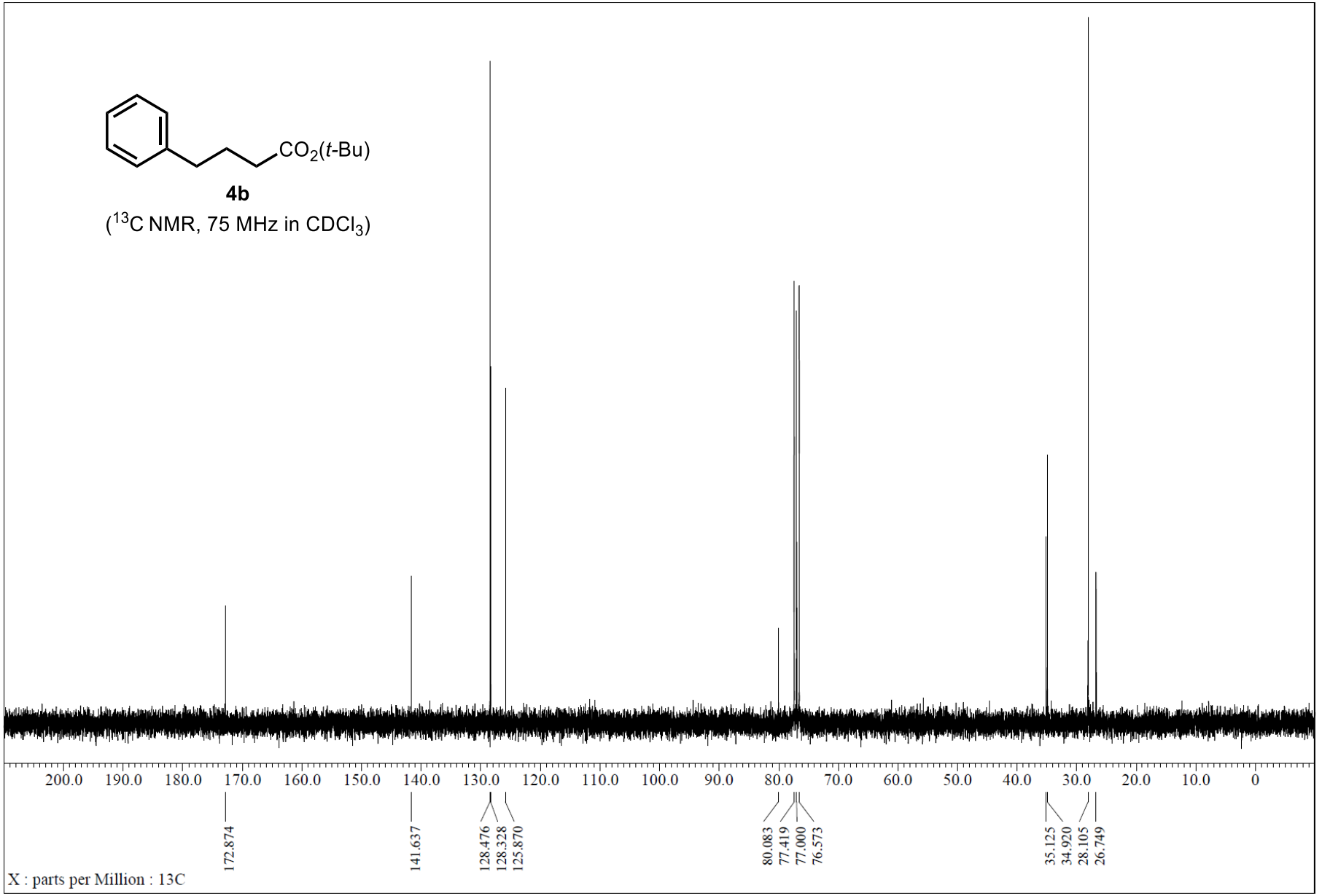

TBSO
O
O
S
S
N
1w
(13C NMR, 75 MHz in CDCl3)
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
165.731
152.734
136.754
127.958
127.588
125.451
122.286
77.427
77.000
76.581
61.957
54.624
30.974
25.779
19.424
18.134
-5.467
X : parts per Million : 13C

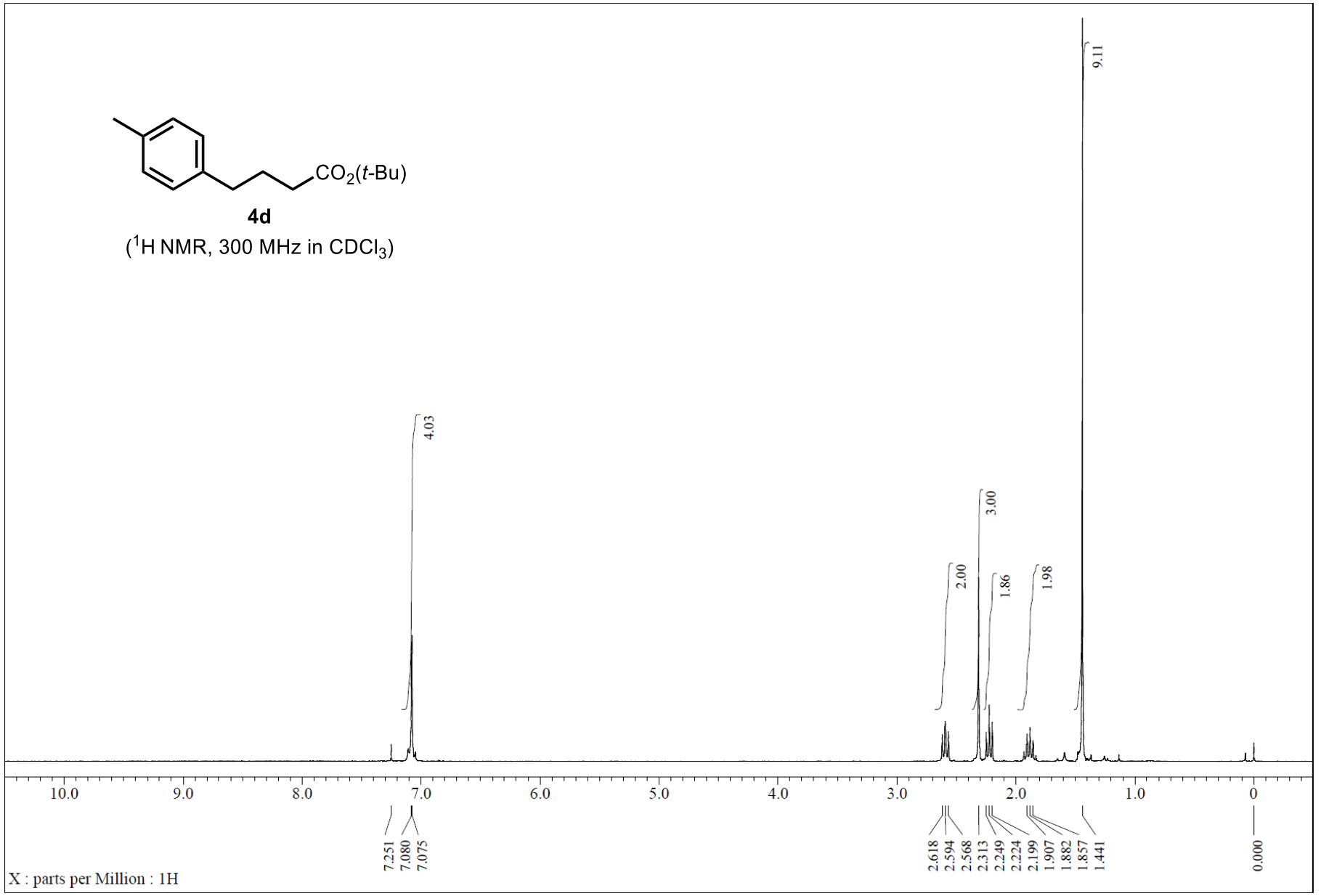

MeO
OMe
2
(1H NMR, 300 MHz in CDCl3)
6.21
4.16
4.08
4.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.254
7.094
7.088
7.072
7.065
6.832
6.825
6.810
6.803
3.787
2.825
0.000
X : parts per Million : 1H

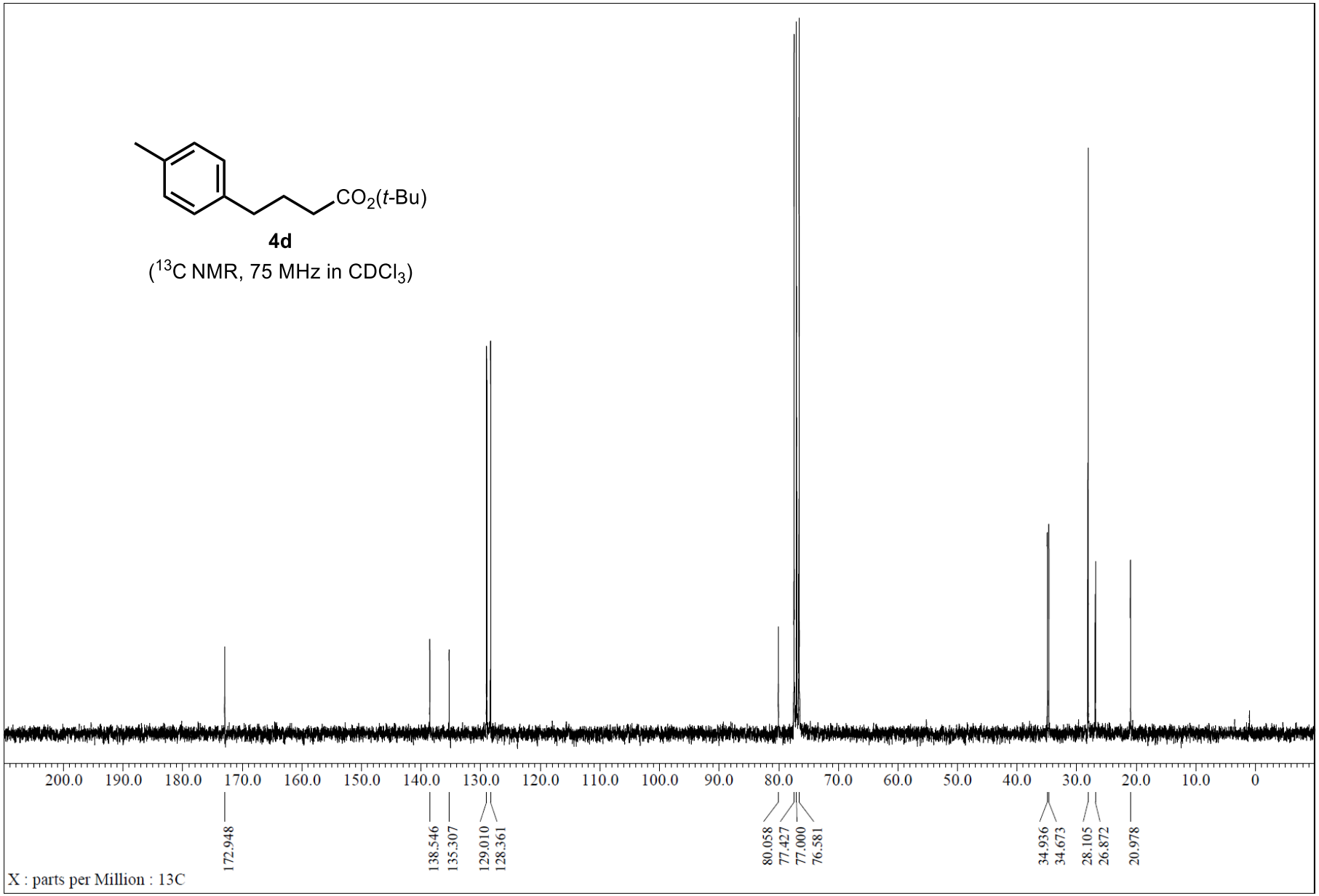

MeO
OMe
2
(^{13}C NMR, 75 MHz in $CDCl_3$)
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
157.764
133.948
129.344
113.674
77.427
77.000
76.581
55.222
37.259
X : parts per Million : 13C

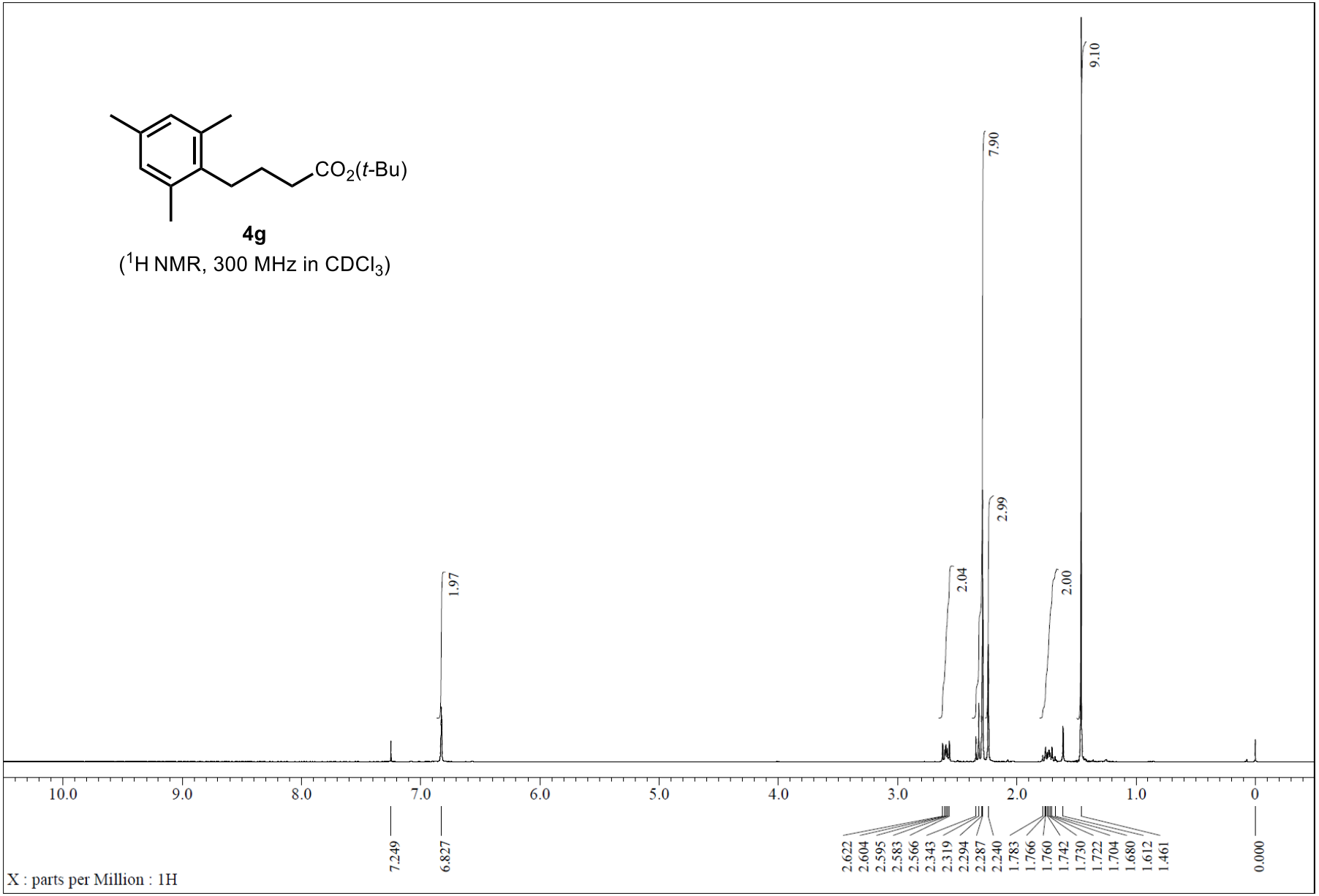

MeO
CO2(t-Bu)
+
MeO
2
4a
(1H NMR, 300 MHz in CDCl3)
8.80
3.24
2.04
2.15
2.00
2.02
2.00
0.19
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.110
7.103
7.094
7.088
7.081
6.841
6.834
6.820
6.813
6.803
6.244
3.787
2.825
2.602
2.577
2.552
2.245
2.221
2.195
1.919
1.894
1.869
1.844
1.444
0.000
X : parts per Million : 1H

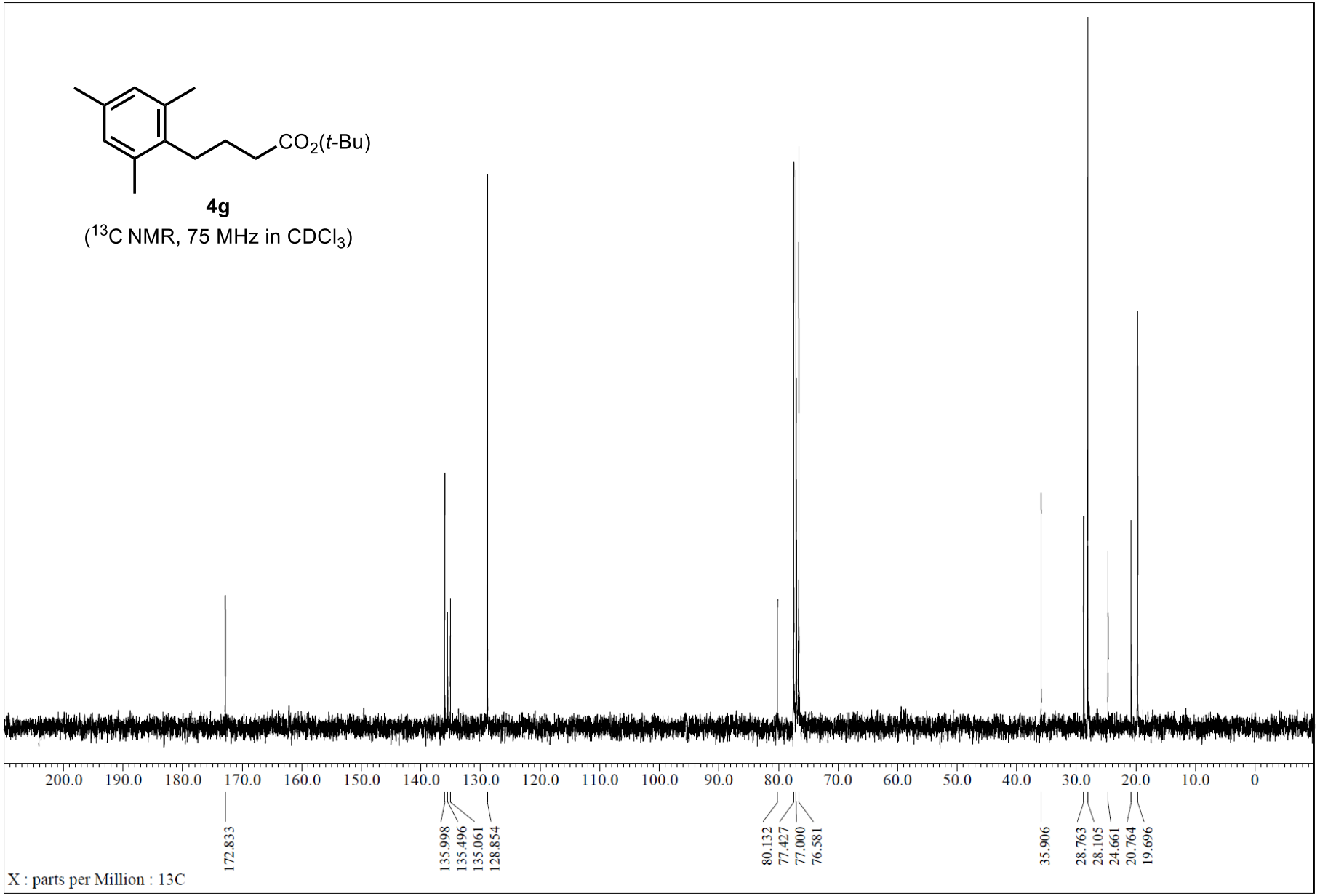

CO2(t-Bu)
4b
(1H NMR, 300 MHz in CDCl3)
8.79
2.91
2.13
2.01
2.01
2.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.285
7.281
7.278
7.258
7.256
7.254
7.205
7.190
7.183
7.166
2.662
2.638
2.612
2.260
2.236
2.211
1.933
1.908
1.883
1.590
1.446
0.000
X : parts per Million : 1H

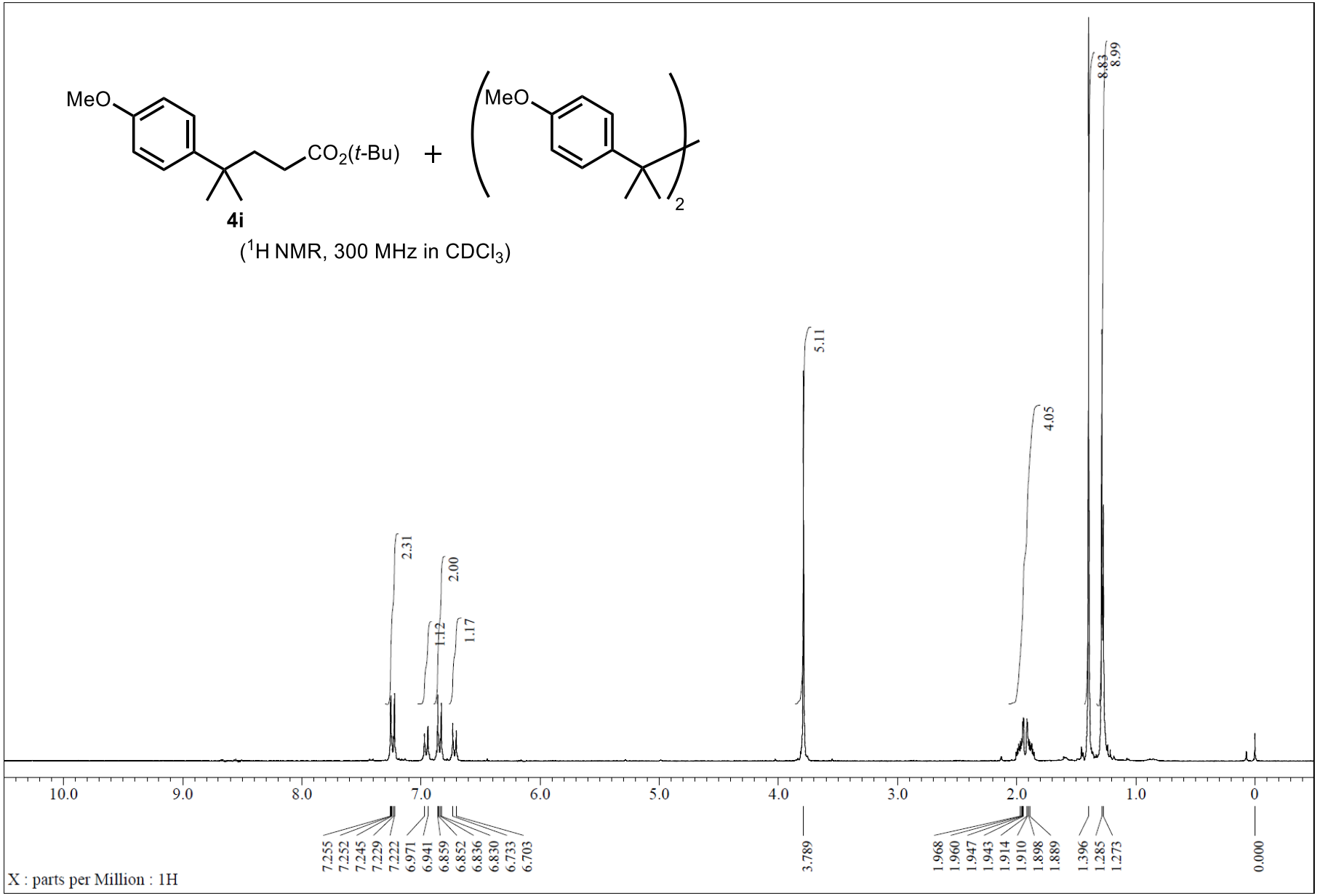

CO2(t-Bu)
4b
(13C NMR, 75 MHz in CDCl3)
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
172.874
141.637
128.476
128.328
125.870
80.083
77.419
77.000
76.573
35.125
34.920
28.105
26.749
X : parts per Million : 13C

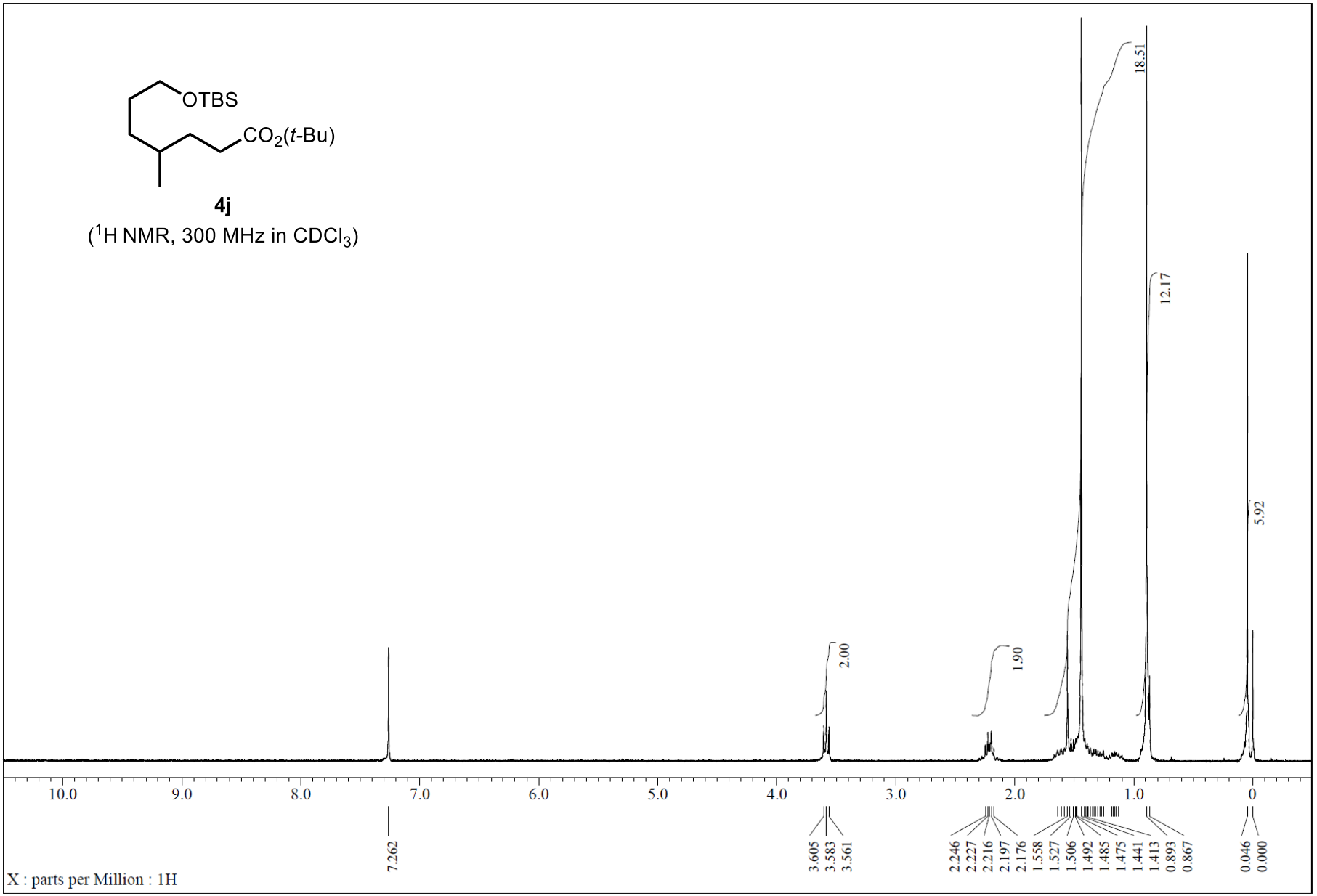

CO2(t-Bu)
4d
(1H NMR, 300 MHz in CDCl3)
9.11
4.03
3.00
2.00
1.86
1.98
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.251
7.080
7.075
2.618
2.594
2.568
2.313
2.249
2.224
2.199
1.907
1.882
1.857
1.441
0.000
X : parts per Million : 1H

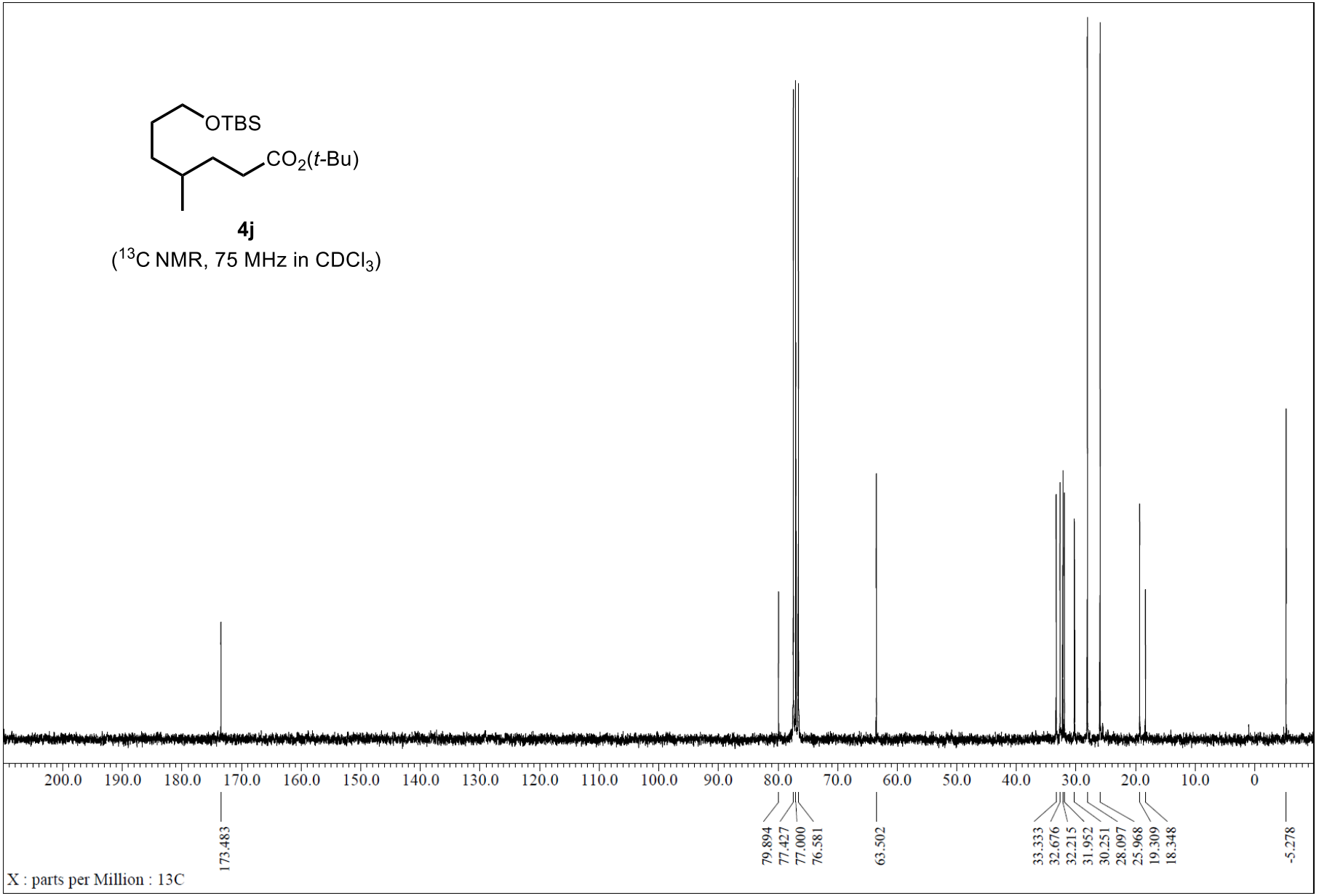

CO2(t-Bu)
4d
(13C NMR, 75 MHz in CDCl3)
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
172.948
138.546
135.307
129.010
128.361
80.058
77.427
77.000
76.581
34.936
34.673
28.105
26.872
20.978
X : parts per Million : 13C

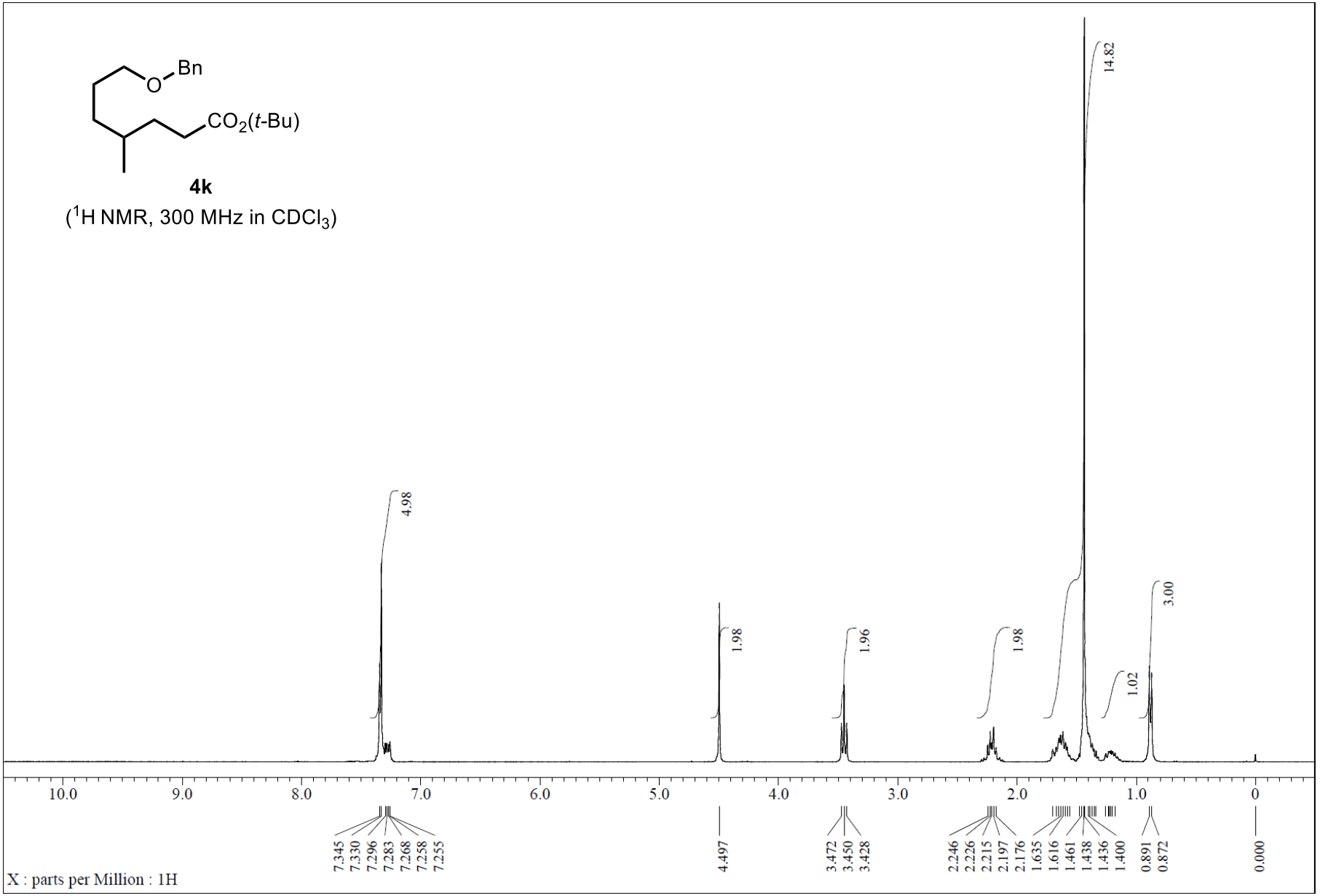

CO2(t-Bu)
4g
(1H NMR, 300 MHz in CDCl3)
9.10
7.90
2.99
2.04
2.00
1.97
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.249
6.827
2.622
2.604
2.595
2.583
2.566
2.343
2.319
2.294
2.287
2.240
1.783
1.766
1.760
1.742
1.730
1.722
1.704
1.680
1.612
1.461
0.000
X : parts per Million : 1H

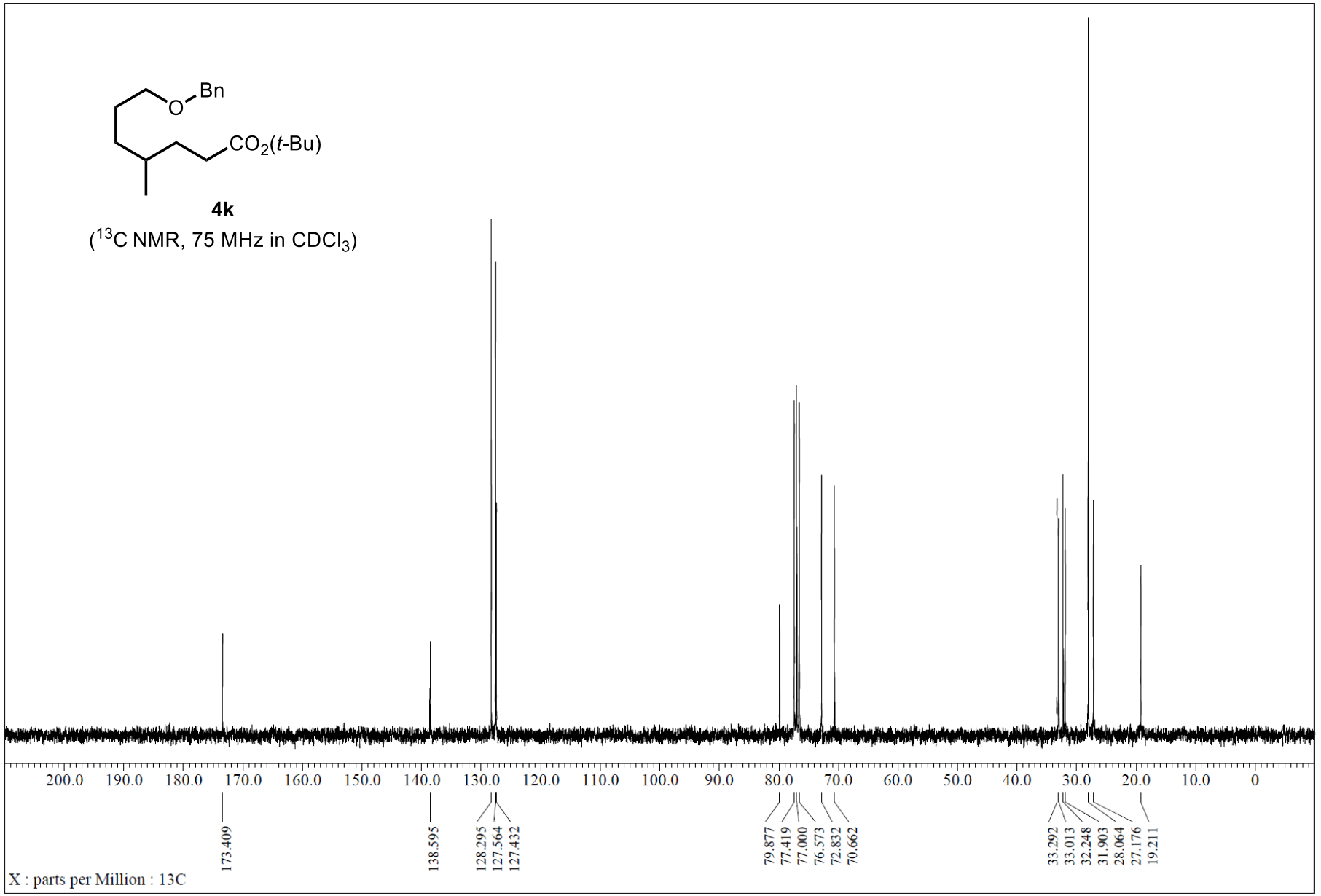

CO2(t-Bu)
4g
(13C NMR, 75 MHz in CDCl3)
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
172.833
135.998
135.496
135.061
128.854
80.132
77.427
77.000
76.581
35.906
28.763
28.105
24.661
20.764
19.696
X : parts per Million : 13C

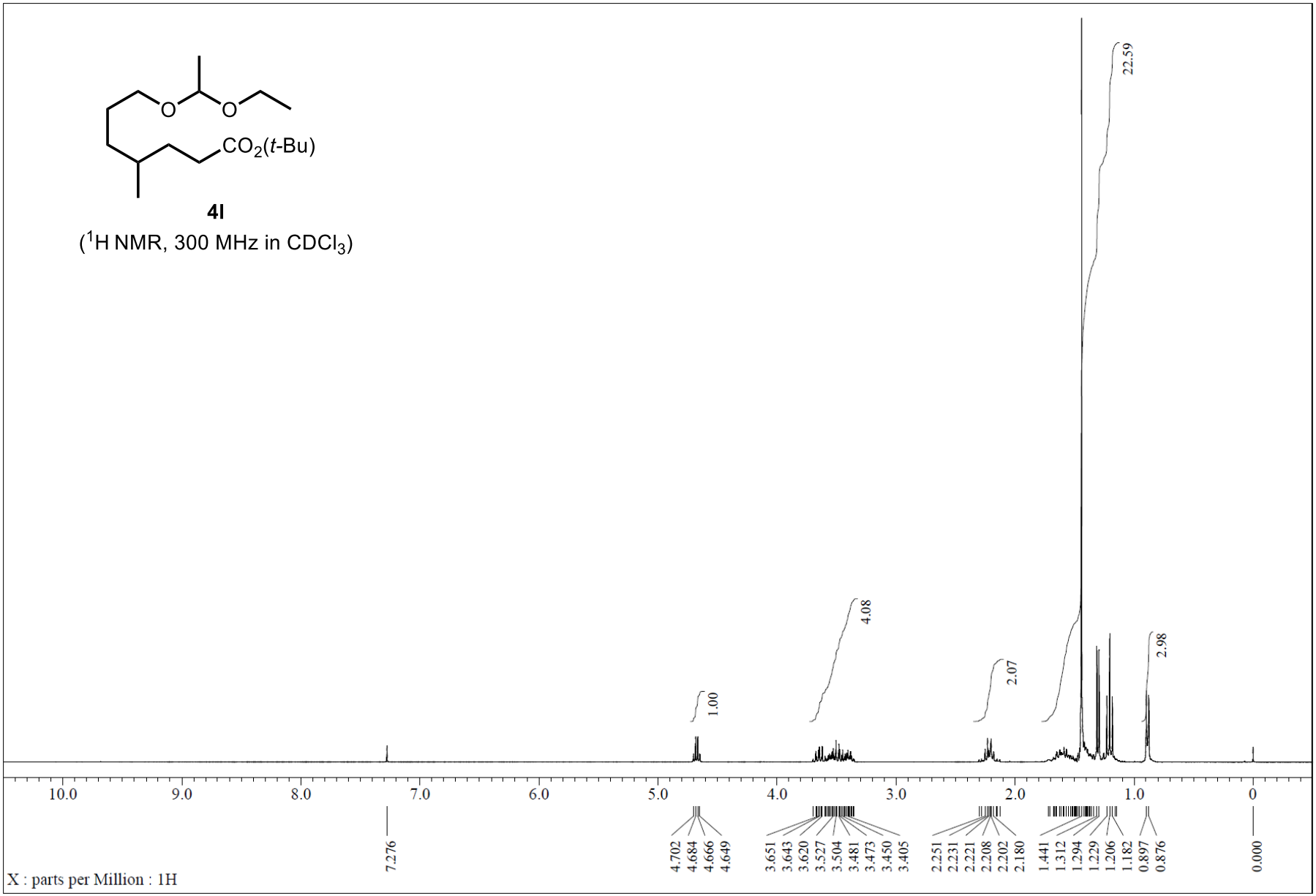

MeO
CO2(t-Bu)
+
MeO
2
4i
(1H NMR, 300 MHz in CDCl3)
8.99
8.83
5.11
4.05
2.31
2.00
1.12
1.17
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.255
7.252
7.245
7.229
7.222
6.971
6.941
6.859
6.852
6.836
6.830
6.733
6.703
3.789
1.968
1.960
1.947
1.943
1.914
1.910
1.898
1.889
1.396
1.285
1.273
0.000
X : parts per Million : 1H

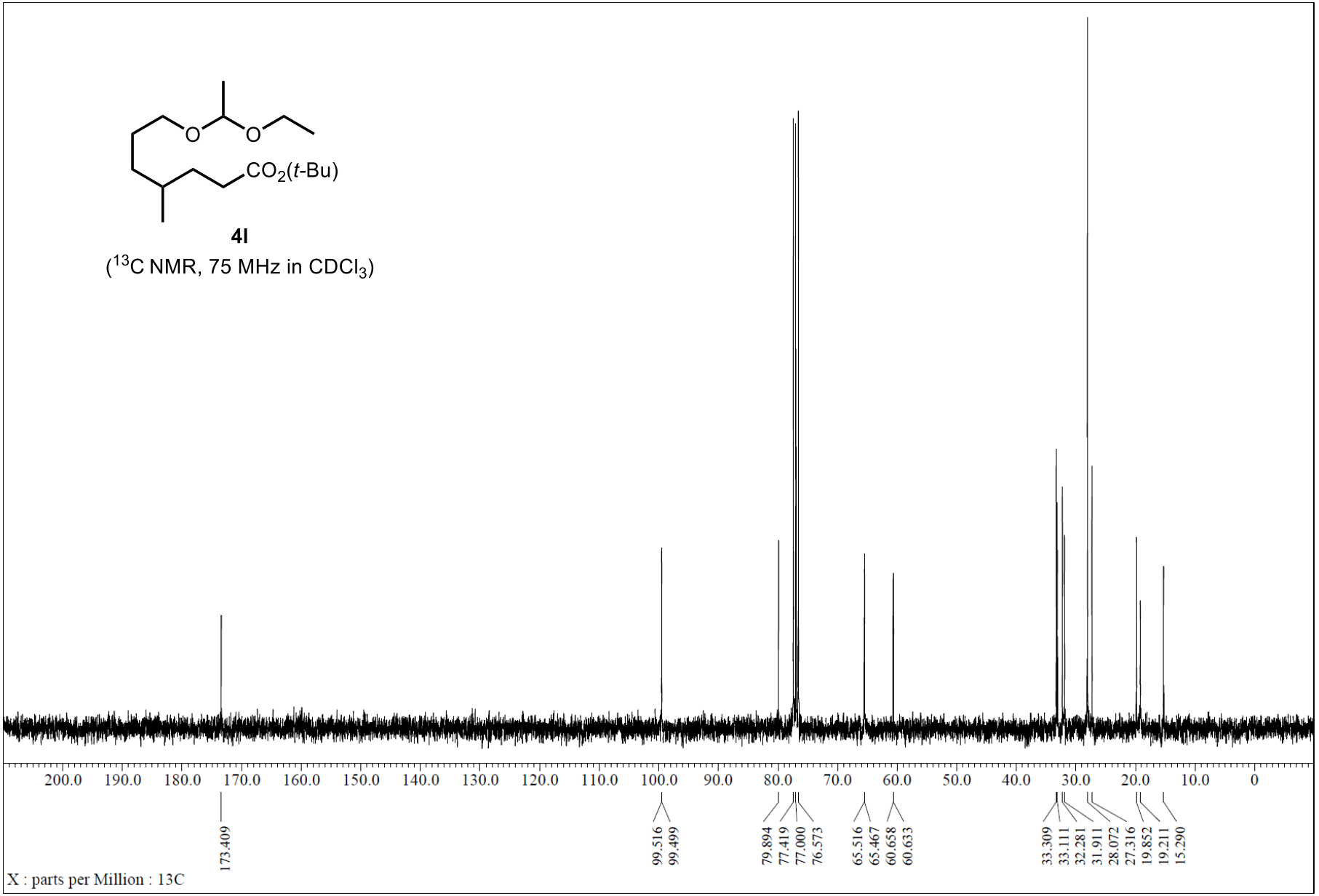

OTBS
CO2(t-Bu)
4j
(1H NMR, 300 MHz in CDCl3)
18.51
12.17
5.92
2.00
1.90
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.262
3.605
3.583
3.561
2.246
2.227
2.216
2.197
2.176
1.558
1.527
1.506
1.492
1.485
1.475
1.441
1.413
0.893
0.867
0.046
0.000
X : parts per Million : 1H

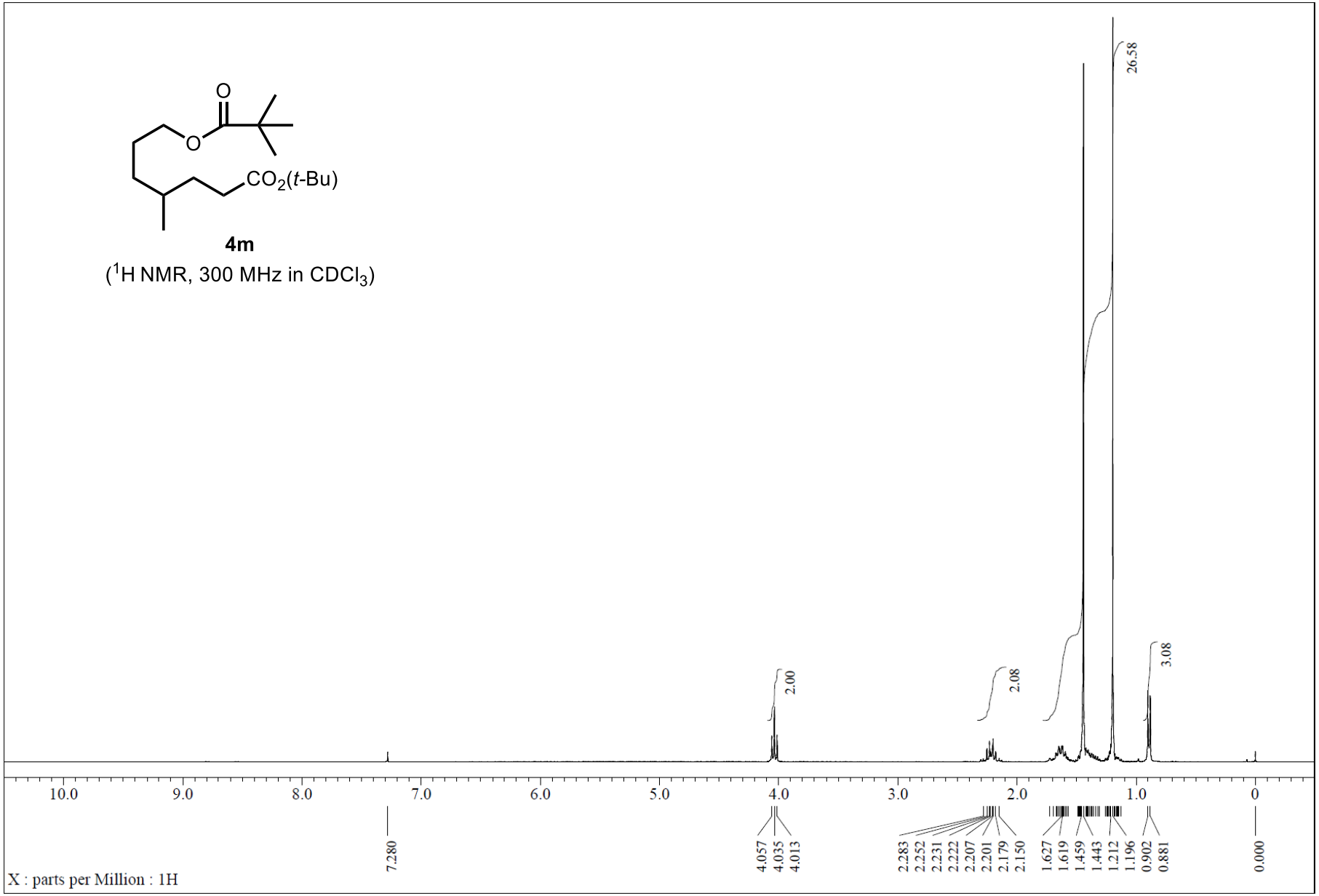

OTBS
CO2(t-Bu)
4j
(13C NMR, 75 MHz in CDCl3)
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
173.483
79.894
77.427
77.000
76.581
63.502
33.333
32.676
32.215
31.952
30.251
28.097
25.968
19.309
18.348
-5.278
X : parts per Million : 13C

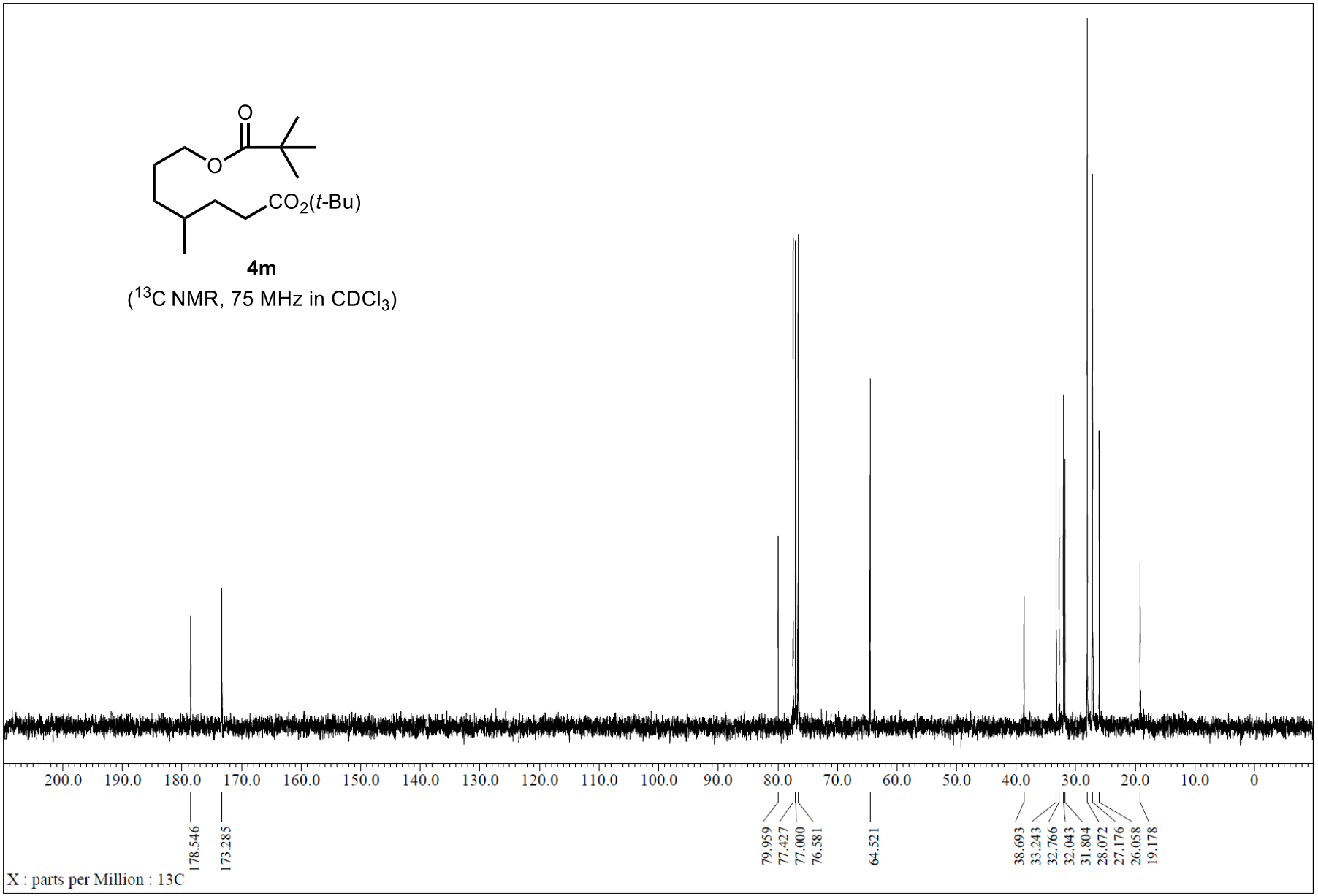

Bn
O
CO2(t-Bu)
4k
(1H NMR, 300 MHz in CDCl3)
14.82
4.98
1.98
1.96
1.98
1.02
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.345
7.330
7.296
7.283
7.268
7.258
7.255
4.497
3.472
3.450
3.428
2.246
2.226
2.215
2.197
2.176
1.635
1.616
1.461
1.438
1.436
1.400
0.891
0.872
0.000
X : parts per Million : 1H

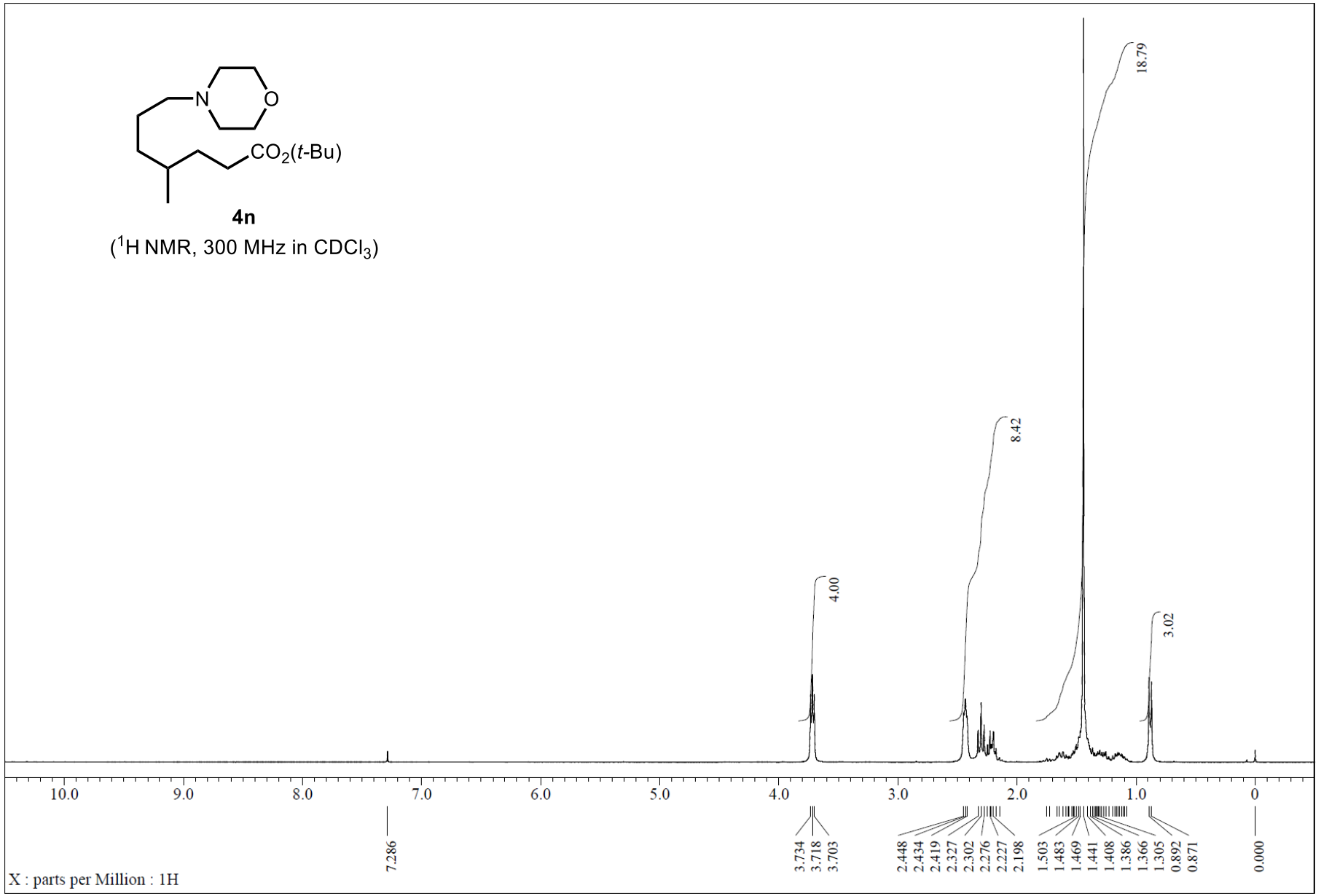

Bn
O
CO2(t-Bu)
4k
(13C NMR, 75 MHz in CDCl3)
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
173.409
138.595
128.295
127.564
127.432
79.877
77.419
77.000
76.573
72.832
70.662
33.292
33.013
32.248
31.903
28.064
27.176
19.211
X : parts per Million : 13C

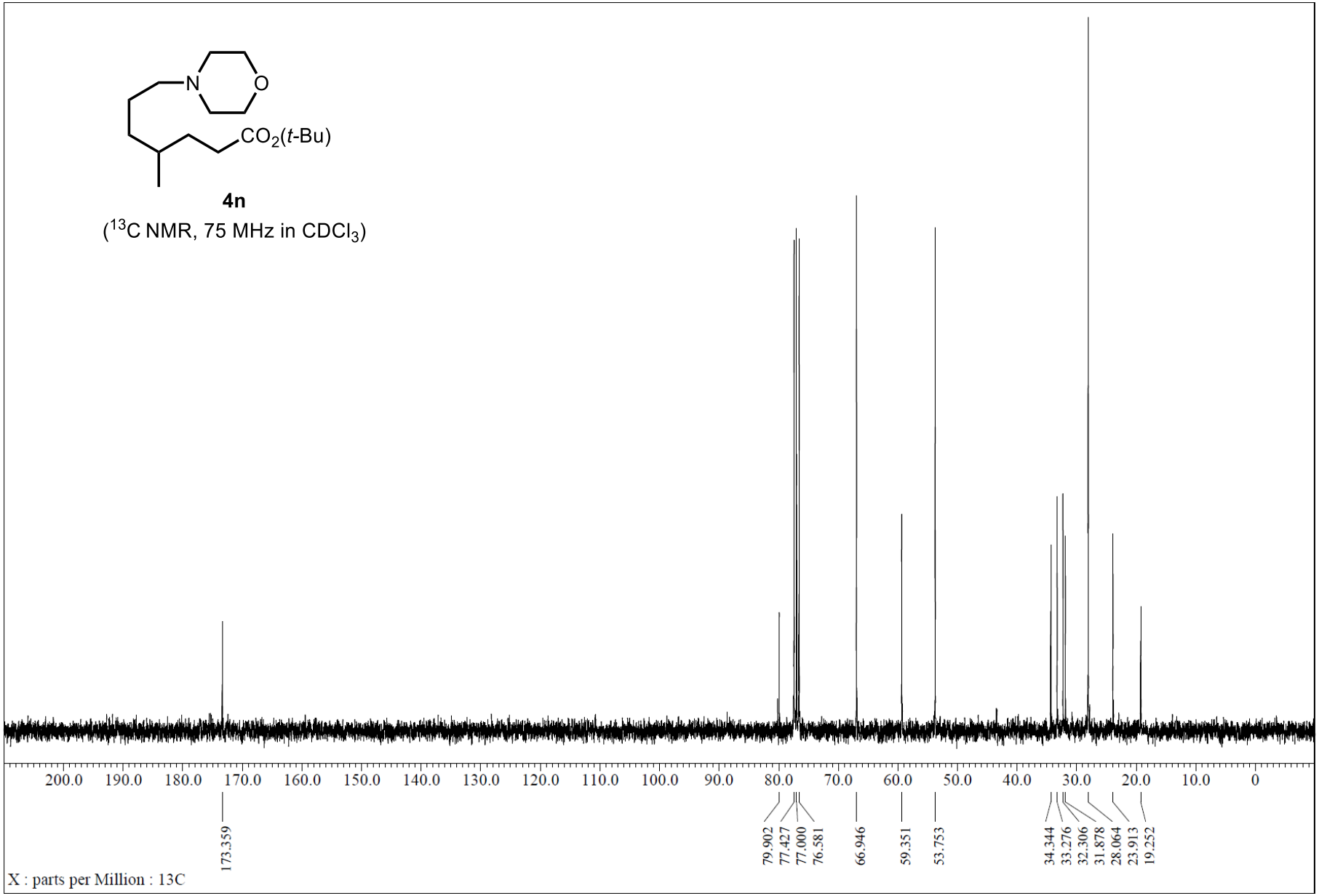

O
O
CO2(t-Bu)
4l
(1H NMR, 300 MHz in CDCl3)
22.59
4.08
2.07
2.98
1.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.276
4.702
4.684
4.666
4.649
3.651
3.643
3.620
3.527
3.504
3.481
3.473
3.450
3.405
2.251
2.231
2.221
2.208
2.202
2.180
1.441
1.312
1.294
1.229
1.206
1.182
0.897
0.876
0.000
X : parts per Million : 1H

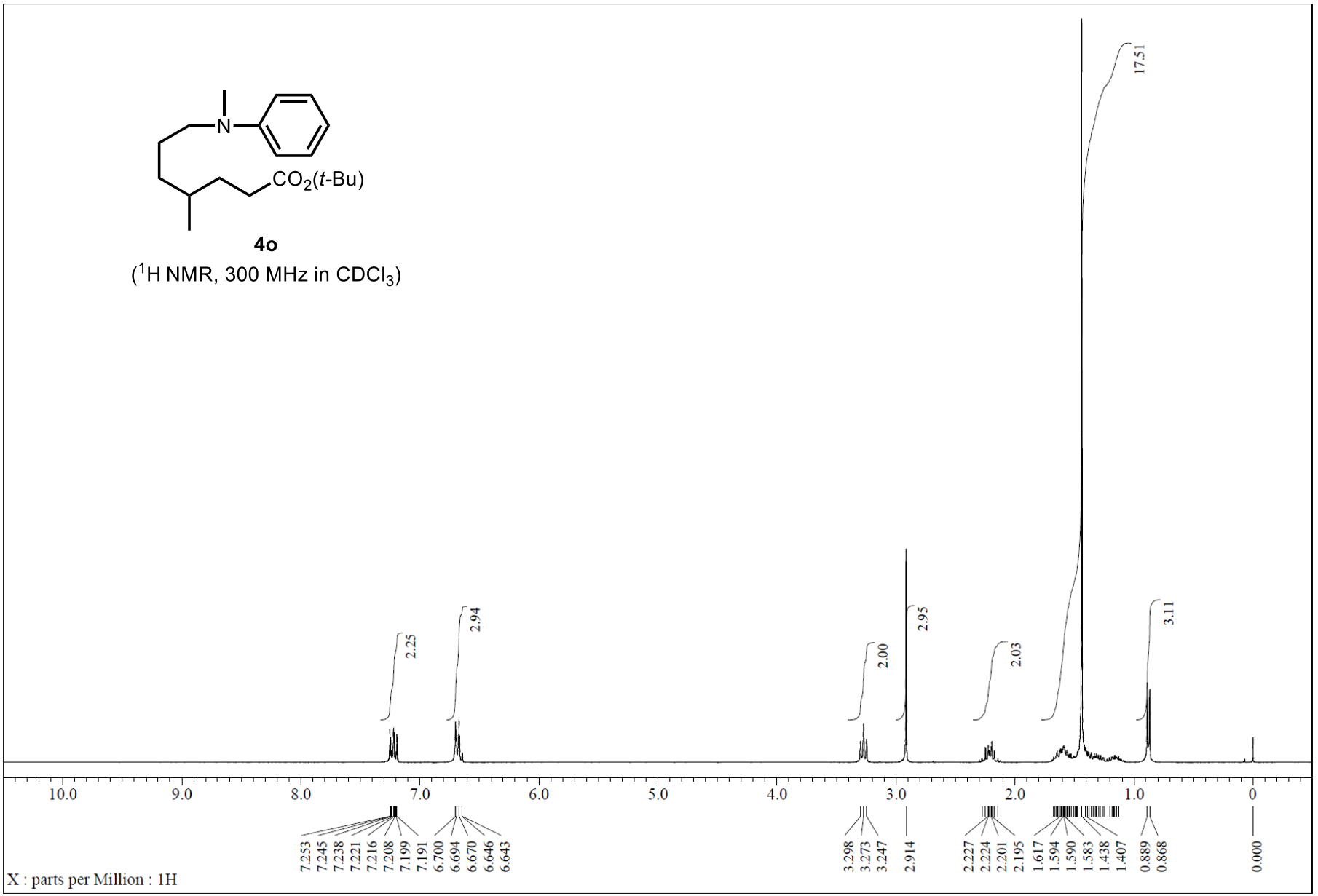

CO2(t-Bu)
4l
(13C NMR, 75 MHz in CDCl3)
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
173.409
99.516
99.499
79.894
77.419
77.000
76.573
65.516
65.467
60.658
60.633
33.309
33.111
32.281
31.911
28.072
27.316
19.852
19.211
15.290
X : parts per Million : 13C

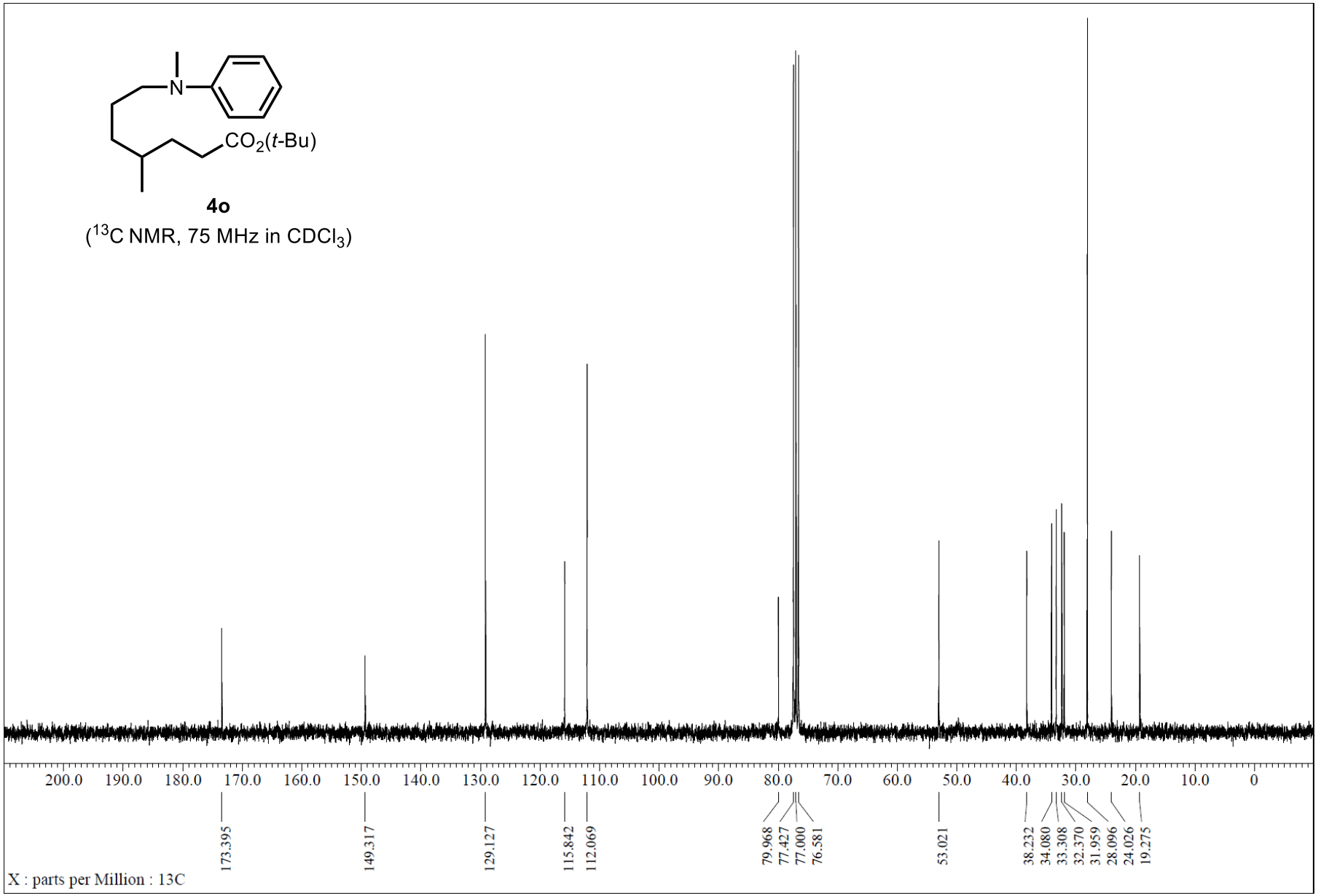

O
O
CO2(t-Bu)
4m
(1H NMR, 300 MHz in CDCl3)
26.58
2.00
2.08
3.08
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.280
4.057
4.035
4.013
2.283
2.252
2.231
2.222
2.207
2.201
2.179
2.150
1.627
1.619
1.459
1.443
1.212
1.196
0.902
0.881
0.000
X : parts per Million : 1H

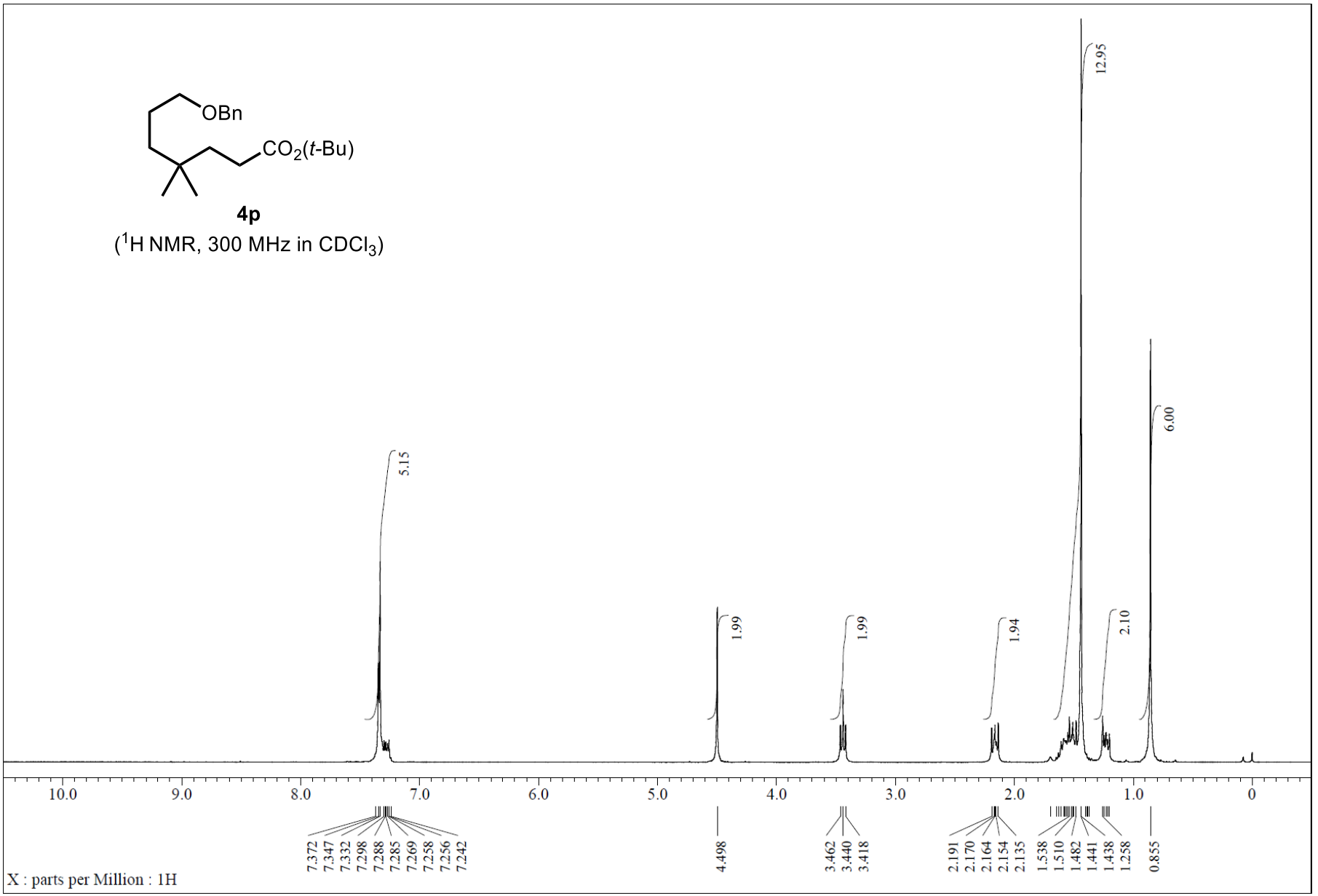

O
O
CO2(t-Bu)
4m
(13C NMR, 75 MHz in CDCl3)
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
178.546
173.285
79.959
77.427
77.000
76.581
64.521
38.693
33.243
32.766
32.043
31.804
28.072
27.176
26.058
19.178
X : parts per Million : 13C

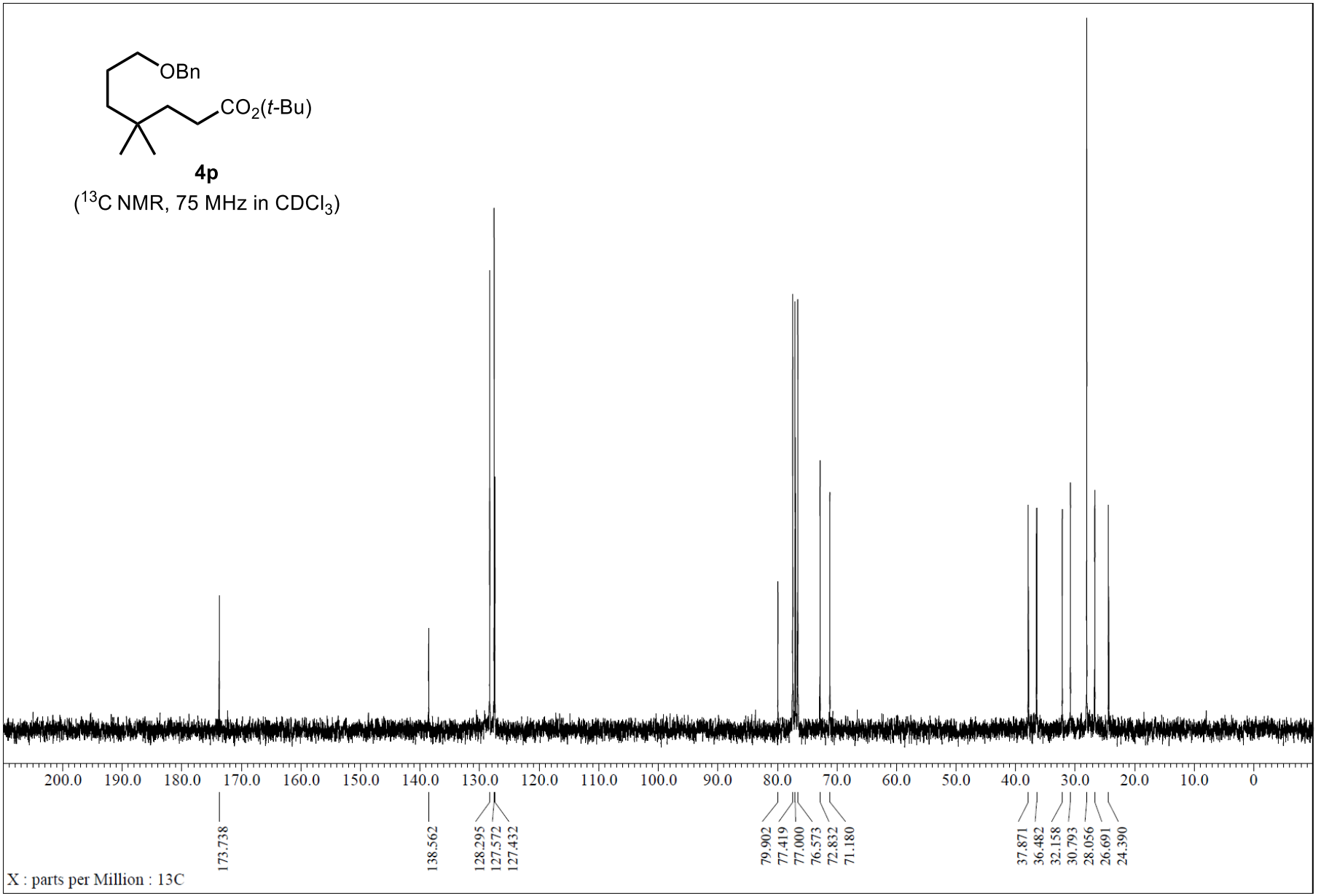

N
O
CO2(t-Bu)
4n
(1H NMR, 300 MHz in CDCl3)
18.79
8.42
4.00
3.02
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.286
3.734
3.718
3.703
2.448
2.434
2.419
2.327
2.302
2.276
2.227
2.198
1.503
1.483
1.469
1.441
1.408
1.386
1.366
1.305
0.892
0.871
0.000
X : parts per Million : 1H

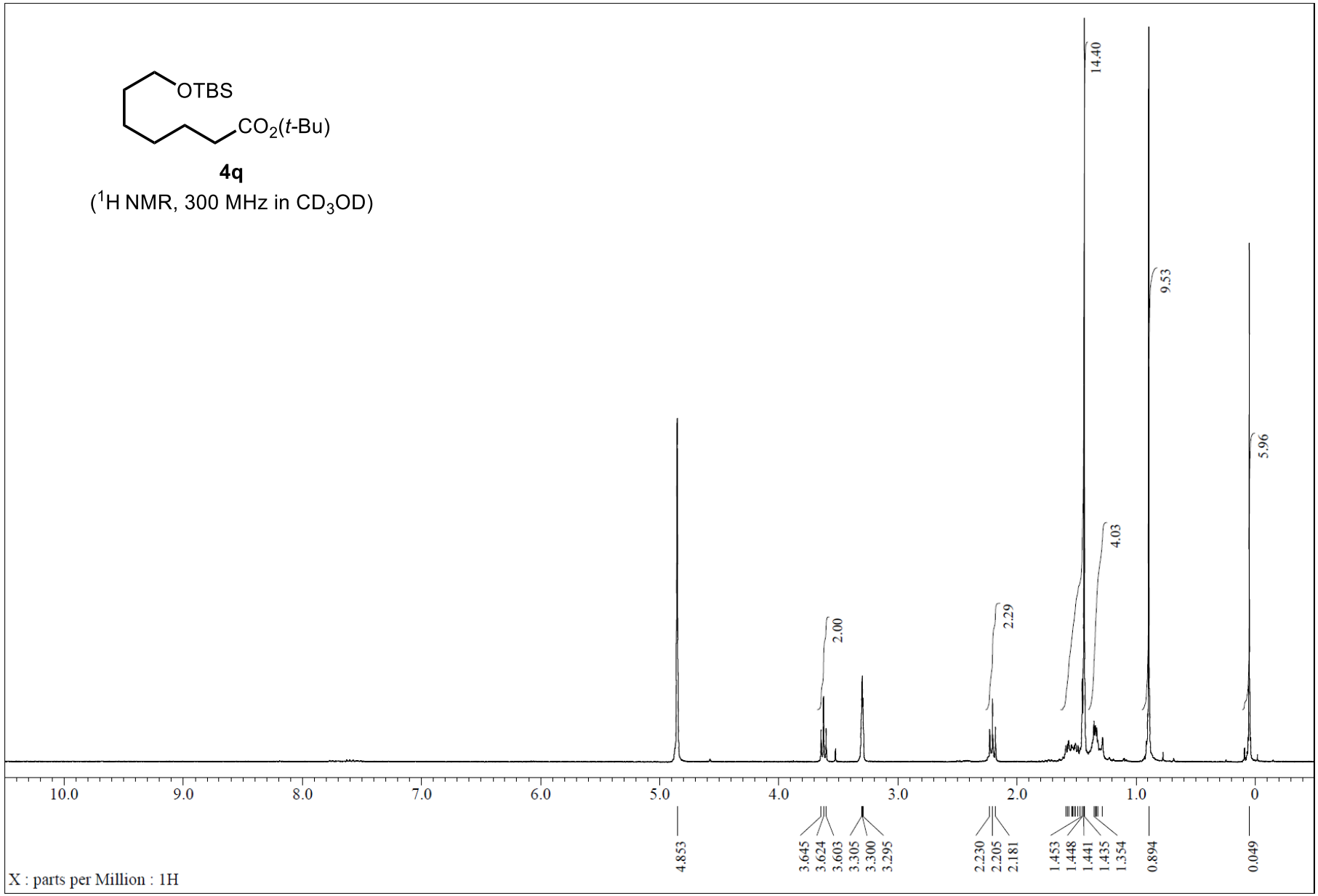

N
O
CO2(t-Bu)
4n
(13C NMR, 75 MHz in CDCl3)
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
173.359
79.902
77.427
77.000
76.581
66.946
59.351
53.753
34.344
33.276
32.306
31.878
28.064
23.913
19.252
X : parts per Million : 13C

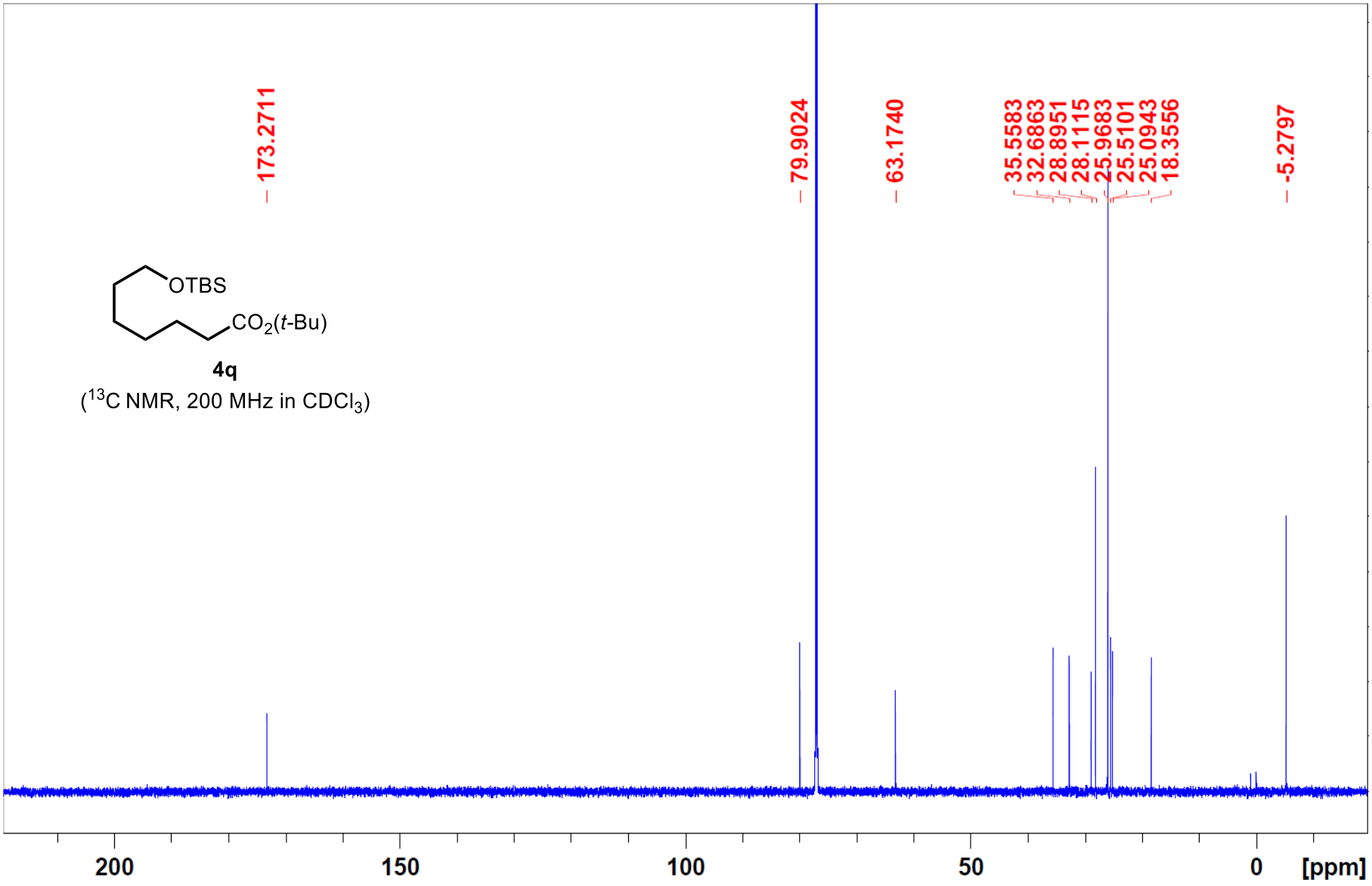

CO2(t-Bu)
4o
(1H NMR, 300 MHz in CDCl3)
17.51
2.25
2.94
2.00
2.95
2.03
3.11
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.253
7.245
7.238
7.221
7.216
7.208
7.199
7.191
6.700
6.694
6.670
6.646
6.643
3.298
3.273
3.247
2.914
2.227
2.224
2.201
2.195
1.617
1.594
1.590
1.583
1.438
1.407
0.889
0.868
0.000
X : parts per Million : 1H

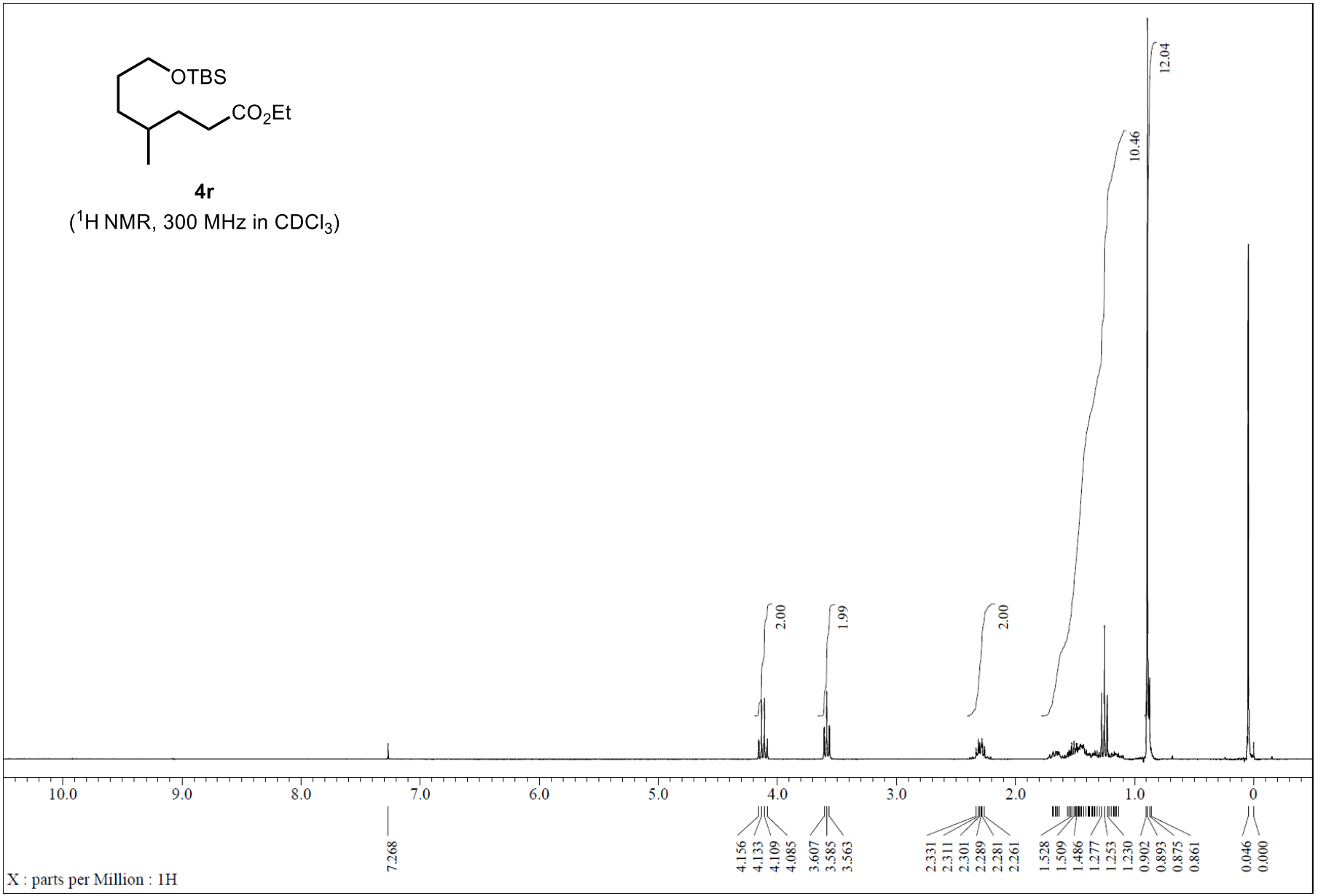

N
CO2(t-Bu)
4o
(13C NMR, 75 MHz in CDCl3)
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
173.395
149.317
129.127
115.842
112.069
79.968
77.427
77.000
76.581
53.021
38.232
34.080
33.308
32.370
31.959
28.096
24.026
19.275
X : parts per Million : 13C

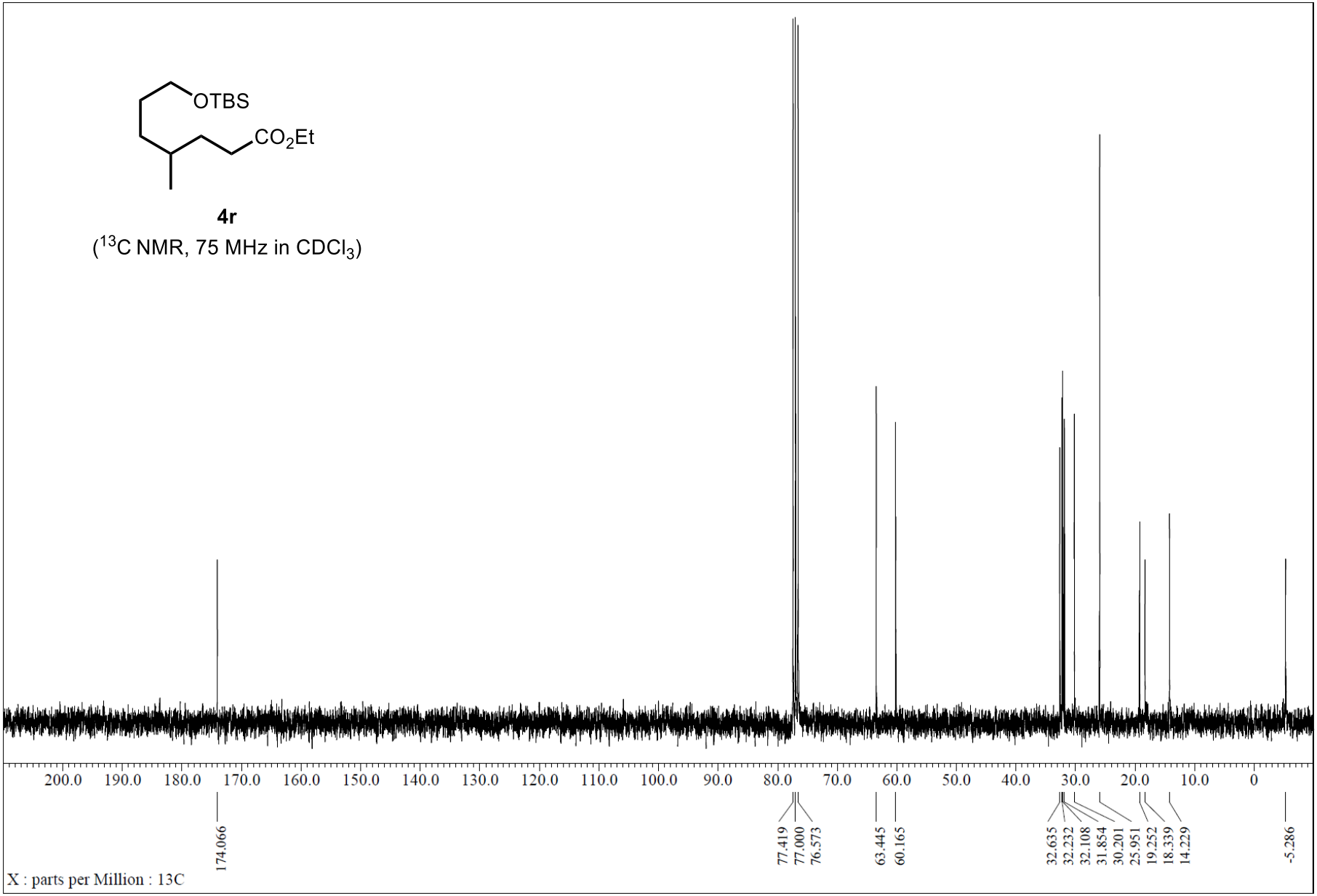

OBn
CO2(t-Bu)
4p
(1H NMR, 300 MHz in CDCl3)
12.95
6.00
5.15
1.99
1.99
1.94
2.10
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.372
7.347
7.332
7.298
7.288
7.285
7.269
7.258
7.256
7.242
4.498
3.462
3.440
3.418
2.191
2.170
2.164
2.154
2.135
1.538
1.510
1.482
1.441
1.438
1.258
0.855
X : parts per Million : 1H

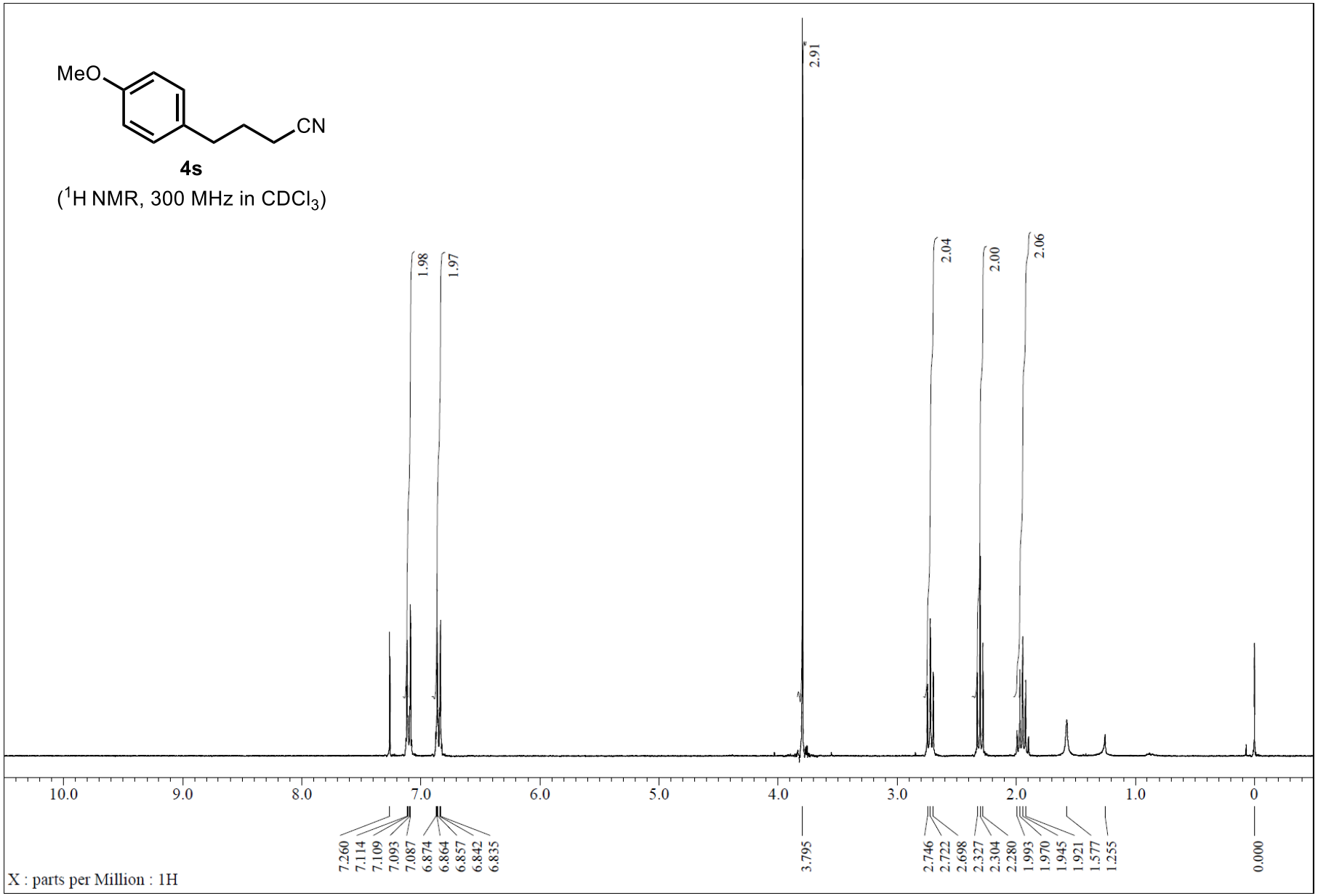

OBn
CO2(t-Bu)
4p
(13C NMR, 75 MHz in CDCl3)
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
173.738
138.562
128.295
127.572
127.432
79.902
77.419
77.000
76.573
72.832
71.180
37.871
36.482
32.158
30.793
28.056
26.691
24.390
X : parts per Million : 13C

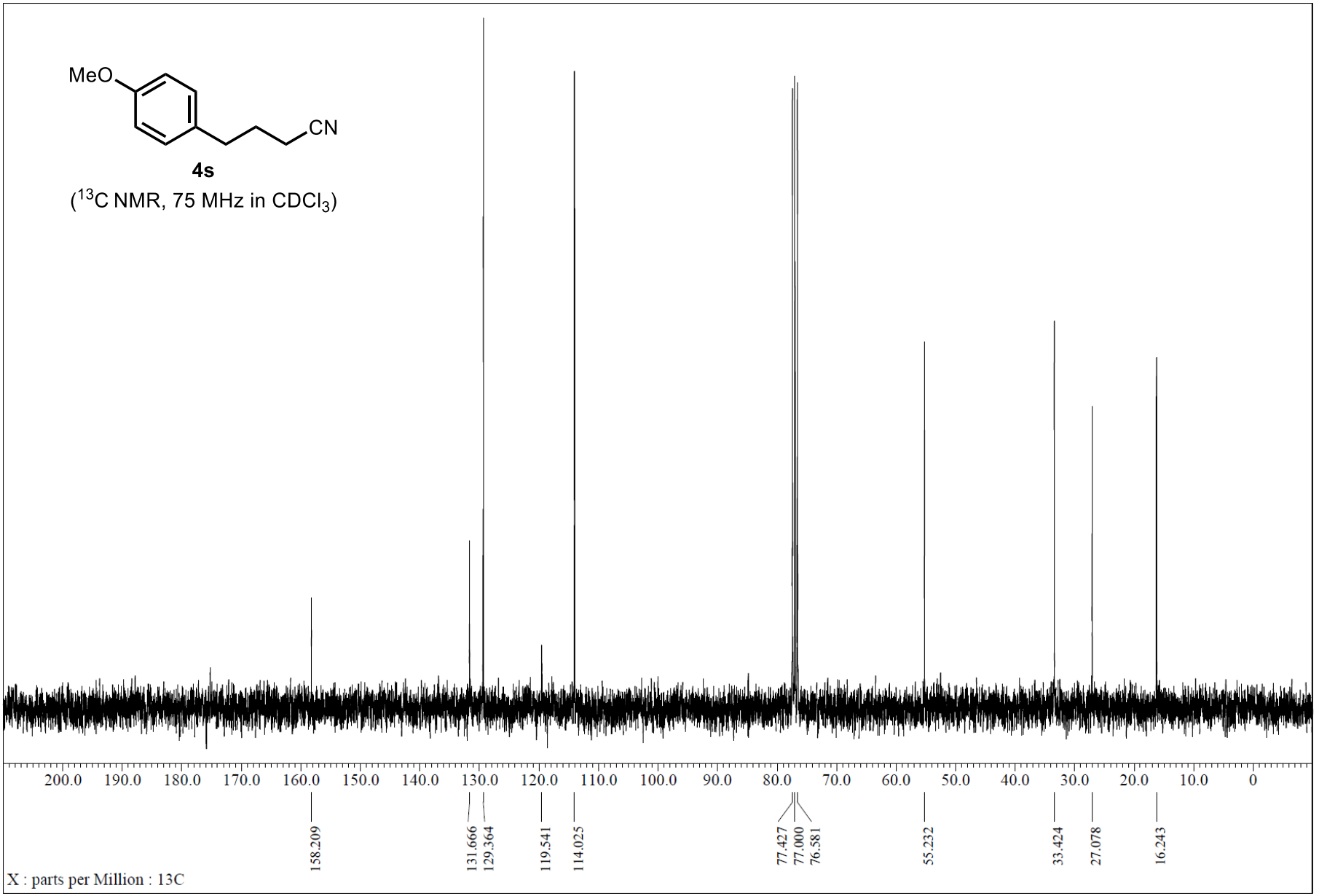

OTBS
CO2(t-Bu)
4q
(1H NMR, 300 MHz in CD3OD)
14.40
9.53
5.96
4.03
2.29
2.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
4.853
3.645
3.624
3.603
3.305
3.300
3.295
2.230
2.205
2.181
1.453
1.448
1.441
1.435
1.354
0.894
0.049
X : parts per Million : 1H

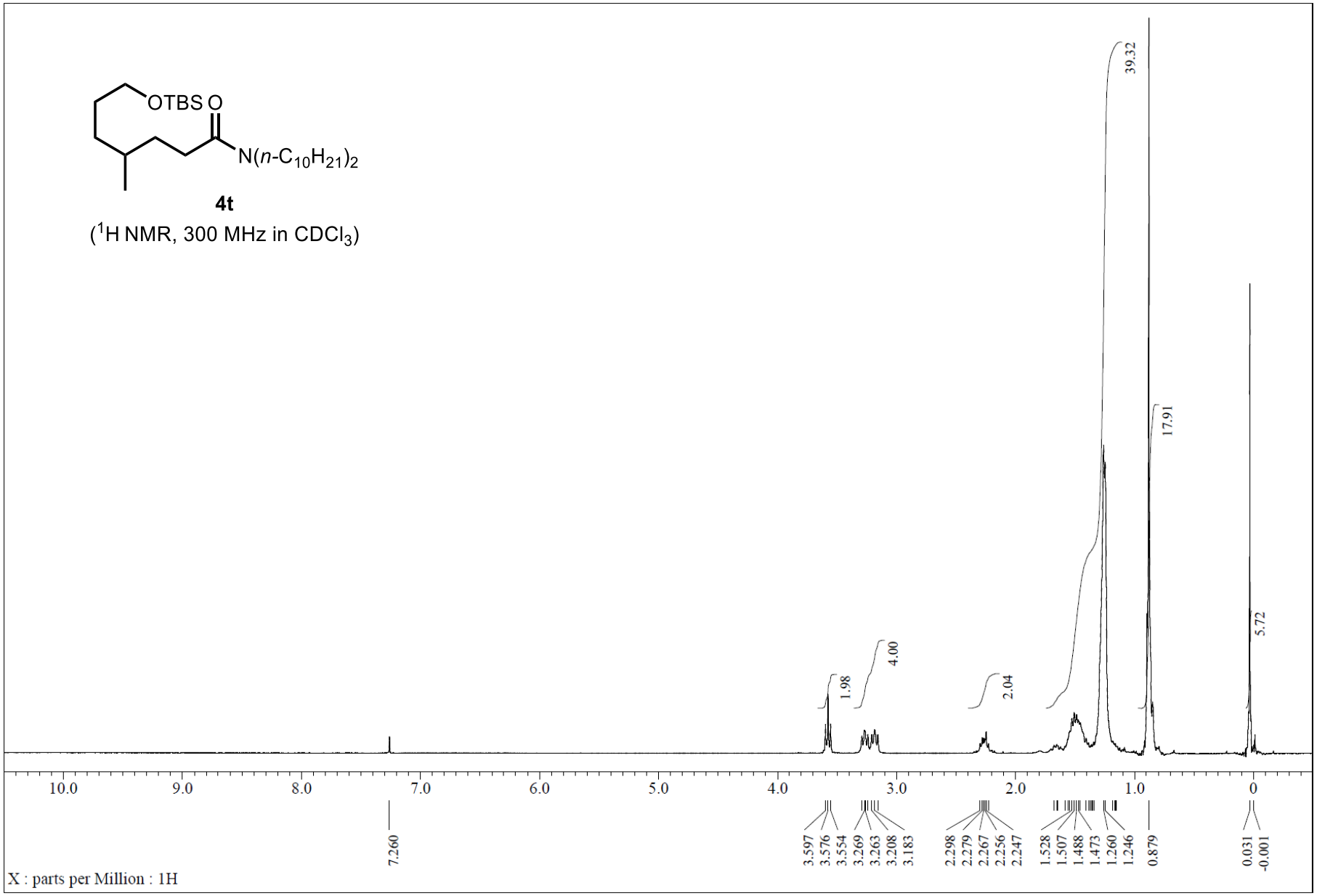

173.2711
79.9024
63.1740
35.5583
32.6863
28.8951
28.1115
25.9683
25.5101
25.0943
18.3556
-5.2797
OTBS
CO2(t-Bu)
4q
(13C NMR, 200 MHz in CDCl3)
200
150
100
50
0
[ppm]

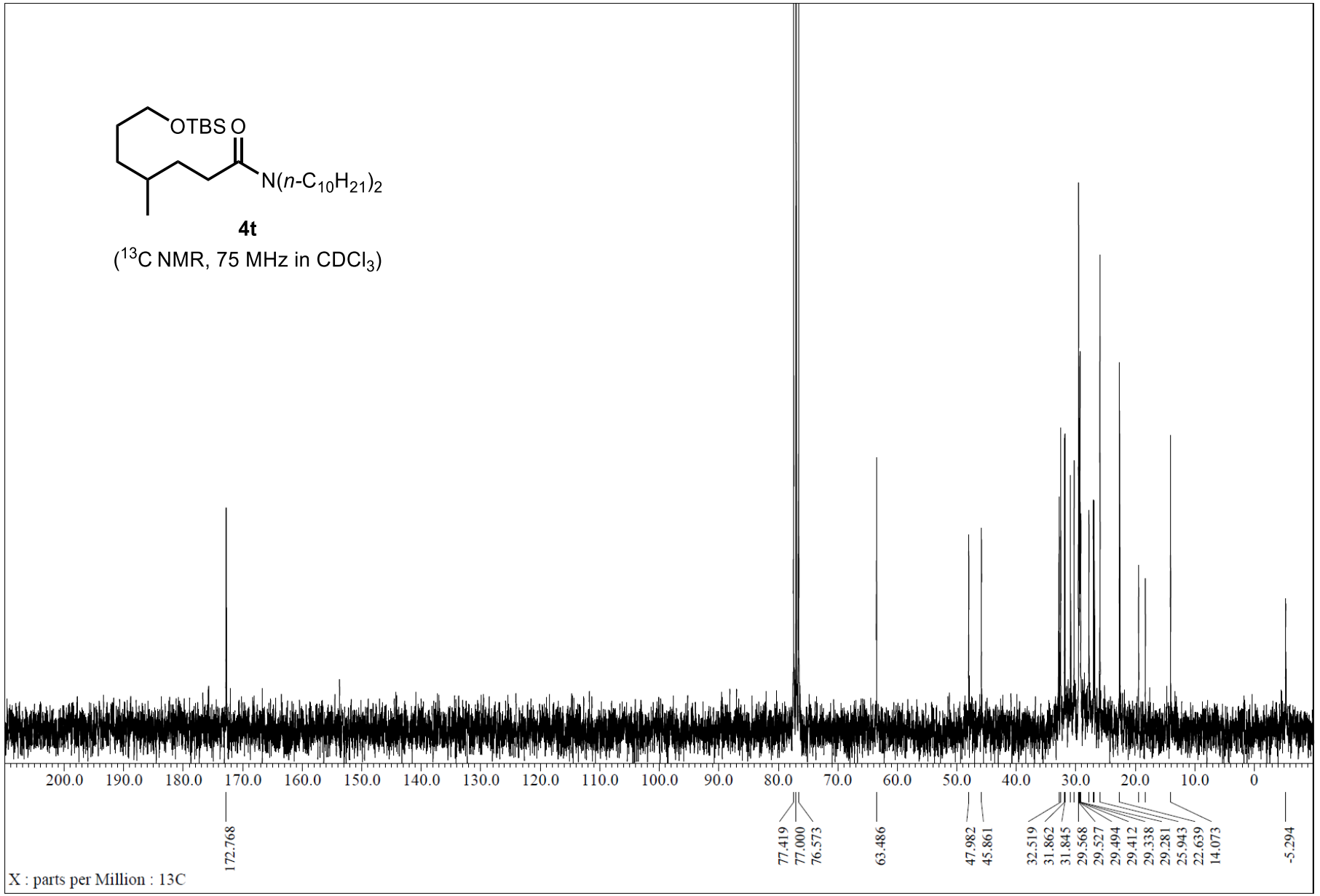

OTBS
CO2Et
4r
(1H NMR, 300 MHz in CDCl3)
12.04
10.46
2.00
1.99
2.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.268
4.156
4.133
4.109
4.085
3.607
3.585
3.563
2.331
2.311
2.301
2.289
2.281
2.261
1.528
1.509
1.486
1.277
1.253
1.230
0.902
0.893
0.875
0.861
0.046
0.000
X : parts per Million : 1H

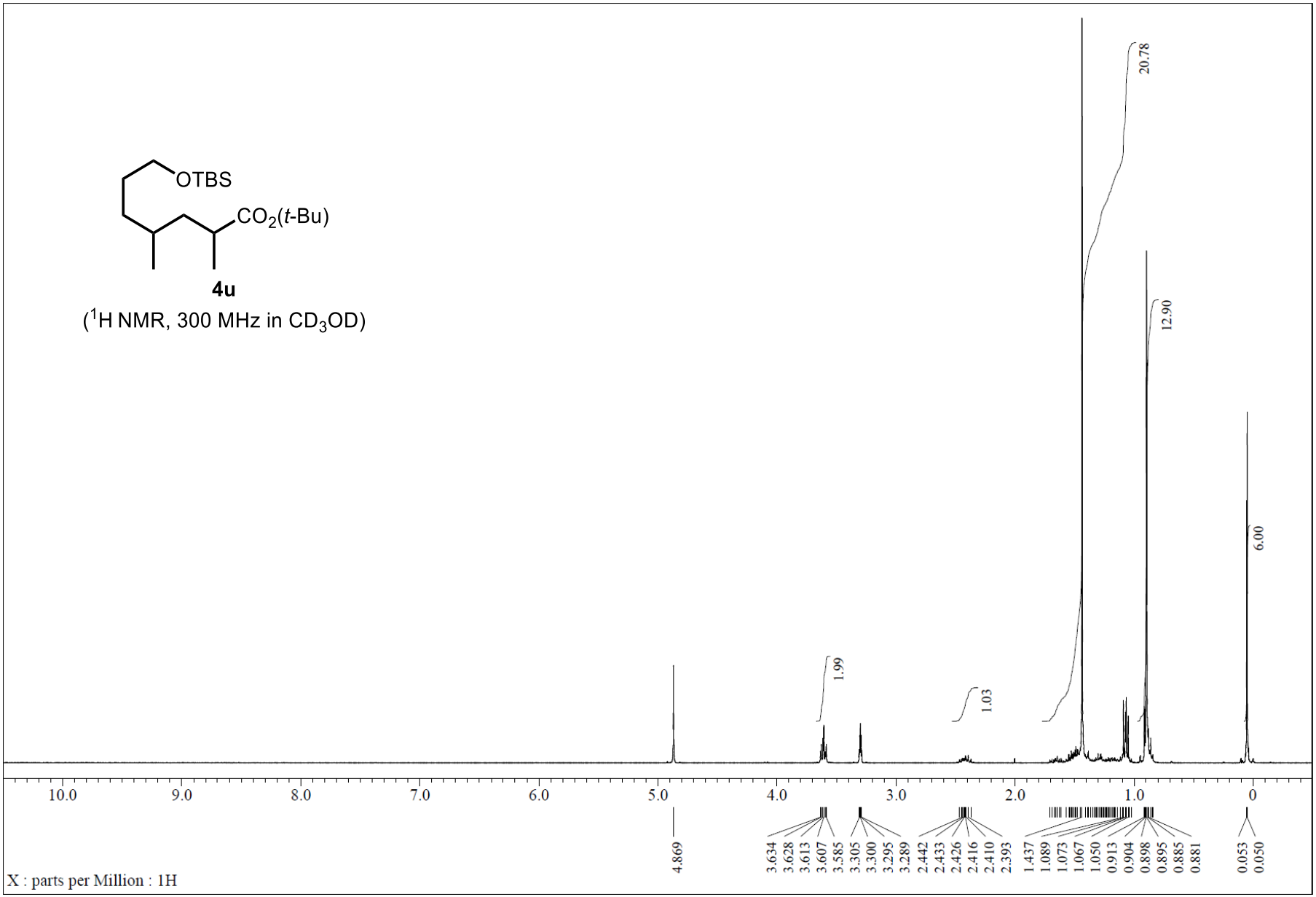

OTBS
CO2Et
4r
(13C NMR, 75 MHz in CDCl3)
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
174.066
77.419
77.000
76.573
63.445
60.165
32.635
32.232
32.108
31.854
30.201
25.951
19.252
18.339
14.229
-5.286
X : parts per Million : 13C

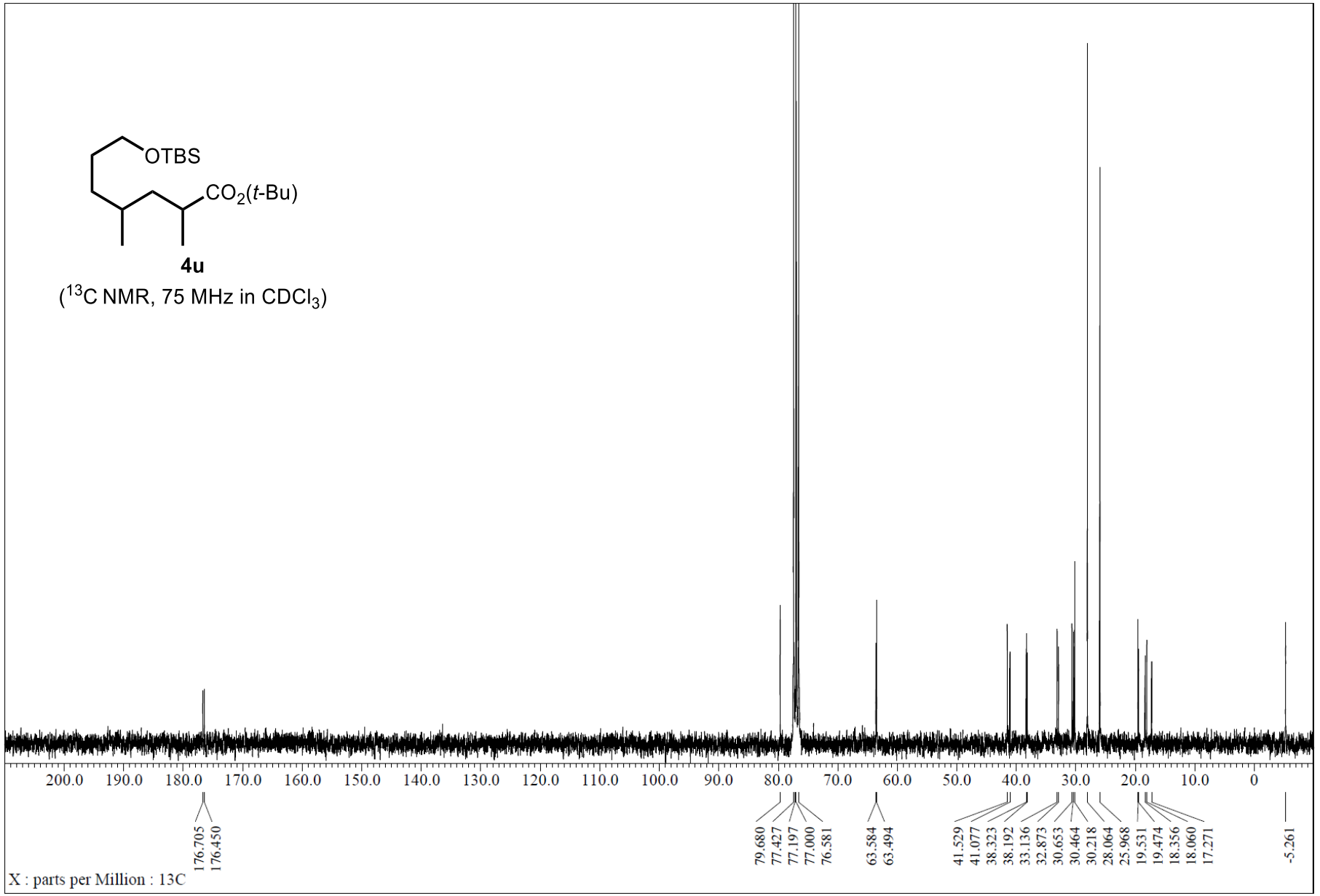

MeO
CN
4s
(1H NMR, 300 MHz in CDCl3)
1.98
1.97
2.91
2.04
2.00
2.06
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.260
7.114
7.109
7.093
7.087
6.874
6.864
6.857
6.842
6.835
3.795
2.746
2.722
2.698
2.327
2.304
2.280
1.993
1.970
1.945
1.921
1.577
1.255
0.000
X : parts per Million : 1H

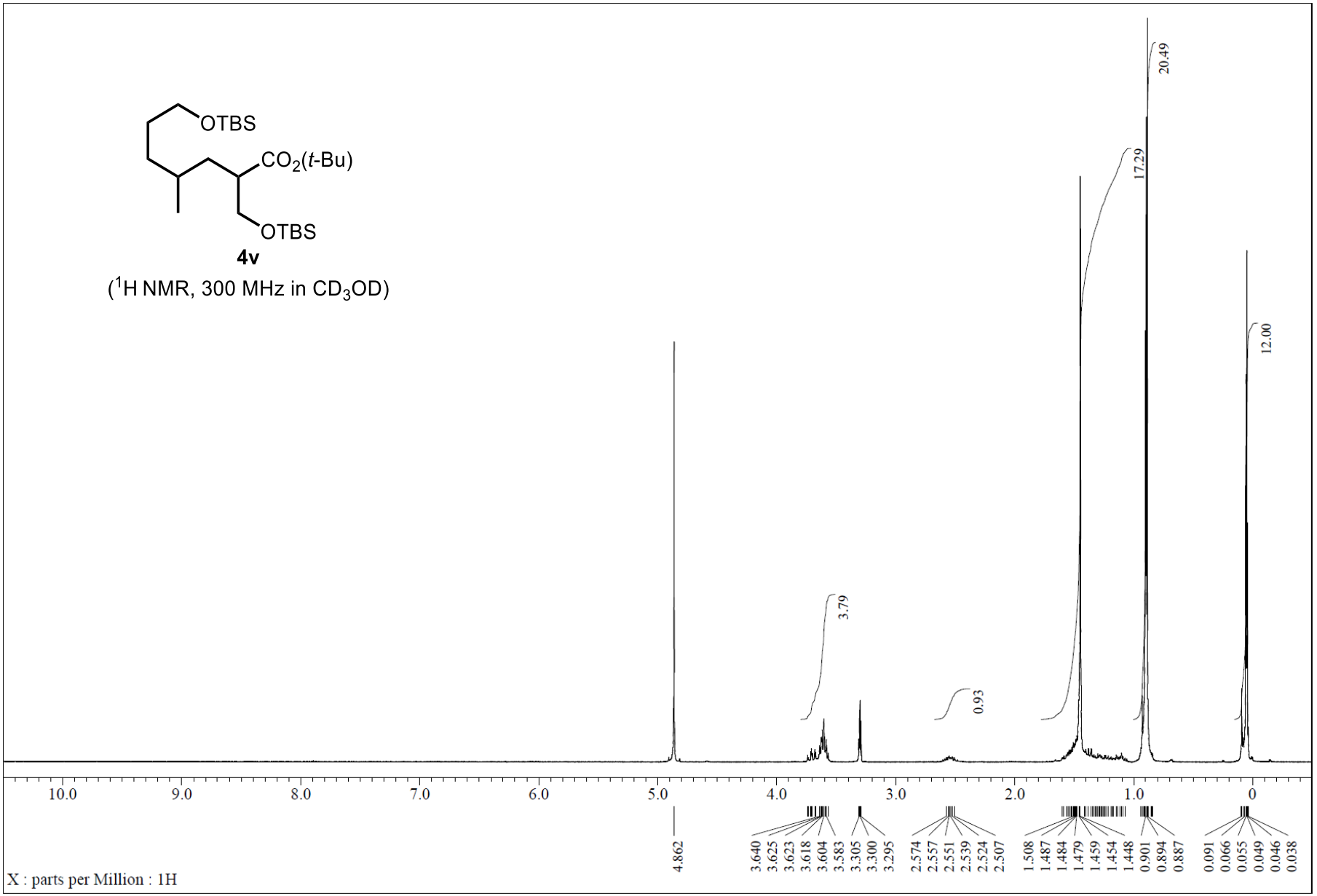

MeO
CN
4s
(13C NMR, 75 MHz in CDCl3)
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
158.209
131.666
129.364
119.541
114.025
77.427
77.000
76.581
55.232
33.424
27.078
16.243
X : parts per Million : 13C

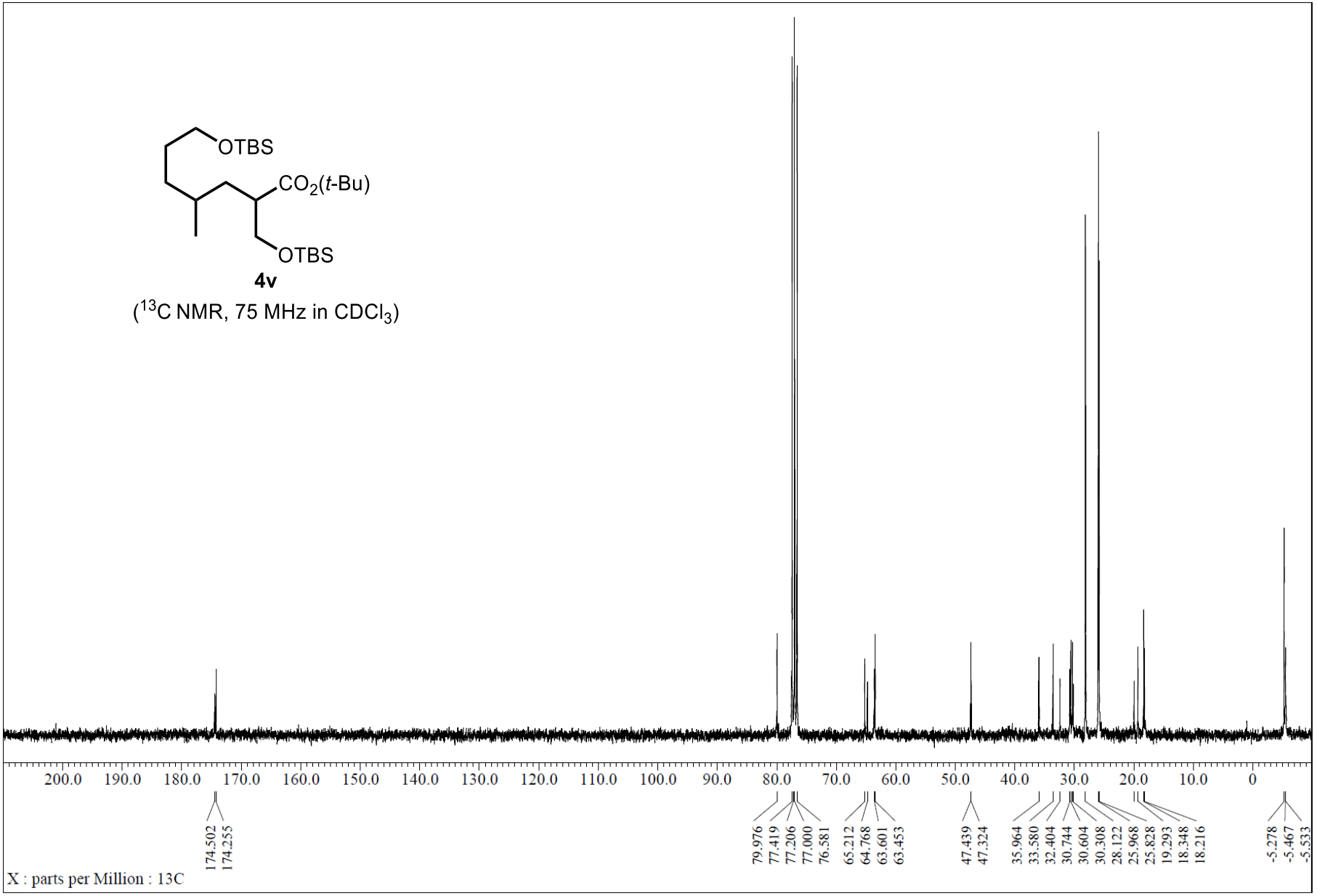

OTBS O
N(n-C10H21)2
4t
(1H NMR, 300 MHz in CDCl3)
39.32
17.91
5.72
4.00
1.98
2.04
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.260
3.597
3.576
3.554
3.269
3.263
3.208
3.183
2.298
2.279
2.267
2.256
2.247
1.528
1.507
1.488
1.473
1.260
1.246
0.879
0.031
-0.001
X : parts per Million : 1H

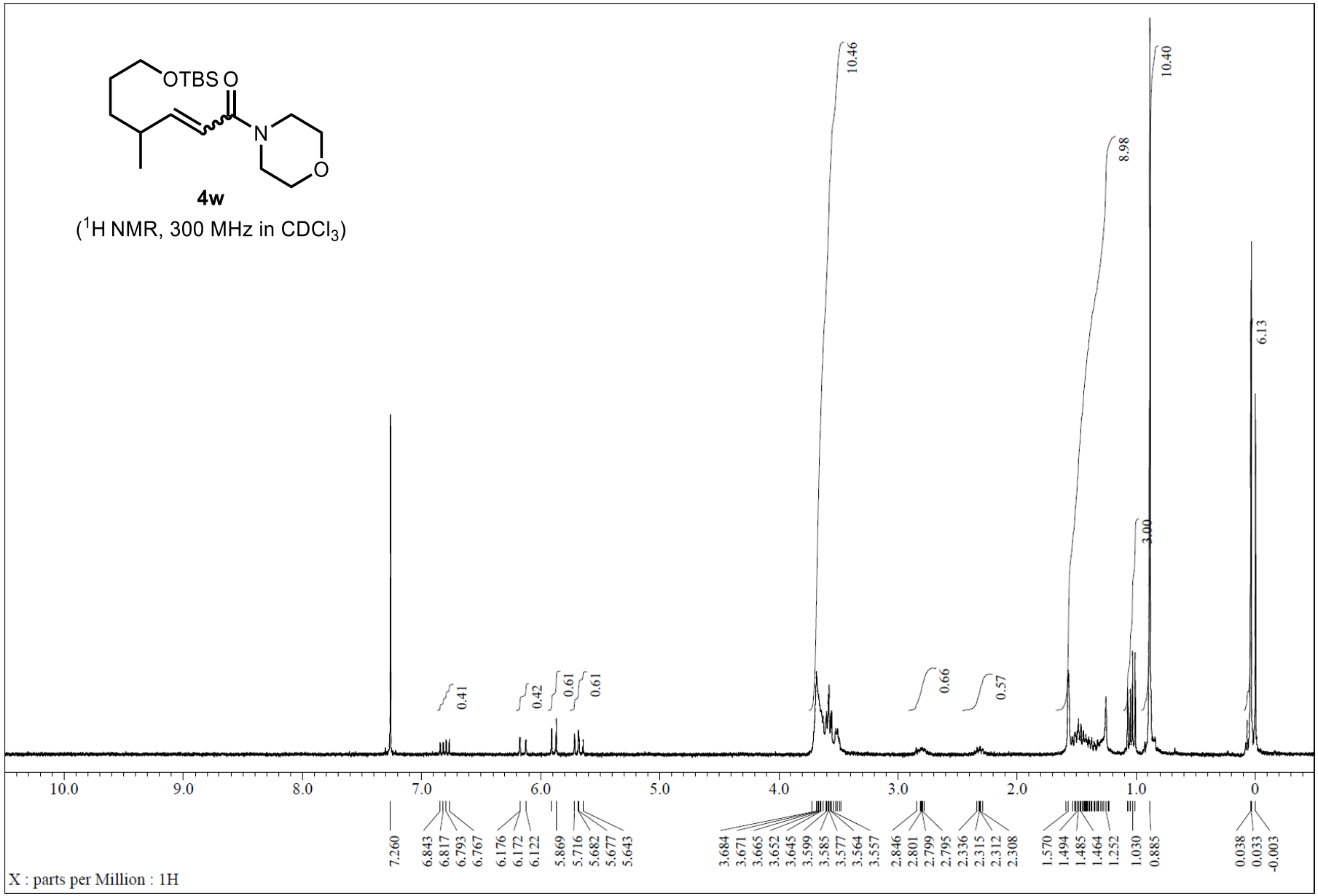

OTBS O
N(n-C10H21)2
4t
(13C NMR, 75 MHz in CDCl3)
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
172.768
77.419
77.000
76.573
63.486
47.982
45.861
32.519
31.862
31.845
29.568
29.527
29.494
29.412
29.338
29.281
25.943
22.639
14.073
-5.294
X : parts per Million : 13C

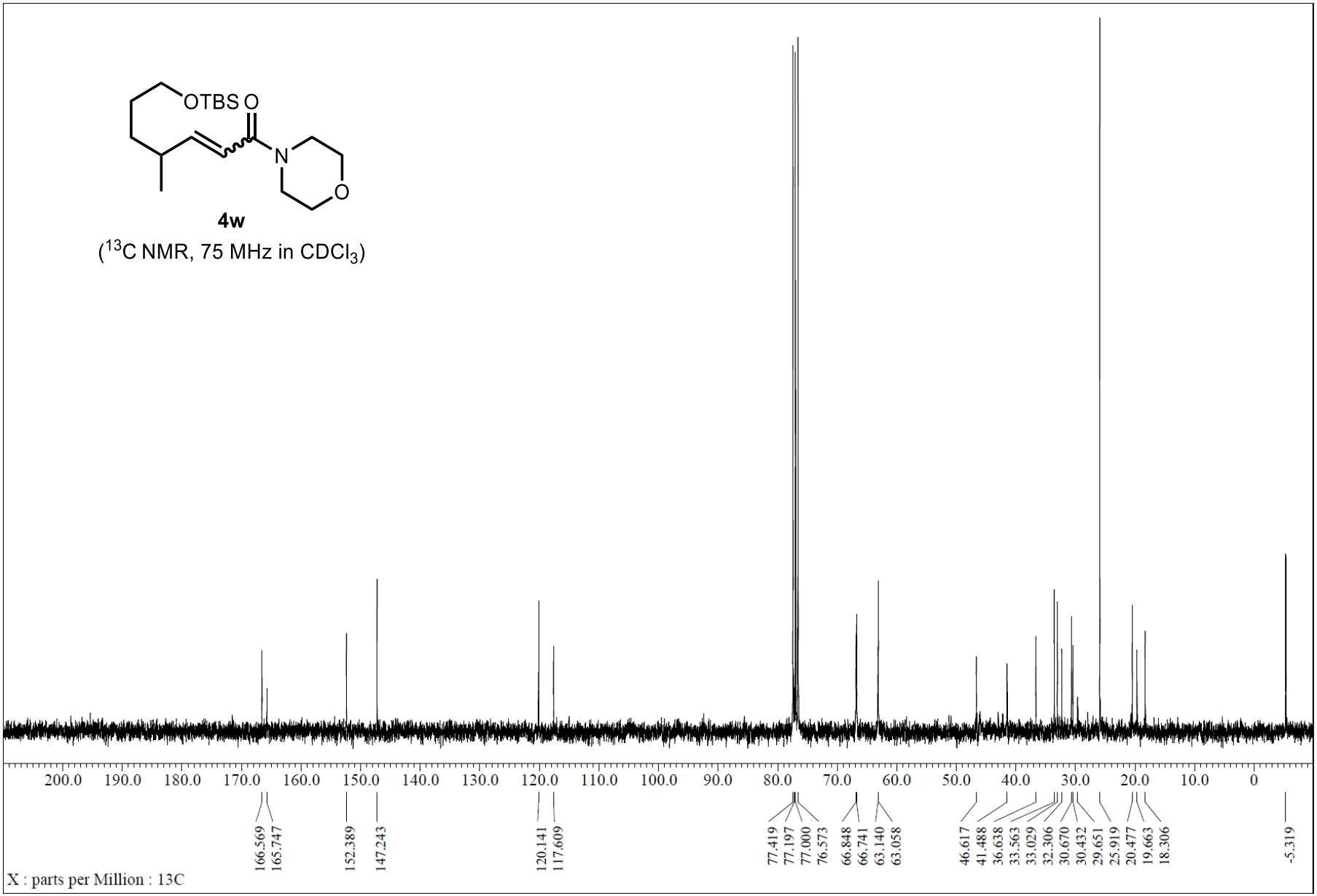

OTBS
CO2(t-Bu)
4u
(1H NMR, 300 MHz in CD3OD)
20.78
12.90
6.00
1.99
1.03
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
4.869
3.634
3.628
3.613
3.607
3.585
3.305
3.300
3.295
3.289
2.442
2.433
2.426
2.416
2.410
2.393
1.437
1.089
1.073
1.067
1.050
0.913
0.904
0.898
0.895
0.885
0.881
0.053
0.050
X : parts per Million : 1H

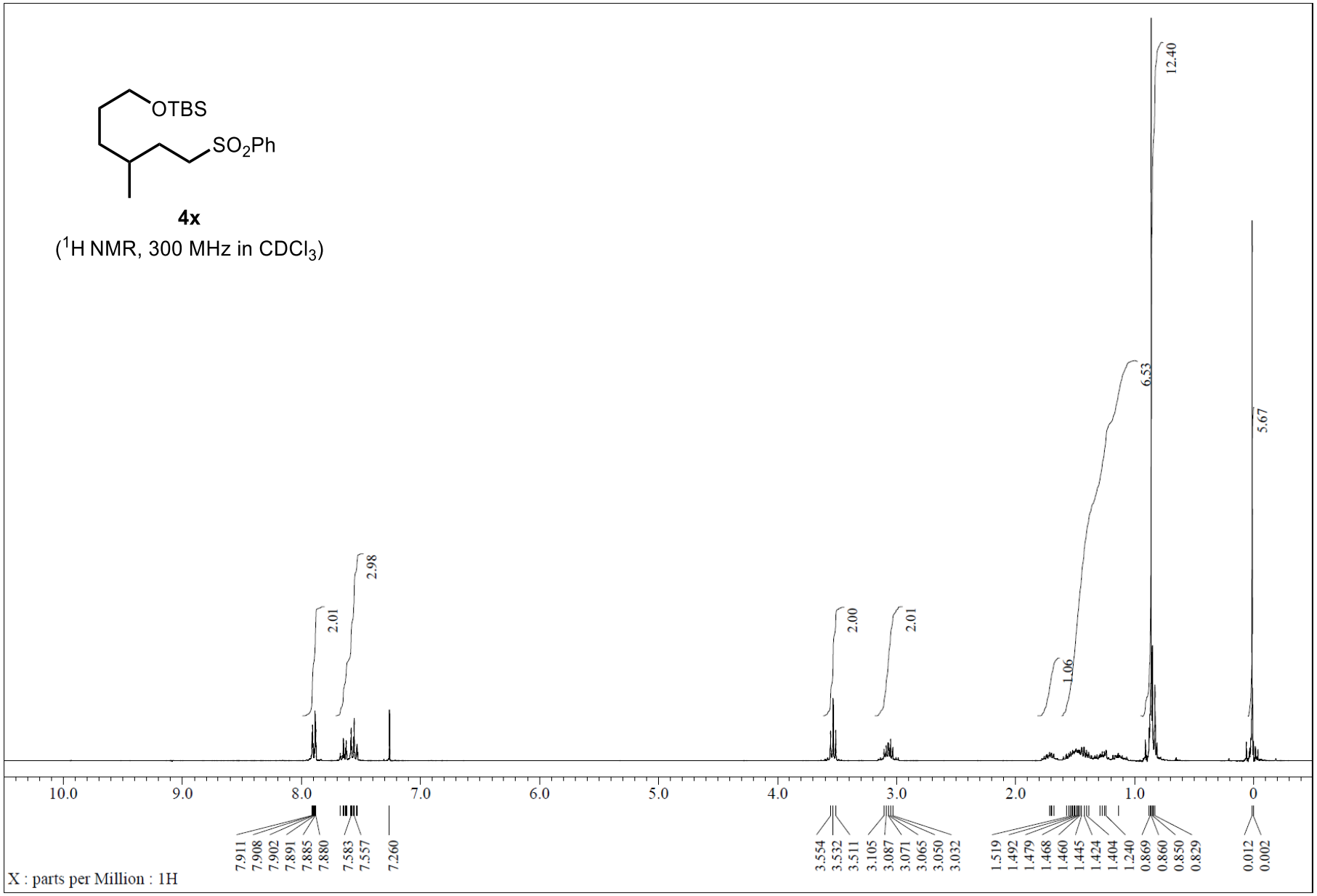

OTBS
CO2(t-Bu)
4u
(13C NMR, 75 MHz in CDCl3)
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
176.705
176.450
79.680
77.427
77.197
77.000
76.581
63.584
63.494
41.529
41.077
38.323
38.192
33.136
32.873
30.653
30.464
30.218
28.064
25.968
19.531
19.474
18.356
18.060
17.271
-5.261
X : parts per Million : 13C

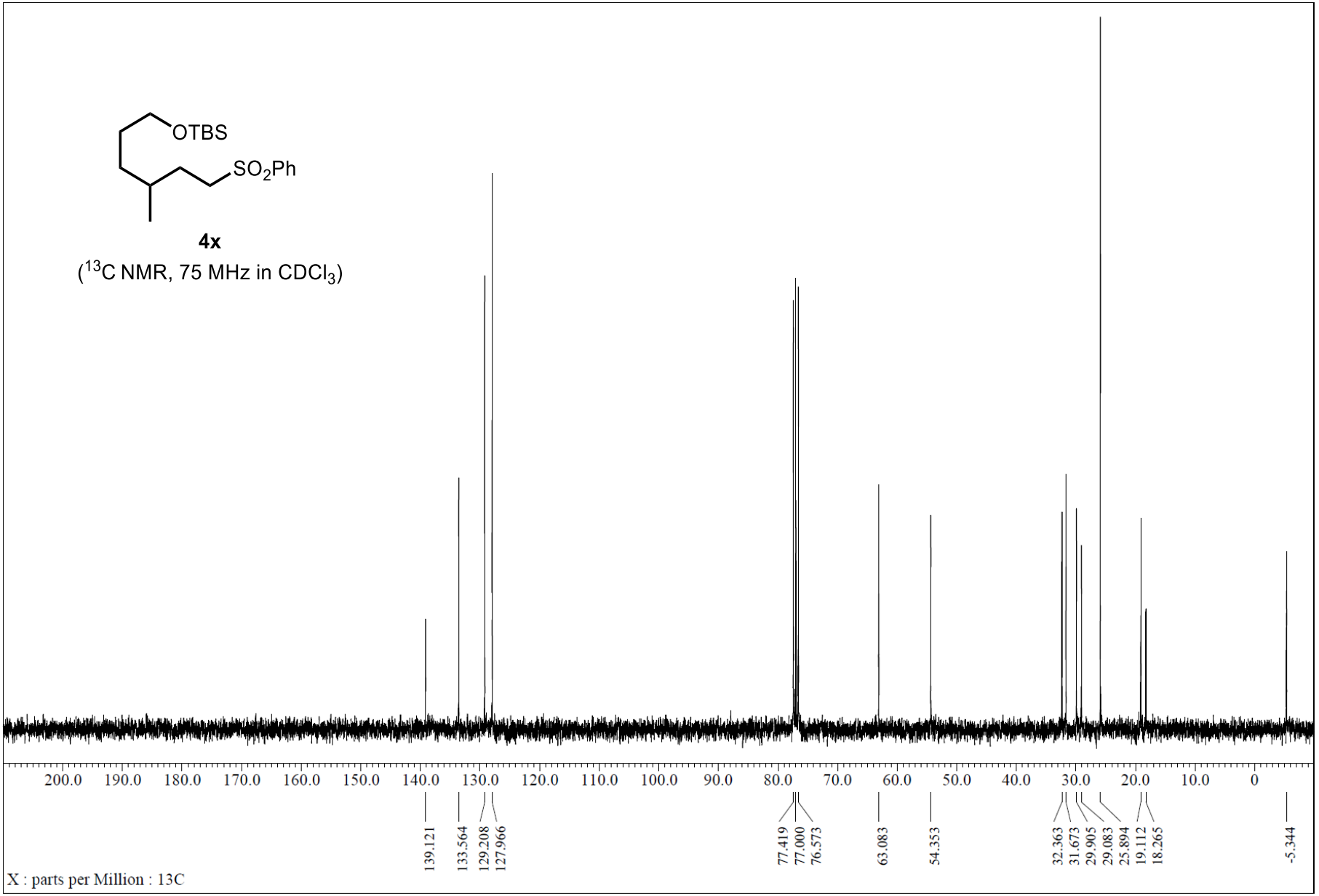

OTBS
CO2(t-Bu)
OTBS
4v
(1H NMR, 300 MHz in CD3OD)
20.49
17.29
12.00
3.79
0.93
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
4.862
3.640
3.625
3.623
3.618
3.604
3.583
3.305
3.300
3.295
2.574
2.557
2.551
2.539
2.524
2.507
1.508
1.487
1.484
1.479
1.459
1.454
1.448
0.901
0.894
0.887
0.091
0.066
0.055
0.049
0.046
0.038
X : parts per Million : 1H

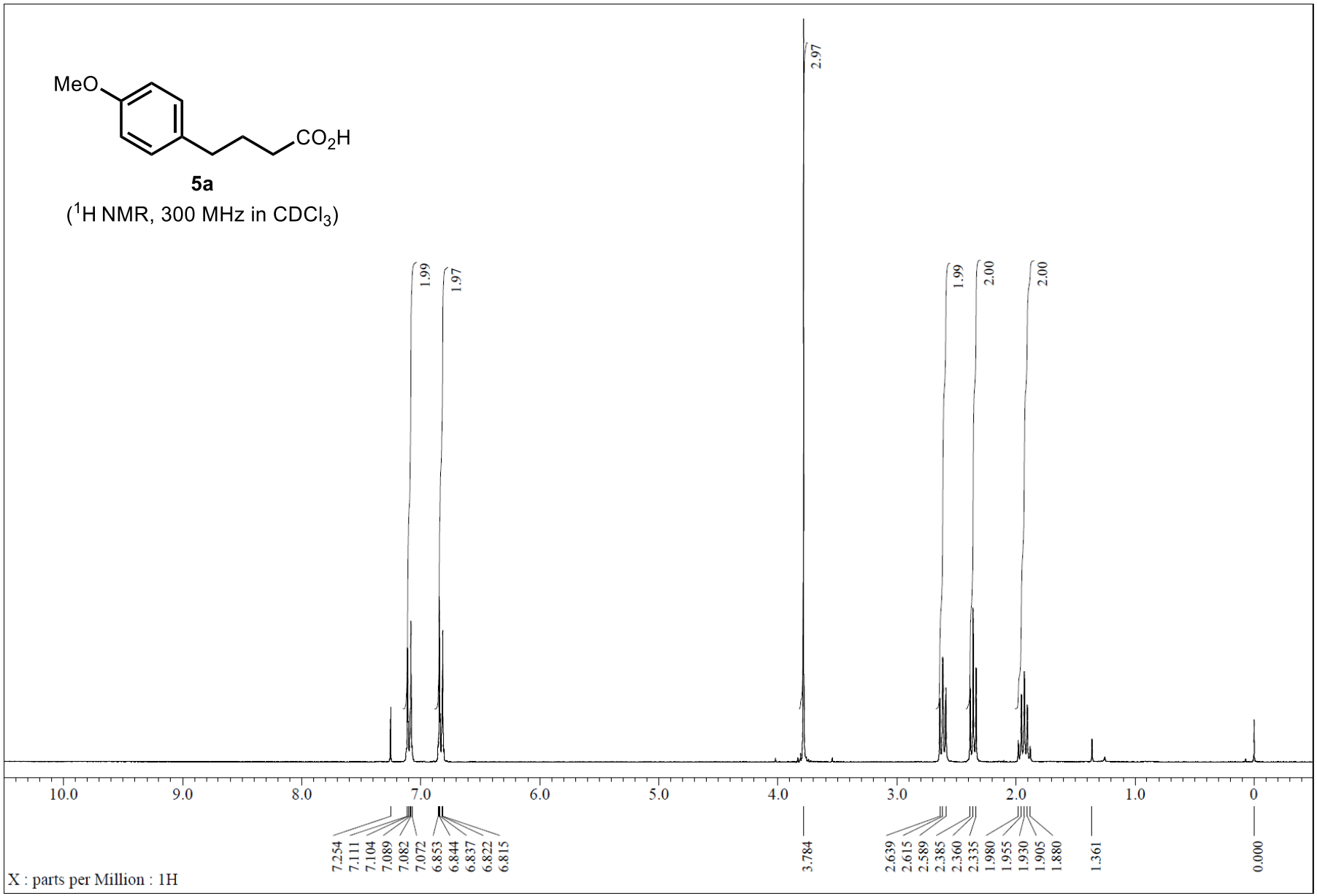

OTBS
CO2(t-Bu)
OTBS
4v
(13C NMR, 75 MHz in CDCl3)
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
174.502
174.255
79.976
77.419
77.206
77.000
76.581
65.212
64.768
63.601
63.453
47.439
47.324
35.964
33.580
32.404
30.744
30.604
30.308
28.122
25.968
25.828
19.293
18.348
18.216
-5.278
-5.467
-5.533
X : parts per Million : 13C

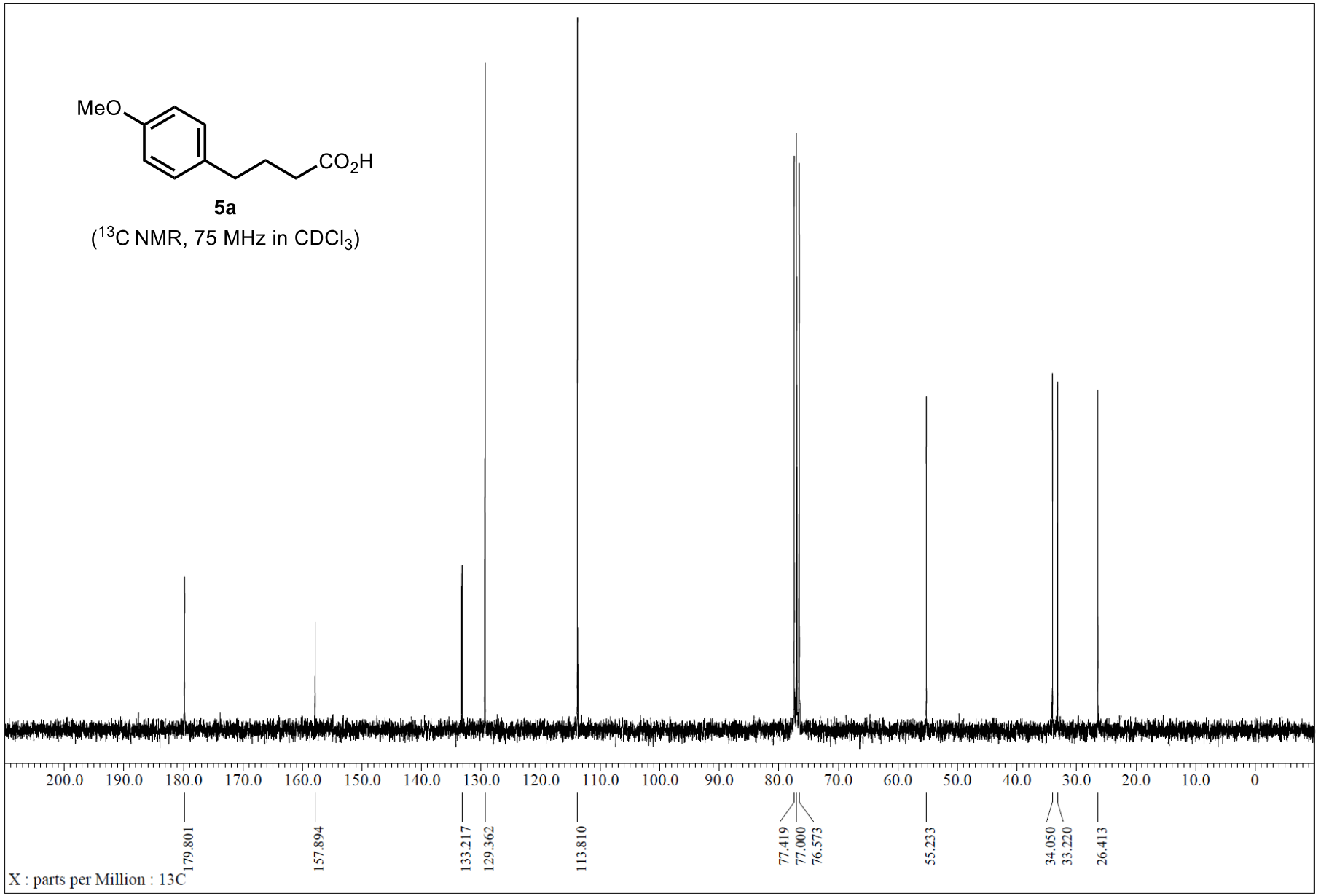

OTBS
O
N
O
4w
(1H NMR, 300 MHz in CDCl3)
10.46
10.40
8.98
6.13
3.00
0.41
0.42
0.61
0.61
0.66
0.57
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.260
6.843
6.817
6.793
6.767
6.176
6.172
6.122
5.869
5.716
5.682
5.677
5.643
3.684
3.671
3.665
3.652
3.645
3.599
3.585
3.577
3.564
3.557
2.846
2.801
2.799
2.795
2.336
2.315
2.312
2.308
1.570
1.494
1.485
1.464
1.252
1.030
0.885
0.038
0.033
-0.003
X : parts per Million : 1H

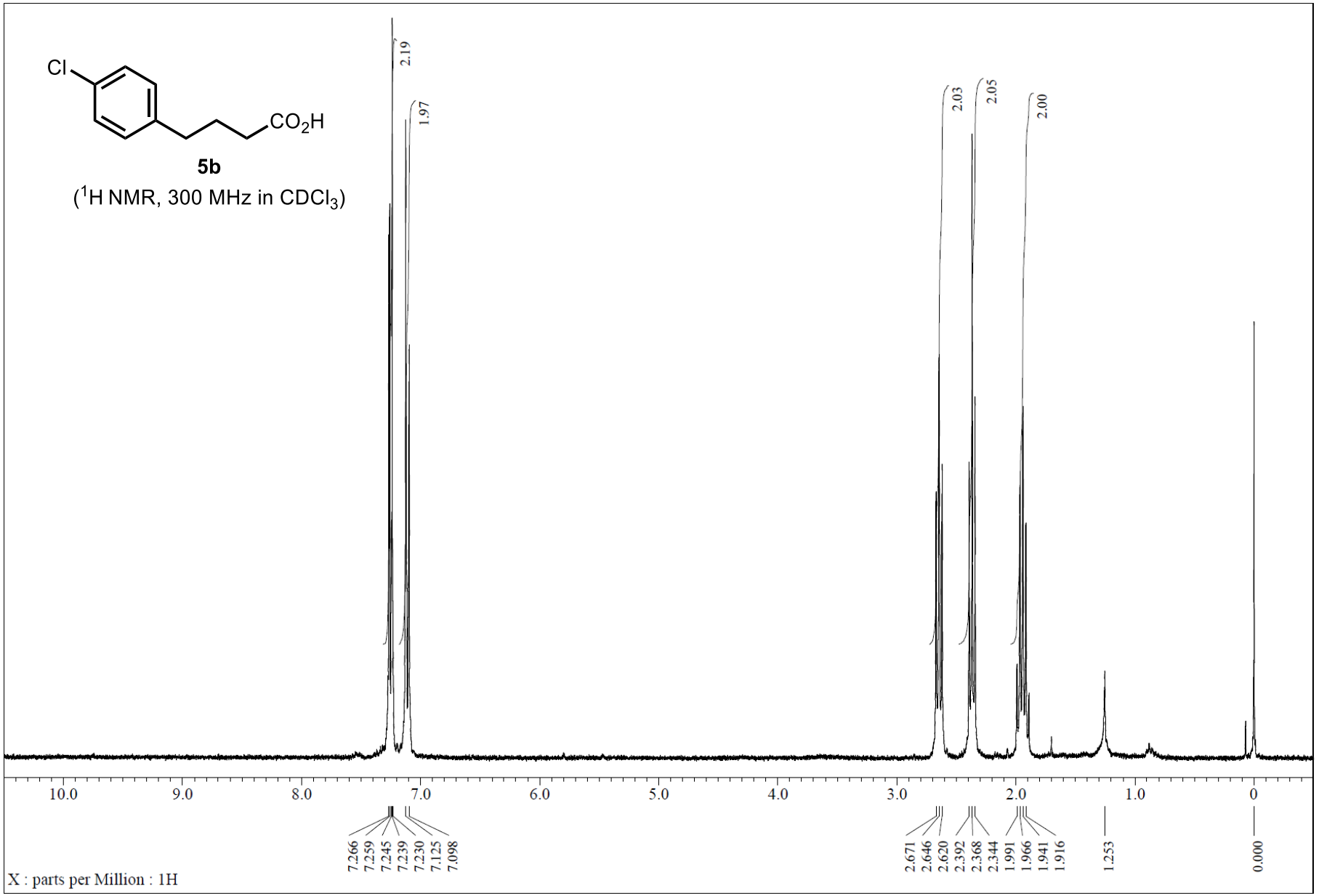

OTBS O
N
O
4w
(13C NMR, 75 MHz in CDCl3)
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
166.569
165.747
152.389
147.243
120.141
117.609
77.419
77.197
77.000
76.573
66.848
66.741
63.140
63.058
46.617
41.488
36.638
33.563
33.029
32.306
30.670
30.432
29.651
25.919
20.477
19.663
18.306
-5.319
X : parts per Million : 13C

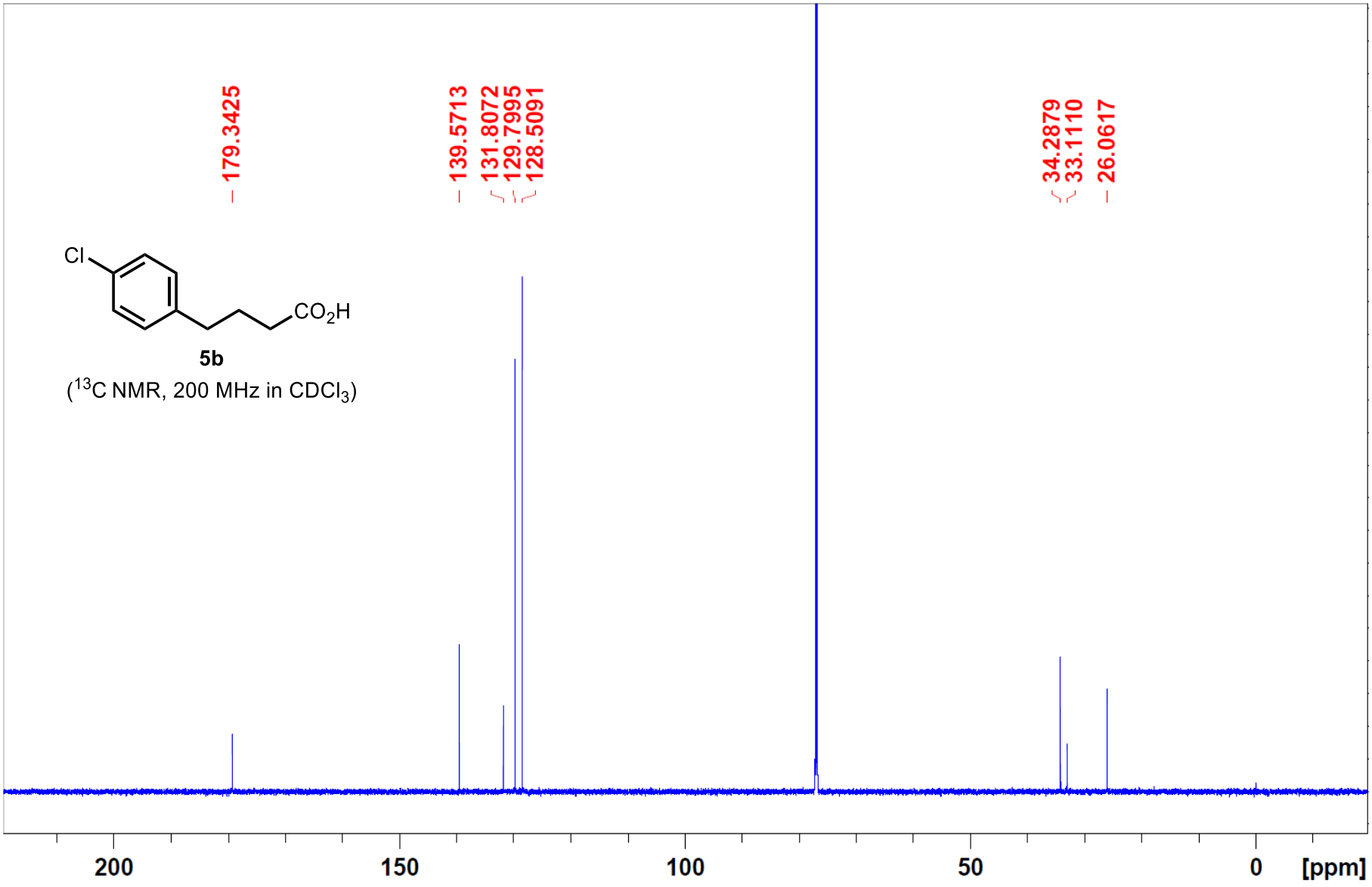

OTBS
SO2Ph
4x
(1H NMR, 300 MHz in CDCl3)
12.40
6.53
5.67
2.98
2.01
2.00
2.01
1.06
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.911
7.908
7.902
7.891
7.885
7.880
7.583
7.557
7.260
3.554
3.532
3.511
3.105
3.087
3.071
3.065
3.050
3.032
1.519
1.492
1.479
1.468
1.460
1.445
1.424
1.404
1.240
0.869
0.860
0.850
0.829
0.012
0.002
X : parts per Million : 1H

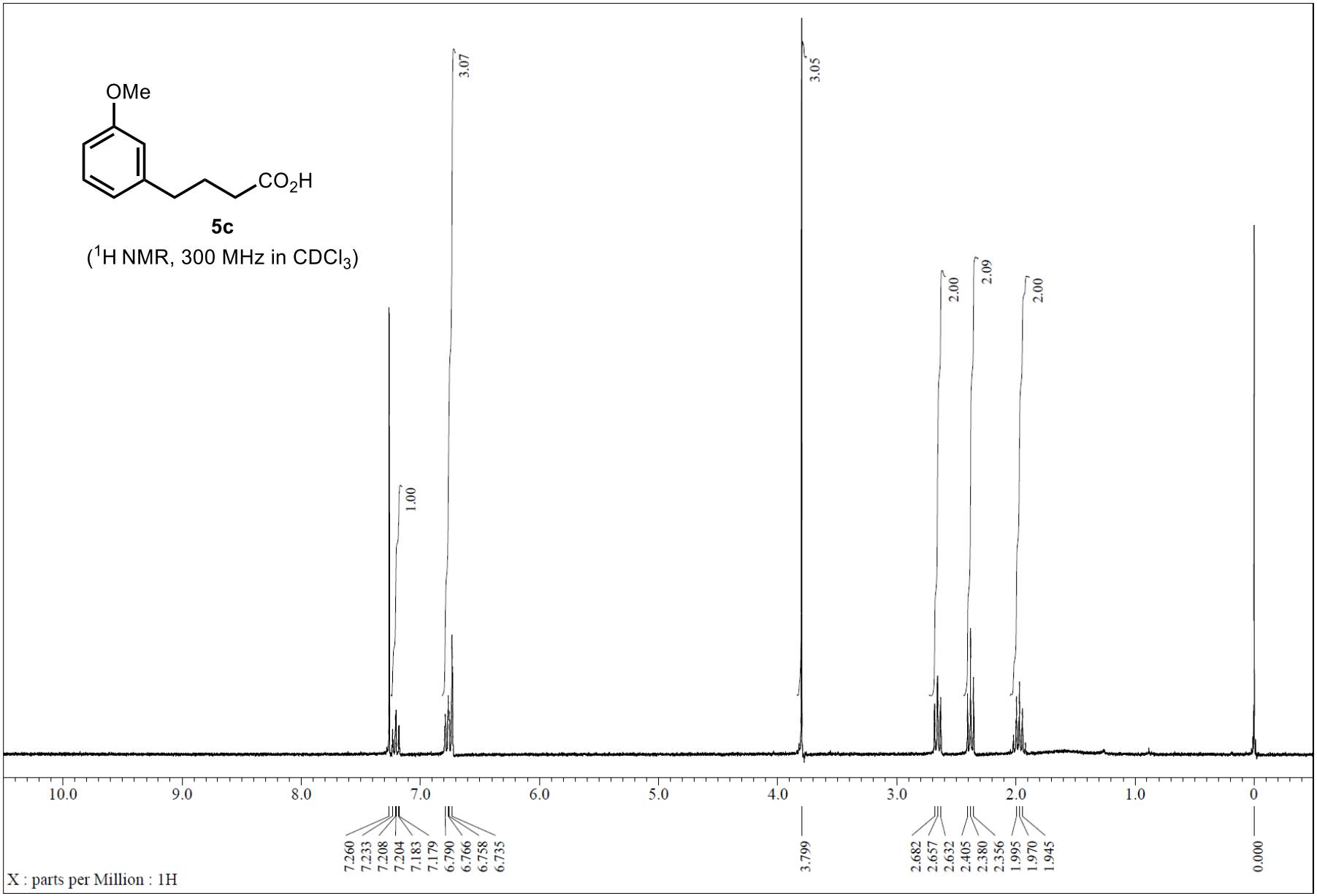

OTBS
SO2Ph
4x
(13C NMR, 75 MHz in CDCl3)
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
139.121
133.564
129.208
127.966
77.419
77.000
76.573
63.083
54.353
32.363
31.673
29.905
29.083
25.894
19.112
18.265
-5.344
X : parts per Million : 13C

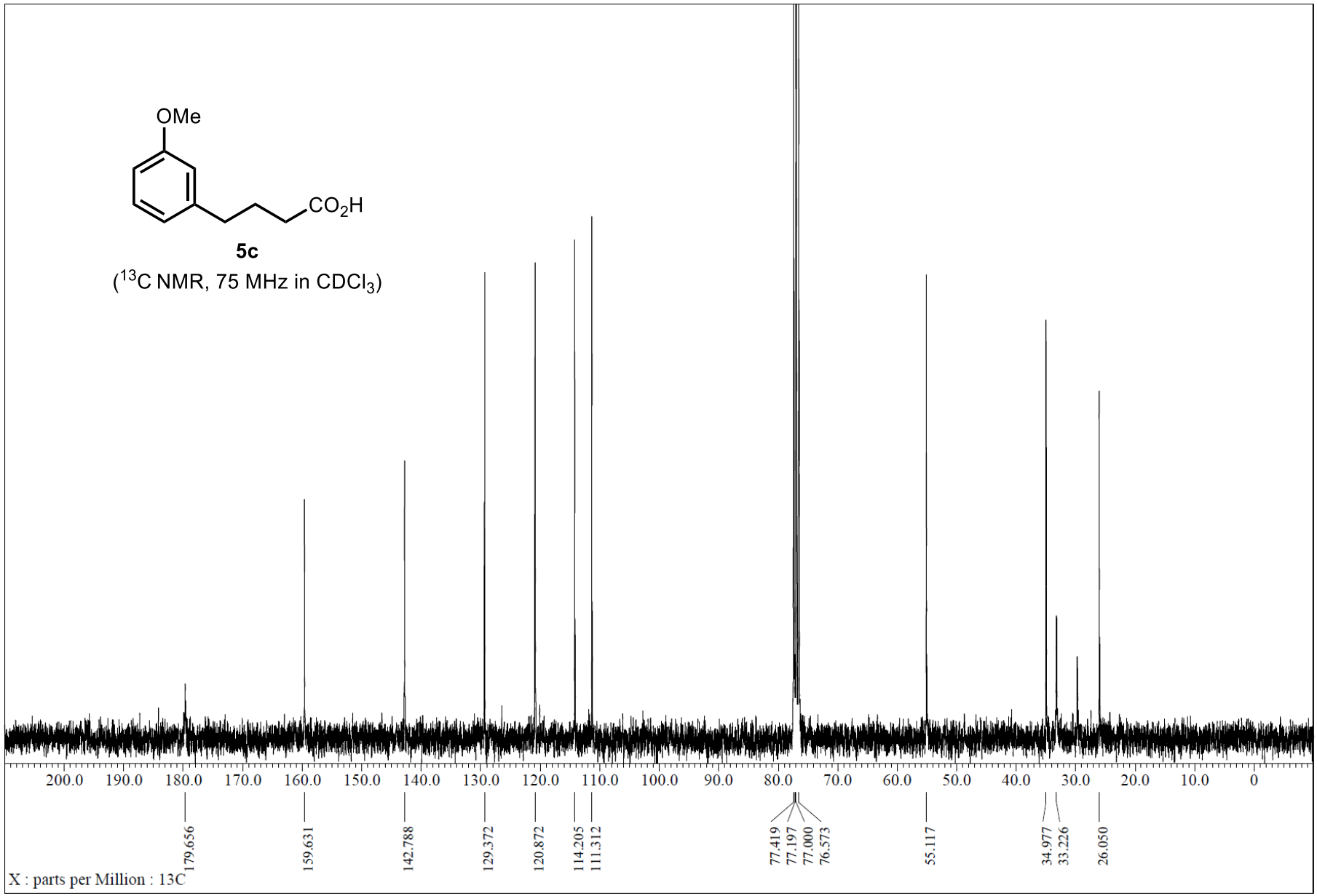

MeO
CO2H
5a
(1H NMR, 300 MHz in CDCl3)
2.97
1.99
1.97
1.99
2.00
2.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.254
7.111
7.104
7.089
7.082
7.072
6.853
6.844
6.837
6.822
6.815
3.784
2.639
2.615
2.589
2.385
2.360
2.335
1.980
1.955
1.930
1.905
1.880
1.361
0.000
X : parts per Million : 1H

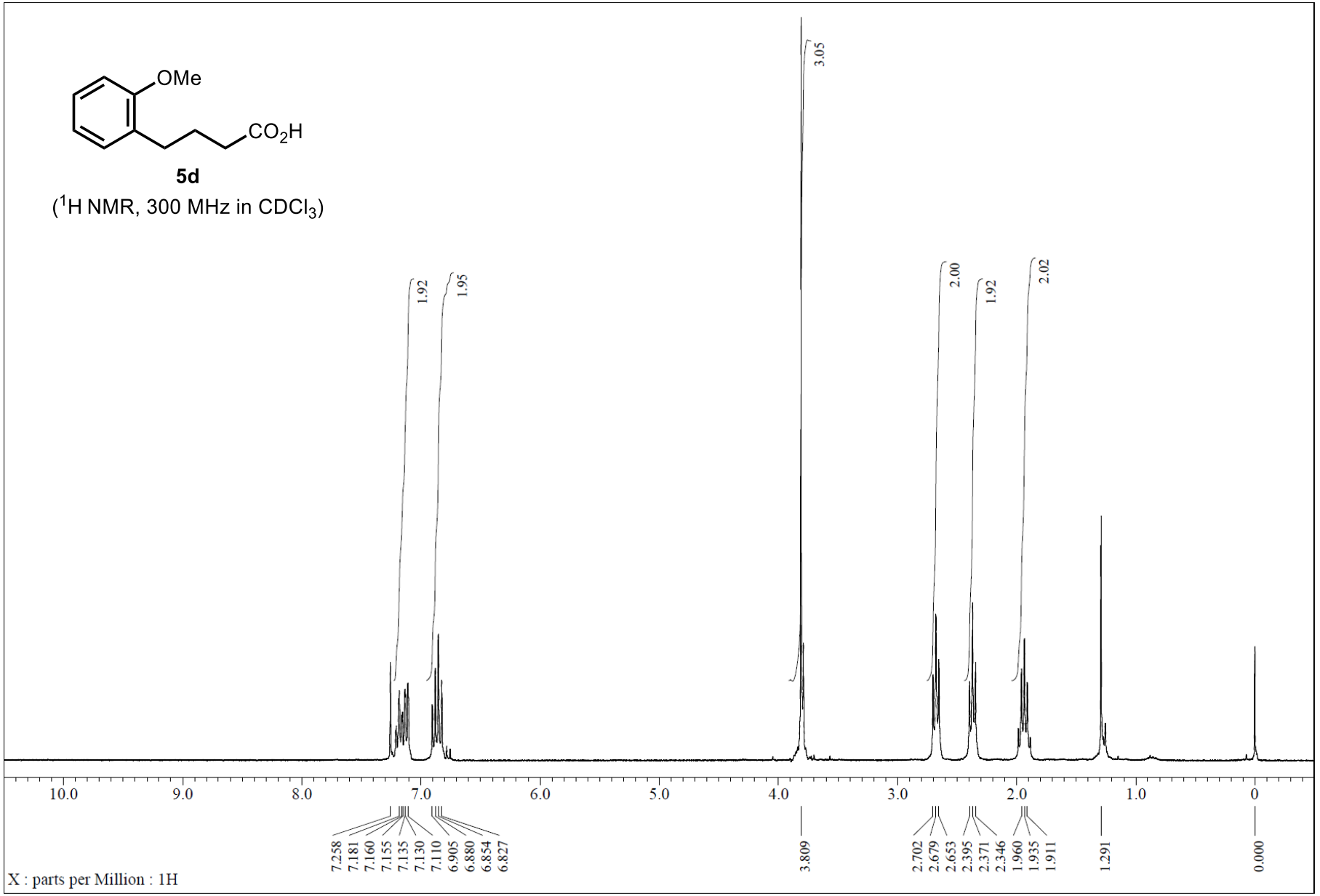

MeO
CO2H
5a
(13C NMR, 75 MHz in CDCl3)
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
179.801
157.894
133.217
129.362
113.810
77.419
77.000
76.573
55.233
34.050
33.220
26.413
X : parts per Million : 13C

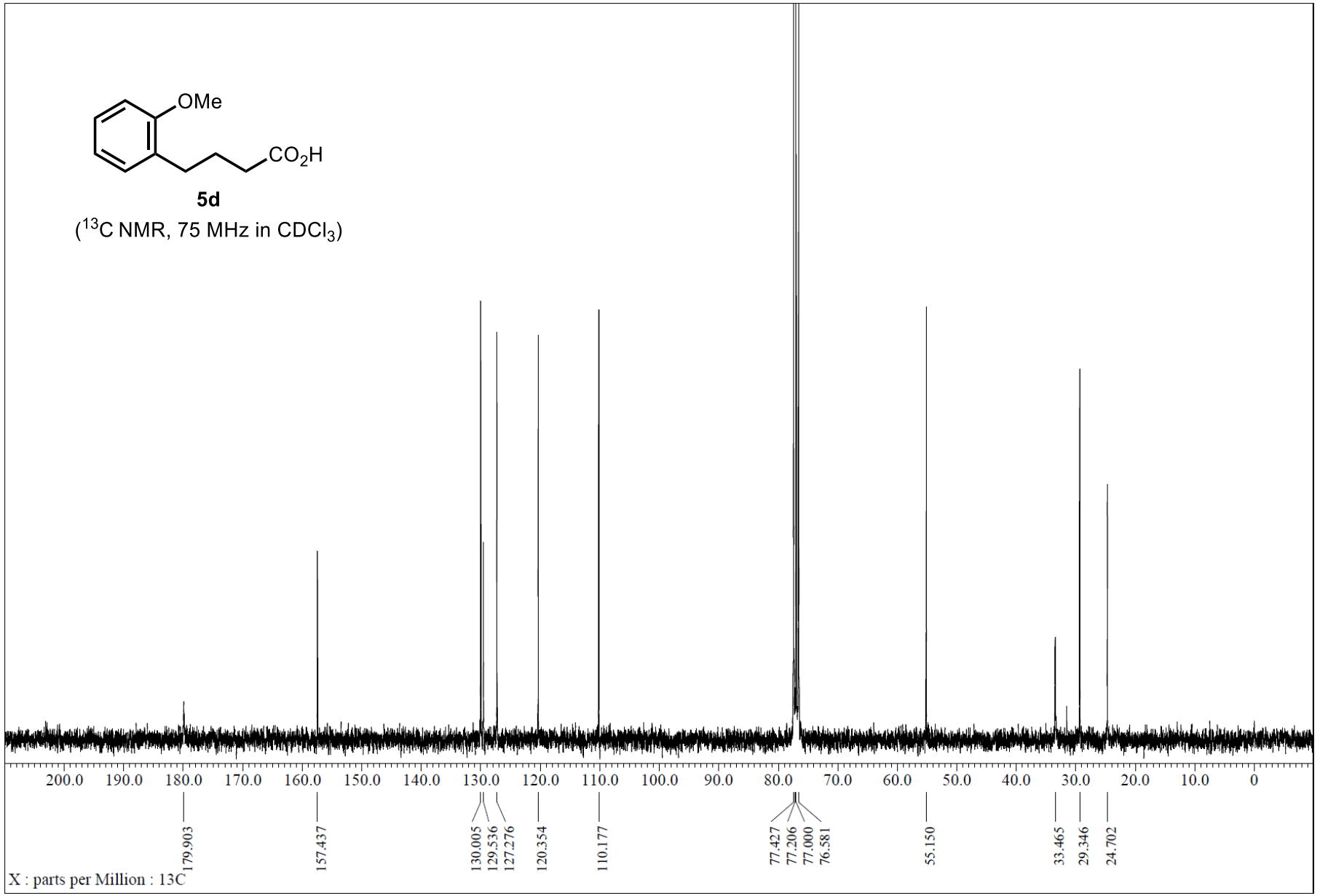

Cl
CO2H
5b
(1H NMR, 300 MHz in CDCl3)
2.19
1.97
2.03
2.05
2.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.266
7.259
7.245
7.239
7.230
7.125
7.098
2.671
2.646
2.620
2.392
2.368
2.344
1.991
1.966
1.941
1.916
1.253
0.000
X : parts per Million : 1H

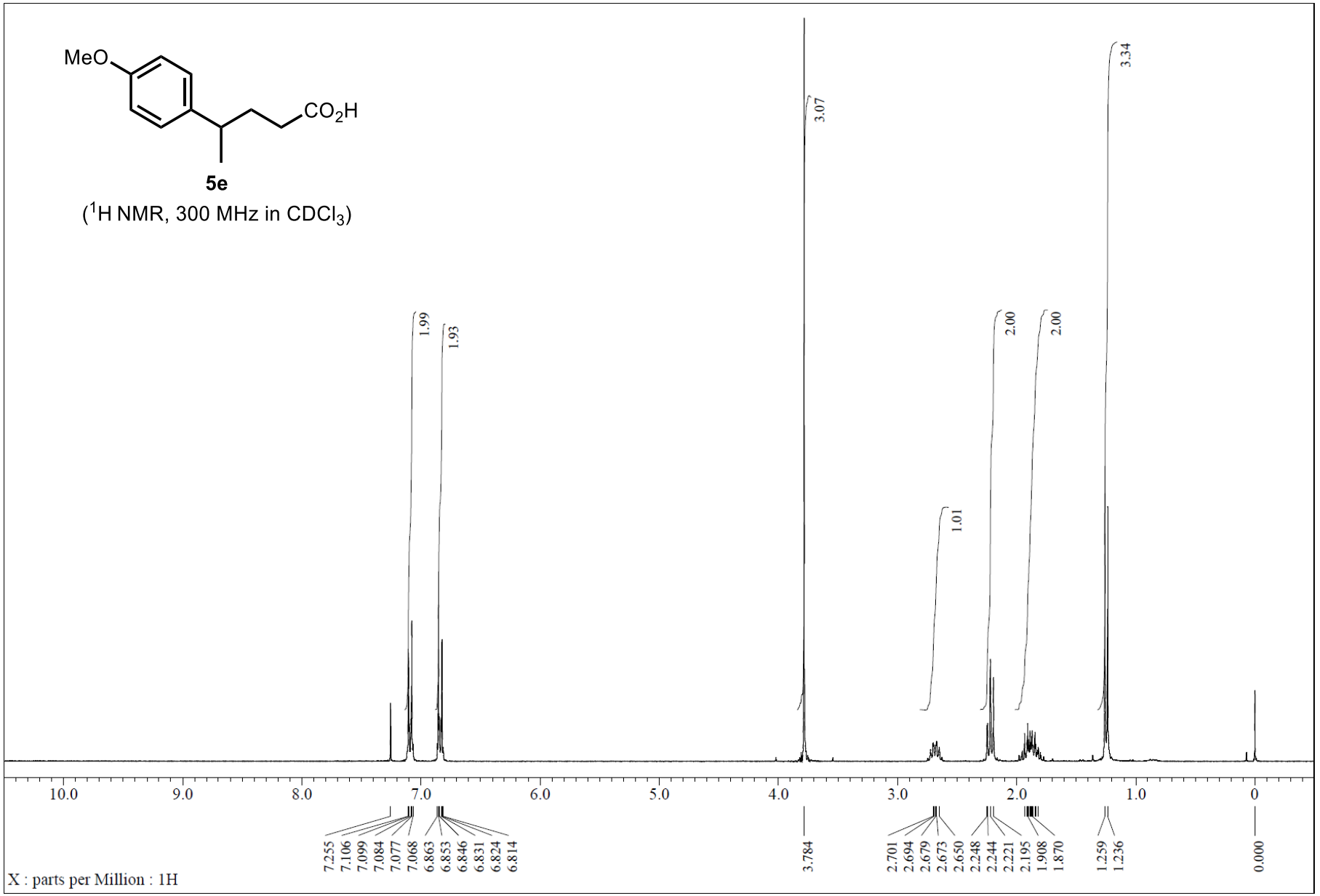

179.3425
139.5713
131.8072
129.7995
128.5091
34.2879
33.1110
26.0617
Cl
CO2H
5b
(13C NMR, 200 MHz in CDCl3)
200
150
100
50
0
[ppm]

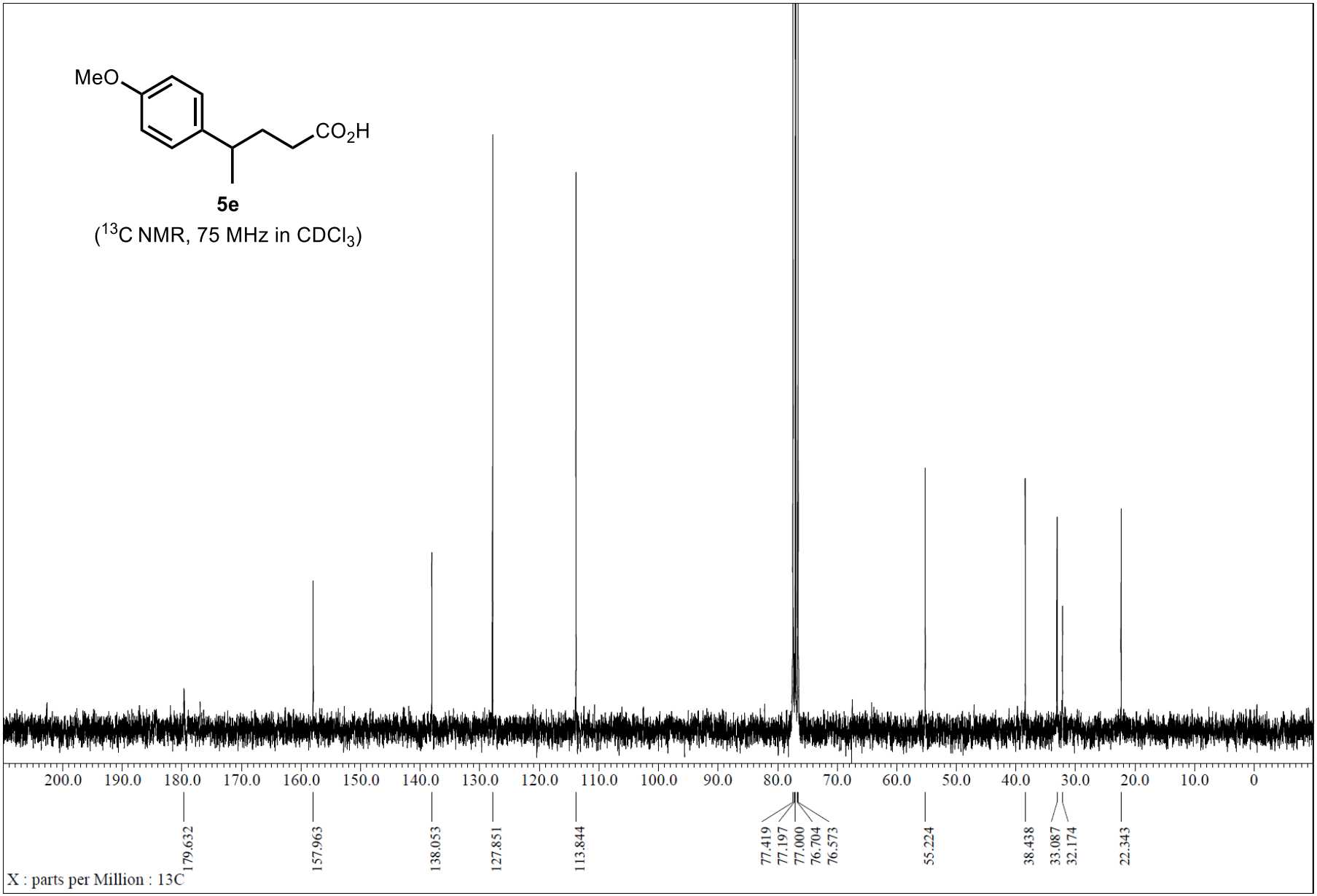

OMe
CO2H
5c
(1H NMR, 300 MHz in CDCl3)
3.07
3.05
2.00
2.09
2.00
1.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.260
7.233
7.208
7.204
7.183
7.179
6.790
6.766
6.758
6.735
3.799
2.682
2.657
2.632
2.405
2.380
2.356
1.995
1.970
1.945
0.000
X : parts per Million : 1H

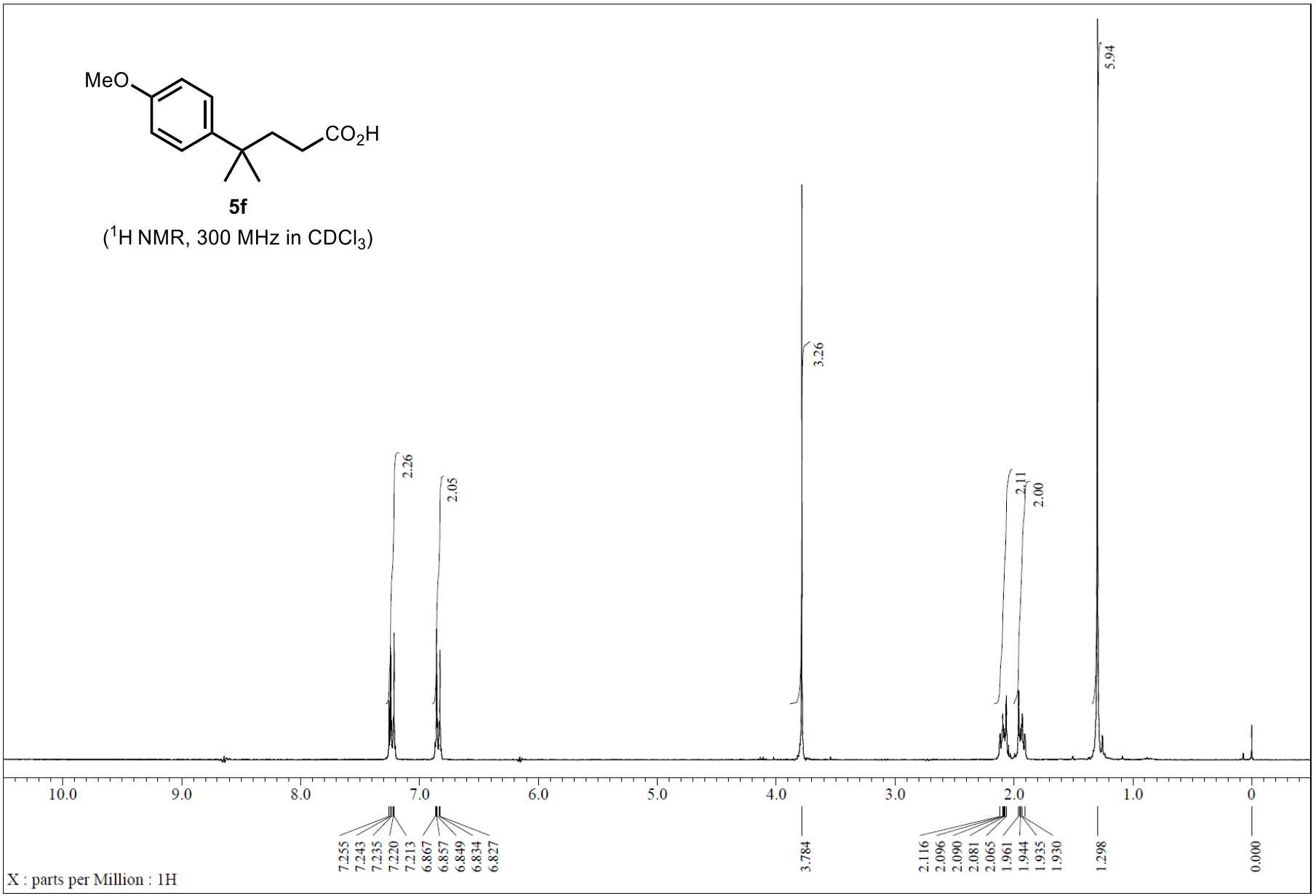

OMe
CO2H
5c
(13C NMR, 75 MHz in CDCl3)
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
179.656
159.631
142.788
129.372
120.872
114.205
111.312
77.419
77.197
77.000
76.573
55.117
34.977
33.226
26.050
X : parts per Million : 13C

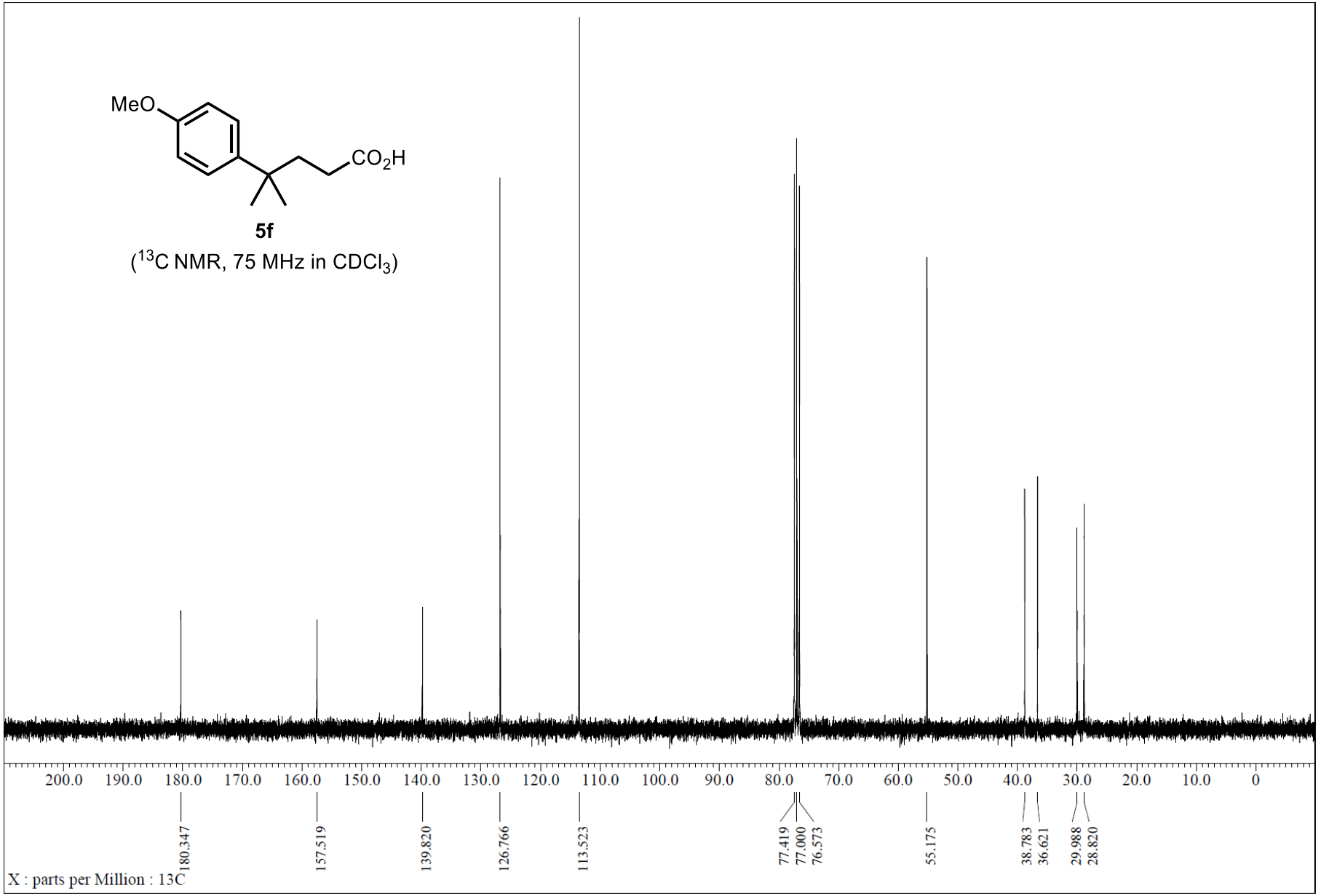

OMe
CO2H
5d
(1H NMR, 300 MHz in CDCl3)
3.05
1.92
1.95
2.00
1.92
2.02
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.258
7.181
7.160
7.155
7.135
7.130
7.110
6.905
6.880
6.854
6.827
3.809
2.702
2.679
2.653
2.395
2.371
2.346
1.960
1.935
1.911
1.291
0.000
X : parts per Million : 1H

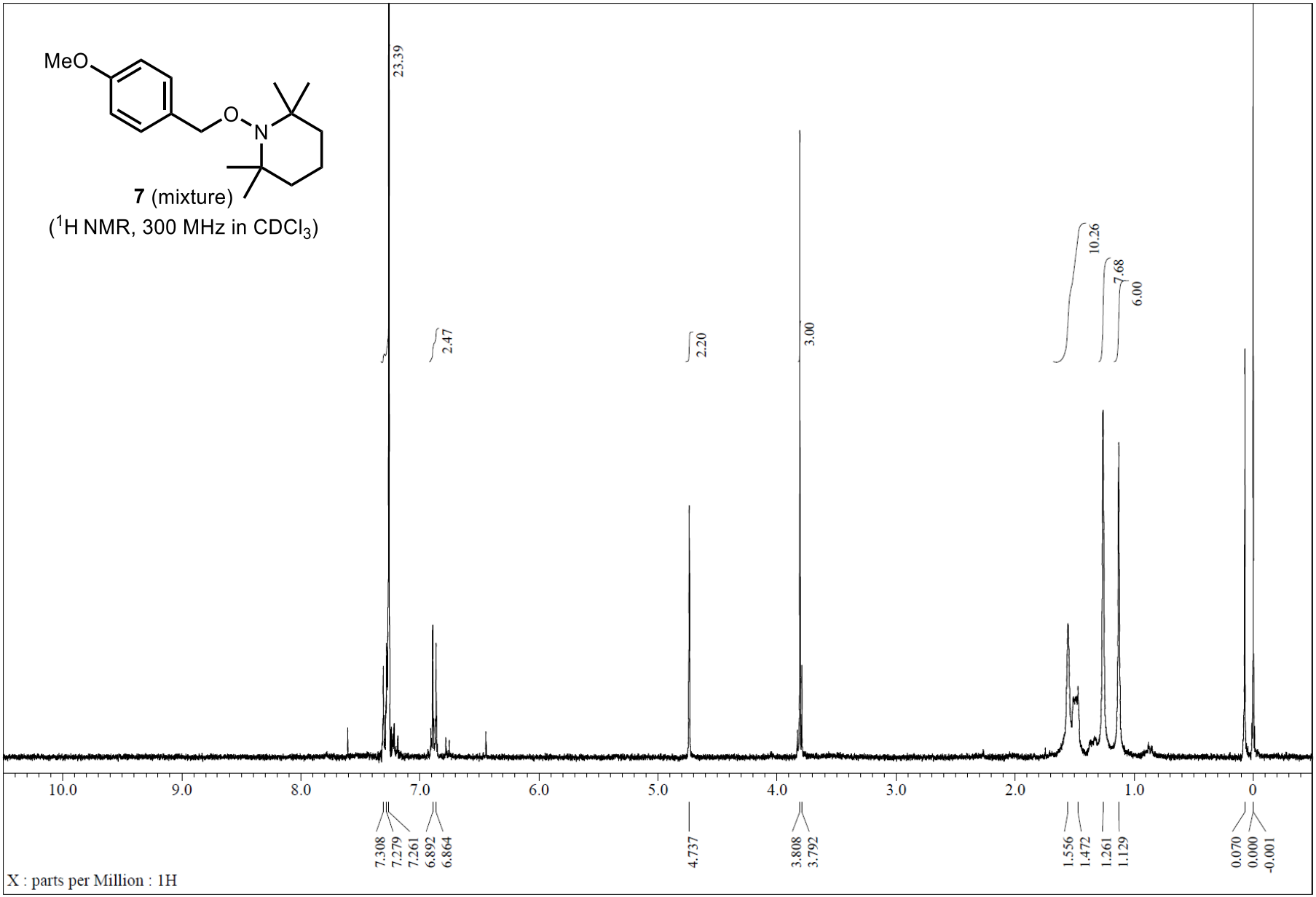

OMe
CO2H
5d
(13C NMR, 75 MHz in CDCl3)
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
179.903
157.437
130.005
129.536
127.276
120.354
110.177
77.427
77.206
77.000
76.581
55.150
33.465
29.346
24.702
X : parts per Million : 13C


MeO
CO2H
5e
(1H NMR, 300 MHz in CDCl3)
3.34
3.07
2.00
2.00
1.99
1.93
1.01
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.255
7.106
7.099
7.084
7.077
7.068
6.863
6.853
6.846
6.831
6.824
6.814
3.784
2.701
2.694
2.679
2.673
2.650
2.248
2.244
2.221
2.195
1.908
1.870
1.259
1.236
0.000
X : parts per Million : 1H


MeO
CO2H
5e
(13C NMR, 75 MHz in CDCl3)
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
179.632
157.963
138.053
127.851
113.844
77.419
77.197
77.000
76.704
76.573
55.224
38.438
33.087
32.174
22.343
X : parts per Million : 13C


MeO
CO2H
5f
(1H NMR, 300 MHz in CDCl3)
5.94
3.26
2.26
2.05
2.11
2.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.255
7.243
7.235
7.220
7.213
6.867
6.857
6.849
6.834
6.827
3.784
2.116
2.096
2.090
2.081
2.065
1.961
1.944
1.935
1.930
1.298
0.000
X : parts per Million : 1H


MeO
CO2H
5f
(13C NMR, 75 MHz in CDCl3)
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
180.347
157.519
139.820
126.766
113.523
77.419
77.000
76.573
55.175
38.783
36.621
29.988
28.820
X : parts per Million : 13C


MeO
O
N
7 (mixture)
(1H NMR, 300 MHz in CDCl3)
23.39
2.47
2.20
3.00
10.26
7.68
6.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.308
7.279
7.261
6.892
6.864
4.737
3.808
3.792
1.556
1.472
1.261
1.129
0.070
0.000
-0.001
X : parts per Million : 1H