Supporting Information

Visible-light-induced radical switching using benzothiazolyl sulfides for geminal carbon–carbon bond formation

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The following data are included in this material:

General Information:

All solvents and reagents were of reagent grade quality and used without further purification unless otherwise stated. Acetonitrile, *N*,*N*-dimethylformamide (DMF), dichloromethane (DCM), 1,2-dichloroethane (DCE) and toluene were dried over MS 4 Å under a nitrogen atmosphere. Methanol was dried over MS 3 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 with the light irradiation device (for details, see the next page). 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 (CHROMATOREXPSQ 100B) from Fuji Silysia Chemical LTD. and eluting with the indicated solvent system. All new compounds were characterized by NMR, IR, and HRMS. The ^{1}H NMR spectra operating at the frequency of 400 MHz on a Bruker AVANCE III HD400 spectrometer, respectively, were recorded in chloroform-*d* ($CDCl_3$) unless otherwise noted. The ^{13}C NMR spectra operating at the frequencies of 101 MHz on a Bruker AVANCE III HD400 spectrometer were recorded in chloroform-*d* ($CDCl_3$) unless otherwise noted. Chemical shifts are reported in parts per million (ppm) relative to TMS and the solvent used as internal standards, and the coupling constants are reported in hertz (Hz). Fourier transform infrared (FTIR) spectra were recorded on a JASCO FT/IR-4100 spectrometer. Mass spectra were recorded on a Bruker micrOTOF system. UV-vis spectra were recorded on a JASCO V-630 spectrophotometer. Emission spectra were recorded on a JASCO FP6200 spectrophotometer. Melting points were measured with a Yanaco MP–S3 micro melting point apparatus. Redox potentials were measured by cyclic voltammetry on a Hokuto Denko HAB-151A.

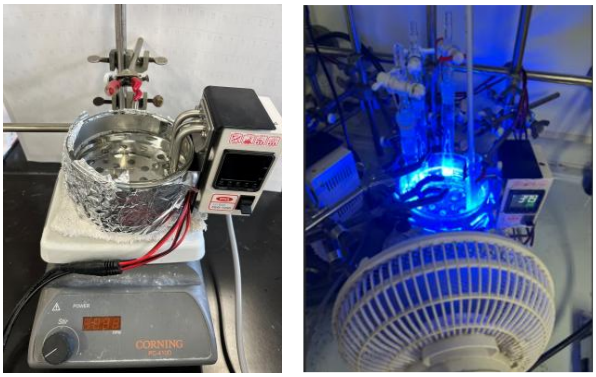
Reaction device for photochemical reactions:

The light irradiation setup for the α-C–H functionalization of alkyl benzothiazolyl sulfides was constructed by wrapping three 2.88 W blue LED strips around an oil bath. The LED strips were positioned 2 cm from the reaction tube. To regulate the temperature of the oil bath (35–40 °C), a fan was used to cool the setup, keeping the solution temperature within 32–36 °C.

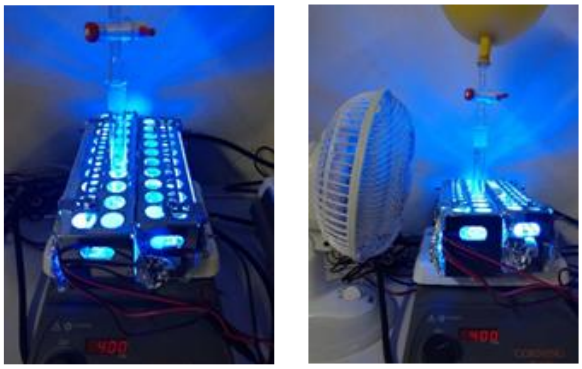
The light irradiation system for desulfurative coupling was adapted from the design reported by Murakami and Itami.[a] In this setup, three 2.88 W blue LED strips were placed 3 cm from the reaction tube. A fan was used to maintain a stable reaction temperature of approximately 35 °C.

Reactions on a 1.2 mmol scale were conducted in a 100 mL flask and irradiated using the same setup as for α-C–H functionalization. The reaction device was fan-cooled to ensure proper temperature control of the oil bath.

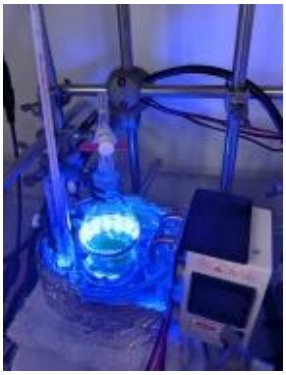
(a) reaction setup for the α-C–H functionalization



(b) reaction setup for the desulfurative coupling



(c) reaction setup for the 1.2 mmol scale reactions



(d) spectral irradiance of blue LEDs

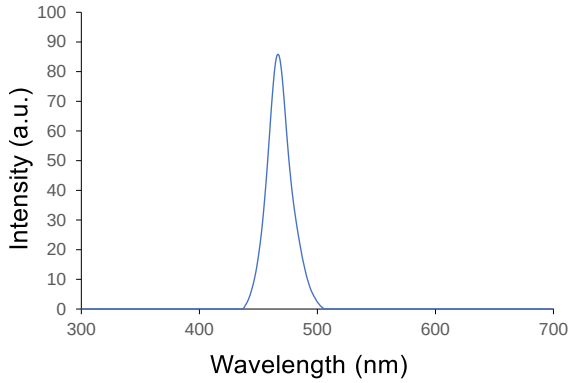
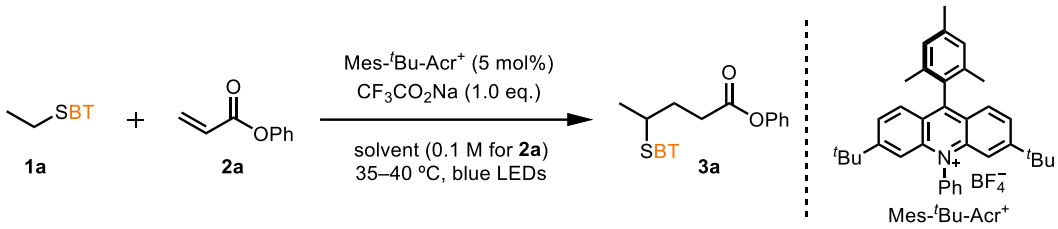


Figure S1. Reaction devices for photochemical reactions used in this study.

Optimization of reaction conditions for α-C–H functionalization:

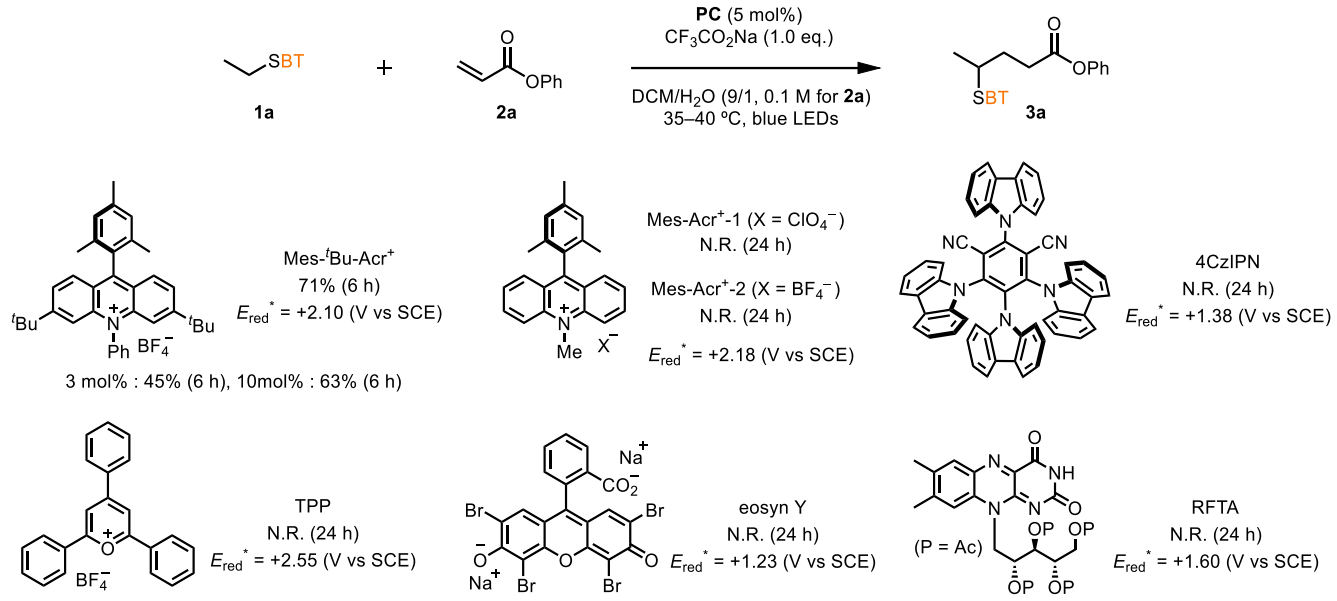
Table S1. Screening of solvents for α-C–H functionalization of **1a** with **2a**.[a]



entry	solvent	Time (h)	**3a** (%)
1	DCM/MeOH (9/1)	6	0[b]
2	DCM/^{i}PrOH (9/1)	6	11
3	DCM/^{t}BuOH (9/1)	6	33
4	DCM/H_2O (9/1)	6	71
5	DCM/H_2O (1/1)	6	45
6	DCM/H_2O (19/1)	6	24
7	DCM	24	47

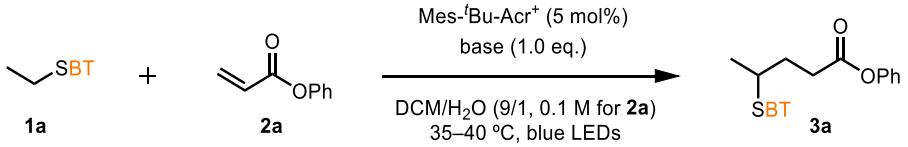
entry	solvent	Time (h)	**3a** (%)
1	DCE/H_2O (9/1)	24	33
2	$CHCl_3$/H_2O (9/1)	24	15
3	PhMe/H_2O (9/1)	24	0[c]
4	MeCN/H_2O (9/1)	24	0[c]
5	1,4-dioxane/H_2O (9/1)	24	0[b]
6[d]	THF/H_2O (9/1)	24	0[b]
7	DMF/H_2O (9/1)	24	0[b]

[a]The reactions were performed with **1a** (0.300 mmol), **2a** (0.100 mmol), Mes-^{t}Bu-Acr^{+} (5 mol%) and CF_3CO_2Na (0.100 mmol) in solvents (1.0 mL) under blue light irradiation. [b]Complete consumption of sulfide **1a** was observed on TLC analysis. [c]No reaction. BT: 2-benzothiazolyl, DCM: dichloromethane, DCE: 1,2-dichloroethane, DMF: *N*,*N*-dimethylformamide.



Scheme S1. Screening of photoredox catalysts for α-C–H functionalization of **1a** with **2a**. The reactions were performed with **1a** (0.300 mmol), **2a** (0.100 mmol), Mes-^{t}Bu-Acr$^+$ (5 mol%) and CF_3CO_2Na (0.100 mmol) in DCM/H_2O (9/1, 1.0 mL) under blue light irradiation. The excitation reduction potentials were taken from references.[b–g]

Table S2. Screening of base additives for α-C–H functionalization of **1a** with **2a**.[a]



entry	solvent	Time (h)	**3a** (%)	entry	solvent	Time (h)	**3a** (%)
1	none	24	27	1	K_3PO_4	24	trace
2	CF_3CO_2Na	6	71	2	tetramethylurea	24	trace
3	NaOBz	24	<4	3	aniline	24	trace
4	NaOAc	24	trace	4	pyridine	24	trace
5	$NaHCO_3$	24	trace	5	tetramethylguanidine	24	trace
6	K_2HPO_4	24	trace	6[d]	TFA	24	<3
7	$NaCO_3$	24	trace	7	TFA・tBuNH$_2$ salt	6	33

[a]The reactions were performed with **1a** (0.300 mmol), **2a** (0.100 mmol), Mes-^{t}Bu-Acr$^+$ (5 mol%) and base (0.100 mmol) in DCM/H_2O (9/1, 1.0 mL) under blue light irradiation. Bz: benzoyl, Ac: acetyl, TFA: trifluoroacetic acid.

List of sulfides and radical acceptors:

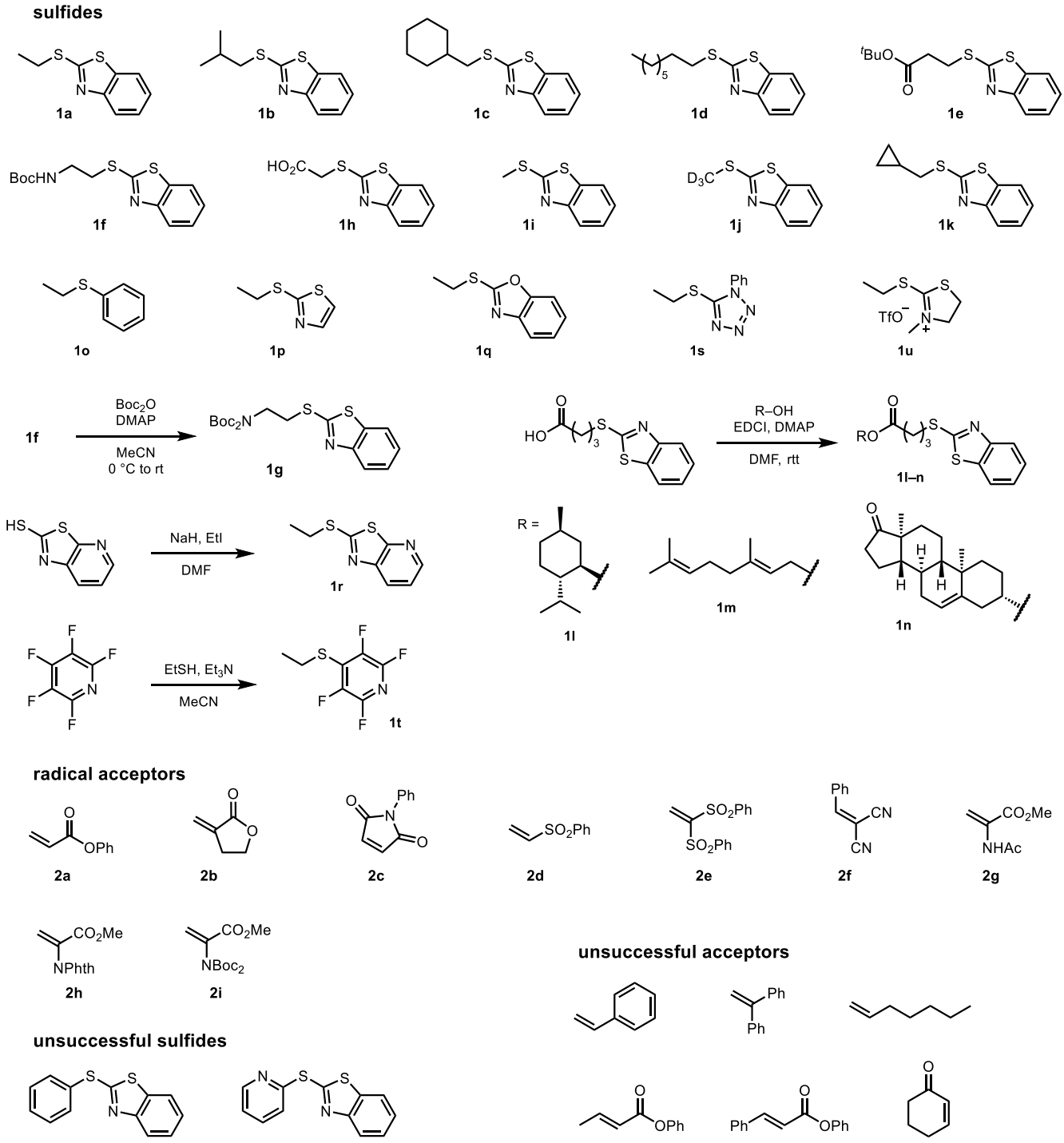
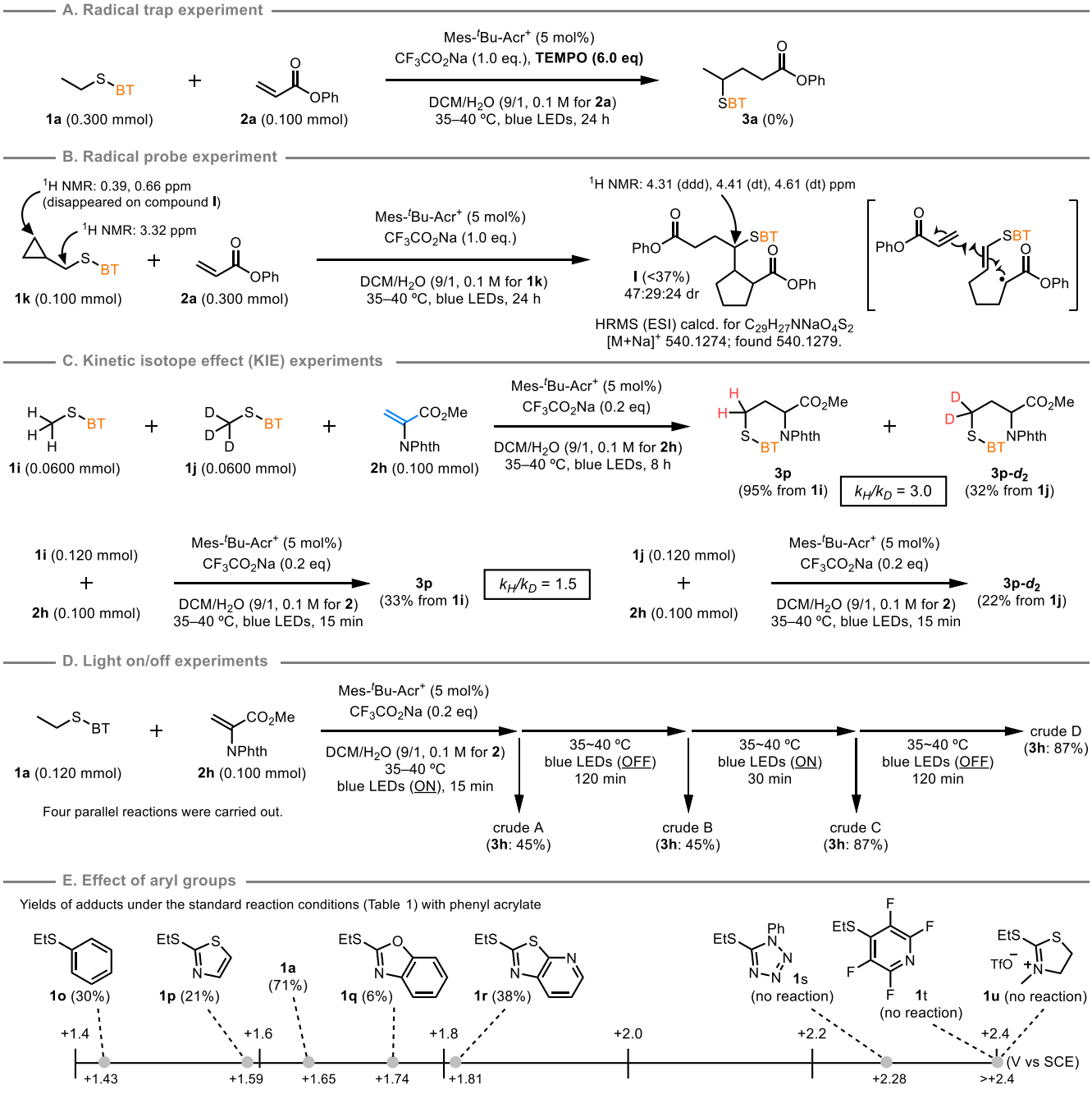


Figure S2. Structures of sulfides and radical acceptors used in this study.

Compound **1o** is commercially available. Compounds **1g,l–n,r,t** were synthesized according to the above scheme. The other sulfones are known compounds (**1a**[h], **1b**[i], **1c**[j], **1d**[k], **1e**[l], **1f**[m], **1h**[n], **1i**[o], **1j**[p], **1k**[q], **1p**[r], **1q**[s], **1s**[t], **1u**[u]). Radical acceptors **2d,e,g,h,i** are known compounds (**2d**[v], **2e**[w], **2g**[x], **2h**[y], **2i**[y]), and **2a,b,c,f** are commercially available.

Mechanistic investigations:



Scheme S2. Mechanistic investigations through (A) the radical trap experiment, (B) the radical probe experiment and (C) the KIE experiments, (D) the light on/off experiments (for details, see the next page) and (E) the effect of aryl groups (for details of the potentials, see page S11).

Light on-off experiments:

The reactions were conducted in parallel using four test tubes (A–D). All reagents [**1a**, **2h**, sodium trifluoroacetate, Mes-^{t}Bu-Acr$^+$, and CH_2Cl_2/H_2O (9/1)] were added to each test tube, and after degassing by three freeze-pump-thaw cycles, the mixtures were irradiated with blue light. After stirring for 15 minutes, the reaction mixture in test tube A was roughly purified by silica gel column chromatography (hexane/EtOAc = 40/1 to 10/1 to 5/1) to give crude A. The remaining three test tubes were wrapped in aluminum foil to shield them from light and stirred for an additional 120 minutes. The reaction mixture in test tube B was then roughly purified by silica gel column chromatography (hexane/EtOAc = 40/1 to 10/1 to 5/1) to give crude B. The reaction mixtures in the remaining two test tubes were re-exposed to blue light and stirred for 30 minutes. The reaction mixture in test tube C was then roughly purified by silica gel column chromatography (hexane/EtOAc = 40/1 to 10/1 to 5/1) to give crude C. In contrast, the reaction mixture in test tube D was stirred in the dark for a further 120 minutes before being roughly purified by silica gel column chromatography (hexane/EtOAc = 40/1 to 10/1 to 5/1) to give crude D. The yields of **3h** in each sample were calculated from their ^{1}H NMR spectra.

Table S3. Reagent amounts added in test tubes A–D.

test tube	**1a**	**2h**	CF_3COONa	Mes-^{t}Bu-Acr$^+$	CH_2Cl_2/H_2O	crude	**3h**
A	23.4 mg (0.120 mmol)	23.1 mg (0.100 mmol)	2.9 mg (0.020 mmol)	2.9 mg (5 mol%)	9/1	31.4 mg	45%[a]
B	23.4 mg (0.120 mmol)	23.1 mg (0.100 mmol)	2.9 mg (0.020 mmol)	2.9 mg (5 mol%)	9/1	32.2 mg	45%[a]
C	23.4 mg (0.120 mmol)	22.3 mg (0.0964 mmol)	2.9 mg (0.020 mmol)	2.9 mg (5 mol%)	9/1	39.9 mg	87%[a]
D	23.4 mg (0.120 mmol)	23.8 mg (0.103 mmol)	2.9 mg (0.020 mmol)	2.9 mg (5 mol%)	9/1	41.8 mg	87%[a]

[a]NMR yield.

UV–Vis absorption spectra:

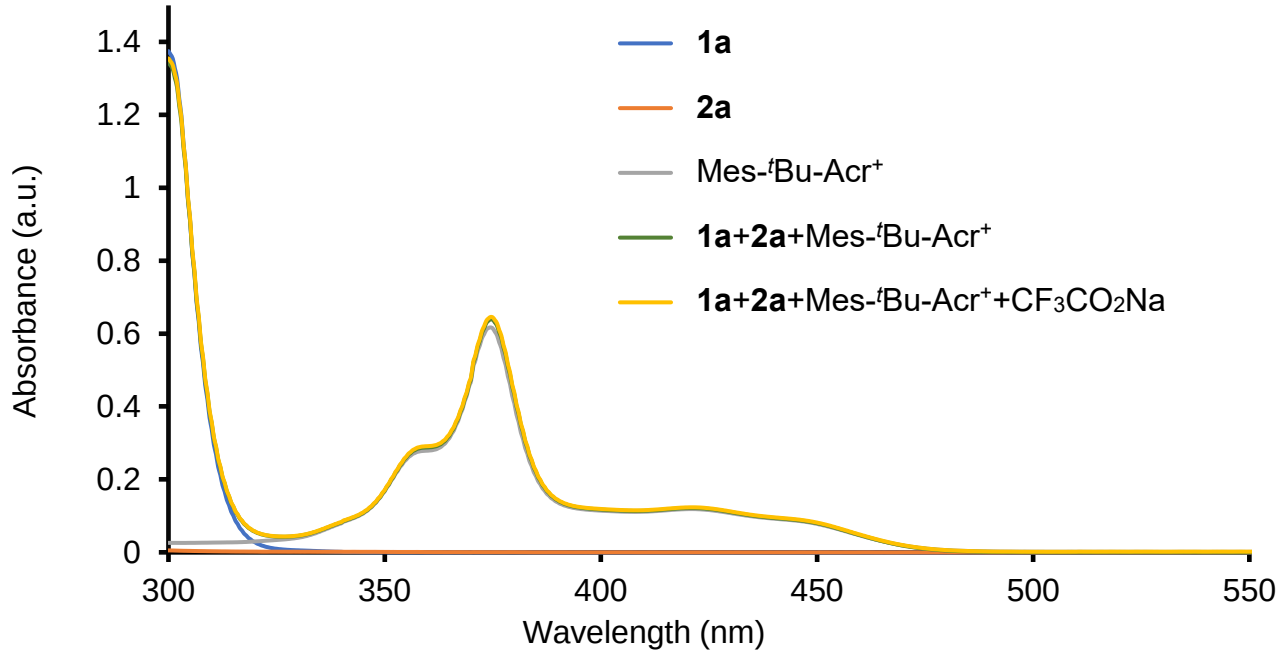


Figure S3. UV-vis absorption spectra of **1a** (blue line, 1.2×10^{-4} M in CH_2Cl_2), **2a** (orange line, 1.0×10^{-4} M in CH_2Cl_2), Mes-^{t}Bu-Acr$^+$ (gray line, 5.0×10^{-6} M in CH_2Cl_2), a 1.2:1:0.05 mixture of **1a**, **2a**, and Mes-^{t}Bu-Acr$^+$ (green line, 1.0×10^{-4} M in CH_2Cl_2), and a 1.2:1:0.05:20 mixture of **1a**, **2a**, Mes-^{t}Bu-Acr$^+$ and CF_3CO_2Na (yellow line, 1.0×10^{-4} M in CH_2Cl_2).

Emission studies:

The emission spectra were recorded on a JASCO FP6200 spectrophotometer. The excitation wavelength was fixed at 460 nm.

For emission spectra of Mes-^{t}Bu-Acr$^+$ in the presence of the quencher (**1a** or **2a**) excited at 460 nm, the samples were prepared by mixing a solution of the quencher (0.005, 0.01, 0.02, 0.04, 0.05 mmol) in 2.5 mL of CH_2Cl_2 with 2.5 mL of 0.0002 M stock solution of Mes-^{t}Bu-Acr$^+$. Then, the solution was placed in a quartz cuvette for spectral measurements.

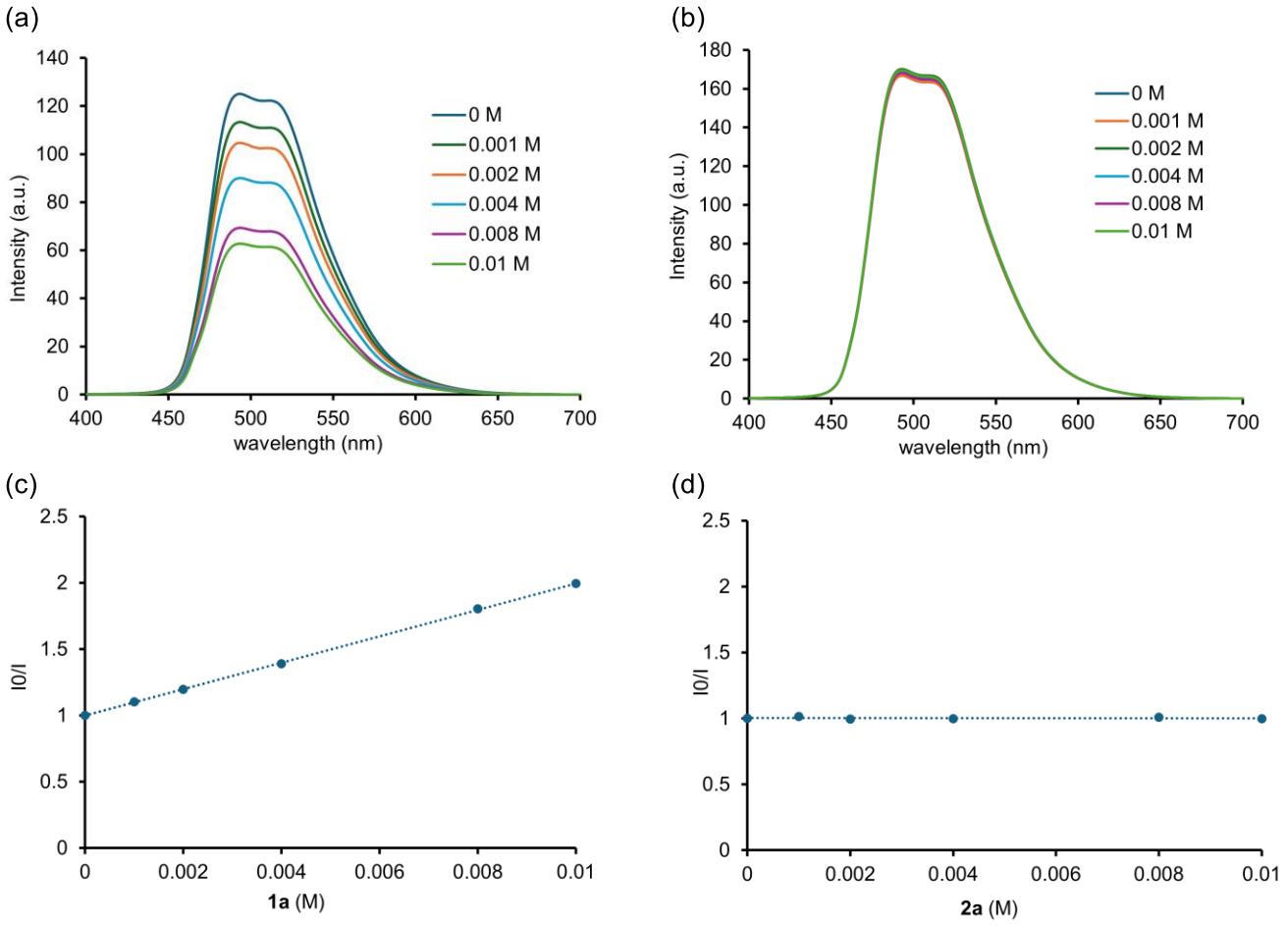


Figure S4. (a) Emission spectra of Mes-^{t}Bu-Acr$^+$ in the presence of increasing **1a** concentrations (0.001–0.01 M) excited at 460 nm. (b) Emission spectra of Mes-^{t}Bu-Acr$^+$ in the presence of increasing **2a** concentrations (0.001–0.01 M) excited at 460 nm. (c) Stern-Volmer plot of I_0/I versus **1a** concentration in Mes-^{t}Bu-Acr$^+$-CH_2Cl_2 solution (I_0 and I represent the intensities of the emission in the absence and presence of the quencher). (d) Stern-Volmer plot of I_0/I versus **2a** concentration in Mes-^{t}Bu-Acr$^+$-CH_2Cl_2 solution.

Cyclic voltammetry:

Cyclic voltammetry was performed with Hokuto Denko HAB-151A. A glassy carbon working electrode (Φ = 3 mm), a platinum wire counter electrode and a reference electrode (Ag/AgCl) were used. The working electrode was polished by a commercially available polishing pad and alumina (Al_2O_3) before data collection. The experiments were conducted by using **1a** (10 mM) in acetonitrile with *n*-Bu_4NPF_6 (0.1 M) as a supporting electrolyte under an argon atmosphere at room temperature. The solution of interest was sparged with argon for 5 minutes. These experiments were carried out at a scan rate of 0.05 V/s starting from 0 V. Ferrocene/ferrocenium ion redox couple was used as an external reference. Reduction potentials were measured vs Fc/Fc^+ and converted to V vs SCE using $E^0_{1/2}$ (Fc/Fc^+) = +0.38 V vs SCE.[z]

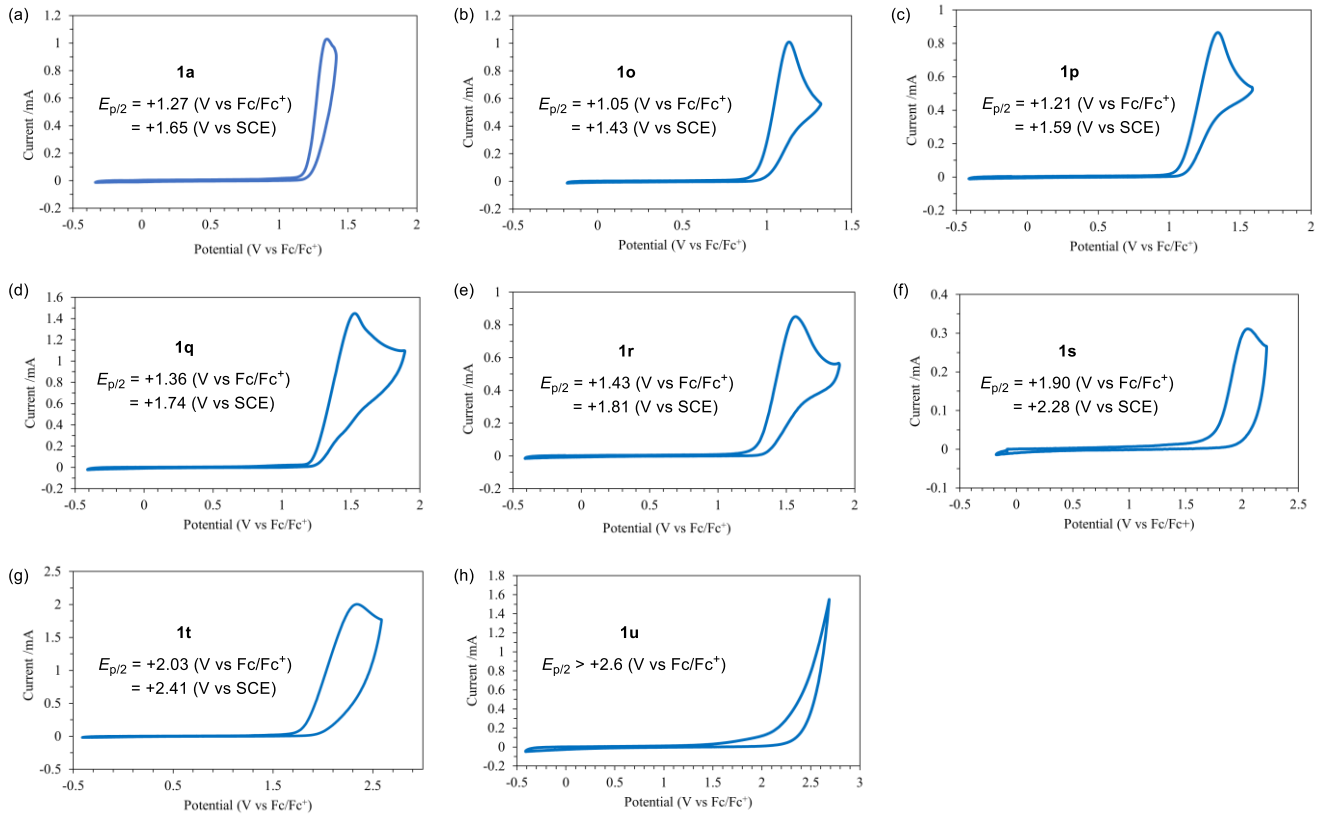
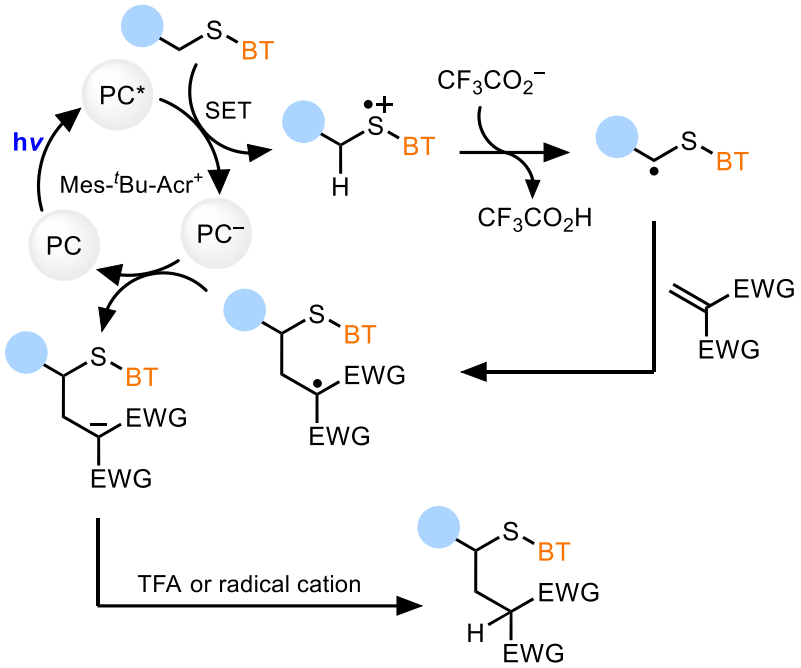


Figure S5. Cyclic voltammograms of **1a**, (b) **1o**, (c) **1p**, (d) **1q**, (e) **1r**, (f) **1s**, (g) **1t**, and (h) **1u** in acetonitrile with a 0.1 M *n*-Bu_4NPF_6 as a supporting electrolyte. Working electrode: glassy carbon; Counter electrode: Pt wire; Reference electrode: $Ag/AgNO_3$; Scan rate: 0.05 V/s. Ferrocene/ferrocenium ion redox couple was used as an external reference.

Reaction mechanism:



Scheme S3. Proposed reaction mechanism for α-C–H functionalization of alkyl benzothiazolyl sulfides

Experimental procedures and characterization data:

Synthesis and characterization of di-*tert*-butyl (2-(benzo[*d*]thiazol-2-ylthio)ethyl)iminodicarbonate (1g)

To a solution of *tert*-butyl (2-(benzo[*d*]thiazol-2-ylthio)ethyl)carbamate (**1f**, 219 mg, 0.705 mmol) in acetonitrile (1.2 mL) were added di-*tert*-butyl dicarbonate (0.26 mL, 1.09 mmol) and 4-dimethylaminopyridine (9.0 mg, 0.07 mmol) under a nitrogen atmosphere. The resulting solution was stirred for 20 h at room temperature. The reaction was then quenched by addition of water (10 mL), and the resulting mixture was extracted with EtOAc (10 mL). The combined organic extracts were 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 = 20/1 to 10/1 to 5/1) to give **1g** (281 mg, 97%) as a colorless oil: R_f = 0.40 (hexane/EtOAc = 3/1); IR (NaCl) 2979, 2930, 1789, 1748, 1698, 1459 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 (m, 1H), 7.75 (m, 1H), 7.40 (m, 1H), 7.29 (m, 1H), 4.07 (t, *J* = 6.8 Hz, 2H), 3.56 (t, *J* = 6.8 Hz, 2H), 1.49 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 153.3, 152.2, 135.3, 126.0, 124.2, 121.6, 121.0, 82.7, 45.5, 32.2, 28.1, 27.9, 27.4. HRMS (ESI) calcd. for $C_{19}H_{26}N_2NaO_4S_2$ $[M+Na]^+$ 433.1226; found 433.1218.

Synthesis and characterization of (1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 4-(benzo[*d*]thiazol-2-ylthio)butanoate (1l)

To a solution of thiazolo[5,4-*b*]pyridine-2-thiol (250 mg, 1.00 mmol) in *N*,*N*-dimethylformamide (1.25 mL) were added 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (293 mg, 1.53 mmol), L-menthol (160 mg, 1.00 mmol), and 4-dimethylaminopyridine (26.2 mg, 0.210 mmol) at 0 ºC under a nitrogen atmosphere. The resulting solution was warmed to room temperature and stirred for 17 h. The reaction was then quenched by addition of saturated aqueous $NaHCO_3$ (20 mL), and the resulting mixture was extracted with EtOAc (20 mL). The organic extract was washed with 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, $CHCl_3$/MeOH = 100/1) to give **1l** (364 mg, 93%) as a colorless oil: R_f = 0.50 (hexane/EtOAc = 5/1); $[\alpha]^{26}_D$ -32.9 (*c* 0.97, $CHCl_3$); IR (NaCl) 2959, 2928, 2871, 1720, 1458, 1428 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.86 (m, 1H), 7.75 (m, 1H), 7.40 (m, 1H), 7.29 (m, 1H), 4.70 (dt, *J* = 4.4, 10.9 Hz, 1H), 3.41 (t, *J* = 6.9 Hz, 2H), 2.50 (t, *J* = 7.3 Hz, 2H), 2.17 (quint. *J* = 7.1 Hz, 2H), 1.98 (m, 1H), 1.84 (m, 1H), 1.71–1.63 (m, 2H), 1.48 (m, 1H), 1.36 (m, 1H), 1.10–0.84 (m, 3H), 0.89 (d, *J* = 6.3 Hz, 3H), 0.88 (d, *J* = 6.9 Hz, 3H), 0.75 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.2, 166.5, 153.2, 135.2, 126.0, 124.2, 121.5, 120.9, 74.4, 46.9, 40.9, 34.2, 33.2, 32.7, 31.3, 26.3, 24.7, 23.4, 22.0, 20.7, 16.3. HRMS (ESI) calcd. for $C_{21}H_{30}NO_2S_2$ $[M+H]^+$ 392.1712; found 392.1707.

Synthesis and characterization of (*E*)-3,7-dimethylocta-2,6-dien-1-yl 4-(benzo[*d*]thiazol-2-ylthio)butanoate (1m)

To a solution of thiazolo[5,4-*b*]pyridine-2-thiol (197 mg, 0.778 mmol) in *N*,*N*-dimethylformamide (1.0 mL) were added 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (228 mg, 1.19 mmol), geraniol (126 mg, 0.817 mmol), and 4-dimethylaminopyridine (21.5 mg, 0.175 mmol) at 0 ºC under a nitrogen atmosphere. The resulting solution was warmed to room temperature and stirred for 2 h. The reaction was then quenched by addition of saturated aqueous $NaHCO_3$ (20 mL), and the resulting mixture was extracted with EtOAc (20 mL). The organic extract was washed with 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, $CHCl_3$/MeOH = 100/1) to give **1m** (161 mg, 63%) as a colorless oil: R_f = 0.50 ($CHCl_3$/MeOH = 100/1); IR (NaCl) 2979, 2928, 2857, 1726, 1458, 1428 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.0 Hz, 1H), 7.74 (d, *J* = 7.5 Hz, 1H), 7.38 (m, 1H), 7.28 (m, 1H), 5.33 (m, 1H), 5.07 (m, 1H), 4.61 (d, *J* = 7.1 Hz, 2H), 3.41 (t, *J* = 7.1 Hz, 2H), 2.52 (t, *J* = 7.3 Hz, 2H), 2.21–2.01 (m, 6H), 1.70 (s, 3H), 1.68 (s, 3H), 1.59 (S, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.7, 166.4, 153.2,

142.3, 135.2, 131.8, 125.9, 124.2, 123.7, 121.5, 120.9, 118.1, 61.4, 39.5, 32.8, 32.6, 26.2, 25.6, 24.6, 17.6, 16.4. HRMS (ESI) calcd. for $C_{21}H_{27}NNaO_2S_2$ $[M+Na]^+$ 412.1375; found 412.1375.

Synthesis and characterization of (3*S*,8*R*,9*S*,10*R*,13*S*,14*S*)-10,13-dimethyl-17-oxo-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl 4-(benzo[*d*]thiazol-2-ylthio)butanoate (1n)

To a solution of thiazolo[5,4-*b*]pyridine-2-thiol (250 mg, 1.00 mmol) in *N*,*N*-dimethylformamide (1.25 mL) were added 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (293 mg, 1.53 mmol), dehydroepiandrosterone (291 mg, 1.00 mmol), and 4-dimethylaminopyridine (26.2 mg, 0.210 mmol) at 0 ºC under a nitrogen atmosphere. The resulting solution was warmed to room temperature and stirred for 17 h. The reaction was then quenched by addition of saturated aqueous $NaHCO_3$ (20 mL), and the resulting mixture was extracted with EtOAc (20 mL). The organic extract was washed with 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, $CHCl_3$/MeOH = 100/1) to give **1n** (293 mg, 56%) as a white solid: R_f = 0.20 (hexane/EtOAc = 5/1); m.p. 158.1–159.6 ºC; $[\alpha]^{25}_D$ +19.1 (*c* 0.52, $CHCl_3$); IR (KBr) 2971, 2950, 2905, 2868, 1731, 1458, 1429 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.1 Hz, 1H), 7.75 (d, *J* = 7.6 Hz, 1H), 7.41 (m, 1H), 7.29 (m, 1H), 5.40 (d, *J* = 5.0 Hz, 1H), 4.63 (m, 1H), 3.42 (t, *J* = 7.1 Hz, 2H), 2.50 (t, *J* = 7.3 Hz, 2H), 2.46 (dd, *J* = 8.6, 19.3 Hz, 1H), 2.39–2.29 (m, 2H), 2.21–2.04 (m, 4H), 1.98–1.82 (m, 4H), 1.70–1.43 (m, 7H), 1.32–1.26 (m, 2H), 1.15 (m, 1H), 1.04 (s, 3H), 0.88 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 221.0, 172.0, 166.4, 153.2, 139.8, 135.2, 126.0, 124.2, 121.9, 121.5, 120.9, 73.9, 51.6, 50.1, 47.6, 38.0, 36.9, 36.7, 35.8, 33.1, 32.6, 31.4, 31.3, 30.7, 27.7, 24.7, 21.8, 20.3, 19.3, 13.5. HRMS (ESI) calcd. for $C_{30}H_{38}NO_3S_2$ $[M+H]^+$ 524.2288; found 524.2275.

Synthesis and characterization of 2-(ethylthio)thiazolo[5,4-*b*]pyridine (1r)

To a solution of thiazolo[5,4-*b*]pyridine-2-thiol (150 mg, 0.892 mmol) in *N*,*N*-dimethylformamide (4.5 mL) was added NaH (55%, 50.6 mg, 1.16 mmol) at 0 ºC under a nitrogen atmosphere. After stirring the solution for 2 min at the same temperature, iodoethane (0.14 mL, 1.78 mmol) was added. The resulting solution was warmed to room temperature and stirred for 23 h. The reaction was then quenched by addition of saturated aqueous NH_4Cl (20 mL), and the resulting mixture was extracted with EtOAc (20 mL). The organic extract was washed with 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 = 15/1 to 7/1) to give **1r** (159 mg, 91%) as a white solid: R_f = 0.50 (hexane/EtOAc = 3/1); m.p. 47.8–48.5 ºC; IR (NaCl) 3054, 2969, 2928, 2870, 1577, 1553, 1436 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, *J* = 4.6 Hz, 1H), 8.05 (dd, *J* = 8.2 Hz, 1H), 7.35 (dd, *J* = 4.7 Hz, 7.6 Hz, 1H), 3.38 (q, *J* = 7.1 Hz, 2H), 1.50 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.7, 158.7, 146.4, 145.5, 127.7, 121.0, 27.3, 14.4. HRMS (ESI) calcd. for $C_8H_9N_2S_2$ $[M+H]^+$ 197.0202; found 197.0196.

Synthesis and characterization of 4-(ethylthio)-2,3,5,6-tetrafluoropyridine (1t)

To a solution of ethanethiol (0.14 mL, 1.88 mmol) in acetonitrile (19 mL) were added triethylamine (0.40 mL, 2.82 mmol) and pentafluoropyridine (0.20 mL, 1.88 mmol) under a nitrogen atmosphere. The resulting solution was stirred for 1 h at room temperature. The reaction was then quenched by addition of saturated aqueous NH_4Cl (20 mL), and the resulting mixture was extracted with EtOAc (3×10 mL). The combined organic extracts were 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 = 20/1) to give **1t** (311 mg, 78%) as a colorless oil: R_f = 0.60 (hexane/CH_2Cl_2 = 10/1); ^1H NMR (400 MHz, $CDCl_3$) δ 3.22 (q, *J* = 7.4 Hz, 2H), 1.37 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.6 (ddd, *J* = 2.9, 14.0, 17.5 Hz), 142.2 (m), 139.6 (m), 131.4 (tt, *J* = 2.8, 17.3 Hz), 27.5 (t, *J* = 5.2 Hz), 15.0. NMR data were in accordance with the literature[aa].

General procedure for α-C–H functionalization of alkyl benzothiazolyl sulfide with electron deficient alkenes

All the experiments for α-C–H functionalization of alkyl benzothiazolyl sulfide with electron deficient alkenes were carried out as described in the following typical procedure. The synthesis of **3a** was exemplified as follows.

Synthesis and characterization of phenyl 4-(benzo[*d*]thiazol-2-ylthio)pentanoate (3a)

Benzothiazolyl ethyl sulfide (**1a**, 61.3 mg, 0.314 mmol), phenyl acrylate (**2a**, 17.8 mg, 0.118 mmol), sodium trifluoroacetate (13.6 mg, 0.100 mmol), and photocatalyst (Mes-^{t}Bu-Acr$^+$, 2.9 mg, 0.005 mmol) were dissolved in CH_2Cl_2/H_2O (9/1, 1.0 mL). The mixture was degassed by three freeze-pump-thaw cycles. Afterward, the mixture was stirred and irradiated with blue LEDs for 6 h. During the reaction, the temperature of the oil bath was controlled to be in the range of 35 °C to 40 °C. The reaction mixture was diluted with CH_2Cl_2 (15 mL), and the organic extract was washed with 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 = 50/1 to 40/1 to 30/1 to 10/1 to 5/1) to give **3a** (28.8 mg, 71%) as a pale yellow oil: R_f = 0.45 (hexane/EtOAc = 10/1); IR (NaCl) 3073, 3036, 3014, 2979, 2960, 2927, 2858, 1753, 1593 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 8.0 Hz, 1H), 7.75 (d, J = 8.0 Hz, 1H), 7.43–7.20 (m, 5H), 7.07 (d, J = 7.6 Hz, 2H), 4.17 (sext, J = 6.8 Hz, 1H), 2.81 (t, J = 7.6 Hz, 2H), 2.24 (m, 2H), 1.58 (d, J = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.5, 165.7, 153.3, 150.7, 135.4, 129.4, 126.1, 125.8, 124.4, 121.7, 121.5, 121.0, 43.6, 31.9, 31.8, 21.6. HRMS (ESI) calcd. for $C_{18}H_{17}NNaO_2S_2$ $[M+Na]^+$ 366.0593; found 366.0609.

Synthesis and characterization of 3-(2-(benzo[*d*]thiazol-2-ylthio)propyl)dihydrofuran-2(3*H*)-one

(3b)

According to the synthetic procedure for **3a**, **1a** (58.6 mg, 0.300 mmol), α-methylene-γ-butyrolactone (**2b**, 10.3 mg, 0.100 mmol), sodium trifluoroacetate (13.6 mg, 0.100 mmol), and Mes-^{t}Bu-Acr$^+$ (2.9 mg, 0.005 mmol) in CH_2Cl_2/H_2O (9/1, 1.0 mL) were stirred for 24 h. The crude product was purified by column chromatography (silica gel, hexane/EtOAc = 50/1 to 30/1 to 10/1 to 5/1 to 1/1) to give **3b** (22.9 mg, 78%, 50:50 d.r.) as a pale yellow oil: R_f = 0.50 (hexane/EtOAc = 2/1); IR (NaCl) 3060, 2966, 2921, 2866, 1766 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 8.0 Hz, 1H), 7.76 (d, J = 8.0 Hz, 1H), 7.42 (t, J = 8.0 Hz, 1H), 7.31 (t, J = 8.0 Hz, 1H), 4.37 (m, 1H), 4.17 (m, 1H), 2.83 (m, 1H), 2.55 (m, 1H), 2.42–2.44 (m, 1H), 2.19–1.80 (m, 2H), 1.60–1.55 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.9 (2C), 165.6, 165.4, 153.3, 153.2, 135.4, 135.3, 126.1 (2C), 124.5 (2C), 121.6 (2C), 121.0, 66.6 (2C), 42.6, 42.5, 37.8, 37.7 (2C), 29.4, 29.2, 22.6, 21.1. HRMS (ESI) calcd. for $C_{14}H_{15}NNaO_2S_2$ $[M+Na]^+$ 316.0436; found 316.0454.

Synthesis and characterization of 3-(1-(benzo[*d*]thiazol-2-ylthio)ethyl)-1-phenylpyrrolidine-2,5-dione (3c)

According to the synthetic procedure for **3a**, **1a** (58.6 mg, 0.300 mmol), *N*-phenylmaleimide (**2c**, 17.7 mg, 0.100 mmol), sodium trifluoroacetate (13.6 mg, 0.100 mmol), and Mes-^{t}Bu-Acr$^+$ (2.9 mg, 0.005 mmol) in CH_2Cl_2/H_2O (9/1, 1.0 mL) were stirred for 24 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 **3c** (12.9 mg, 35%) as a pale yellow oil: R_f = 0.25 (hexane/EtOAc = 5/1); IR (NaCl) 3060, 2987, 2925, 2852, 1778, 1709, 1599, 1501, 1455 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 8.0 Hz, 1H), 7.78 (d, J = 7.6 Hz, 1H), 7.50–7.38 (m, 4H), 7.35–7.26 (m, 3H), 4.80 (m, 1H), 3.86 (m, 1H), 3.01 (dd, J = 9.0, 18.7 Hz, 1H), 2.93 (dd, J = 5.6, 18.7 Hz, 1H), 1.56 (d, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.3, 175.0, 164.1, 153.1, 135.4, 131.7, 129.3, 128.8, 126.5, 126.3, 124.8, 122.0, 121.1, 44.5, 43.4, 31.2, 16.3. HRMS (ESI) calcd.

for $C_{19}H_{16}N_2NaO_2S_2$ $[M+Na]^+$ 391.0545; found 391.0557.

Synthesis and characterization of 2-((4-(phenylsulfonyl)butan-2-yl)thio)benzo[*d*]thiazole (3d)

According to the synthetic procedure for **3a**, **1a** (58.9 mg, 0.300 mmol), phenyl vinyl sulfone (**2d**, 14.2 mg, 0.100 mmol), sodium trifluoroacetate (13.6 mg, 0.100 mmol), and Mes-^{t}Bu-Acr$^+$ (2.9 mg, 0.005 mmol) in CH_2Cl_2/H_2O (9/1, 1.0 mL) were stirred for 24 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 **3d** (11.7 mg, 32%) as a pale yellow oil: R_f = 0.25 (hexane/EtOAc = 5/1); IR (NaCl) 3064, 2982, 1457, 1428 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91–7.26 (m, 9H), 4.08 (m, 1H), 3.34 (m, 2H), 2.22 (m, 2H), 1.49 (d, J = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.6, 153.1, 138.7, 135.3, 133.7, 129.2, 128.0, 126.0, 124.5, 121.7, 121.0, 53.7, 42.6, 29.5, 21.2. HRMS (ESI) calcd. for $C_{17}H_{17}NNaO_2S_3$ $[M+Na]^+$ 386.0314; found 386.0306.

Synthesis and characterization of 2-((4,4-bis(phenylsulfonyl)butan-2-yl)thio)benzo[*d*]thiazole (3e)

According to the synthetic procedure for **3a**, **1a** (58.6 mg, 0.300 mmol), 1,1-bis(phenylsulfonyl)ethylene (**2c**, 30.7 mg, 0.0996 mmol), sodium trifluoroacetate (13.6 mg, 0.100 mmol), and Mes-^{t}Bu-Acr$^+$ (2.9 mg, 0.005 mmol) in CH_2Cl_2/H_2O (9/1, 1.0 mL) were stirred for 8 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 **3e** (49.3 mg, 98%) as a reddish brown oil: R_f = 0.20 (hexane/EtOAc = 5/1); IR (NaCl) 3069, 3031, 2924, 1448, 1428 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04–8.02 (m, 2H), 7.81–7.74 (m, 4H), 7.67 (t, J = 7.5 Hz, 1H), 7.54–7.42 (m, 4H), 7.36–7.30 (m, 3H), 5.34 (m, 1H), 4.27 (sext, J = 7.0 Hz, 1H), 2.71–2.68 (m, 2H), 1.58 (d, J = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.8, 152.9, 138.6, 137.3, 135.5, 134.6, 134.4, 129.5, 129.4, 129.1, 129.0, 126.2, 124.7, 121.7, 121.1, 80.9, 43.6, 33.5, 22.3. HRMS (ESI) calcd. for $C_{23}H_{22}NO_4S_4$ $[M+H]^+$ 504.0429; found 504.0426.

Synthesis and characterization of 2-(2-(benzo[*d*]thiazol-2-ylthio)-1-phenylpropyl)malononitrile (3f)

According to the synthetic procedure for **3a**, **1a** (58.6 mg, 0.300 mmol), benzalmalononitrile (**2f**, 15.7 mg, 0.100 mmol), sodium trifluoroacetate (13.6 mg, 0.100 mmol), and Mes-^{t}Bu-Acr$^+$ (2.9 mg, 0.005 mmol) in CH_2Cl_2/H_2O (9/1, 1.0 mL) were stirred for 24 h. The crude product was purified by column chromatography (silica gel, hexane/EtOAc = 30/1 to 25/1 to 15/1 to 7/1 to 5/1) to give **3f** (30.8 mg, 88%, 58:42 d.r.) as a light brown oil: R_f = 0.50 (hexane/EtOAc = 5/1); IR (NaCl) 3063, 3033, 2960, 2924, 2847, 2254, 1497, 1455, 1428, 1379, 1309, 1275, 1239 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99 (m, 1H), 7.79 (m, 1H), 7.53–7.32 (m, 7H), 5.07 (d, *J* = 4.6 Hz, 1H, minor isomer), 4.78 (m, 1H, major isomer), 4.66 (d, *J* = 9.5 Hz, major isomer), 4.22 (m, 1H, minor isomer), 3.76 (m, 1H), 1.57 (d, *J* = 7.1 Hz, 3H, major isomer), 1.40 (d, *J* = 6.8 Hz, 3H, minor isomer); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.9, 161.8, 153.2, 152.9, 135.8, 135.6, 134.7, 133.7, 129.5 (2C), 129.4, 129.1, 128.7, 128.6, 126.6, 126.4, 125.3, 124.9, 122.5, 122.1, 121.2, 121.1, 112.4, 112.3, 111.9, 52.0, 51.9, 46.3, 46.2, 29.1, 27.4, 21.1, 20.1. HRMS (ESI) calcd. for $C_{19}H_{15}N_3NaS_2$ $[M+H]^+$ 372.0600; found 372.0592.

Synthesis and characterization of methyl 2-acetamido-4-(benzo[*d*]thiazol-2-ylthio)pentanoate (3g)

According to the synthetic procedure for **3a**, **1a** (58.6 mg, 0.300 mmol), methyl 2-acetamidoacrylate (**2g**, 14.3 mg, 0.100 mmol), sodium trifluoroacetate (13.6 mg, 0.100 mmol), and Mes-^{t}Bu-Acr$^+$ (2.9 mg, 0.005 mmol) in CH_2Cl_2/H_2O (9/1, 1.0 mL) were stirred for 8 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 **3g** (9.7 mg, 28%, 57:43 d.r.) as a pale yellow oil: R_f = 0.35 (hexane/EtOAc = 2/1); IR (NaCl) 3281, 2952, 2925, 2847, 1746, 1656, 1542, 1456 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.1 Hz, 1H), 7.77 (m, 1H), 7.44 (m, 1H), 7.33 (m, 1H) 7.03 (brd, *J* = 7.1 Hz, 1H, major isomer), 6.61 (brd, *J* = 7.0 Hz, 1H, minor isomer), 4.67

(m, 1H), 4.12 (m, 1H), 3.78 (s, 3H, minor isomer), 3.71 (s, 3H, major isomer), 2.37 (m, 1H), 2.25–2.14 (m, 3H), 2.05 (s, 1H), 1.54 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.2 (2C), 170.3, 169.8, 166.7, 166.0, 153.0, 152.8, 135.2, 134.9, 126.2, 124.6, 121.4, 121.2, 121.1, 121.0, 52.5 (2C), 51.0, 50.9, 40.7, 39.6, 39.2, 23.2 (2C), 21.5, 20.2. HRMS (ESI) calcd. for $C_{15}H_{18}N_2NaO_3S_2$ $[M+Na]^+$ 361.0651; found 361.0637.

Synthesis and characterization of methyl 4-(benzo[*d*]thiazol-2-ylthio)-2-(1,3-dioxoisoindolin-2-yl)pentanoate (3h)

According to the synthetic procedure for **3a**, **1a** (58.6 mg, 0.300 mmol), methyl 2-(1,3-dioxoisoindolin-2-yl)acrylate (**2h**, 23.1 mg, 0.100 mmol), sodium trifluoroacetate (13.6 mg, 0.100 mmol), and Mes-^{t}Bu-Acr^+ (2.9 mg, 0.005 mmol) in CH_2Cl_2/H_2O (9/1, 1.0 mL) were stirred for 6 h. The crude product was purified by column chromatography (silica gel, hexane/EtOAc = 20/1 to 10/1 to 5/1 to 3/1) to give **3h** (37.5 mg, 88%, 64:36 d.r.) as a pale yellow oil: R_f = 0.20 (hexane/EtOAc = 5/1); IR (NaCl) 3031, 2960, 1739, 1716, 1457 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7,88 (m, 1H, major isomer), 7.77 (m, 1H, major isomer), 7.67–7.65 (m, 3H), 7.50 (d, J = 8.0 Hz, 1H, minor isomer), 7.32–7.21 (m, 3H), 5.32 (dd, J = 4.3, 11.6 Hz, 1H, major isomer), 5.10 (dd, J = 4.5, 10.2 Hz, 1H, minor isomer), 4.19–4.16 (m, 1H), 3.73 (s, 3H), 2.98 (ddd, J = 3.8, 11.5, 15.0 Hz, 1H, major isomer), 2.80 (ddd, J = 5.3, 9.8, 14.5 Hz, 1H, minor isomer), 2.62 (m, 1H), 1.58 (d, J = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.7, 169.3, 167.6, 167.4, 165.5, 165.1, 153.1, 152.7, 135.4, 135.3, 134.3, 134.0, 131.9 (2C), 125.8, 125.7, 124.3, 124.1, 123.7, 123.5, 121.5, 121.3, 120.9, 53.0 (2C), 50.4, 49.9, 40.9, 40.8, 36.5, 35.5, 22.8, 20.2. HRMS (ESI) calcd. for $C_{21}H_{18}N_2NaO_4S_2$ $[M+Na]^+$ 449.0600 found 449.0623.

Synthesis and characterization of methyl 4-(benzo[*d*]thiazol-2-ylthio)-2-(bis(*tert*-butoxycarbonyl)amino)pentanoate (3i)

According to the synthetic procedure for **3a**, **1a** (58.6 mg, 0.300 mmol), methyl 2-(bis(*tert*-butoxycarbonyl)amino)acrylate (**2i**, 30.1 mg, 0.100 mmol), sodium trifluoroacetate (13.6 mg, 0.100 mmol), and Mes-^{t}Bu-Acr$^+$ (2.9 mg, 0.005 mmol) in CH_2Cl_2/H_2O (9/1, 1.0 mL) were stirred for 8 h. The crude product was purified by column chromatography (silica gel, hexane/EtOAc = 50/1 to 30/1 to 20/1 to 10/1) to give **3i** (49.0 mg, 99%, 64:36 d.r.) as a pale yellow oil: R_f = 0.40 (hexane/EtOAc = 5/1); IR (NaCl) 3031, 2983, 2956, 1789, 1742, 1702, 1457 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (m, 1H), 7.74 (m, 1H), 7.40 (m, 1H), 7.29 (m, 1H), 5.25 (dd, *J* = 4.4, 9.5 Hz, 1H, major isomer), 5.15 (dd, *J* = 5.4, 7.9 Hz, 1H, minor isomer), 4.05 (m, 1H), 3.73 (s, 3H), 2.62 (m, 1H), 2.34 (m, 1H), 1.59 (d, *J* = 6.8 Hz, 3H, major isomer), 1.57 (d, *J* = 7.0 Hz, 3H, minor isomer), 1.46–1.43 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0, 170.9, 165.6, 165.5, 153.4, 151.9, 151.8, 135.4, 135.3, 125.9, 124.3, 124.2, 121.9, 121.7, 120.9, 120.8, 83.4 (2C), 56.4, 56.3, 52.4 (2C), 41.7, 41.5, 38.0, 36.7, 28.0 (2C), 22.5, 21.3. HRMS (ESI) calcd. for $C_{23}H_{32}N_2NaO_6S_2$ $[M+Na]^+$ 519.1594; found 519.1598.

Synthesis and characterization of methyl 4-(benzo[*d*]thiazol-2-ylthio)-2-(1,3-dioxoisoindolin-2-yl)-5-methylhexanoate (3j)

According to the synthetic procedure for **3a**, **1b** (27.7 mg, 0.124 mmol), methyl 2-(1,3-dioxoisoindolin-2-yl)acrylate (**2h**, 23.5 mg, 0.102 mmol), sodium trifluoroacetate (2.8 mg, 0.0200 mmol), and Mes-^{t}Bu-Acr$^+$ (2.9 mg, 0.005 mmol) in CH_2Cl_2/H_2O (9/1, 1.0 mL) were stirred for 8 h. The crude product was purified by column chromatography (silica gel, hexane/EtOAc = 30/1 to 20/1 to 10/1 to 5/1) to give **3j** (44.3 mg, 96%, 71:29 d.r.) as a pale yellow oil: R_f = 0.25 (hexane/EtOAc = 5/1); IR (NaCl) 3027, 2964, 1778, 1745, 1717, 1603, 1457 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (m, 1H, major isomer), 7.68 (m, 1H, major isomer), 7.64–7.57 (m, 4H), 7,42 (m, 1H, minor isomer), 7.29 (m, 1H, minor isomer), 7.23–7.09 (m, 2H), 6.85 (m, 1H, major isomer), 5.40 (dd, *J* = 12.2, 4.6 Hz, 1H, major isomer), 5.14 (dd, *J* = 8.9, 5.6 Hz, 1H, minor isomer), 4.24 (m, 1H), 3.74 (s, 3H), 3.07 (ddd, *J* = 15.0, 12.2, 3.1 Hz, 1H, major

isomer), 2.85 (ddd, J = 14.9, 6.8, 5.9 Hz, 1H, minor isomer), 2.48 (m, 1H), 2.31 (m, 1H, minor isomer), 2.12 (m, 1H, major isomer), 1.06 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 169.4, 167.7, 167.4, 166.8, 166.5, 152.9, 152.3, 135.3, 134.0, 133.8, 131.9 (2C), 125.7, 125.4, 124.1, 123.9, 123.5, 123.3, 121.4, 120.9, 120.8, 53.2, 52.9, 52.1, 50.7, 50.2, 33.6, 33.3, 31.9, 31.6, 20.3, 19.9, 18.8, 18.0. HRMS (ESI) calcd. for $C_{23}H_{22}N_2NaO_4S_2$ $[M+Na]^+$ 477.0913; found 477.0912.

Synthesis and characterization of methyl 4-(benzo[*d*]thiazol-2-ylthio)-4-cyclohexyl-2-(1,3-dioxoisoindolin-2-yl)butanoate (3k)

According to the synthetic procedure for **3a**, **1c** (31.6 mg, 0.120 mmol), methyl 2-(1,3-dioxoisoindolin-2-yl)acrylate (**2h**, 23.3 mg, 0.101 mmol), sodium trifluoroacetate (2.8 mg, 0.0200 mmol), and Mes-^{t}Bu-Acr$^+$ (2.9 mg, 0.005 mmol) in CH_2Cl_2/H_2O (9/1, 1.0 mL) were stirred for 8 h. The crude product was purified by column chromatography (silica gel, hexane/EtOAc = 30/1 to 20/1 to 10/1 to 5/1) to give **3k** (49.0 mg, 98%, 68:32 d.r.) as a pale yellow oil: R_f = 0.32 (hexane/EtOAc = 5/1); IR (NaCl) 2929, 2858, 1745, 1716, 1458, 1455 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (m, 1H, major isomer), 7.68 (m, 1H, major isomer), 7.64–7.56 (m, 3H), 7,42 (m, 1H, minor isomer), 7.28 (m, 1H, minor isomer), 7.23–7.09 (m, 2H), 6.84 (m, 1H, major isomer), 5.39 (dd, J = 12.2, 4.6 Hz, 1H, major isomer), 5.14 (dd, J = 8.9, 5.6 Hz, 1H, minor isomer), 4.20 (m, 1H), 3.74 (s, 3H, minor isomer), 3.72 (s, 3H, major isomer), 3.10 (ddd, J = 15.0, 12.2, 3.1 Hz, 1H, major isomer), 2.89 (ddd, J = 14.9, 6.8, 5.9 Hz, 1H, minor isomer), 2.48 (m, 1H), 1.93–1.62 (m, 6H), 1.40–1.10 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 169.5, 167.7, 167.4, 166.9, 166.7, 152.9, 152.3, 135.3, 134.0, 133.8, 131.9 (2C), 125.7, 125.4, 124.0, 123.8, 123.5, 123.3, 121.3, 120.9, 120.8, 52.9, 52.5, 51.3, 50.7, 50.3, 43.6, 42.0, 33.2, 31.4, 30.6, 30.1, 29.2, 28.7, 26.4, 26.25, 26.20, 26.1. HRMS (ESI) calcd. for $C_{26}H_{27}N_2O_4S_2$ $[M+H]^+$ 495.1407; found 495.1419.

Synthesis and characterization of methyl 4-(benzo[*d*]thiazol-2-ylthio)-2-(1,3-dioxoisoindolin-2-

yl)undecanoate (3l)

According to the synthetic procedure for **3a**, **1d** (33.5 mg, 0.120 mmol), methyl 2-(1,3-dioxoisoindolin-2-yl)acrylate (**2h**, 23.9 mg, 0.103 mmol), sodium trifluoroacetate (2.8 mg, 0.0200 mmol), and Mes-^{t}Bu-Acr$^+$ (2.9 mg, 0.005 mmol) in CH_2Cl_2/H_2O (9/1, 1.0 mL) were stirred for 8 h. The crude product was purified by column chromatography (silica gel, hexane/EtOAc = 30/1 to 20/1 to 10/1 to 5/1) to give **3l** (40.4 mg, 77%, 66:34 d.r.) as a pale yellow oil: R_f = 0.50 (hexane/EtOAc = 3/1); IR (NaCl) 2956, 2929, 2854, 1749, 1717, 1457 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (m, 1H, major isomer), 7.75 (m, 1H, major isomer), 7.66–7.61 (m, 3H), 7,42 (m, 1H, minor isomer), 7.29 (m, 1H, minor isomer), 7.24–7.15 (m, 2H), 7.05 (m, 1H, major isomer), 5.37 (dd, *J* = 12.0, 4.4 Hz, 1H, major isomer), 5.12 (dd, *J* = 9.5, 4.9 Hz, 1H, minor isomer), 4.15 (m, 1H, major isomer), 4.02 (m, 1H, minor isomer), 3.72 (s, 3H), 3.08 (ddd, *J* = 15.1, 12.0, 3.5 Hz, 1H, major isomer), 2.78 (m, 1H, minor isomer), 2.66 (m, 1H, minor isomer), 2.52 (ddd, *J* = 15.1, 11.9, 4.4 Hz, 1H, major isomer), 1.95–1.19 (m, 12H), 0.84 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.9, 169.4, 167.7, 167.4, 166.1, 165.7, 153.1, 152.6, 135.4, 135.3, 134.2, 133.9, 131.9 (2C), 125.7, 125.5, 124.1, 124.0, 123.6, 123.4, 121.4, 121.1, 120.8, 52.9, 50.4, 49.9, 46.6, 46.1, 36.4, 35.2, 33.9, 33.8, 31.8, 29.3 (2C), 29.1, 29.0, 26.7 (2C), 22.6 (2C), 14.1 (2C). HRMS (ESI) calcd. for $C_{27}H_{30}N_2NaO_4S_2$ $[M+Na]^+$ 533.1539; found 533.1535.

Synthesis and characterization of 6-(*tert*-butyl) 1-methyl 4-(benzo[*d*]thiazol-2-ylthio)-2-(1,3-dioxoisoindolin-2-yl)hexanedioate (3m)

According to the synthetic procedure for **3a**, **1e** (35.5 mg, 0.120 mmol), methyl 2-(1,3-dioxoisoindolin-2-yl)acrylate (**2h**, 23.7 mg, 0.103 mmol), sodium trifluoroacetate (2.8 mg, 0.0200 mmol), and Mes-^{t}Bu-Acr$^+$ (2.9 mg, 0.005 mmol) in CH_2Cl_2/H_2O (9/1, 1.0 mL) were stirred for 8 h. The crude product was purified by column chromatography (silica gel, hexane/EtOAc = 30/1 to 20/1 to 10/1 to 5/1 to 3/1) to give **3m** (53.7 mg, 99%, 69:31 d.r.) as a pale yellow oil: R_f = 0.50 (hexane/EtOAc = 3/1); IR (NaCl) 3030,

2981, 1774, 1745, 1718, 1457 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.82 (m, 1H, major isomer), 7.73 (m, 1H, major isomer), 7.68–7.64 (m, 3H), 7.51 (m, 1H, minor isomer), 7.31–7.13 (m, 3H), 5.36 (dd, *J* = 11.8, 4.1 Hz, 1H, major isomer), 5.14 (dd, *J* = 9.2, 5.4 Hz, 1H, minor isomer), 4.39 (m, 1H), 3.73 (s, 3H, major isomer), 3.72 (s, 3H, minor isomer), 3.02 (ddd, *J* = 15.1, 11.9, 3.5 Hz, 1H, major isomer), 2.89 (m, 3H), 1.44 (s, 9H, minor isomer), 1.39 (s, 9H, major isomer); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.7, 169.6, 169.2, 167.6, 167.3, 165.2, 164.9, 153.0, 152.6, 135.4, 135.3, 134.2, 133.9, 131.9 (2C), 125.8, 125.6, 124.3, 124.2, 123.6, 123.4, 121.6, 121.3, 120.9, 81.6, 81.5, 52.9, 50.4, 50.0, 42.4, 42.0, 41.6, 40.1, 34.1, 33.2, 28.1, 28.0. HRMS (ESI) calcd. for $C_{26}H_{27}N_2O_6S_2$ $[M+H]^+$ 527.1305; found 527.1298.

Synthesis and characterization of methyl 4-(benzo[*d*]thiazol-2-ylthio)-5-((*tert*-butoxycarbonyl)amino)-2-(1,3-dioxoisoindolin-2-yl)pentanoate (3n)

According to the synthetic procedure for **3a**, **1f** (37.3 mg, 0.120 mmol), methyl 2-(1,3-dioxoisoindolin-2-yl)acrylate (**2h**, 23.5 mg, 0.102 mmol), sodium trifluoroacetate (2.8 mg, 0.0200 mmol), and Mes-^{t}Bu-Acr^+ (2.9 mg, 0.005 mmol) in CH_2Cl_2/H_2O (9/1, 1.0 mL) was stirred for 8 h. The crude product was purified by column chromatography (silica gel, hexane/EtOAc = 15/1 to 7/1 to 5/1 to 3/1 to 1/1) to give **3n** (41.7 mg, 76%, 70:30 d.r.) as a pale yellow oil: R_f = 0.25 (hexane/EtOAc = 3/1); IR (NaCl) 3450, 3031, 3010, 2981, 1777, 1747, 1716, 1506, 1457 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 50 °C) δ 7.86–7.57 (m, 5H), 7.36–7.24 (m, 3H), 5.39–5.20 (m, 2H), 4.10 (m, 1H), 3.72 (s, 3H), 3.57 (m, 1H), 3.01 (m, 1H, major isomer), 2.83 (m, 1H, minor isomer), 2.56 (m, 1H), 1.39 (m, 9H); ^{13}C NMR (101 MHz, $CDCl_3$, 50 °C) δ 169.4, 169.0, 167.5, 167.3, 164.7, 164.3, 155.8, 153.0, 152.6, 135.6, 135.5, 134.1, 133.9, 132.0, 131.9, 125.9, 125.7, 124.4, 124.3, 123.5, 123.4, 121.7, 121.5, 120.9, 79.5, 52.8 (2C), 50.2, 50.1, 47.7, 46.8, 31.8, 31.2, 28.3 (2C). HRMS (ESI) calcd. for $C_{26}H_{27}N_3NaO_6S_2$ $[M+Na]^+$ 564.1233; found 564.1219.

Synthesis and characterization of methyl 4-(benzo[*d*]thiazol-2-ylthio)-5-(bis(*tert*-

butoxycarbonyl)amino)-2-(1,3-dioxoisoindolin-2-yl)pentanoate (3o)

According to the synthetic procedure for **3a**, **1g** (49.3 mg, 0.120 mmol), methyl 2-(1,3-dioxoisoindolin-2-yl)acrylate (**2h**, 23.2 mg, 0.100 mmol), sodium trifluoroacetate (2.8 mg, 0.0200 mmol), and Mes-^{t}Bu-Acr$^+$ (2.9 mg, 0.005 mmol) in CH_2Cl_2/H_2O (9/1, 1.0 mL) were stirred for 8 h. The crude product was purified by column chromatography (silica gel, hexane/EtOAc = 30/1 to 20/1 to 10/1 to 5/1 to 3/1) to give **3o** (60.5 mg, 94%, 56:44 d.r.) as a pale yellow oil: R_f = 0.45 (hexane/EtOAc = 3/1); IR (NaCl) 3026, 3004, 2982, 2960, 2931, 1781, 1741, 1717, 1462 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (m, 1H), 7.66–7.59 (m, 4H), 7.33 (m, 1H, minor isomer), 7.25–7.12 (m, 2H), 6.91 (m, 1H, major isomer), 5.41 (dd, *J* = 12.0, 4.4 Hz, 1H, major isomer), 5.24 (dd, *J* = 8.3, 6.0 Hz, 1H, minor isomer), 4.55–4.38 (m, 1H), 4.20–3.90 (m, 2H), 3.72 (s, 3H), 3.11 (ddd, *J* = 15.2, 12.0, 3.4 Hz, 1H, major isomer), 2.91 (ddd, *J* = 12.0, 11.5, 5.7 Hz, 1H, minor isomer), 2.57 (m, 1H), 1.46 (s, 18H, major isomer), 1.42 (s, 18H, minor isomer); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.7, 169.2, 167.4, 167.3, 165.0, 164.7, 153.0, 152.4, 151.9, 135.4 (2C), 133.9 (2C), 131.9 (2C), 125.8, 125.5, 124.2, 124.1, 123.4, 123.3, 121.7, 121.1, 120.9, 120.8, 82.8, 82.7, 52.9 (2C), 50.1, 50.0, 49.7, 49.2, 46.9, 45.1, 32.2, 31.0, 28.0, 27.9. HRMS (ESI) calcd. for $C_{31}H_{35}N_3NaO_8S_2$ $[M+Na]^+$ 664.1758; found 664.1758.

Synthesis and characterization of methyl 4-(benzo[*d*]thiazol-2-ylthio)-2-(1,3-dioxoisoindolin-2-yl)butanoate (3p)

According to the synthetic procedure for **3a**, **1i** (21.8 mg, 0.120 mmol), methyl 2-(1,3-dioxoisoindolin-2-yl)acrylate (**2h**, 24.4 mg, 0.106 mmol), sodium trifluoroacetate (2.8 mg, 0.0200 mmol), and Mes-^{t}Bu-Acr$^+$ (2.9 mg, 0.005 mmol) in CH_2Cl_2/H_2O (9/1, 1.0 mL) were stirred for 8 h. The crude product was purified by column chromatography (silica gel, hexane/EtOAc = 30/1 to 20/1 to 10/1 to 5/1 to 3/1 to 1/1) to give **3p** (30.8 mg, 70%) as a reddish brown oil: R_f = 0.20 (hexane/EtOAc = 5/1); IR (NaCl) 3029, 2997, 1745, 1719, 1457 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (m, 2H), 7.75 (m, 2H), 7.71 (m, 1H), 7.64

(m, 1H), 7.35 (ddd, J = 8.4, 7.3, 1.3 Hz, 1H), 7.26 (m, 1H), 5.14 (dd, J = 8.7, 6.5 Hz, 1H), 3.74 (s, 3H), 3.51 (m, 1H), 3.38 (m, 1H), 2.80 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.3, 167.6, 165.8, 153.0, 135.3, 134.3, 131.8, 125.9, 124.2, 123.7, 121.5, 121.0, 53.0, 50.8, 29.9, 29.0. HRMS (ESI) calcd. for $C_{20}H_{16}N_2NaO_4S_2[M+Na]^+$ 435.0444; found 435.0444.

Synthesis and characterization of methyl 4-(benzo[*d*]thiazol-2-ylthio)-2-(1,3-dioxoisoindolin-2-yl)butanoate-4,4-d_2 (3p-d_2)

According to the synthetic procedure for **3a**, **1j** (22.1 mg, 0.120 mmol), methyl 2-(1,3-dioxoisoindolin-2-yl)acrylate (**2h**, 23.1 mg, 0.100 mmol), sodium trifluoroacetate (2.8 mg, 0.0200 mmol), and Mes-^{t}Bu-Acr$^+$ (2.9 mg, 0.005 mmol) in CH_2Cl_2/H_2O (9/1, 1.0 mL) were stirred for 8 h. The crude product was purified by column chromatography (silica gel, hexane/EtOAc = 30/1 to 20/1 to 10/1 to 5/1) to give **3p-d_2** (34.0 mg, 85%) as a reddish brown oil: R_f = 0.38 (hexane/EtOAc = 3/1); IR (NaCl) 3031, 3007, 2956, 1774, 1745, 1719, 1458 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (m, 2H), 7.75 (m, 2H), 7.71 (m, 1H), 7.64 (m, 1H), 7.35 (m, 1H), 7.26 (m, 1H), 5.14 (dd, J = 8.7, 6.5 Hz, 1H), 3.74 (s, 3H), 2.80 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.3, 167.6, 165.8, 153.0, 135.3, 134.3, 131.8, 125.9, 124.2, 123.7, 121.5, 121.0, 53.0, 50.8, 28.8. HRMS (ESI) calcd. for $C_{20}H_{14}D_2N_2NaO_4S_2$ $[M+Na]^+$ 437.0569; found 437.0568.

Synthesis and characterization of 1-((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl) 7-phenyl 4-(benzo[*d*]thiazol-2-ylthio)heptanedioate (3q)

According to the synthetic procedure for **3a**, **1l** (118 mg, 0.300 mmol), phenyl acrylate (15.9 mg, 0.100 mmol), sodium trifluoroacetate (13.9 mg, 0.100 mmol), and Mes-^{t}Bu-Acr$^+$ (2.9 mg, 0.005 mmol) in CH_2Cl_2/H_2O (9/1, 1.0 mL) were stirred for 6.5 h. The crude product was purified by column chromatography (silica gel, hexane/EtOAc = 50/1 to 40/1 to 30/1) to give **3q** (20.8 mg, 39%) as a colorless oil: R_f = 0.4 (hexane/EtOAc = 5/1); $[\alpha]^{25}_D$ -20.5 (*c* 1.00, $CHCl_3$); IR (NaCl) 3018, 2959, 2927,

2871, 1753, 1720, 1520, 1427 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.84 (m, 1H), 7.75 (m, 1H), 7.43–7.28 (m, 4H), 7.21 (tt, *J* = 1.1, 7.4 Hz, 1H), 7.07–7.04 (m, 2H), 4.68 (ddt, *J* = 1.8, 4.4, 10.8 Hz, 1H), 4.15 (m, 1H), 2.92–2.80 (m, 2H), 2.66 –2.53 (m, 2H), 2.39–2.04 (m, 4H), 1.96 (m, 1H), 1.82 (m, 2H), 1.70–1.23 (m, 5H), 1.11–0.93 (m, 2H), 0.89–0.83 (m, 6H), 0.75–0.71 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.4 (2C), 171.5, 165.4 (2C), 153.1, 150.6, 135.4, 129.4, 126.0, 125.8, 124.4, 121.8, 121.5, 120.9, 74.4, 48.6, 48.5, 46.9 (2C), 40.8, 34.2, 32.0 (2C), 31.7 (2C), 31.3, 30.5 (2C), 30.4, 30.3, 26.3, 26.2, 23.4, 23.3, 22.0 (2C), 20.7 (2C), 16.3. HRMS (ESI) calcd. for $C_{30}H_{38}NO_4S_2$ $[M+H]^+$ 540.2237; found 540.2230.

Synthesis and characterization of (*E*)-1-(3,7-dimethylocta-2,6-dien-1-yl) 7-phenyl 4-(benzo[*d*]thiazol-2-ylthio)heptanedioate (3r)

According to the synthetic procedure for **3a**, **1m** (117 mg, 0.300 mmol), phenyl acrylate (15.1 mg, 0.0950 mmol), sodium trifluoroacetate (13.9 mg, 0.100 mmol), and Mes-^{t}Bu-Acr$^+$ (2.9 mg, 0.005 mmol) in CH_2Cl_2/H_2O (9/1, 1.0 mL) were stirred for 6.5 h. The crude product was purified by column chromatography (silica gel, hexane/EtOAc = 50/1 to 40/1 to 30/1 to 20/1) to give **3r** (8.0 mg, <15%) as a colorless oil: R_f = 0.33 (hexane/EtOAc = 5/1); $[\alpha]^{27}_D$ +5.6 (*c* 0.52, $CHCl_3$); IR (NaCl) 2925, 2854, 1759, 1732, 1493, 1457, 1428 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ7.87–7.74 (m, 2H), 7.43–7.19 (m, 5H), 7.08–7.04 (m, 2H), 5.29 (m, 1H), 5.06 (m, 1H), 4.68–4.55 (m, 2H), 4.16 (m, 1H), 2.85 (t, *J* = 7.5 Hz, 2H), 2.61 (m, 2H), 2.53–1.99 (m, 8H), 1.67 (s, 6H), 1.59 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.9, 171.4, 150.6, 142.4, 131.8, 129.4, 126.0, 125.8, 124.4, 124.2, 123.7, 121.7, 121.5, 120.9, 118.1, 61.5, 48.4, 39.5, 31.7 (2C), 30.4, 30.3, 26.3, 25.7, 17.7, 16.4. HRMS (ESI) calcd. for $C_{30}H_{36}NO_4S_2$ $[M+H]^+$ 538.2080; found 538.2056.

Synthesis and 1-((3*S*,8*R*,9*S*,10*R*,13*S*,14*S*)-10,13-dimethyl-17-oxo-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl) 7-phenyl 4-

(benzo[*d*]thiazol-2-ylthio)heptanedioate (3s)

According to the synthetic procedure for **3a**, **1n** (52.7 mg, 0.100 mmol), phenyl acrylate (45.4 mg, 0.300 mmol), sodium trifluoroacetate (13.9 mg, 0.100 mmol), and Mes-^{t}Bu-Acr$^+$ (2.9 mg, 0.005 mmol) in CH_2Cl_2/H_2O (9/1, 1.0 mL) were stirred for 22 h. The crude product was purified by column chromatography (silica gel, hexane/EtOAc = 10/1 to 5/1 to 4/1) to give **3s** (37.1 mg, 55%) as a colorless oil: R_f = 0.33 (hexane/EtOAc = 3/1); IR (NaCl) 2942, 2854, 1758, 1737, 1493, 1456, 1427 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.1 Hz, 1H), 7.75 (d, *J* = 7.5 Hz, 1H), 7.43–7.28 (m, 4H), 7.21 (m, 1H), 7.07–7.05 (m, 2H), 5.37 (m, 1H), 4.61 (m, 1H), 4.17 (m, 1H), 2.86 (t, *J* = 7.5 Hz, 2H), 2.63–2.55 (m, 2H), 2.46 (dd, *J* = 8.5, 19.3 Hz, 1H), 2.38–2.05 (m, 8H), 1.98–1.78 (m, 4H), 1.70–1.42 (m, 7H), 1.32–1.26 (m, 2H), 1.13 (m, 1H), 1.00 (s, 3H), 0.88 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 221.1, 172.3, 171.5, 165.5, 153.1, 150.6, 139.9, 135.4, 129.4, 126.1, 125.8, 124.5, 121.9 (2C), 121.8, 121.5, 121.0, 74.0, 51.7, 50.1, 48.5, 47.5, 38.0, 36.9, 36.7, 35.9, 32.0, 31.8, 31.5, 31.4, 30.8, 30.4, 29.7, 27.7, 21.9, 20.3, 19.3, 13.6. HRMS (ESI) calcd. for $C_{39}H_{46}NO_5S_2$ $[M+H]^+$ 672.2812; found 672.2812.

Synthesis and characterization of phenyl 4-(phenylthio)pentanoate (3t)

According to the synthetic procedure for **3a**, **1o** (41.1 mg, 0.297 mmol), phenyl acrylate (15.2 mg, 0.100 mmol), sodium trifluoroacetate (13.9 mg, 0.100 mmol), and Mes-^{t}Bu-Acr$^+$ (2.9 mg, 0.005 mmol) in CH_2Cl_2/H_2O (9/1, 1.0 mL) were stirred for 6 h. The crude product was purified by column chromatography (silica gel, hexane/EtOAc = 30/1 to 20/1 to 10/1) to give **3t** (8.7 mg, 30%) as a colorless oil: R_f = 0.43 (hexane/EtOAc = 5/1); IR (NaCl) 2962, 2925, 2866, 1758, 1592, 1493, 1439 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45–7.42 (m, 2H), 7.40–7.35 (m, 2H), 7.32–7.20 (m, 4H), 7.08–7.04 (m, 2H), 3.32 (sext., *J* = 6.7 Hz, 1H), 2.84–2.72 (m, 2H), 2.07–1.96 (m, 2H), 1.35 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.7, 150.6, 134.5, 132.4, 129.4, 128.9, 127.1, 125.8, 121.5, 42.9, 31.7, 31.4, 21.2. HRMS (ESI) calcd. for $C_{17}H_{18}NaO_2S$ $[M+Na]^+$ 309.0920; found 309.0910.

Synthesis and characterization of phenyl 4-(thiazol-2-ylthio)pentanoate (3u)

According to the synthetic procedure for **3a**, **1p** (44.0 mg, 0.303 mmol), phenyl acrylate (15.6 mg, 0.105 mmol), sodium trifluoroacetate (13.9 mg, 0.100 mmol), and Mes-^{t}Bu-Acr$^+$ (2.9 mg, 0.005 mmol) in CH_2Cl_2/H_2O (9/1, 1.0 mL) were stirred for 6 h. The crude product was purified by column chromatography (silica gel, hexane/EtOAc = 15/1 to 7/1 to 5/1) to give **3u** (6.3 mg, 21%) as a colorless oil: R_f = 0.33 (hexane/EtOAc = 5/1); IR (NaCl) 2963, 2924, 2862, 1758, 1593, 1493, 1456 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 3.4 Hz, 1H), 7.40–7.35 (m, 2H), 7.27–7.20 (m, 2H), 7.09–7.06 (m, 2H), 3.83 (m, 1H), 2.83–2.76 (m, 2H), 2.21–2.08 (m, 2H), 1.50 (d, J = 6.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.5, 162.9, 150.6, 143.1, 129.4, 125.8, 121.5, 120.0, 44.5, 31.8, 31.6, 21.4. HRMS (ESI) calcd. for $C_{14}H_{15}NNaO_2S_2$ $[M+Na]^+$ 316.0436; found 316.0432.

Synthesis and characterization of phenyl 4-(benzo[*d*]oxazol-2-ylthio)pentanoate (3v)

According to the synthetic procedure for **3a**, **1q** (55.2 mg, 0.308 mmol), phenyl acrylate (14.9 mg, 0.100 mmol), sodium trifluoroacetate (2.8 mg, 0.0200 mmol), and Mes-^{t}Bu-Acr$^+$ (2.9 mg, 0.005 mmol) in CH_2Cl_2/H_2O (9/1, 1.0 mL) were stirred for 6 h. The crude product was purified by column chromatography (silica gel, hexane/EtOAc = 15/1 to 7/1 to 5/1) to give **3v** (1.9 mg, 6%) as a colorless oil: R_f = 0.37 (hexane/EtOAc = 5/1); IR (NaCl) 2959, 2925, 2865, 1758, 1593, 1497, 1454 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (m, 1H), 7.44 (m, 1H), 7.40–7.35 (m, 2H), 7.31–7.20 (m, 3H), 7.11–7.07 (m, 2H), 4.08 (m, 1H), 2.81 (t, J = 7.6 Hz, 2H), 2.33–2.19 (m, 2H), 1.61 (d, J = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.3, 164.0, 151.7, 150.6, 141.9, 129.4, 125.8, 124.3, 124.0, 121.5, 118.5, 109.9, 42.7, 31.8, 31.6, 21.7. HRMS (ESI) calcd. for $C_{18}H_{18}NO_3S$ $[M+H]^+$ 328.1002; found 328.0998.

Synthesis and characterization of phenyl 4-(thiazolo[5,4-*b*]pyridin-2-ylthio)pentanoate (3w)

According to the synthetic procedure for **3a**, **1r** (59.4 mg, 0.303 mmol), phenyl acrylate (15.3 mg, 0.103 mmol), sodium trifluoroacetate (14.2 mg, 0.102 mmol), and Mes-^{t}Bu-Acr$^+$ (2.9 mg, 0.005 mmol) in CH_2Cl_2/H_2O (9/1, 1.0 mL) were stirred for 6 h. The crude product was purified by column chromatography (silica gel, hexane/EtOAc = 15/1 to 7/1 to 5/1) to give **3w** (13.1 mg, 38%) as a colorless oil: R_f = 0.20 (hexane/EtOAc = 5/1); IR (NaCl) 2959, 2925, 2858, 1757, 1592, 1493, 1434 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 4.0 Hz, 1H), 8.02 (dd, *J* = 3.2, 8.2 Hz, 1H), 7.40–7.33 (m, 3H), 7.22 (m, 1H), 7.10–7.06 (m, 2H), 4.26 (m, 1H), 2.85–2.76 (m, 2H), 2.33–2.18 (m, 2H), 1.60 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4, 167.5, 158.7, 150.6, 146.3, 145.7, 129.4, 128.0, 125.8, 121.5, 121.1, 42.9, 31.8, 31.7, 21.5. HRMS (ESI) calcd. for $C_{17}H_{16}N_2NaO_2S_2$ $[M+Na]^+$ 367.0545; found 367.0540.

Synthesis and characterization of methyl 4-(benzo[*d*]thiazol-2-ylthio)-2-(bis(*tert*-butoxycarbonyl)amino)-5-methylhexanoate (3x)

According to the synthetic procedure for **3a**, **1b** (67.1 mg, 0.300 mmol), methyl 2-(bis(*tert*-butoxycarbonyl)amino)acrylate (**2i**, 29.6 mg, 0.0982 mmol), sodium trifluoroacetate (13.6 mg, 0.100 mmol), and Mes-^{t}Bu-Acr$^+$ (2.9 mg, 0.005 mmol) were stirred for 24 h. The crude product was purified by column chromatography (silica gel, hexane/EtOAc = 30/1 to 20/1 to 10/1 to 5/1) to give **3x** (48.2 mg, 97%) as a pale yellow oil: R_f = 0.55 (hexane/EtOAc = 3/1); IR (NaCl) 3031, 2981, 2942, 2872, 1789, 1742, 1698, 1457 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (m, 1H), 7.71 (m, 1H), 7.38 (m, 1H), 7.26 (m, 1H), 5.32 (dd, *J* = 10.6, 3.9 Hz, 1H, major isomer), 5.20 (t, *J* = 6.5 Hz, 1H, minor isomer), 4.19 (ddd, *J* = 8.8, 5.7, 3.5 Hz, 1H, minor isomer), 3.91 (dt, *J* = 11.5, 3.3 Hz, 1H, major isomer), 3.74 (s, 3H, minor isomer), 3.73 (s, 3H, major isomer), 2.80 (dt, *J* = 14.8, 6.0 Hz, 1H, minor isomer), 2.47 (m, 1H, major isomer), 2.36–2.21 (m, 2H), 2.04 (ddd, *J* = 15.0, 8.5, 6.3 Hz, 1H, minor isomer), 1.44 (s, 18H, minor isomer), 1.39 (s, 18H, major isomer), 1.09 (d, *J* = 4.9 Hz, 3H, minor isomer), 1.07 (d, *J* = 5.2 Hz, 3H,

minor isomer), 1.06 (d, J = 2.4 Hz, 3H, major isomer), 1.04 (d, J = 2.4 Hz, 3H, major isomer); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.3, 171.1, 166.9, 166.6, 153.3, 152.0, 151.7, 135.3, 125.8 (2C), 124.1, 124.0, 121.8, 121.6, 120.8 (2C), 83.3, 83.2, 56.5, 54.0, 52.4 (2C), 52.3, 34.5, 32.8, 32.0, 30.5, 28.0 (2C), 27.9, 19.9, 19.5, 18.6, 18.4. HRMS (ESI) calcd. for $C_{25}H_{36}N_2NaO_6S_2$ $[M+Na]^+$ 547.1907; found 547.1908.

Synthesis and characterization of methyl 4-(benzo[*d*]thiazol-2-ylthio)-2-(bis(*tert*-butoxycarbonyl)amino)-4-cyclohexylbutanoate (3y)

According to the synthetic procedure for **3a**, **1c** (79.0 mg, 0.300 mmol), methyl 2-(bis(*tert*-butoxycarbonyl)amino)acrylate (**2i**, 30.1 mg, 0.100 mmol), sodium trifluoroacetate (13.6 mg, 0.100 mmol), and ^{t}Bu-Mes-Acr$^+$ (2.9 mg, 0.005 mmol) in CH_2Cl_2/H_2O (9/1, 1.0 mL) was stirred for 24 h. The crude product was purified by column chromatography (silica gel, hexane/EtOAc = 30/1 to 20/1 to 10/1 to 5/1) to give **3y** (53.9 mg, 95%) as a pale yellow oil: R_f = 0.37 (hexane/EtOAc = 5/1); IR (NaCl) 2979, 2928, 2853, 1793, 1746, 1702, 1457, 1429 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (m, 1H), 7.71 (m, 1H), 7.38 (m, 1H), 7.26 (m, 1H), 5.31 (dd, J = 3.9, 10.6 Hz, 1H, major isomer), 5.20 (t, J = 6.5 Hz, 1H, minor isomer), 4.14 (m, 1H, major isomer), 3.88 (dt, J = 3.4, 11.1 Hz, 1H, minor isomer), 3.73 (s, 3H, major isomer), 3.72 (s, 3H, minor isomer), 2.83 (m, 1H, minor 1701, isomer), 2.51 (m, 1H, major isomer), 2.35 (m, 1H, major isomer), 2.06 (m, 1H, minor isomer), 1.93–1.64 (m, 6H), 1.52–1.07 (m, 23H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2, 171.1, 167.1, 166.8, 153.3, 153.2, 152.0, 151.7, 135.2, 125.8, 125.7, 124.0 (2C), 121.7, 121.6, 120.7 (2C), 83.2, 83.1, 56.6, 53.4, 52.3, 52.2, 51.8, 42.9, 42.0, 34.4, 31.0, 30.3, 29.9, 29.2, 28.9, 27.9, 27.8, 26.3 (2C), 26.2. HRMS (ESI) calcd. for $C_{28}H_{41}N_2O_6S_2$ $[M+H]^+$ 565.2401; found 565.2382.

Synthesis and characterization of 6-(*tert*-butyl) 1-methyl 4-(benzo[*d*]thiazol-2-ylthio)-2-(bis(*tert*-butoxycarbonyl)amino)hexanedioate (3z)

According to the synthetic procedure for **3a**, **1e** (88.8 mg, 0.301 mmol), methyl 2-(bis(*tert*-butoxycarbonyl)amino)acrylate (**2i**, 30.2 mg, 0.100 mmol), sodium trifluoroacetate (13.8 mg, 0.100 mmol), and ^{t}Bu-Mes-Acr^{+} (2.9 mg, 0.005 mmol) in CH_2Cl_2/H_2O (9/1, 1.0 mL) was stirred 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 **3z** (60.1 mg, 100%) as a pale yellow oil: R_f = 0.55 (hexane/EtOAc = 5/1); IR (NaCl) 3031, 2982, 2931, 1790, 1740, 1457 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.1 Hz, 1H), 7.73 (t, *J* = 7.1 Hz, 1H), 7.40 (m, 1H), 7.29 (m, 1H), 5.30 (dd, *J* = 10.0, 3.7 Hz, 1H, major isomer), 5.21 (t, *J* = 6.5 Hz, 1H, minor isomer), 4.38 (quint., *J* = 6.4 Hz, 1H, minor isomer), 4.14 (m, 1H, major isomer), 3.73 (s, 3H, minor isomer), 3.71 (s, 3H, major isomer), 3.01–2.70 (m, 3H), 2.54 (ddd, *J* = 13.9, 10.0, 3.8 Hz, 1H, major isomer), 2.41 (quint., *J* = 6.4 Hz, 1H, minor isomer), 1.45–1.44 (m, 27H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0, 170.8, 169.8 (2C), 153.3, 153.2, 152.0, 151.7, 135.4, 135.3, 125.9 (2C), 124.3 (2C), 121.9, 120.9 (2C), 83.4, 83.3, 81.3, 81.1, 56.4, 52.4, 52.3, 43.1, 42.5, 41.4, 40.6, 35.9, 34.1, 28.1 (2C), 27.9 (2C). HRMS (ESI) calcd. for $C_{28}H_{40}N_2NaO_8S_2$ $[M+Na]^+$ 619.2118; found 619.2119.

Synthesis and characterization of methyl 4-(benzo[*d*]thiazol-2-ylthio)-2,5-bis(bis(*tert*-butoxycarbonyl)amino)pentanoate (3aa)

According to the synthetic procedure for **3a**, **1g** (123 mg, 0.300 mmol), methyl 2-(bis(*tert*-butoxycarbonyl)amino)acrylate (**2i**, 30.1 mg, 0.100 mmol), sodium trifluoroacetate (13.6 mg, 0.100 mmol), and ^{t}Bu-Mes-Acr^{+} (2.9 mg, 0.005 mmol) in CH_2Cl_2/H_2O (9/1, 1.0 mL) was stirred for 24 h. The crude product was purified by column chromatography (silica gel, hexane/EtOAc = 50/1 to 40/1 to 15/1 to 7/1 to 3/1) to give **3aa** (65.8 mg, 92%) as a pale yellow oil: R_f = 0.45 (hexane/EtOAc = 5/1); IR (NaCl) 2983, 2927, 1788, 1742, 1698, 1457 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (m, 1H), 7.73 (m, 1H), 7.39 (m, 1H), 7.27 (m, 1H), 5.33 (m, 1H), 4.52–4.01 (m, 3H), 3.712 (s, 3H, minor isomer), 3.705 (s, 3H, major isomer), 2.84 (ddd, *J* = 12.3, 7.7, 4.6 Hz, 1H, minor isomer), 2.61 (m, 1H, major isomer), 2.50 (m,

1H, major isomer), 2.13 (ddd, J = 15.0, 10.1, 5.1 Hz, 1H, minor isomer), 1.48–1.41 (m, 36H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0, 170.7, 165.1, 164.3, 153.4, 153.3, 152.5, 152.2, 151.9, 151.7, 151.6, 135.6, 135.4, 125.9 (2C), 124.3, 124.2, 121.8 (2C), 120.8, 83.3 (2C), 82.6, 56.3, 56.1, 52.4, 52.2, 50.3, 49.6, 47.4, 45.7, 33.7, 31.6, 28.1, 28.0 (2C), 27.9 (2C). HRMS (ESI) calcd. for $C_{33}H_{50}N_3O_{10}S_2$ $[M+H]^+$ 712.2932; found 712.2931.

Synthesis and characterization of phenyl 2-(1-(benzo[*d*]thiazol-2-ylthio)-4-oxo-4-phenoxybutyl)cyclopentane-1-carboxylate (I)

According to the synthetic procedure for **3a**, **1k** (22.3 mg, 0.101 mmol), phenyl acrylate (2a, 45.4 mg, 0.300 mmol), sodium trifluoroacetate (13.9 mg, 0.100 mmol), and Mes-*t*Bu-Acr$^+$ (2.9 mg, 0.005 mmol) in CH_2Cl_2/H_2O (9/1, 1.0 mL) was stirred for 24 h. The crude product was purified by column chromatography (silica gel, hexane/EtOAc = 30/1 to 15/1 to 7/1) to give **I** (18.9 mg, <37%) as a pale yellow oil: R_f = 0.17 (hexane/EtOAc = 5/1); IR (NaCl) 2956, 2871, 1752, 1593, 1493, 1456 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84–7.72 (m, 2H), 7.42–6.88 (m, 12H), 4.60 (dt, J = 4.4, 10.3 Hz, 1H, diastereomer A), 4.41 (dt, J = 3.4, 10.3 Hz, 1H, diastereomer B), 4.31 (ddd, J = 3.4, 9.6, 11.2 Hz, 1H, diastereomer C), 3.86–2.81 (m, 4H), 2.66–1.53 (m, 8H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.4, 201.2, 174.9, 174.2, 173.6, 173.3, 173.0, 172.3, 171.7, 171.6, 171.5, 166.3, 166.2, 165.6, 164.8, 153.2, 153.1, 153.0, 150.8 (2C), 150.6 (2C), 150.5, 150.4, 135.4 (2C), 129.6, 129.4, 129.3 (2C), 129.6, 129.1, 126.1, 126.0 (2C), 125.9, 125.8, 125.7 (3C), 125.6, 125.5, 124.4, 124.3, 121.9, 121.7, 121.6, 121.5 (3C), 121.4, 121.0, 120.9, 54.8, 53.9, 53.2, 52.7, 51.4, 51.0, 49.3, 48.5, 48.4, 48.2, 48.0, 47.8, 47.0, 46.6, 45.9, 43.5, 32.2, 31.9, 31.7 (2C), 31.6, 31.3, 30.7, 30.6, 30.4, 30.3, 30.2, 30.0 (2C), 29.7, 29.6, 29.1 (2C), 28.7, 26.8, 25.9, 25.7, 25.2, 24.9, 24.0, 23.7, 22.9. HRMS (ESI) calcd. for $C_{29}H_{27}NNaO_4S_2$ $[M+Na]^+$ 540.1274; found 540.1279.

General procedure for the synthesis of γ,γ-disubstituted-α-amino acid derivatives

All the experiments for the synthesis of γ,γ-disubstituted-α-amino acid derivatives were performed as described in the following typical procedure. The synthesis of **4a** was exemplified as follows.

Synthesis and characterization of 7-benzyl 1-methyl 2-(bis(*tert*-butoxycarbonyl)amino)-4-isopropylheptanedioate (4a)

3x (48.0 mg, 0.0915 mmol), benzyl acrylate (22.9 mg, 0.137 mmol), HEH-$(OH)_2$ (52.2 mg, 0.183 mmol), 4DPAIPN (0.7 mg, 0.00092 mmol), and potassium carbonate (25.8 mg, 0.183 mmol) were dissolved in DMSO (0.9 mL). The mixture was degassed by three freeze-pump-thaw cycles. Afterward, the mixture was stirred and irradiated with blue LEDs for 24 h. The reaction was then quenched by addition of saturated aqueous NH_4Cl (15 mL), and the resulting mixture was extracted with EtOAc (15 mL). The organic extract was washed with water (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 = 15/1 to 8/1 to 5/1) to give **4a** (24.5 mg, 51%, 71:29 d.r.) as a pale yellow oil: R_f = 0.33 (hexane/EtOAc = 5/1); IR (NaCl) 2958, 1791, 1742, 1699, 1456 cm^{-1}; ^1H NMR (400 MHz, CD_3OD) δ 7.36–7.27 (m, 5H), 5.14–5.04 (m, 2H), 4.93 (dd, J = 4.7, 10.1 Hz, 1H), 3.69 (s, 3H), 2.46–2.23 (m, 2H), 2.10 (m, 1H, minor isomer), 1.95 (m, 1H, major isomer), 1.83–1.62 (m, 4H), 1.47 (s, 18H), 1.43–1.04 (m, 2H), 0.88–0.81 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.6, 173.5, 171.7, 171.6, 152.1, 152.1, 136.1 (2C), 128.5 (2C), 128.2, 128.1 (2C), 83.1, 83.0, 66.1 (2C), 56.6, 56.5, 52.1, 40.0 (2C), 32.6, 32.2, 31.0, 30.0, 28.7, 28.6, 28.0, 27.9, 25.7, 24.8, 19.7 (2C), 17.9, 17.4. HRMS (ESI) calcd. for $C_{28}H_{43}NNaO_8$ $[M+Na]^+$ 544.2881 found 544.2861.

Synthesis and characterization of methyl 2-(bis(*tert*-butoxycarbonyl)amino)-6-cyano-4-

isopropylhexanoate (4b)

According to the synthetic procedure for **4a**, a suspension of **3x** (55.2 mg, 0.105 mmol), acrylonitrile (8.5 mg, 0.158 mmol), HEH-$(OH)_2$ (59.9 mg, 0.211 mmol), 4DPAIPN (0.8 mg, 0.0010 mmol), and potassium carbonate (29.6 mg, 0.211 mmol) in DMSO (1.1 mL) was stirred at room temperature for 24 h. The crude product was purified by column chromatography (hexane/EtOAc = 30/1 to 20/1 to 10/1 to 5/1) to give **4b** (24.5 mg, 57%, 62:38 d.r.) as a pale yellow solid: R_f = 0.35 (hexane/EtOAc = 3/1); m.p. 116.4–127.9 ºC; IR (KBr) 3000, 2963, 2244, 1732, 1692, 1459 cm^{-1}; ^1H NMR (400 MHz, CD_3OD) δ 4.94 (m, 1H), 3.722 (s, 3H, major isomer), 3.718 (s, 3H, minor isomer), 2.43 (m, 2H), 2.13 (ddd, J = 5.1, 8.1, 13.3 Hz, minor isomer), 1.97 (ddd, J = 3.9, 10.0, 14.5 Hz, 1H, major isomer), 1.87–1.60 (m, 4H), 1.513 (s, 18H, minor isomer), 1.507 (s, 18H, major isomer), 1.33 (m, 1H) 0.93–0.85 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.5, 171.4, 152.4, 152.2, 119.9, 119.7, 83.4, 56.3, 56.2, 52.3, 39.9, 39.7, 30.7, 29.8, 28.43, 28.36, 28.0, 26.5, 25.8, 19.7, 19.5, 17.7, 17.3, 15.5, 15.3. HRMS (ESI) calcd. for $C_{21}H_{36}N_2NaO_6$ $[M+Na]^+$ 435.2466; found 435.2441.

Synthesis and characterization of 7-benzyl 1-methyl 2-(bis(*tert*-butoxycarbonyl)amino)-4-cyclohexylheptanedioate (4c)

According to the synthetic procedure for **4a**, a suspension of **3y** (39.7 mg, 0.0703 mmol), benzyl acrylate (17.6 mg, 0.105 mmol), HEH-$(OH)_2$ (40.2 mg, 0.141 mmol), 4DPAIPN (0.6 mg, 0.00070 mmol), and potassium carbonate (19.9 mg, 0.141 mmol) in DMSO (0.7 mL) was stirred at room temperature for 24 h. The crude product was purified by column chromatography (silica gel, hexane/EtOAc = 15/1 to 8/1 to 5/1) to give **4c** (14.7 mg, 37%, 88:12 d.r.) as a pale yellow oil: R_f = 0.29 (hexane/EtOAc = 5/1); IR (NaCl) 3021, 2982, 2929, 2854, 1789, 1739, 1487, 1456 cm^{-1}; ^1H NMR (400 MHz, CD_3OD) δ 7.36–7.30 (m, 5H), 5.11–5.07 (m, 2H), 4.92 (dd, J = 4.5, 10.2 Hz, 1H), 3.70 (s, 3H), 2.46–2.22 (m, 2H), 2.13 (m, 1H, minor isomer), 1.99 (m, 1H, major isomer), 1.85–1.60 (m, 7H), 1.48–1.44 (m, 20H), 1.40–0.89 (m, 6H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.6, 171.7, 152.1, 149.7, 136.1, 128.5, 128.2, 128.1, 83.0, 82.0, 66.1 (2C), 56.8, 56.6, 52.2, 39.8, 39.7, 39.6, 39.5, 32.7, 32.3, 31.0, 30.5, 30.3, 30.2, 28.6, 28.2, 28.0 (2C), 26.7 (2C), 25.7, 25.6. HRMS (ESI) calcd. for $C_{31}H_{47}NNaO_8$ $[M+Na]^+$ 584.3194; found 584.3183.

Synthesis and characterization of methyl 2-(bis(*tert*-butoxycarbonyl)amino)-6-cyano-4-cyclohexylhexanoate (4d)

According to the synthetic procedure for **4a**, a suspension of **3y** (38.3 mg, 0.0678 mmol), acrylonitrile (5.5 mg, 0.102 mmol), HEH-$(OH)_2$ (38.7 mg, 0.136 mmol), 4DPAIPN (0.5 mg, 0.00068 mmol), and potassium carbonate (19.2 mg, 0.136 mmol) in DMSO (0.7 mL) was stirred at room temperature for 24 h. The crude product was purified by column chromatography (silica gel, hexane/EtOAc = 30/1 to 20/1 to 10/1 to 5/1) to give **4d** (13.2 mg, 43%, 72:28 d.r.) as a pale yellow solid: R_f = 0.35 (hexane/EtOAc = 3/1); m.p. 80.2–84.0 ºC; IR (NaCl) 3033, 2981, 2929, 2854, 2251, 1786, 1740, 1694, 1450 cm^{-1}; ^{1}H NMR (400 MHz, CD_3OD) δ 4.93 (m, 1H), 3.71 (s, 3H), 2.53–2.28 (m, 2H), 2.15 (ddd, J = 5.0, 8.5, 13.6 Hz, 1H, minor isomer), 1.99 (ddd, J = 4.1, 10.0, 14.5 Hz, 1H, major isomer), 1.87–1.65 (m, 7H), 1.503 (s, 18H, minor isomer), 1.499 (s, 18H, major isomer), 1.34–0.96 (m, 8H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.5 (2C), 152.4, 152.2, 119.9, 119.7, 83.3, 56.5, 56.4, 52.3, 39.8, 39.6, 39.4, 39.3, 30.7, 30.4, 30.3, 30.1, 28.5, 28.2, 28.0, 26.7, 26.6 (3C), 15.6, 15.4. HRMS (ESI) calcd. for $C_{24}H_{40}N_2NaO_6$ $[M+Na]^+$ 475.2779; found 475.2779.

Synthesis and characterization of 7-benzyl 1-methyl 2-(bis(*tert*-butoxycarbonyl)amino)-4-(2-(*tert*-butoxy)-2-oxoethyl)heptanedioate (4e)

According to the synthetic procedure for **4a**, a suspension of **3z** (83.5 mg, 0.140 mmol), benzyl acrylate (35.1 mg, 0.210 mmol), HEH-$(OH)_2$ (79.9 mg, 0.280 mmol), 4DPAIPN (1.1 mg, 0.0014 mmol), and potassium carbonate (39.5 mg, 0.280 mmol) in DMSO (1.4 mL) was stirred at room temperature for 24

h. The crude product was purified by column chromatography (silica gel, hexane/EtOAc = 15/1 to 8/1 to 5/1 and 10/1 to 5/1 to 2/1 and 50/1 to 20/1 to 10/1) to give **4e** (59.6 mg, 72%, 58:42 d.r.) as a pale yellow oil: R_f = 0.11 (hexane/EtOAc = 5/1); IR (NaCl) 3029, 3010, 2981, 2935, 1789, 1736, 1477, 1456 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.38-7.28 (m, 5H), 5.10 (m, 2H), 4.99 (dd, *J* = 4.9, 9.7 Hz, 1H, minor-isomer), 4.91 (dd, *J* = 5.3, 8.2 Hz, 1H, major-isomer), 3.70 (s, 3H), 2.47–1.65 (m, 9H), 1.49 (s, 18H), 1.42 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.1, 173.0, 171.5, 171.4, 171.3, 171.2, 152.0 (2C), 137.8, 136.0, 129.0, 128.4, 128.3, 128.2, 128.1 (2C), 125.2, 83.2 (2C), 80.4, 80.3, 66.1 (2C), 56.0, 55.8, 52.2 (2C), 39.7, 38.6, 34.2, 33.3, 32.1, 31.7, 31.6, 31.2, 29.0, 28.0, 27.9, 21.4. HRMS (ESI) calcd. for $C_{31}H_{47}NNaO_{10}$ $[M+Na]^+$ 616.3092 found 616.3088.

Synthesis and characterization of 6-(*tert*-butyl) 1-methyl 2-(bis(*tert*-butoxycarbonyl)amino)-4-(2-cyanoethyl)hexanedioate (4f)

According to the synthetic procedure for **4a**, a suspension of **3z** (64.5 mg, 0.108 mmol), acrylonitrile (8.8 mg, 0.162 mmol), HEH-$(OH)_2$ (61.6 mg, 0.216 mmol), 4DPAIPN (0.9 mg, 0.0011 mmol), and potassium carbonate (30.5 mg, 0.216 mmol) in DMSO (1.1 mL) was stirred at room temperature for 24 h. The crude product was purified by column chromatography (silica gel, hexane/EtOAc = 30/1 to 20/1 to 10/1 to 5/1) to give **4f** (33.0 mg, 63%, 55:45 d.r.) as a pale yellow oil: R_f = 0.33 (hexane/EtOAc = 3/1); IR (NaCl) 2983, 2934, 2248, 1789, 1737, 1476, 1451 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.99 (dd, *J* = 4.8, 9.7 Hz, 1H, minor isomer), 4.87 (dd, *J* = 5.9, 7.5 Hz,1H, major isomer), 3.72 (s, 3H), 2.46–2.30 (m, 3H), 2.27–2.17 (m, 1H), 2.13–1.90 (m, 2H), 1.85–1.63 (m, 3H), 1.51 (s, 18H), 1.45 (s, 9H, minor isomer), 1.44 (s, 9H, major isomer); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1 (2C), 171.0, 152.3, 152.1, 119.5, 119.3, 83.5, 80.9, 80.8, 55.8, 55.6, 52.4, 39.4, 38.1, 34.2, 32.9, 32.2, 31.4, 29.8, 29.1, 28.1, 28.0 (2C), 14.7, 14.6. HRMS (ESI) calcd. for $C_{24}H_{40}N_2NaO_8$ $[M+Na]^+$ 507.2677; found 507.2679.

Synthesis and characterization of 7-benzyl 1-methyl 2-(bis(*tert*-butoxycarbonyl)amino)-4-((bis(*tert*-butoxycarbonyl)amino)methyl)heptanedioate (4g)

According to the synthetic procedure for **4a**, a suspension of **3aa** (62.8 mg, 0.0882 mmol), benzyl acrylate (22.1 mg, 0.132 mmol), HEH-$(OH)_2$ (50.3 mg, 0.176 mmol), 4DPAIPN (0.7 mg, 0.00088 mmol), and potassium carbonate (24.9 mg, 0.176 mmol) in DMSO (0.9 mL) was stirred at room temperature for 24 h. The crude product was purified by column chromatography (silica gel, hexane/EtOAc = 15/1 to 8/1 to 5/1) to give **4g** (53.6 mg, 86%, 82:18 d.r.) as a pale yellow oil: R_f = 0.20 (hexane/EtOAc = 5/1); IR (NaCl) 3031, 2980, 2935, 1787, 1743, 1697, 1478, 1456 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.36–7.29 (m, 5H), 5.10 (s, 2H, major isomer), 5.09 (s, 2H, minor isomer), 5.00 (m, 1H), 3.69 (s, 3H, major isomer), 3.68 (s, 3H, minor isomer), 3.57 (m, 2H), 2.42 (m, 2H), 2.22 (m, 1H, minor isomer), 2.06 (m, 1H, major isomer), 1.83–1.63 (m, 4H), 1.48 (s, 36H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.2, 173.1, 171.3, 171.2, 153.1, 152.4, 152.0, 151.8, 136.0, 128.4, 128.2, 128.1 (3C), 83.2, 83.1, 82.3, 82.2, 66.1, 66.0, 56.1, 55.6, 52.1 (2C), 49.1, 48.6, 35.2, 34.6, 32.1, 31.8, 31.5, 31.1, 28.0, 27.9, 26.4, 25.9. HRMS (ESI) calcd. For $C_{36}H_{56}N_2NaO_{12}$ $[M+Na]^+$ 731.3725 found 731.3732.

Synthesis and characterization of methyl 2-(bis(*tert*-butoxycarbonyl)amino)-4-((bis(*tert*-butoxycarbonyl)amino)methyl)-6-cyanohexanoate (4h)

According to the synthetic procedure for **4a**, a suspension of **3aa** (51.3 mg, 0.0721 mmol), acrylonitrile (5.9 mg, 0.108 mmol), HEH-$(OH)_2$ (41.1 mg, 0.144 mmol), 4DPAIPN (0.6 mg, 0.00072 mmol), and potassium carbonate (20.3 mg, 0.144 mmol) in DMSO (0.7 mL) was stirred at room temperature for 24 h. The crude product was purified by column chromatography (silica gel, hexane/EtOAc = 30/1 to 20/1 to 10/1 to 5/1) to give **4h** (26.6 mg, 62%, 79:21 d.r.) as a pale yellow oil: R_f = 0.25 (hexane/EtOAc = 3/1); IR (NaCl) 2983, 2931, 2244, 1782, 1741, 1698, 1472, 1455 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.01 (dd, J = 5.8, 8.1 Hz, 1H, minor isomer), 4.94 (dd, J = 6.0, 7.7 Hz, 1H, major isomer), 3.72 (s 3H,

major isomer), 3.70 (s, 3H, minor isomer), 3.60 (m, 2H), 2.43 (m, 2H), 2.13 (m, 1H), 1.94–1.65 (m, 4H), 1.51 (s, 36H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 153.3, 152.7, 152.2, 152.0, 119.8, 119.7, 83.5, 83.4, 82.7 (2C), 55.9, 55.5, 52.3 (2C), 48.6, 47.7, 35.0, 32.0, 31.7, 28.0 (2C), 27.5, 27.2, 14.5, 14.3. HRMS (ESI) calcd. for $C_{29}H_{49}N_3NaO_{10}$ $[M+Na]^+$ 622.3310; found 662.3318.

Synthesis and characterization of 7-benzyl 1-methyl 2-(bis(*tert*-butoxycarbonyl)amino)-4-methylheptanedioate (4i)

According to the synthetic procedure for **4a**, a suspension of **3i** (29.5 mg, 0.0594 mmol), benzyl acrylate (14.8 mg, 0.0888 mmol), HEH-$(OH)_2$ (33.7 mg, 0.118 mmol), 4DPAIPN (0.5 mg, 0.000592 mmol), and potassium carbonate (16.7 mg, 0.118 mmol) in DMSO (0.6 mL) was stirred at room temperature for 45 h. The crude product was purified by column chromatography (silica gel, hexane/EtOAc = 20/1 to 10/1 to 5/1 to 2/1) to give **4i** (27.1 mg, 92%, 57:43 d.r.) as a pale yellow oil: R_f = 0.50 (hexane/EtOAc = 3/1); IR (NaCl) 2979, 2934, 1795, 1743, 1698, 1456 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.29 (m, 5H), 5.10 (m, 2H), 4.93 (m, 1H), 3.70 (d, J = 4.1 Hz, 3H), 2.38 (m, 2H), 2.17 (m, 1H, major isomer), 1.99 (m, 1H, minor isomer), 1.89–1.41 (m, 22H), 0.93 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.5 (2C), 171.7, 171.5, 152.1, 151.9, 149.7, 136.0 (2C), 128.5 (2C), 128.2, 128.1, 83.1 (2C), 82.0, 66.1, 56.3, 56.1, 52.2, 52.1, 37.3, 36.5, 32.2, 32.0, 31.9, 31.1, 29.9, 29.4, 28.0, 27.9, 19.6, 18.8. HRMS (ESI) calcd. for $C_{26}H_{39}NNaO_8$ $[M+Na]^+$ 516.2568; found 516.2566.

Synthesis and characterization of methyl 2-(bis(*tert*-butoxycarbonyl)amino)-6-cyano-4-methylhexanoate (4j)

According to the synthetic procedure for **4a**, a suspension of **3i** (42.4 mg, 0.0854 mmol), acrylonitrile (6.8 mg, 0.128 mmol), HEH-$(OH)_2$ (48.8 mg, 0.171 mmol), 4DPAIPN (0.7 mg, 0.000855 mmol), and potassium carbonate (24.1 mg, 0.171 mmol) in DMSO (0.9 mL) was stirred at room temperature for 45

h. The crude product was purified by column chromatography (silica gel, hexane/EtOAc = 20/1 to 10/1 to 5/1 to 2/1) to give **4j** (20.8 mg, 63%, 55:45 d.r.) as a pale yellow solid: R_f = 0.35 (hexane/EtOAc = 3/1); m.p. 56.8–58.5 ºC; IR (NaCl) 2975, 2877, 2240, 1730, 1692, 1454, 1420 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.93 (m, 1H), 3.72 (s, 3H), 2,37 (m, 2H), 2.18 (m, 1H, major isomer), 2.00 (m, 1H, minor isomer), 1.85 (m, 1H), 1.74–1.44 (m, 21H), 0.99 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4, 171.3, 152.3, 152.0, 119.7, 119.5, 83.3 (2C), 55.9, 55.8, 52.3 (2C), 37.0, 36.0, 32.7, 31.6, 29.7, 29.0, 28.0 (2C), 19.3, 18.4, 14.8 (2C). HRMS (ESI) calcd. for $C_{19}H_{32}N_2NaO_6$ $[M+Na]^+$ 407.2153; found 407.2145.

A 1 mmol-scale experiment for the synthesis of 4i

Benzothiazolyl ethyl sulfide (**1a**, 234 mg, 1.20 mmol), phenyl acrylate (**2a**, 301 mg, 1.00 mmol), sodium trifluoroacetate (27.8 mg, 0.200 mmol), and photocatalyst (Mes-*t*Bu-Acr^+, 29.0 mg, 0.05 mmol) were dissolved in CH_2Cl_2/H_2O (9/1, 10.0 mL). The mixture was degassed by three freeze-pump-thaw cycles. Afterward, the mixture was stirred and irradiated with blue LEDs for 20 h. During the reaction, the temperature of the oil bath was controlled to be in the range of 35 °C to 40 °C. The reaction mixture was diluted with CH_2Cl_2 (15 mL), and the organic extract was washed with 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 = 30/1 to 15/1 to 10/1 to 8/1) to give **3i** (468 mg, 94%) as a pale yellow oil.

3i (468.0 mg, 0.942 mmol), benzyl acrylate (236 mg, 1.41 mmol), HEH-$(OH)_2$ (536 mg, 1.88 mmol), 4DPAIPN (7.5 mg, 0.00942 mmol), and potassium carbonate (265 mg, 1.88 mmol) were dissolved in DMSO (9.4 mL). The mixture was degassed by three freeze-pump-thaw cycles. Afterward, the mixture was stirred and irradiated with blue LEDs for 24 h. The reaction was then quenched by addition of saturated aqueous NH_4Cl (50 mL), and the resulting mixture was extracted with EtOAc (50 mL). The organic extract was washed with water (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 = 20/1 to 10/1 to 5/1) to give **4i** (387 mg, 83%, 57:43 d.r.) as a pale yellow oil.

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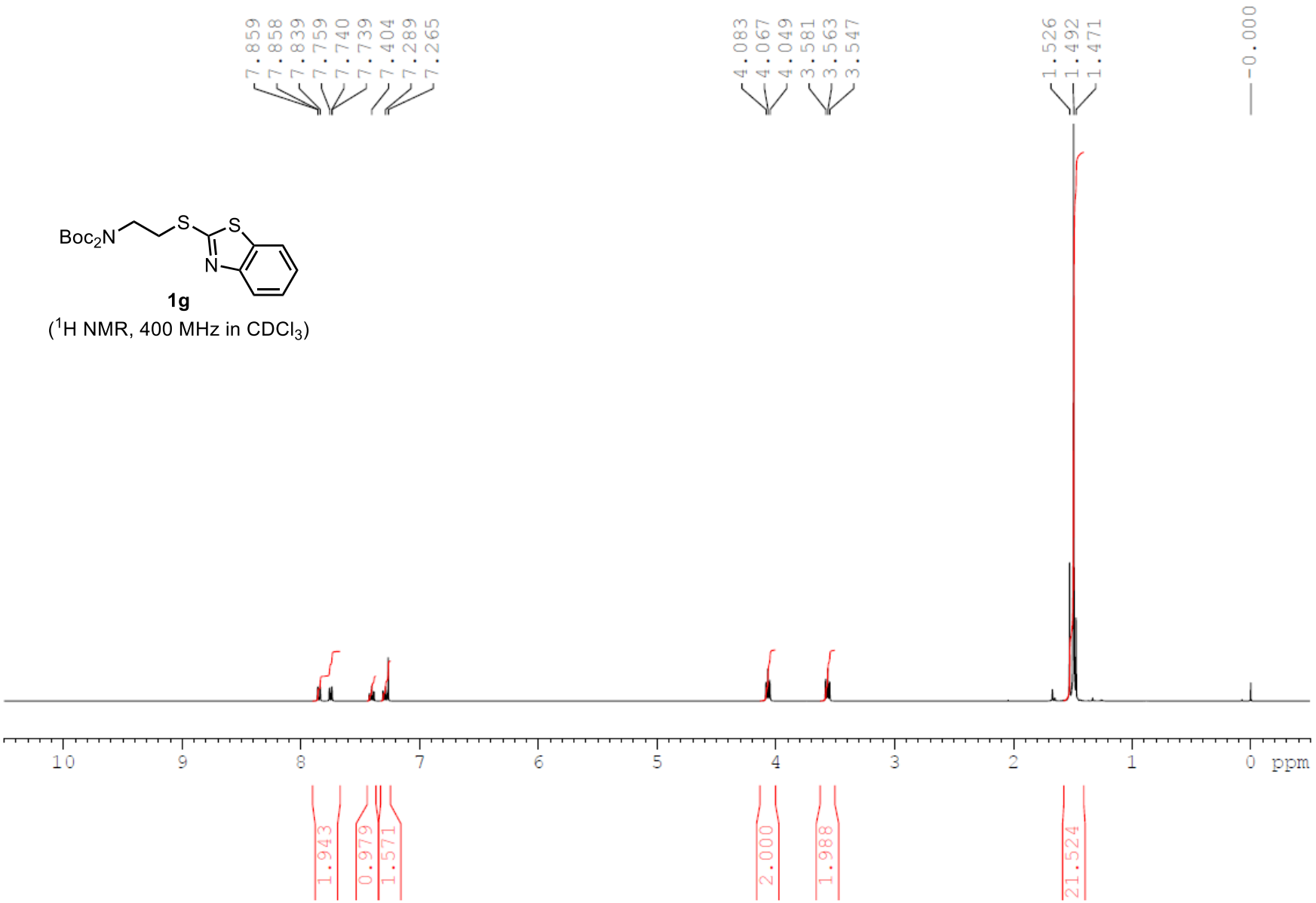

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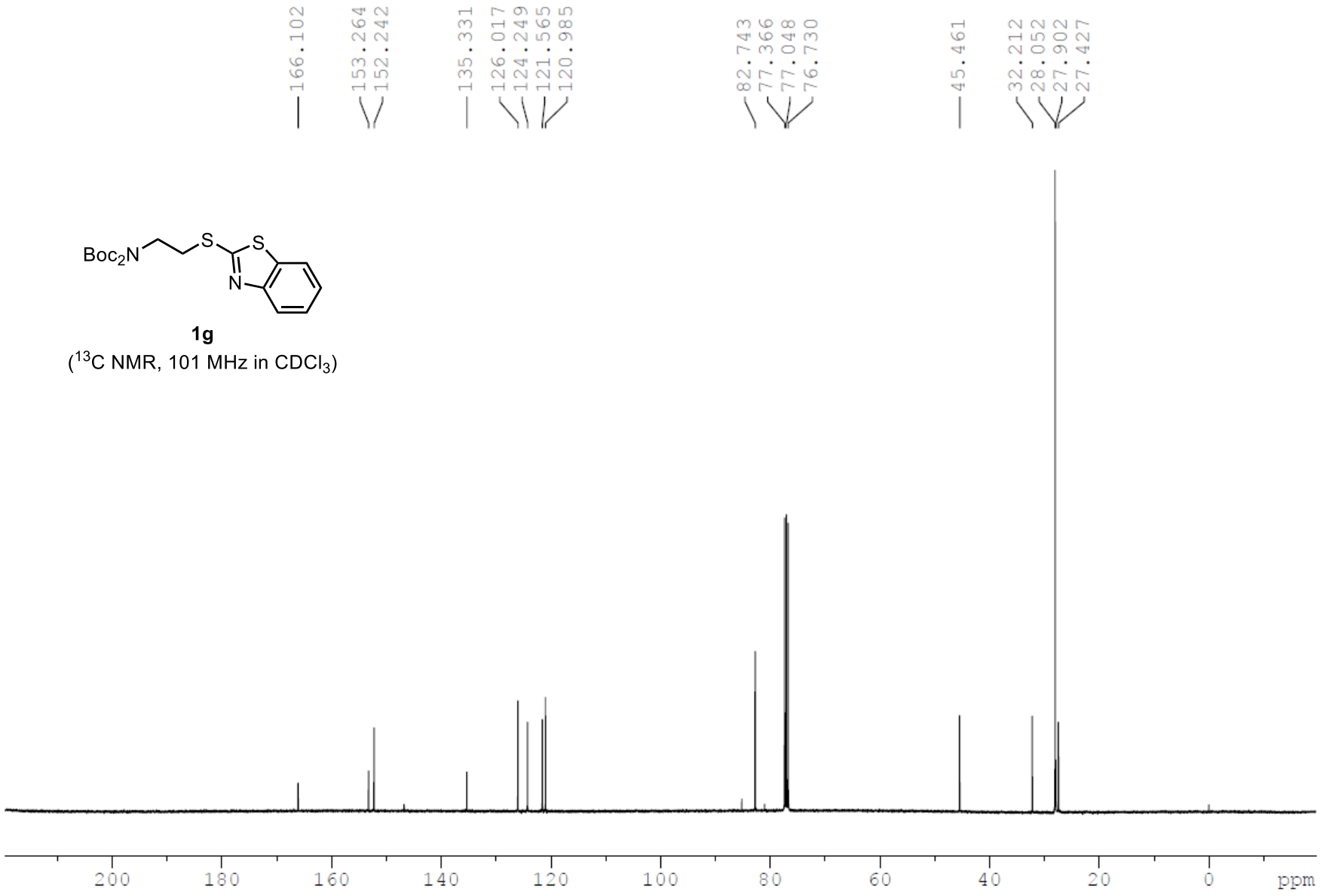

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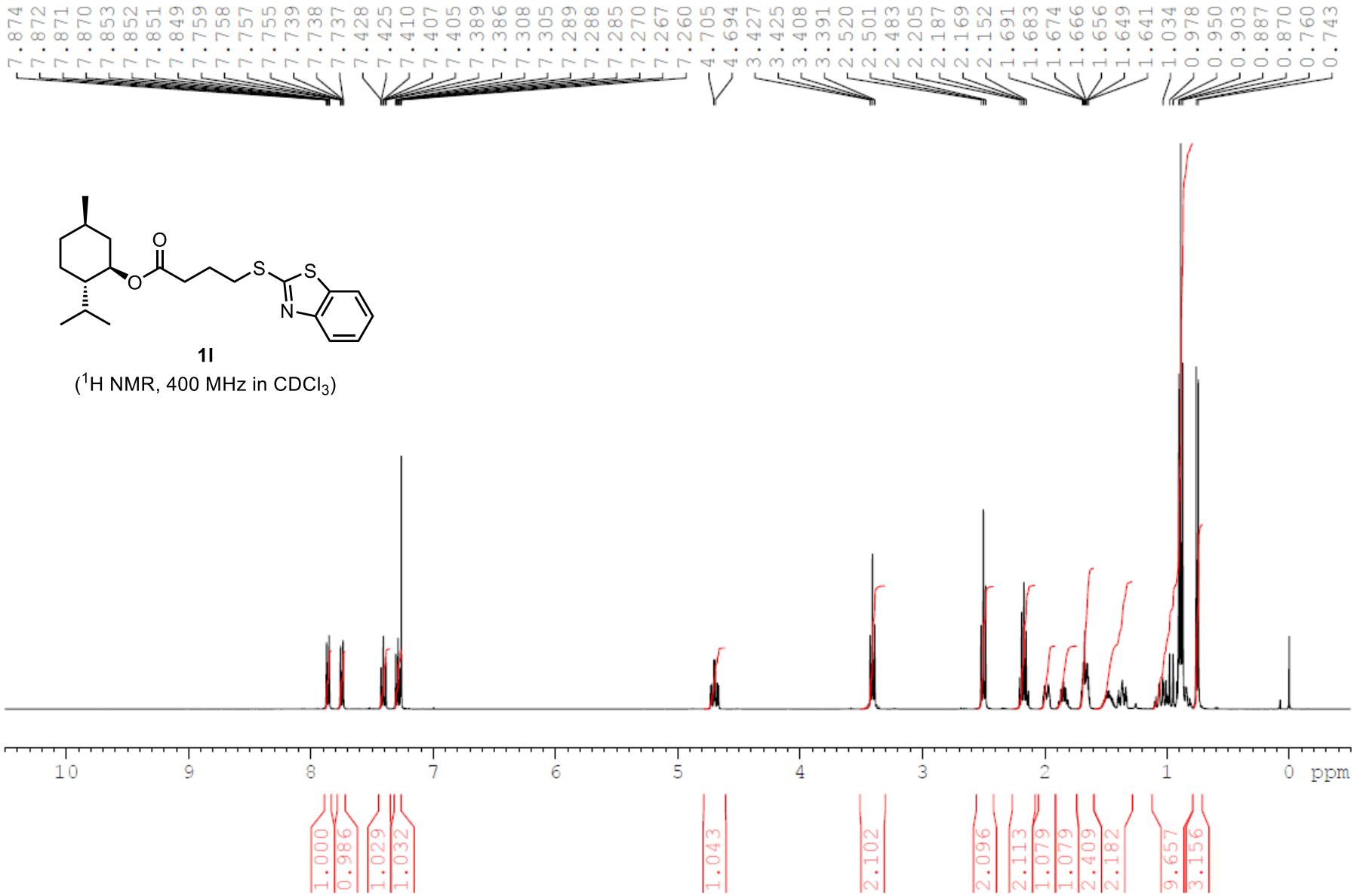

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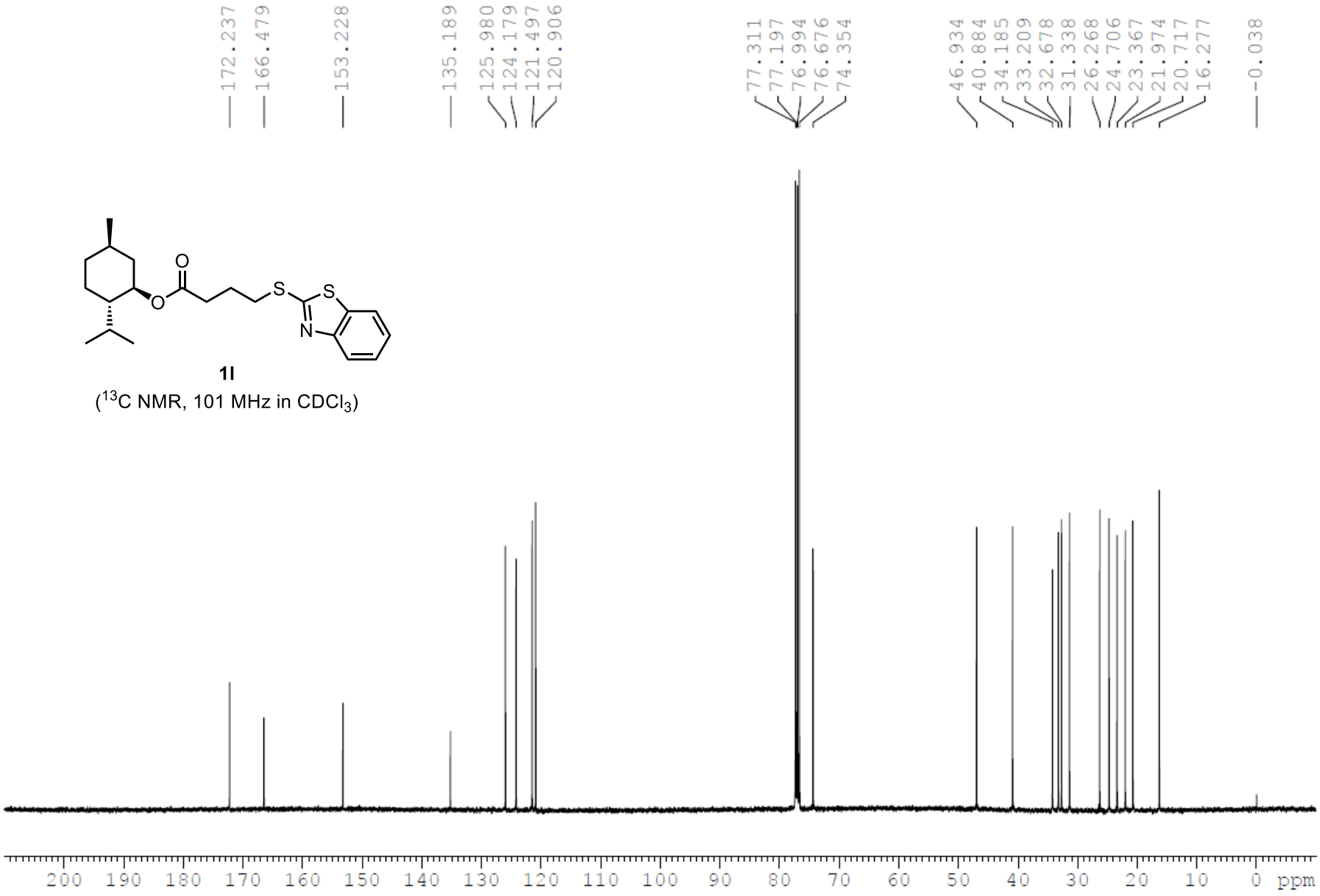

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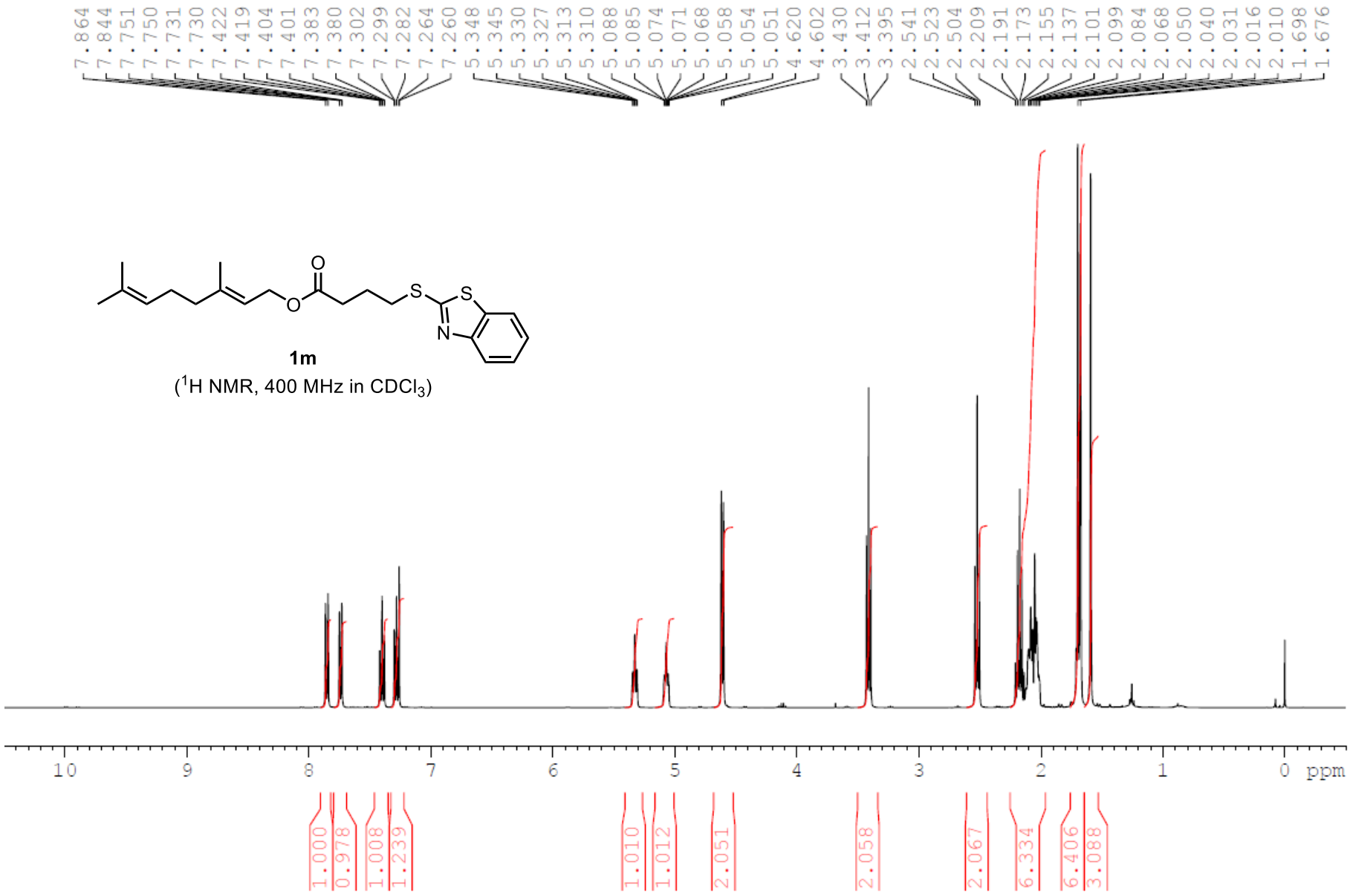

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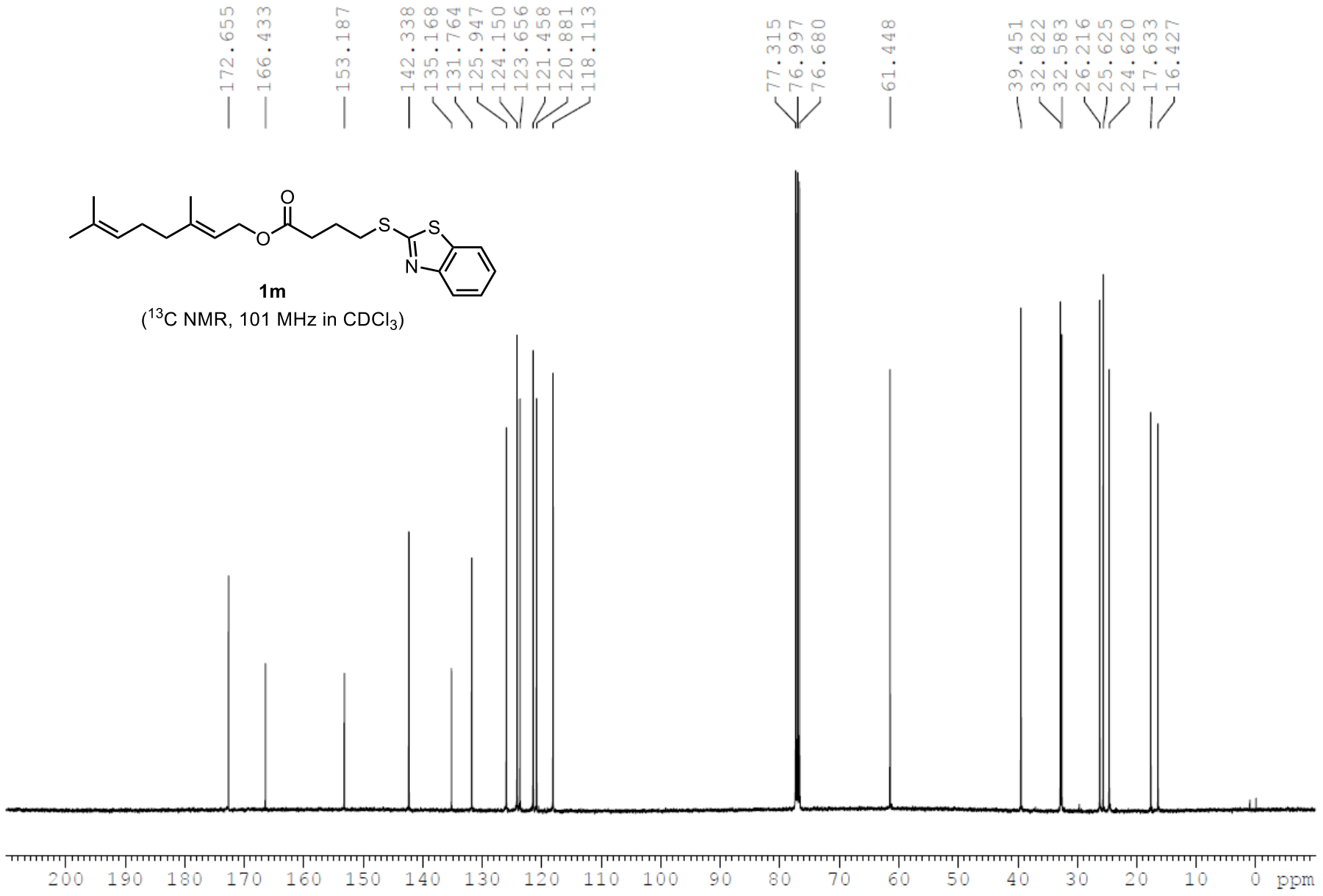

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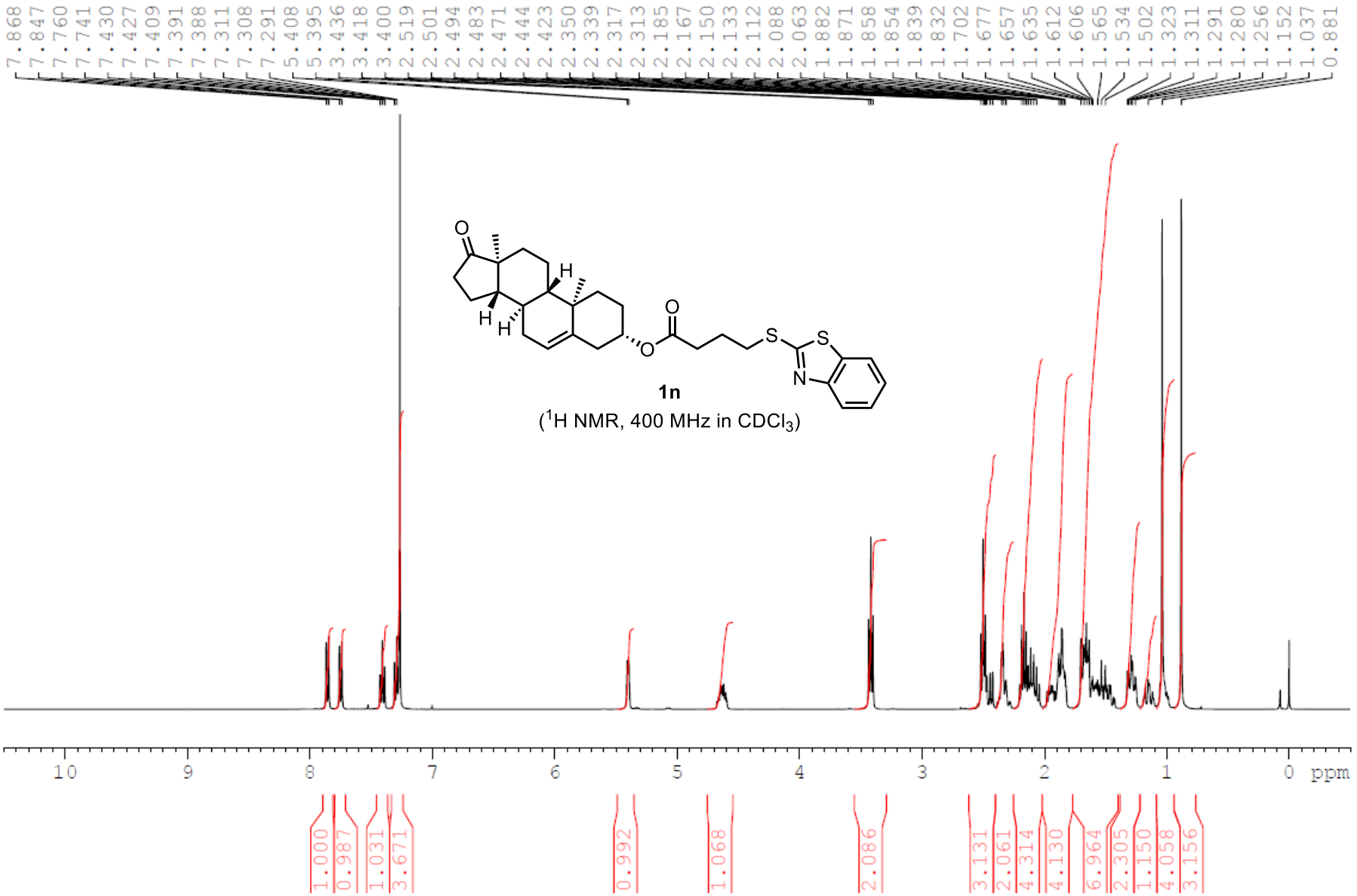

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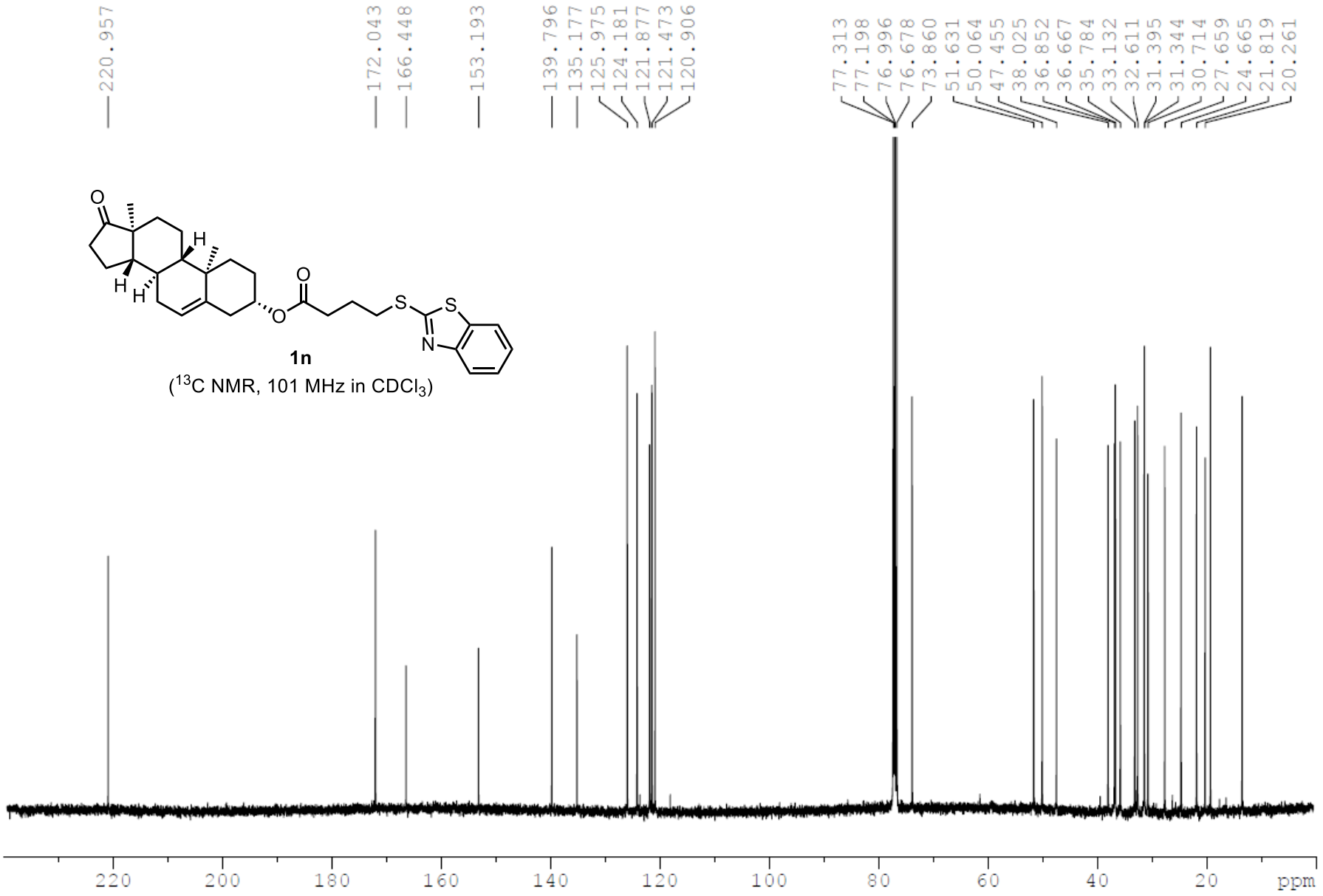

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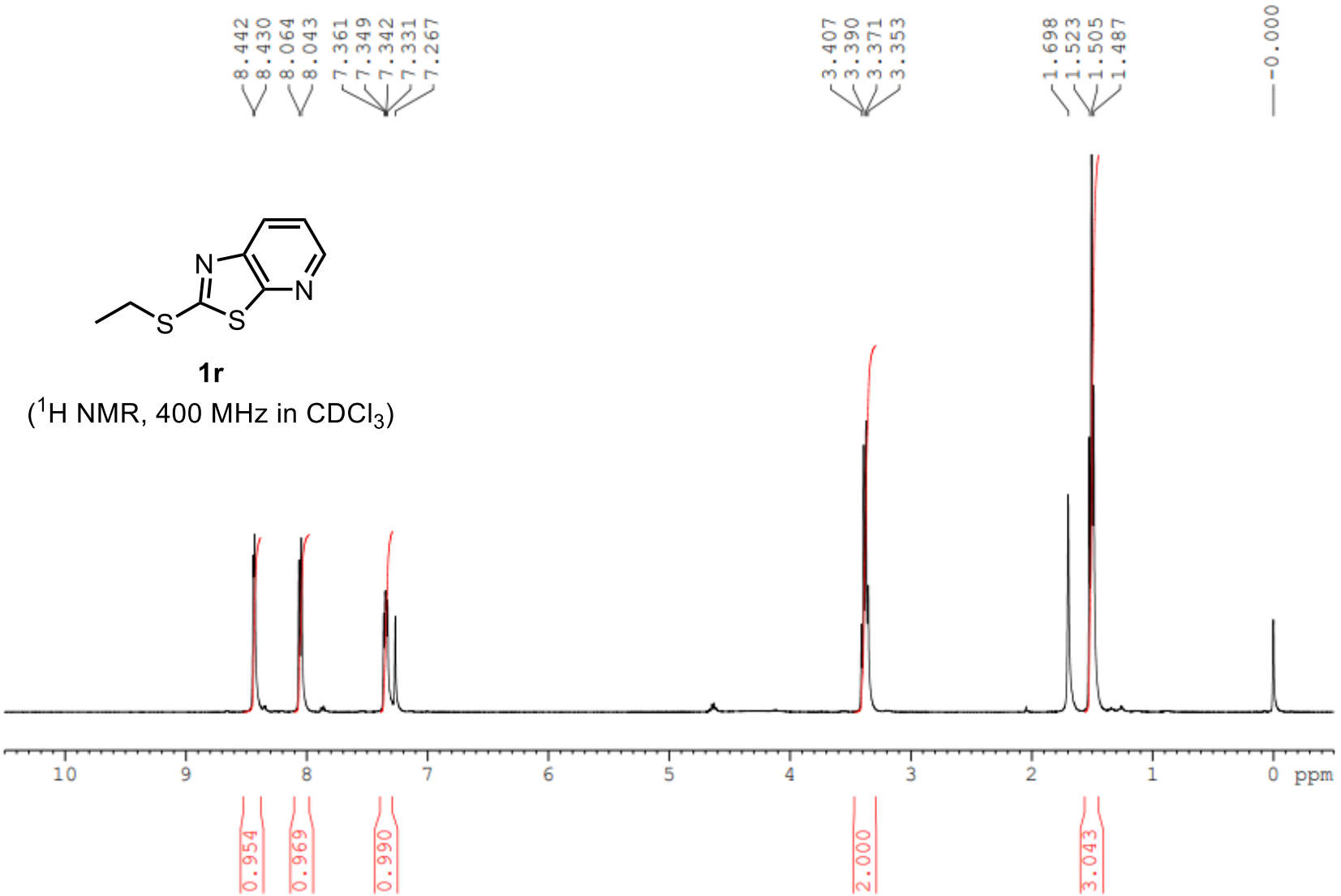

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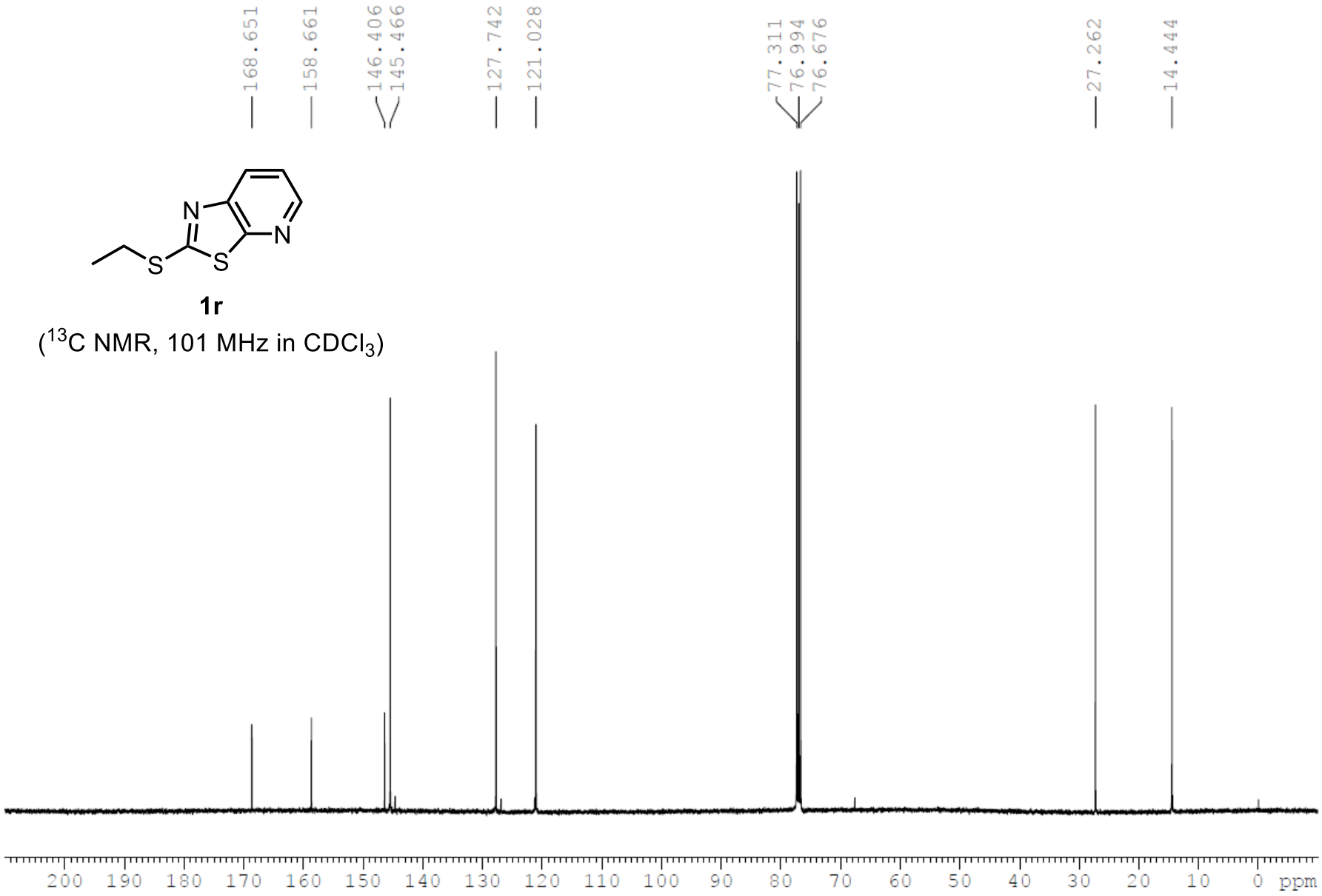
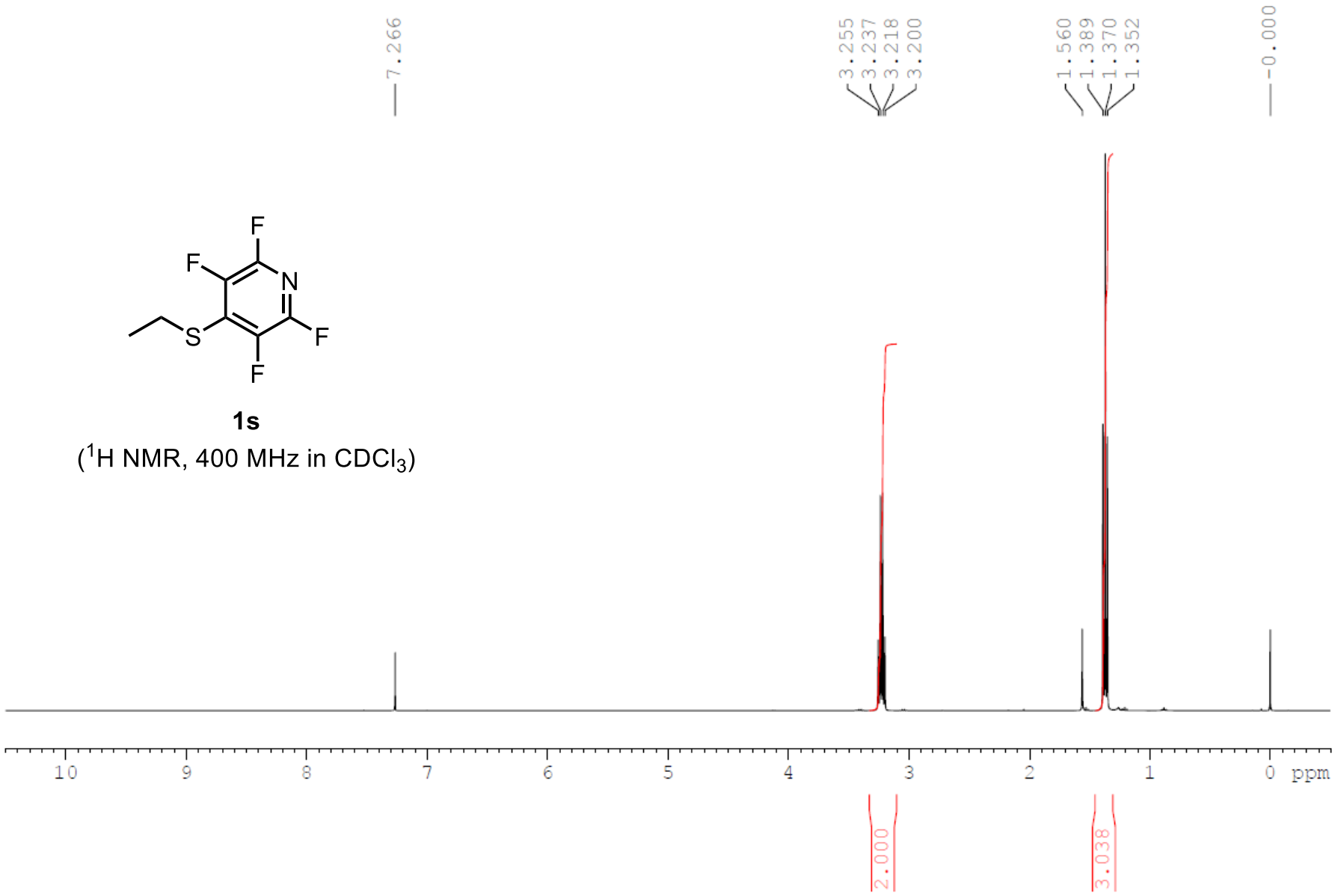


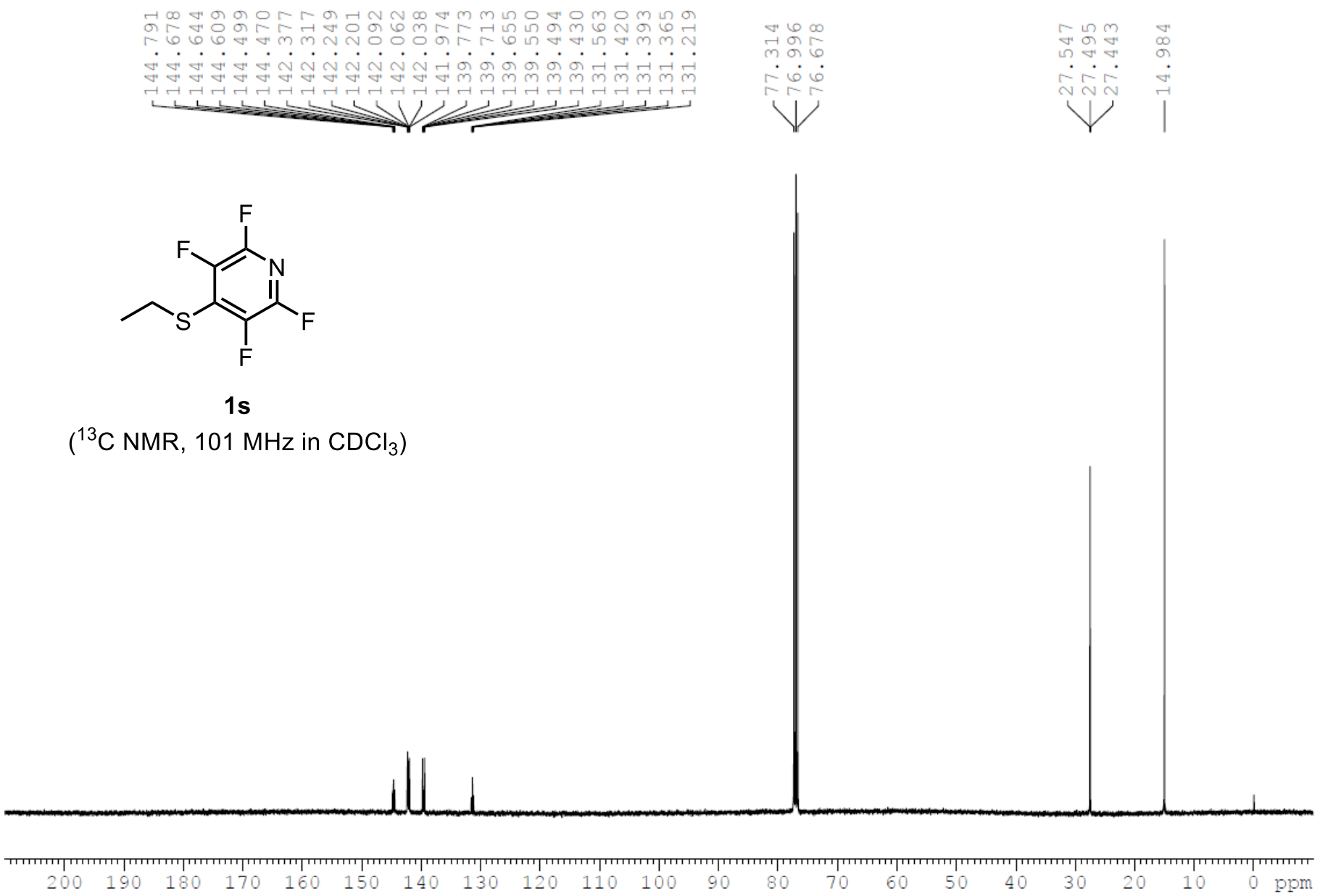
1r

(^{13}C NMR, 101 MHz in $CDCl_3$)



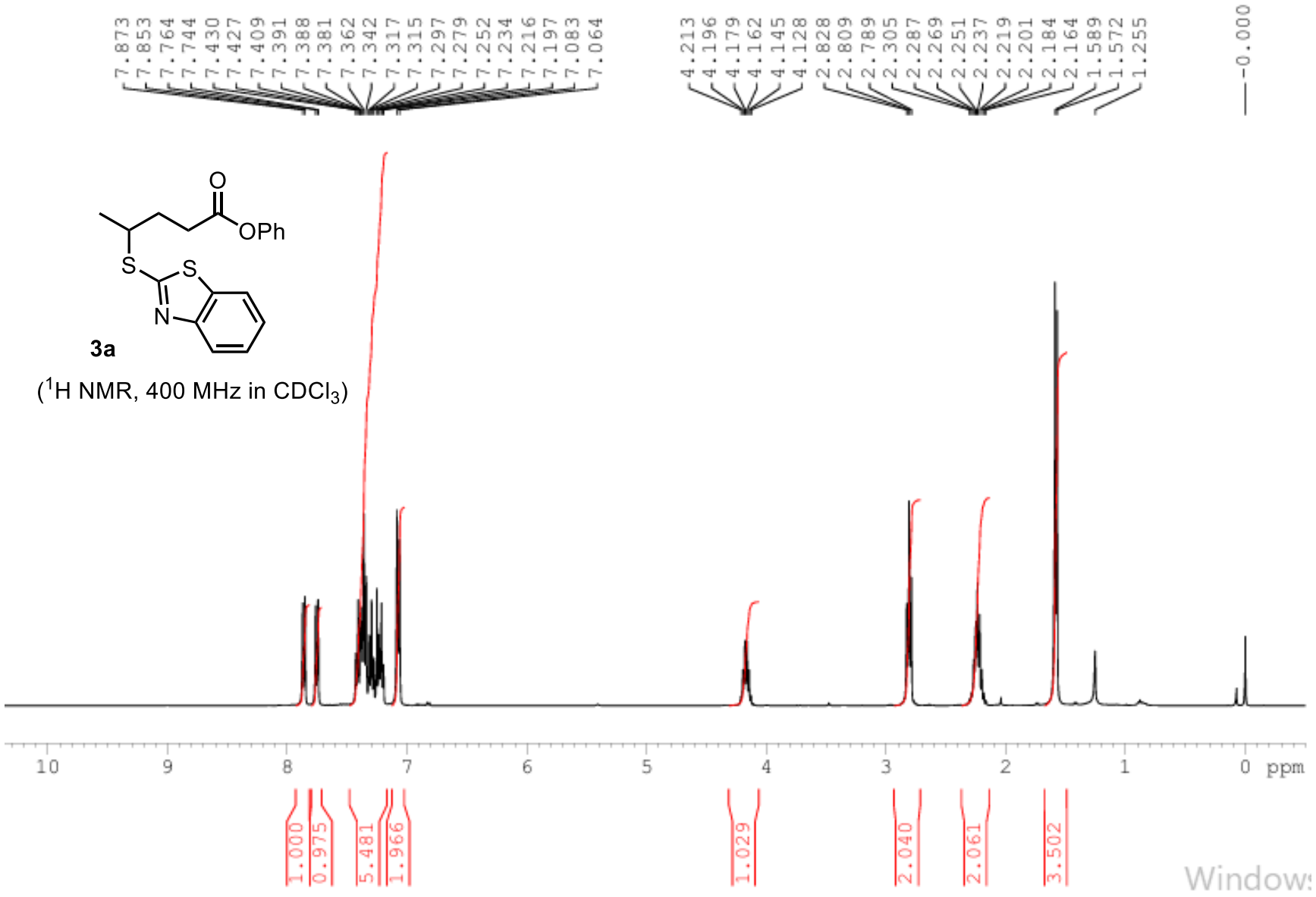
1s

(^{1}H NMR, 400 MHz in $CDCl_3$)



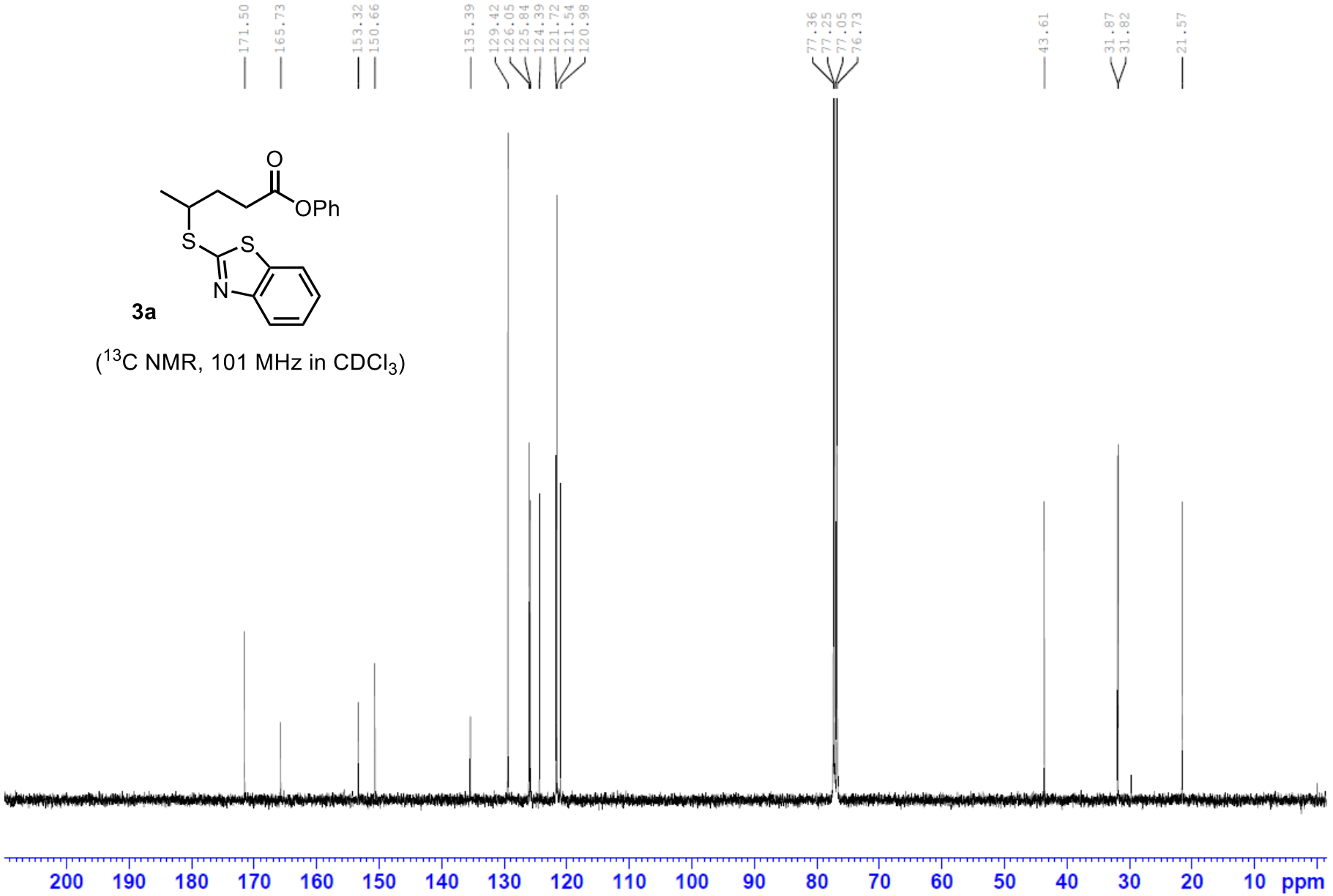
1s

(^{13}C NMR, 101 MHz in $CDCl_3$)



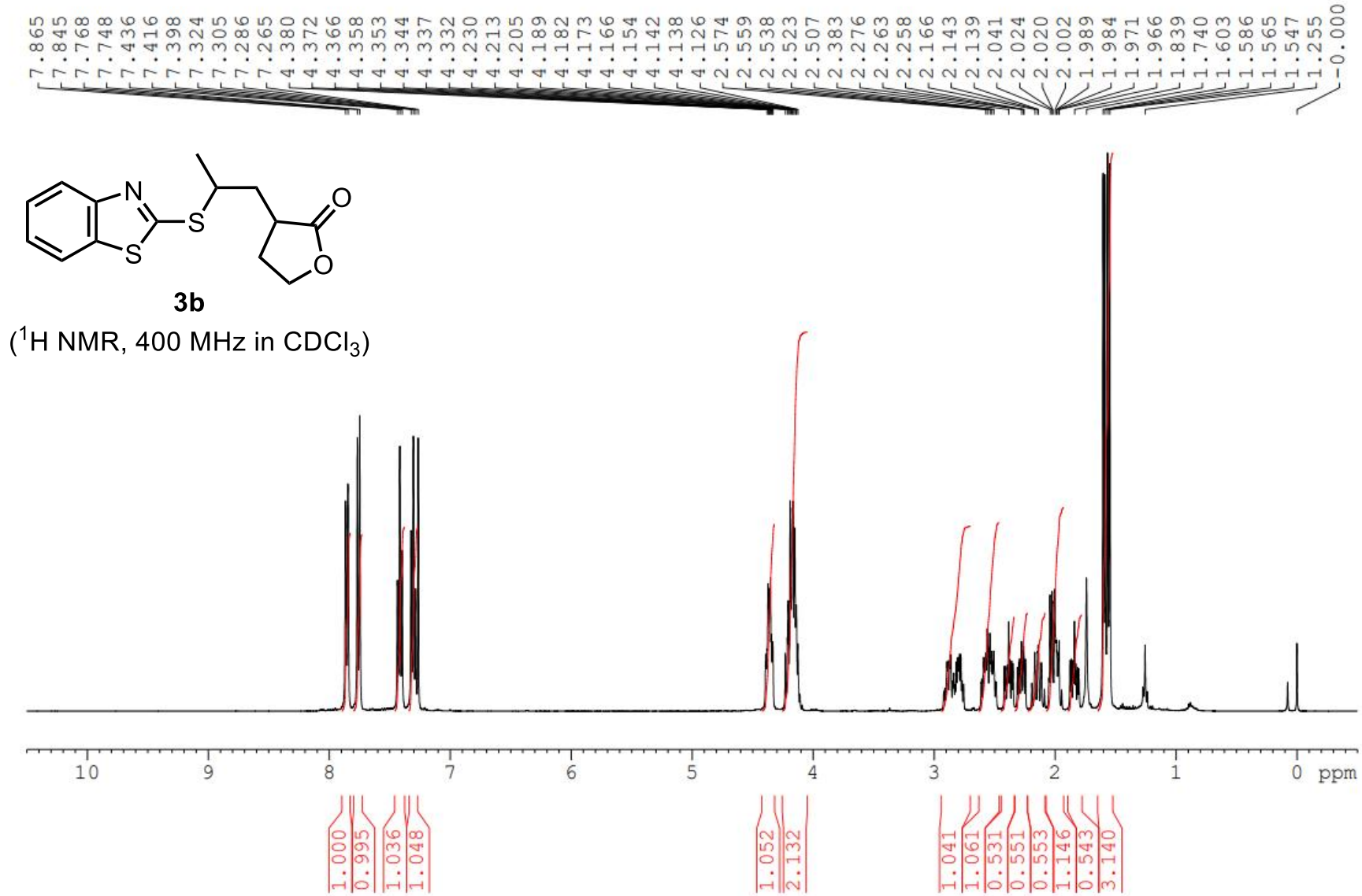
3a

(^{1}H NMR, 400 MHz in $CDCl_3$)



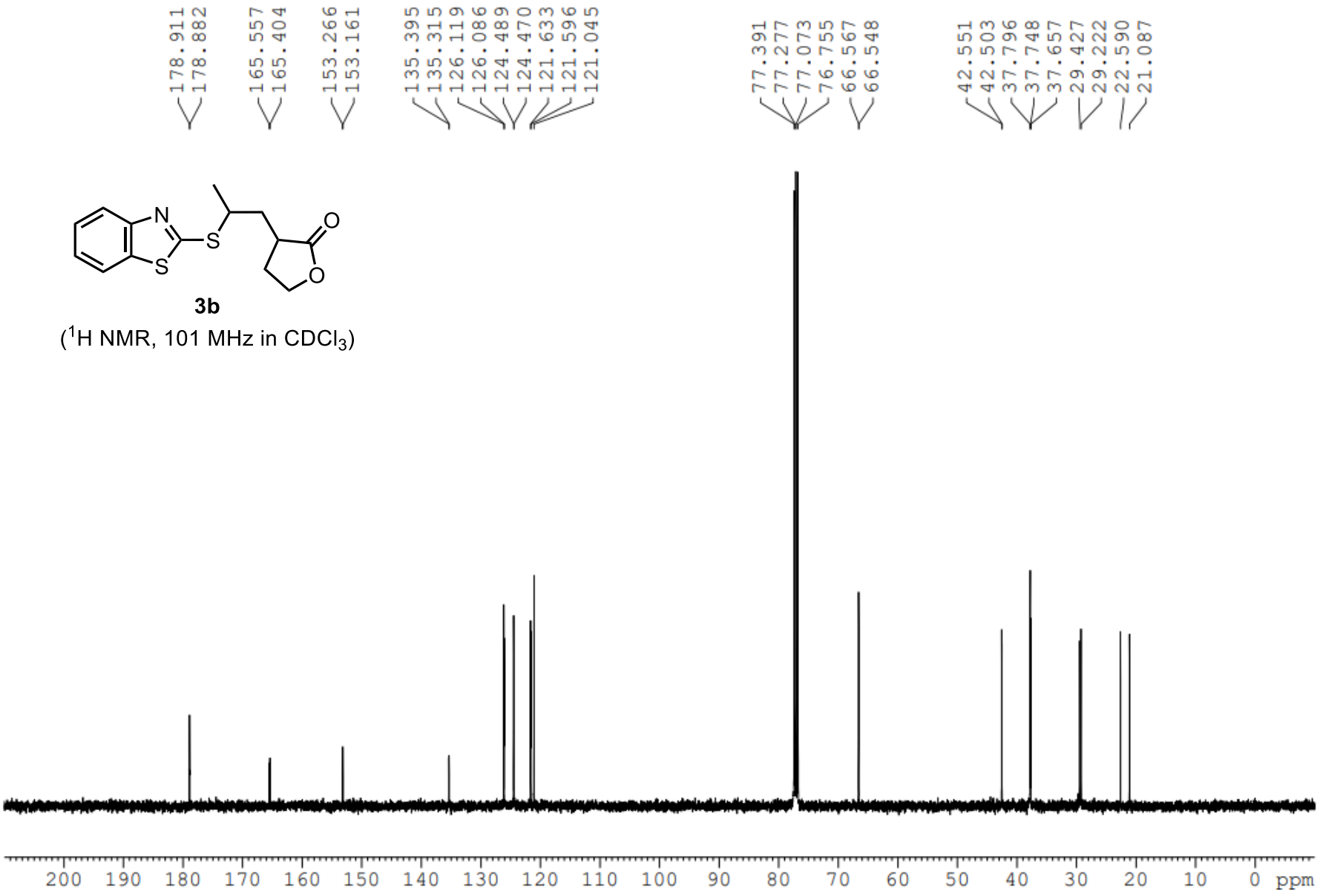
3a

(^{13}C NMR, 101 MHz in $CDCl_3$)



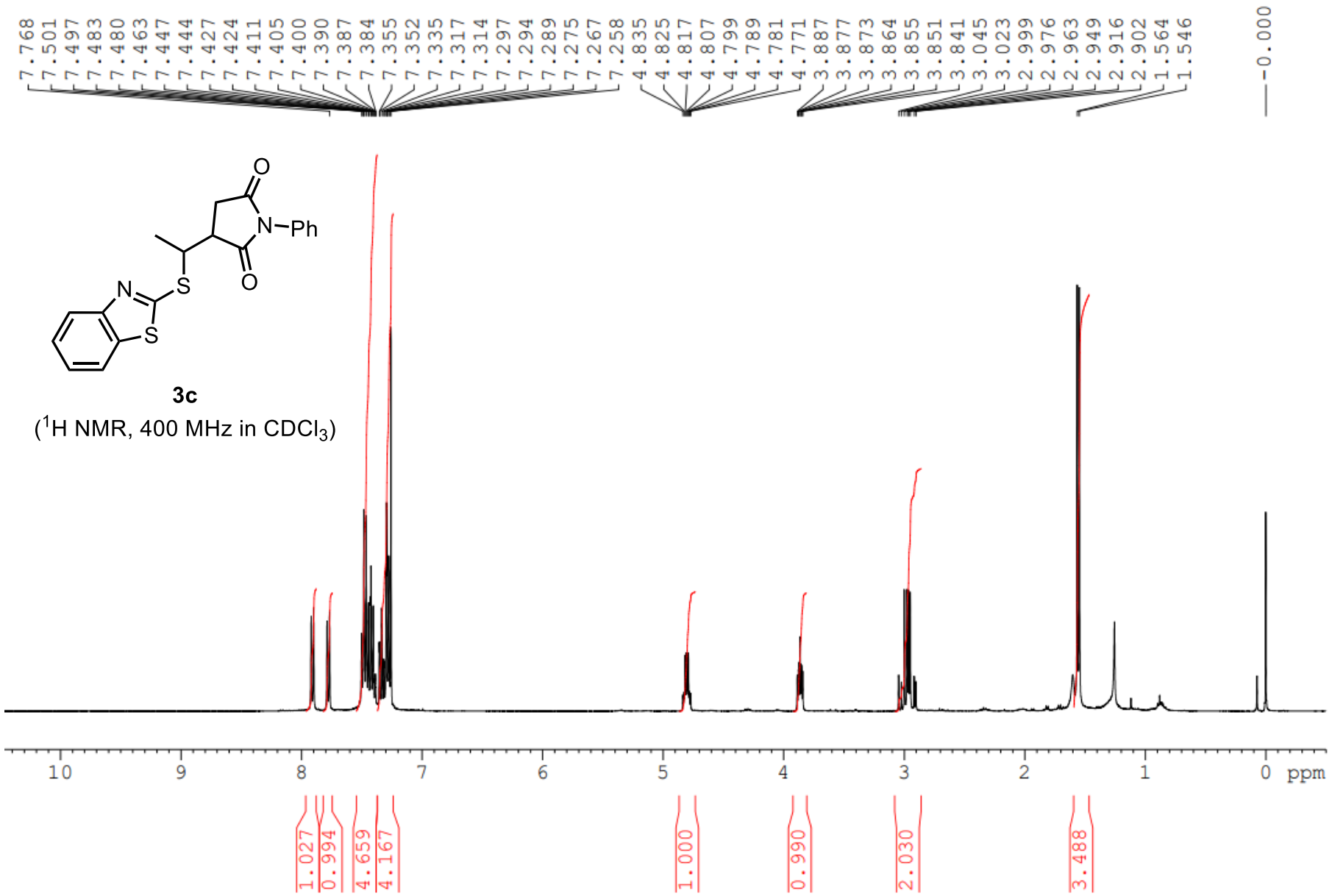
3b

(^{1}H NMR, 400 MHz in $CDCl_3$)



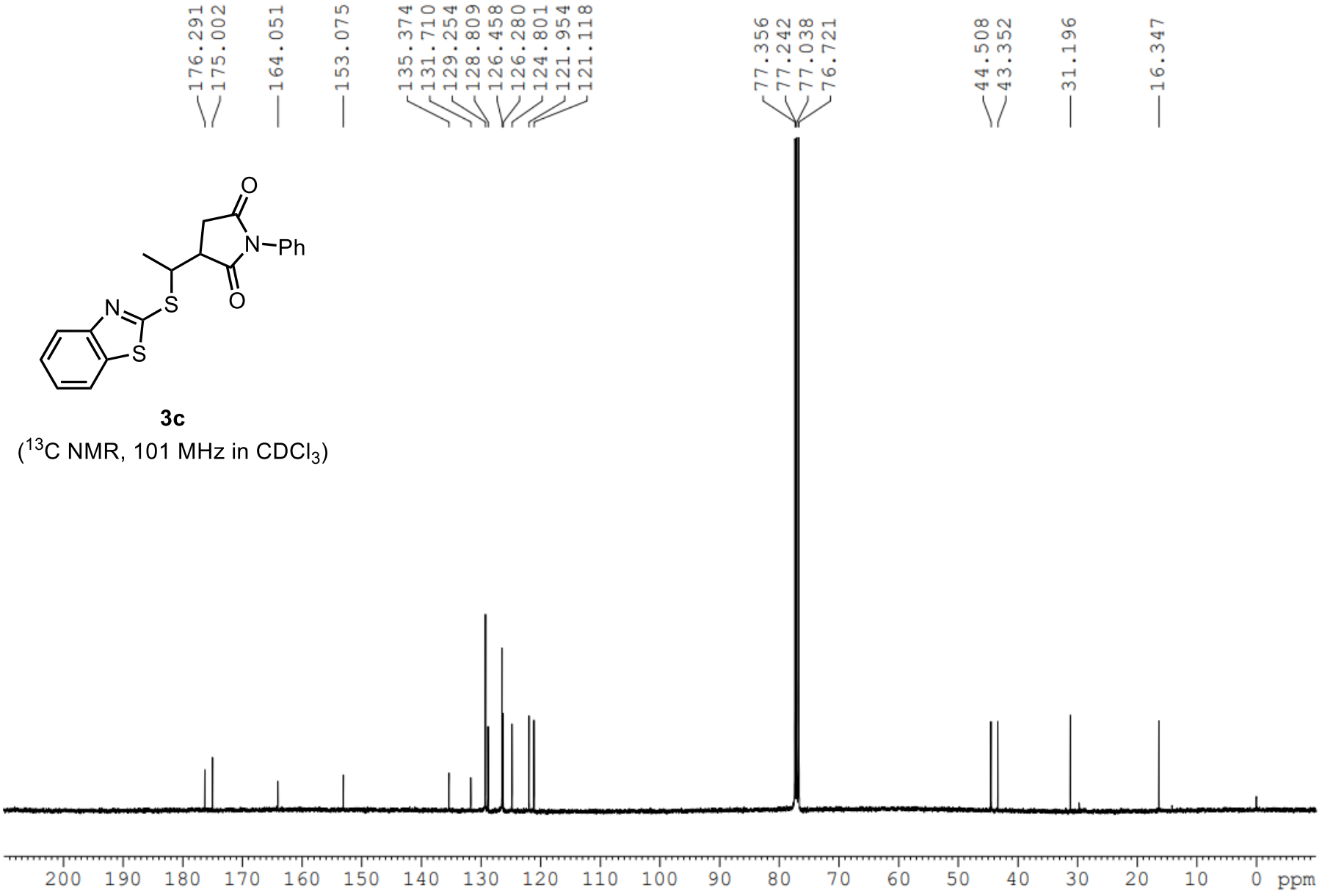
3b

(^{1}H NMR, 101 MHz in $CDCl_3$)



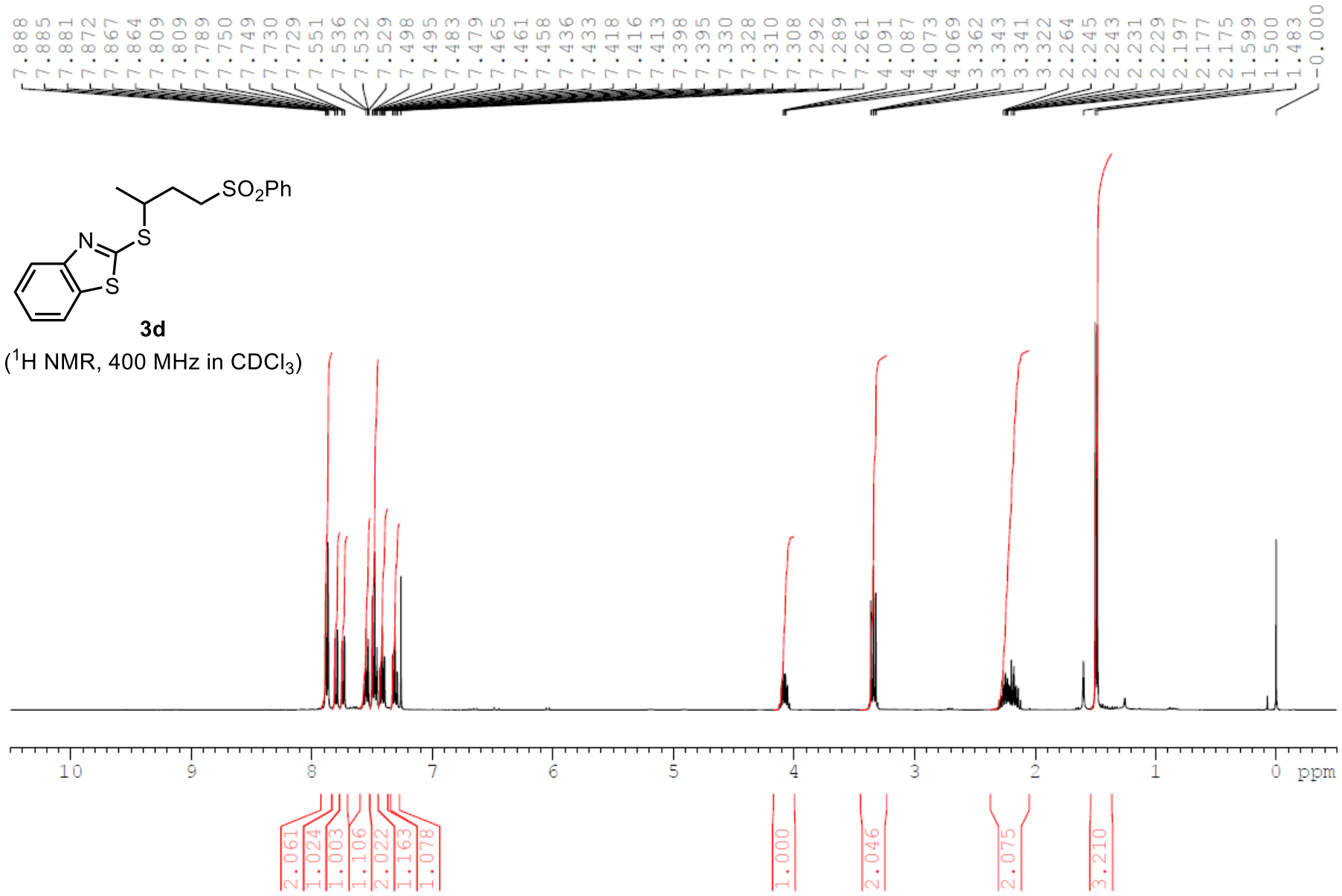
3c

(^{1}H NMR, 400 MHz in $CDCl_3$)



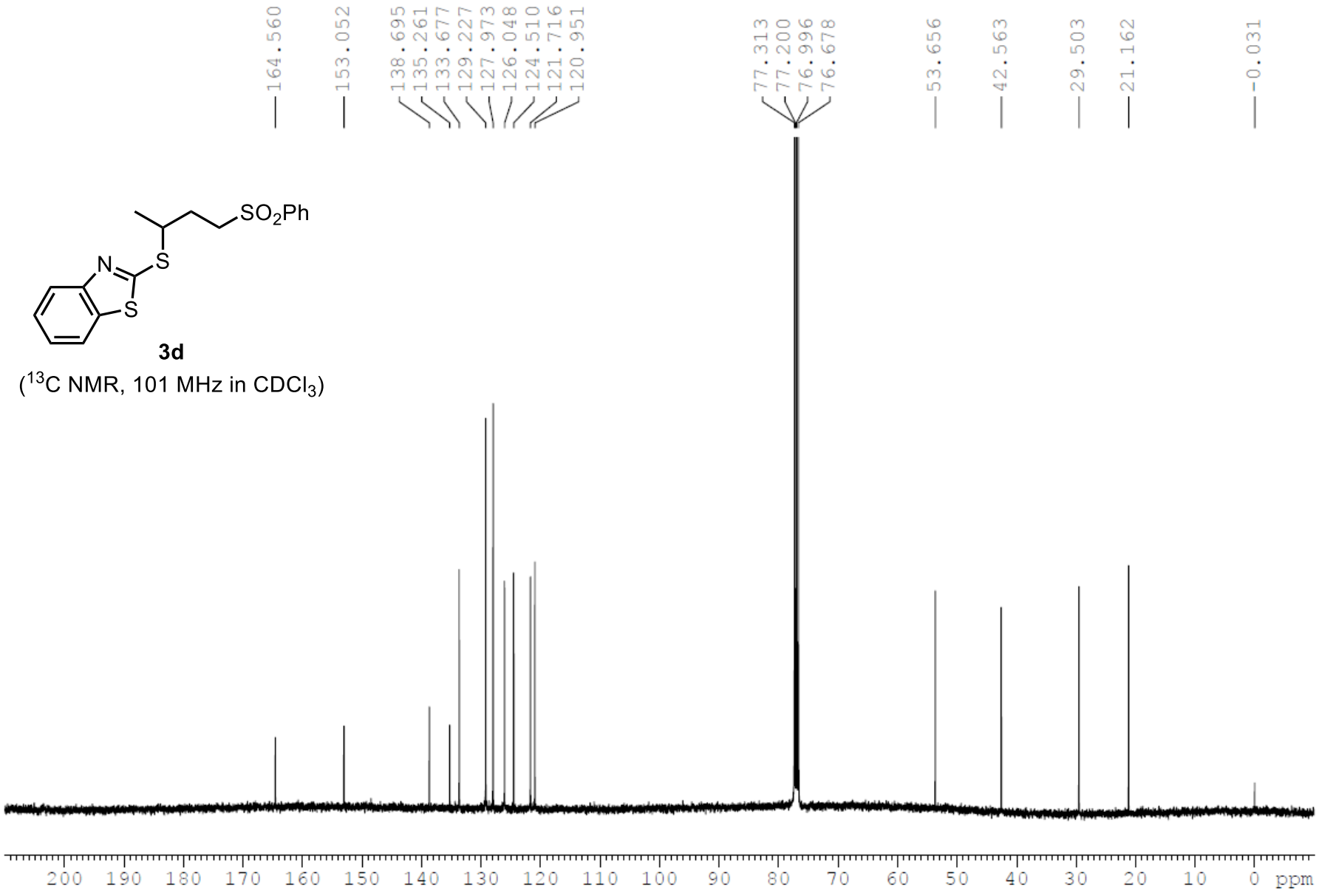
3c

(^{13}C NMR, 101 MHz in $CDCl_3$)



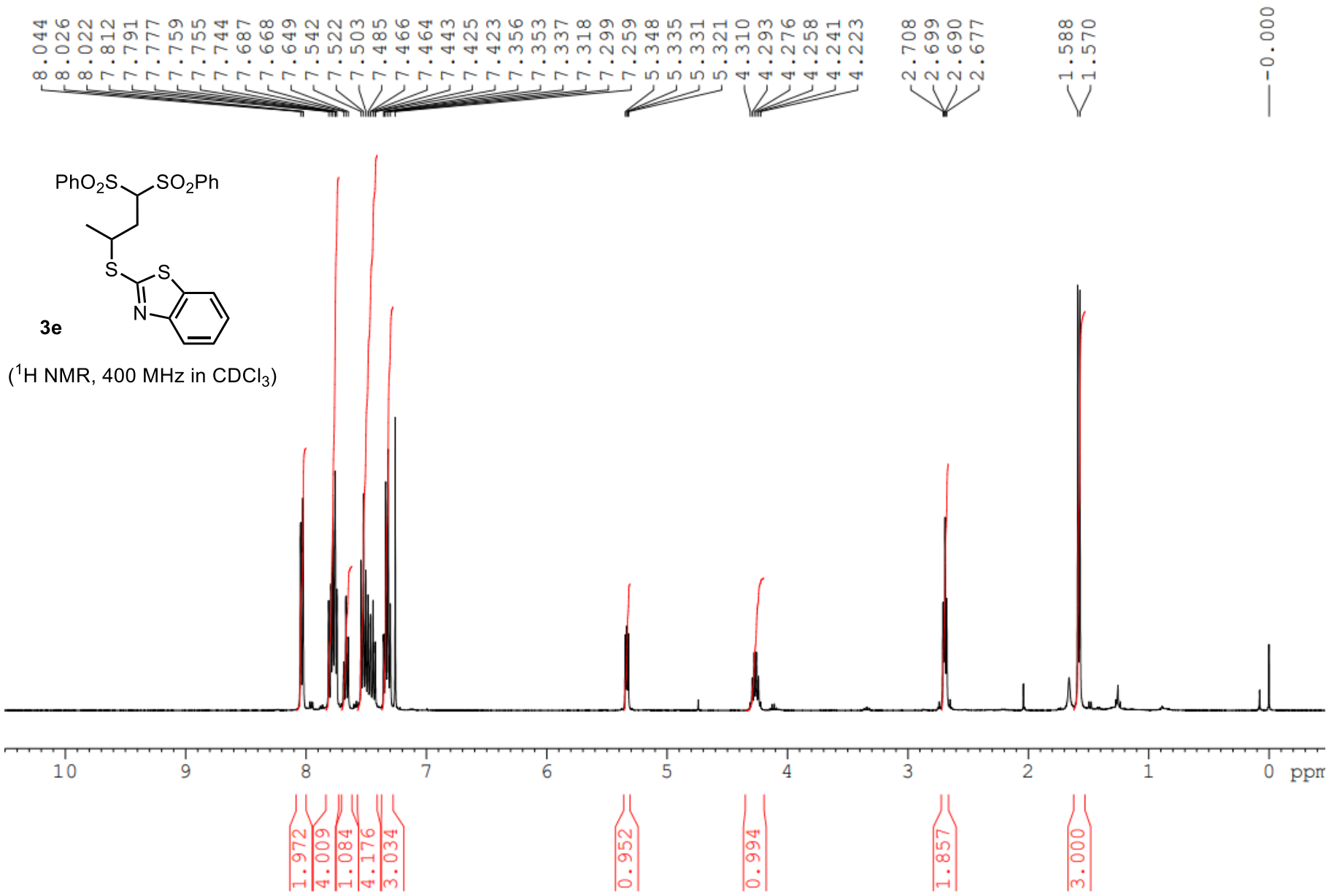
3d

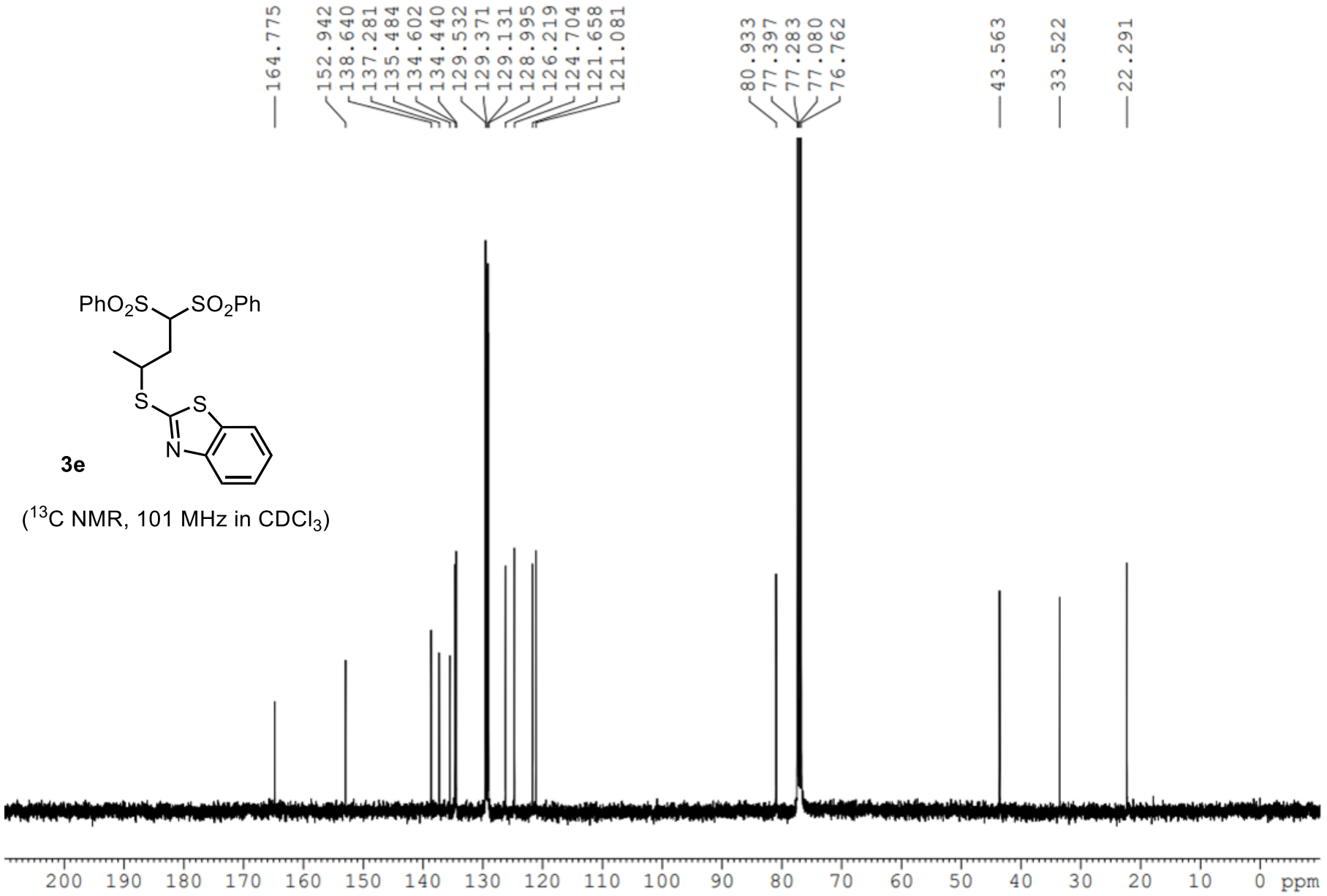
(^{1}H NMR, 400 MHz in $CDCl_3$)



3d

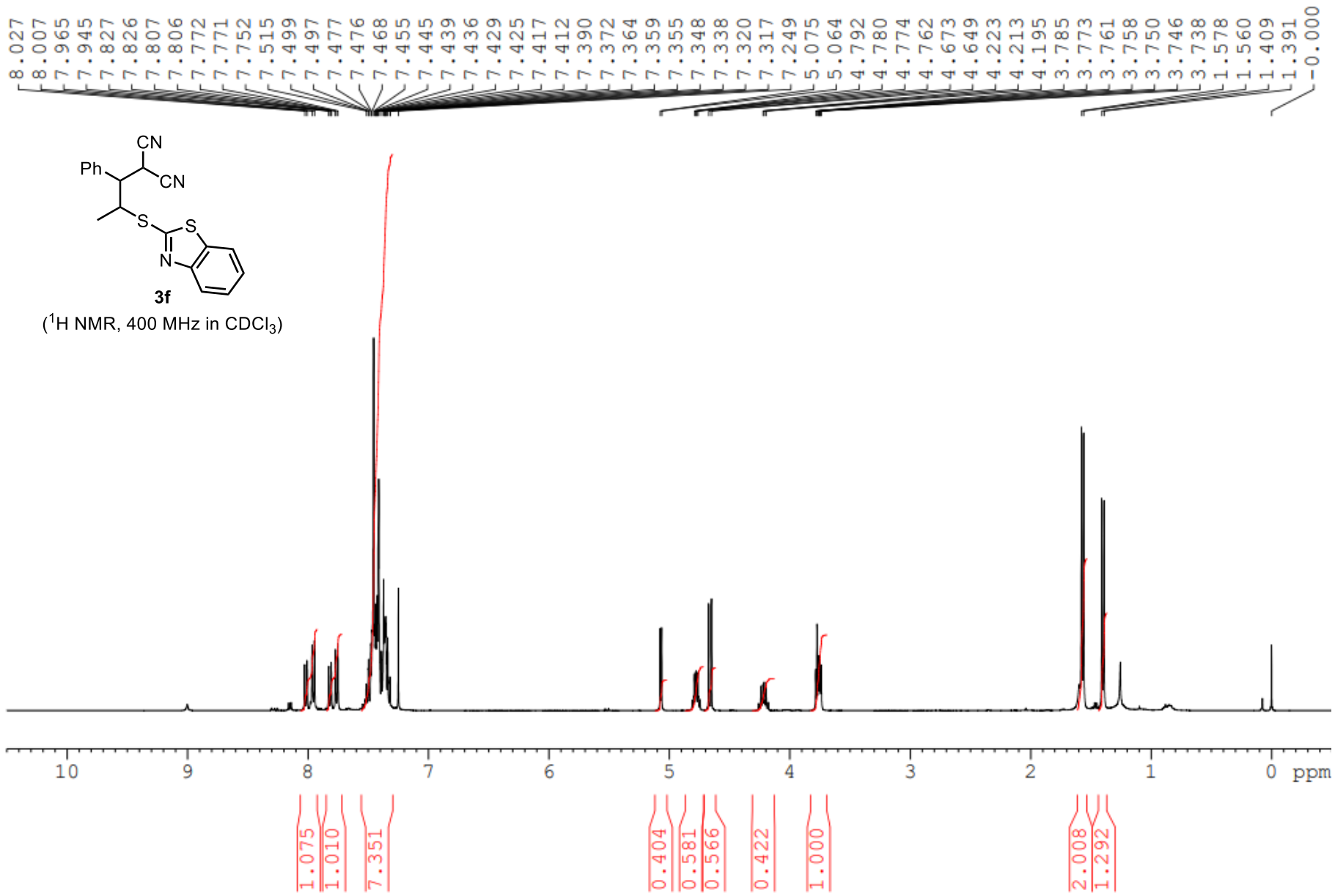
(^{13}C NMR, 101 MHz in $CDCl_3$)

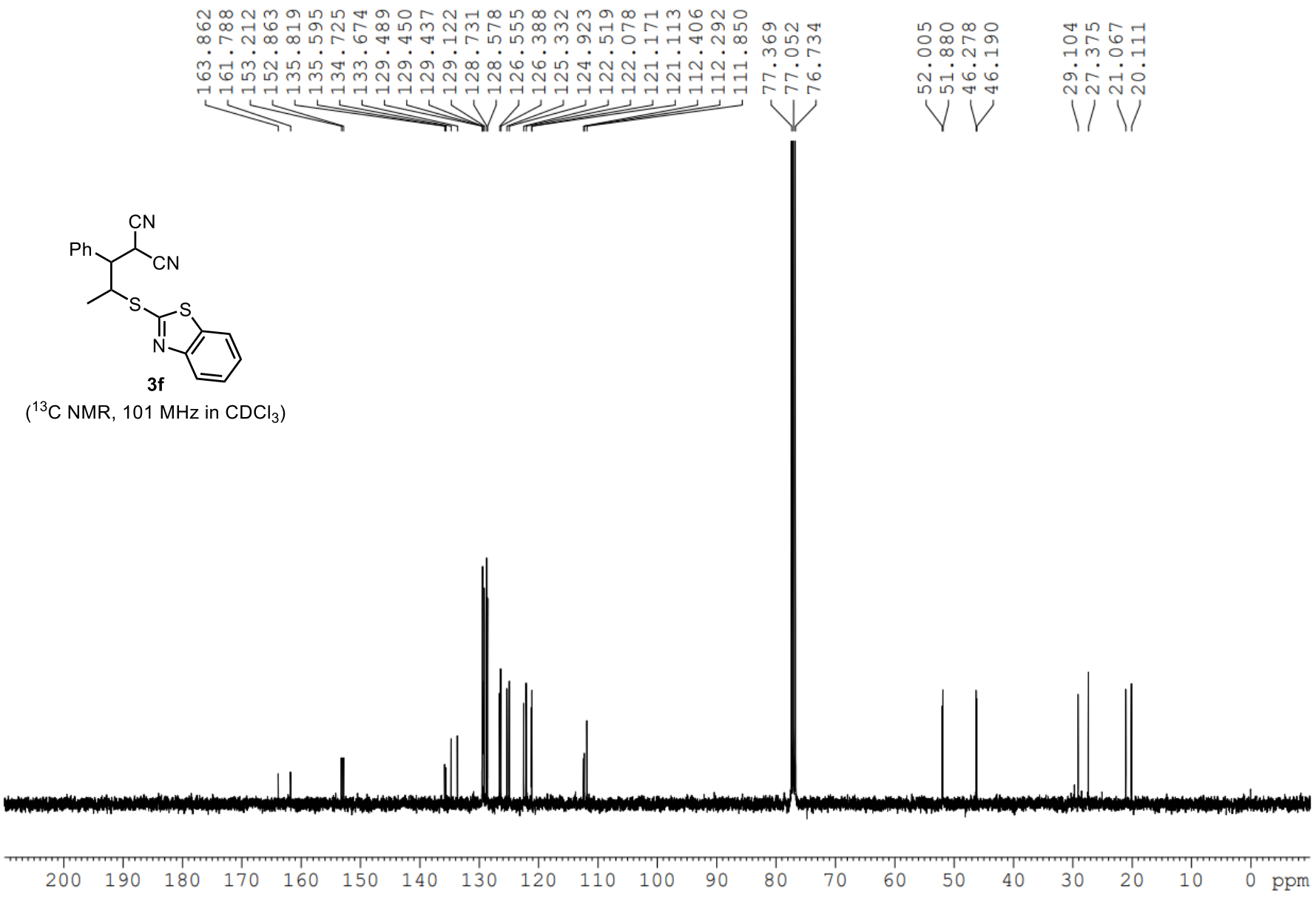

8.044
8.026
8.022
7.812
7.791
7.777
7.759
7.755
7.744
7.687
7.668
7.649
7.542
7.522
7.503
7.485
7.466
7.464
7.443
7.425
7.423
7.356
7.353
7.337
7.318
7.299
7.259
5.348
5.335
5.331
5.321
4.310
4.293
4.276
4.258
4.241
4.223
2.708
2.699
2.690
2.677
1.588
1.570
0.000
PhO2S
SO2Ph
S
S
N
3e
(1H NMR, 400 MHz in CDCl3)
10
9
8
7
6
5
4
3
2
1
0 ppm
1.972
4.009
1.084
4.176
3.034
0.952
0.994
1.857
3.000



3e

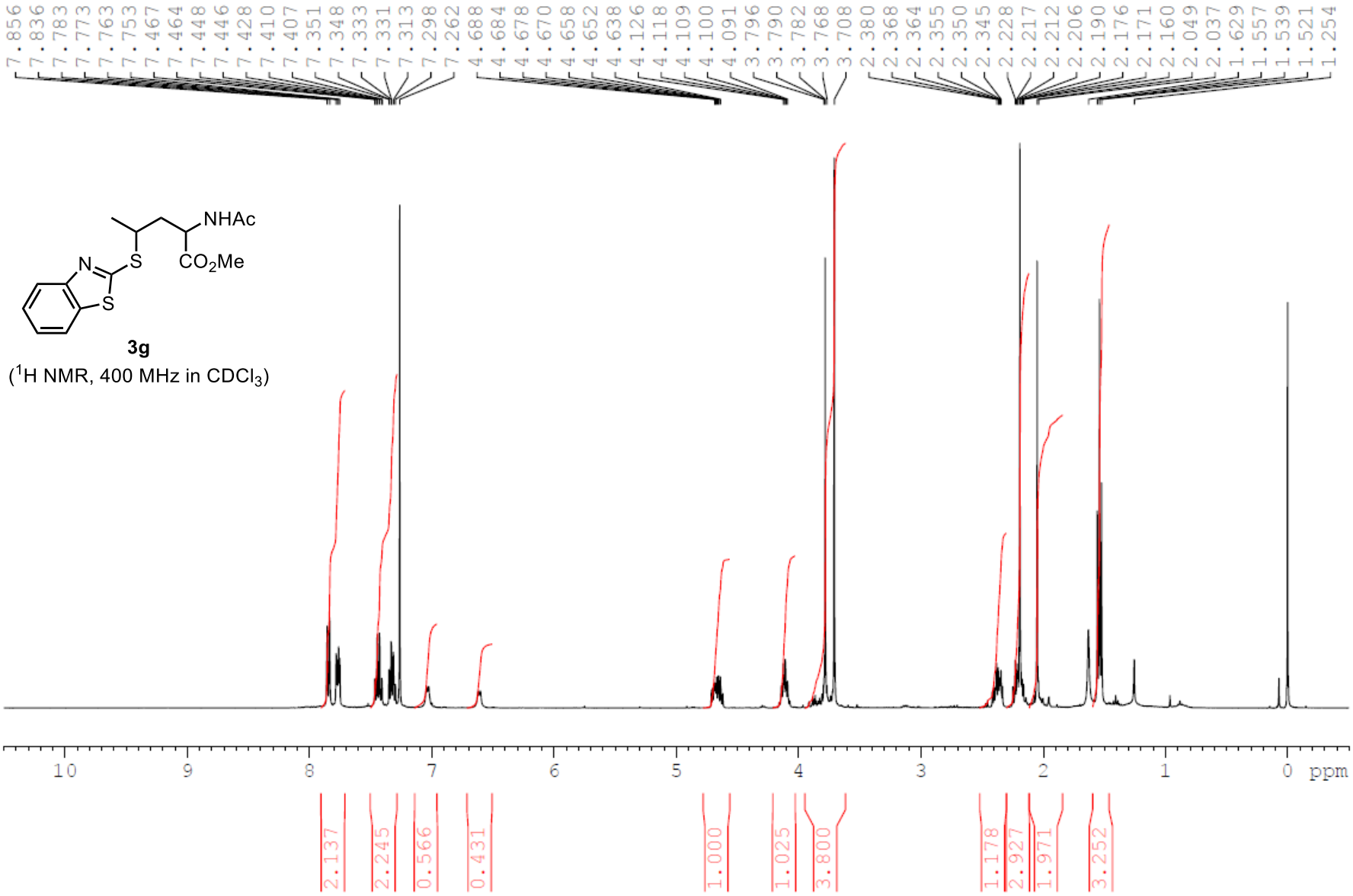
(^{13}C NMR, 101 MHz in $CDCl_3$)

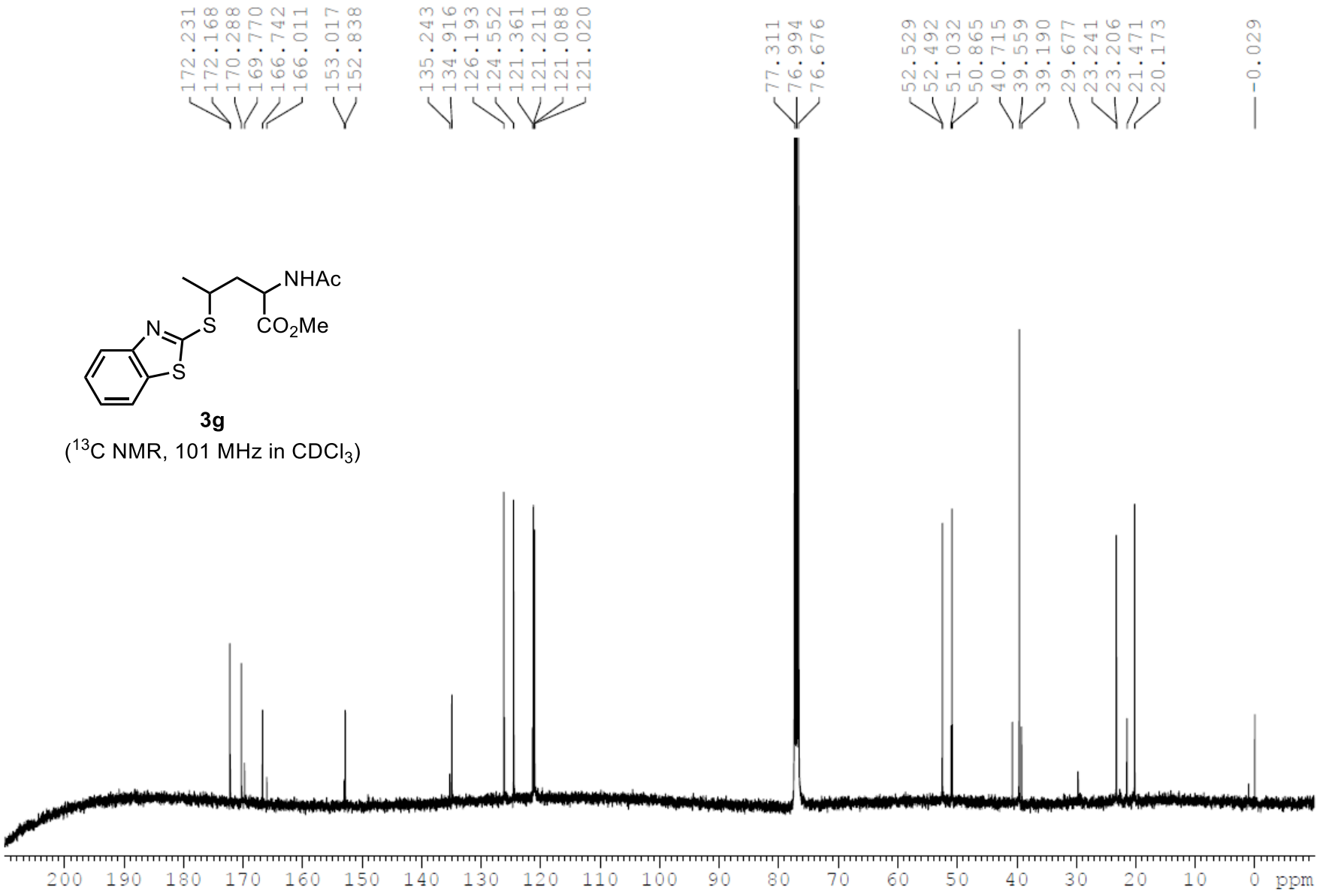

8.027
8.007
7.965
7.945
7.827
7.826
7.807
7.806
7.772
7.771
7.752
7.515
7.499
7.497
7.477
7.476
7.468
7.455
7.445
7.439
7.436
7.429
7.425
7.417
7.412
7.390
7.372
7.364
7.359
7.355
7.348
7.338
7.320
7.317
7.249
5.075
5.064
4.792
4.780
4.774
4.762
4.673
4.649
4.223
4.213
4.195
3.785
3.773
3.761
3.758
3.750
3.746
3.738
1.578
1.560
1.409
1.391
-0.000
CN
Ph
CN
S
S
N
3f
(1H NMR, 400 MHz in CDCl3)
10
9
8
7
6
5
4
3
2
1
0 ppm
1.075
1.010
7.351
0.404
0.581
0.566
0.422
1.000
2.008
1.292



3f

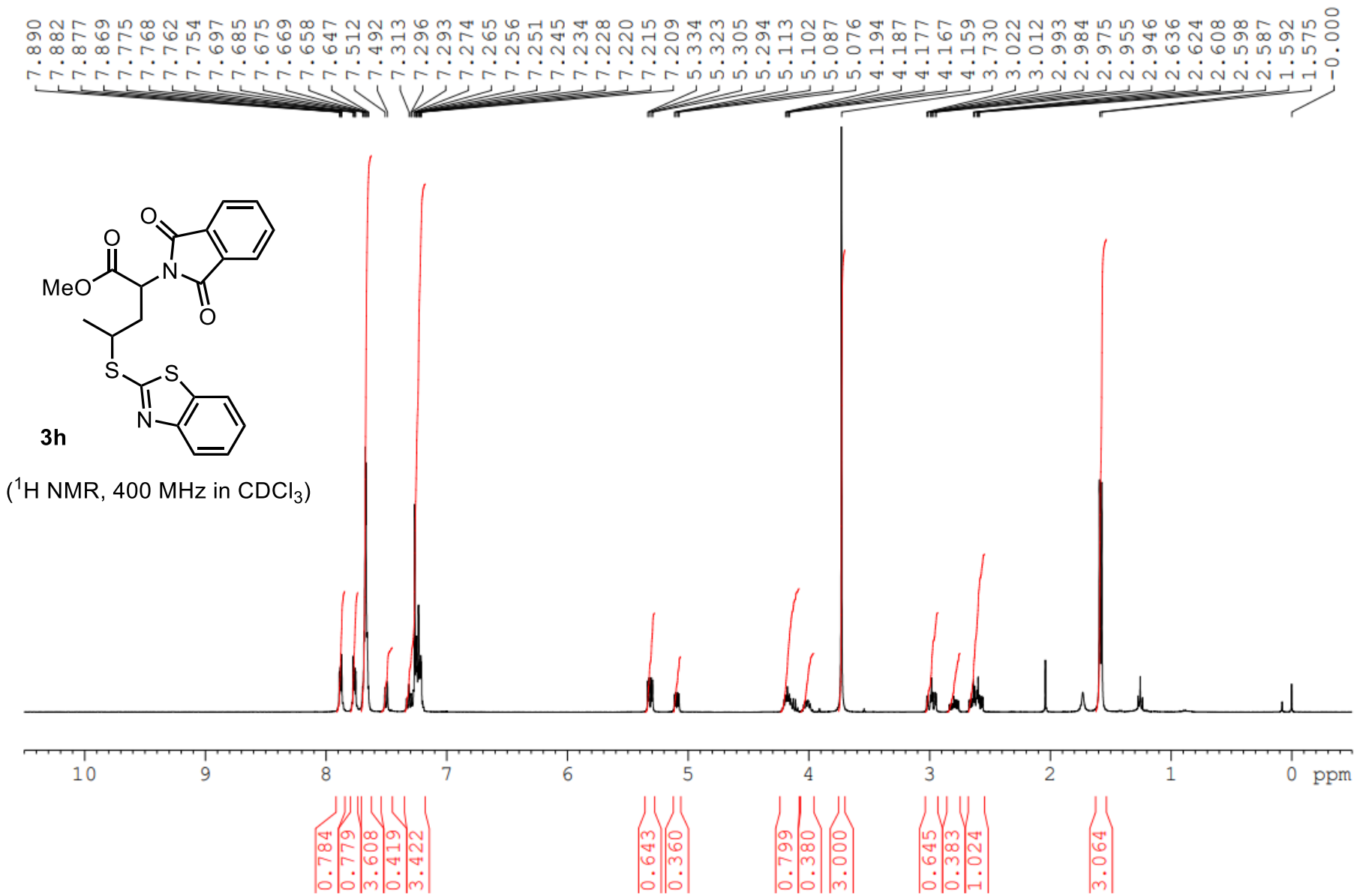
(^{13}C NMR, 101 MHz in $CDCl_3$)


7.856
7.836
7.783
7.773
7.763
7.753
7.467
7.464
7.448
7.446
7.428
7.410
7.407
7.351
7.348
7.333
7.331
7.313
7.298
7.262
4.688
4.684
4.678
4.670
4.658
4.652
4.638
4.126
4.118
4.109
4.100
4.091
3.796
3.790
3.782
3.768
3.708
2.380
2.368
2.364
2.355
2.350
2.345
2.228
2.217
2.212
2.206
2.190
2.176
2.171
2.160
2.049
2.037
1.629
1.557
1.539
1.521
1.254
NHAc
CO2Me
N
S
S
3g
(1H NMR, 400 MHz in CDCl3)
10
9
8
7
6
5
4
3
2
1
0 ppm
2.137
2.245
0.566
0.431
1.000
1.025
3.800
1.178
2.927
1.971
3.252



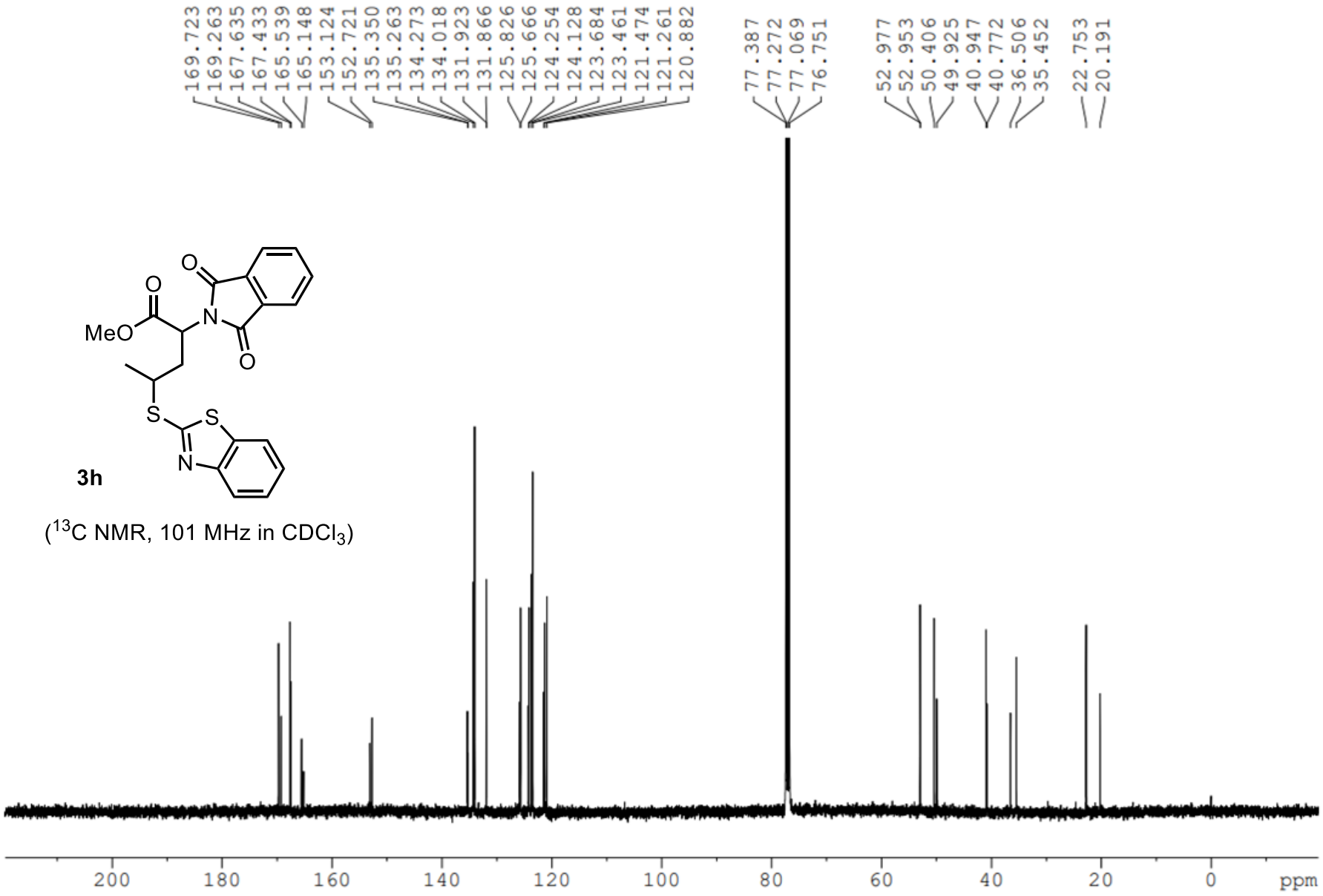
3g

(^{13}C NMR, 101 MHz in $CDCl_3$)



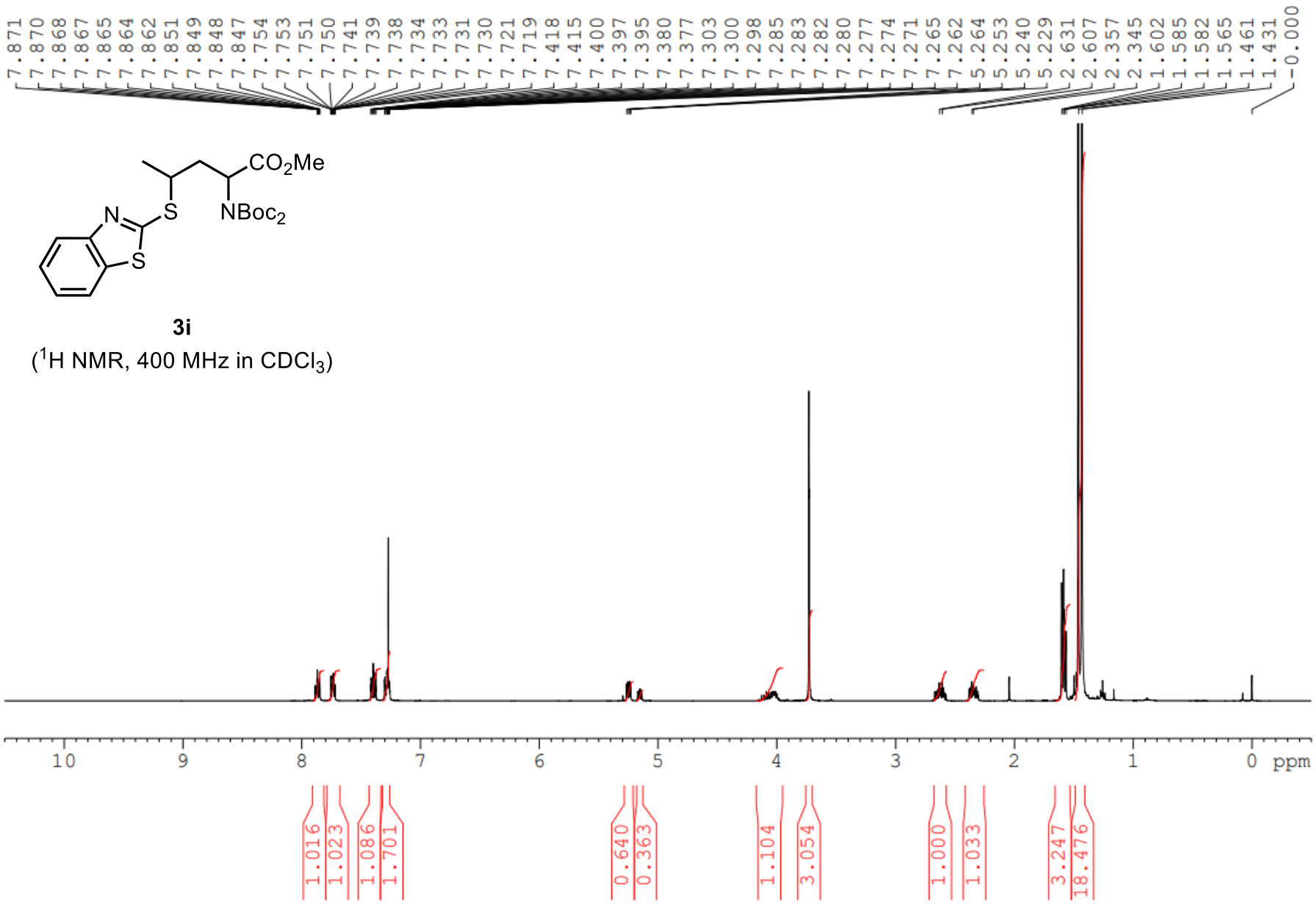
3h

(^{1}H NMR, 400 MHz in $CDCl_3$)



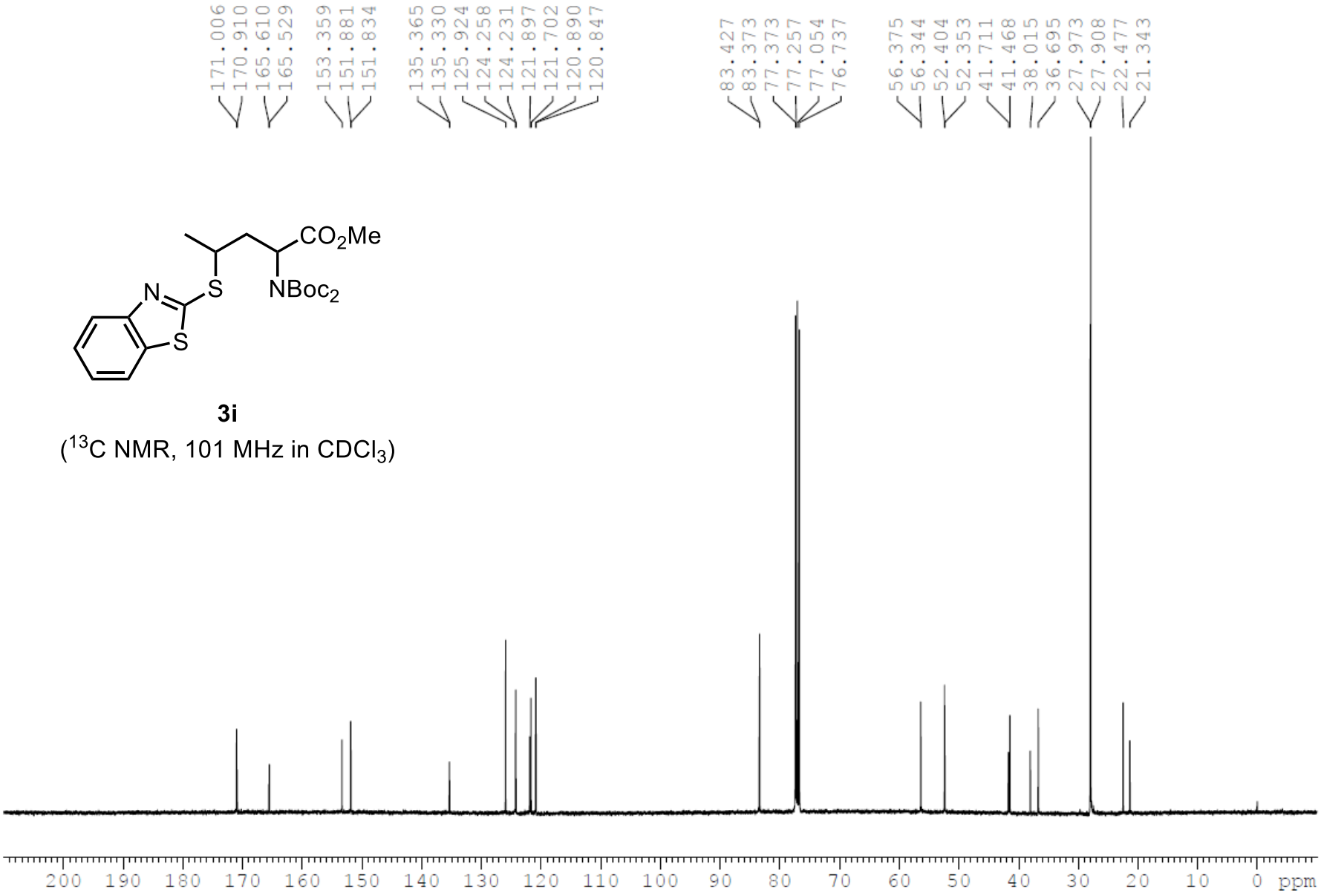
3h

(^{13}C NMR, 101 MHz in $CDCl_3$)



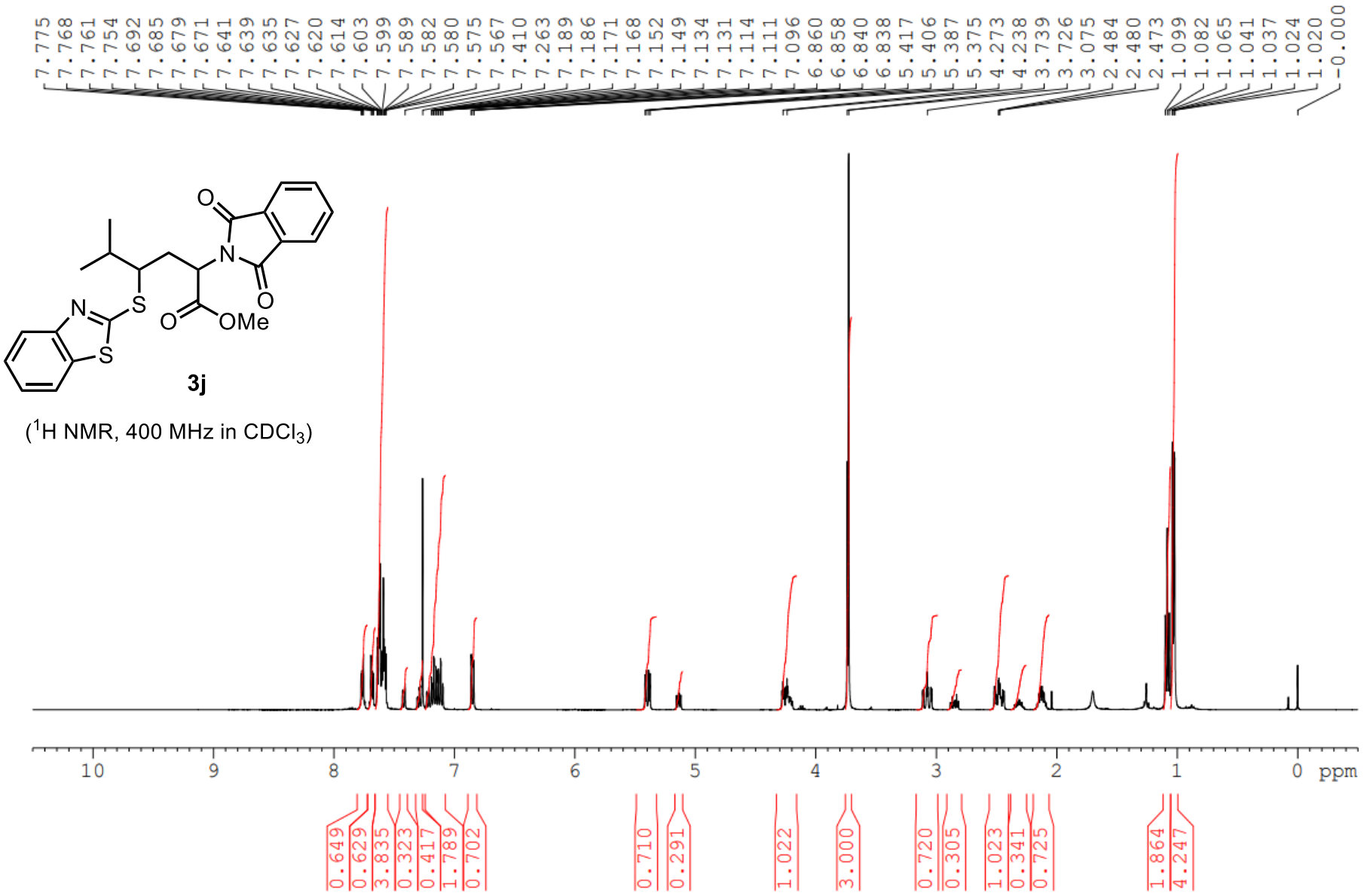
3i

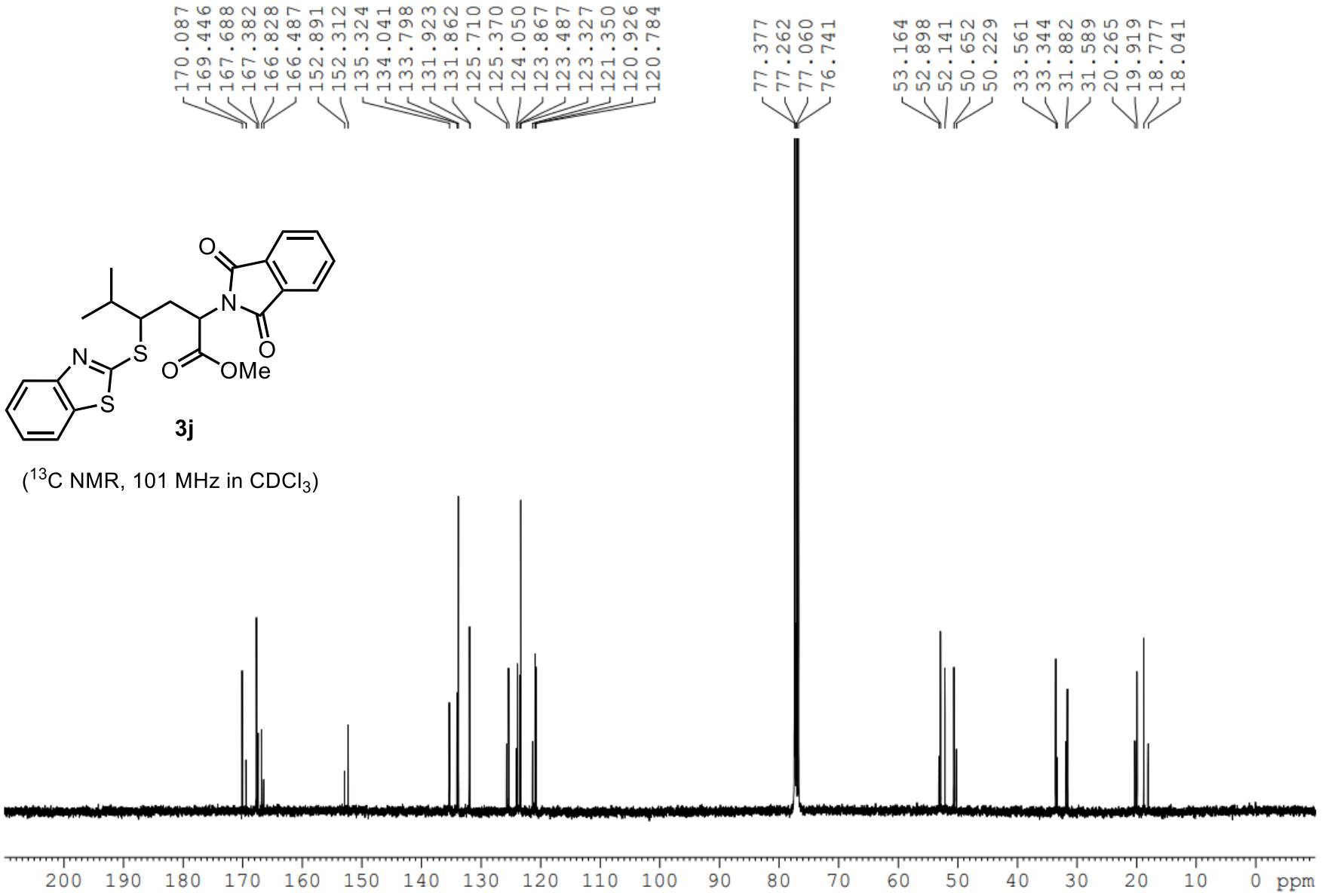
(^{1}H NMR, 400 MHz in $CDCl_3$)



3i

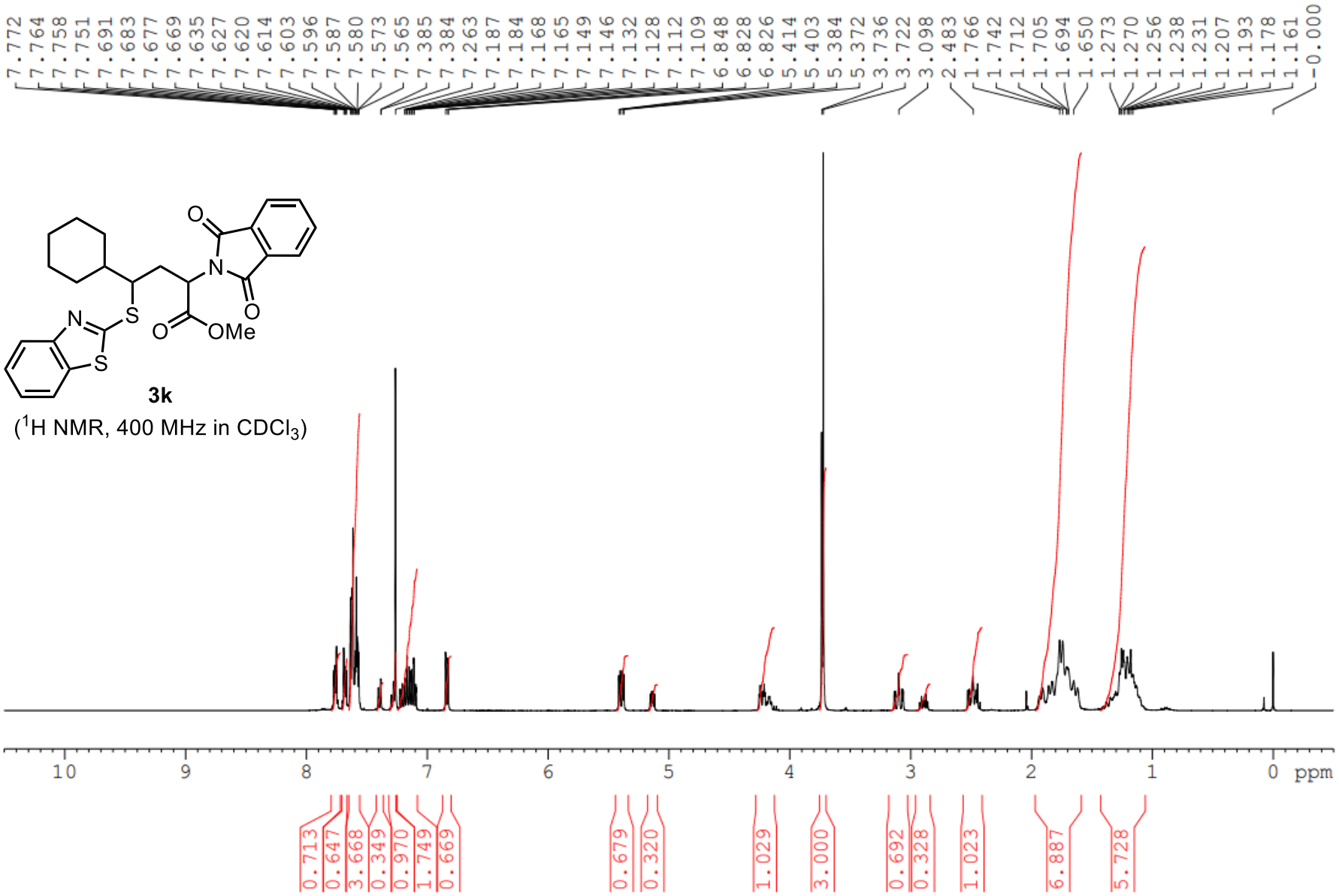
(^{13}C NMR, 101 MHz in $CDCl_3$)


7.775
7.768
7.761
7.754
7.692
7.685
7.679
7.671
7.641
7.639
7.635
7.627
7.620
7.614
7.603
7.599
7.589
7.582
7.580
7.575
7.567
7.410
7.263
7.189
7.186
7.171
7.168
7.152
7.149
7.134
7.131
7.114
7.111
7.096
6.860
6.858
6.840
6.838
5.417
5.406
5.387
5.375
4.273
4.238
3.739
3.726
3.075
2.484
2.480
2.473
1.099
1.082
1.065
1.041
1.037
1.024
1.020
-0.000
O
N
O
S
N
O
O
OMe
S
3j
(1H NMR, 400 MHz in CDCl3)
10
9
8
7
6
5
4
3
2
1
0
ppm
0.649
0.629
3.835
0.323
0.417
1.789
0.702
0.710
0.291
1.022
3.000
0.720
0.305
1.023
0.341
0.725
1.864
4.247



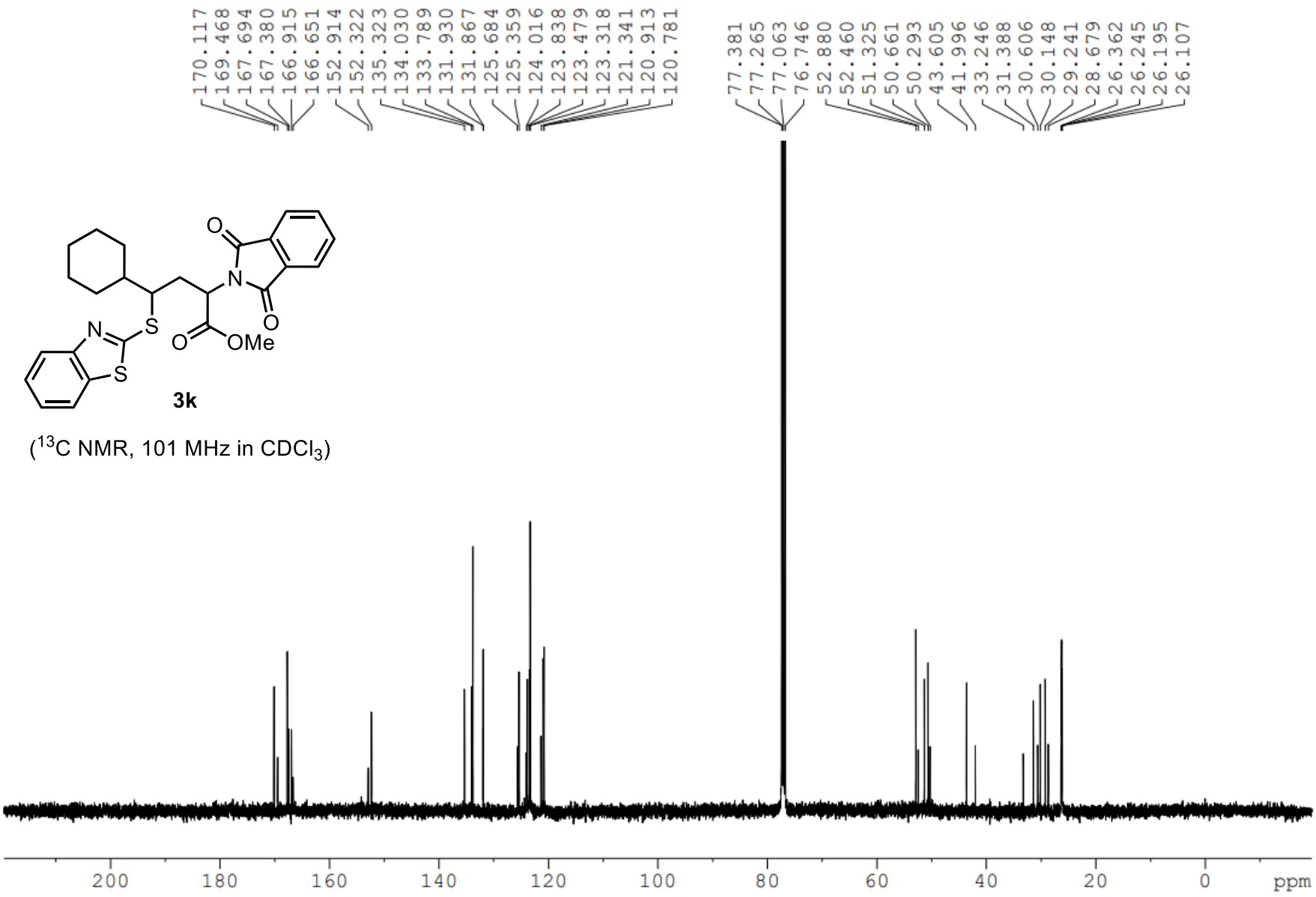
3j

(^{13}C NMR, 101 MHz in $CDCl_3$)

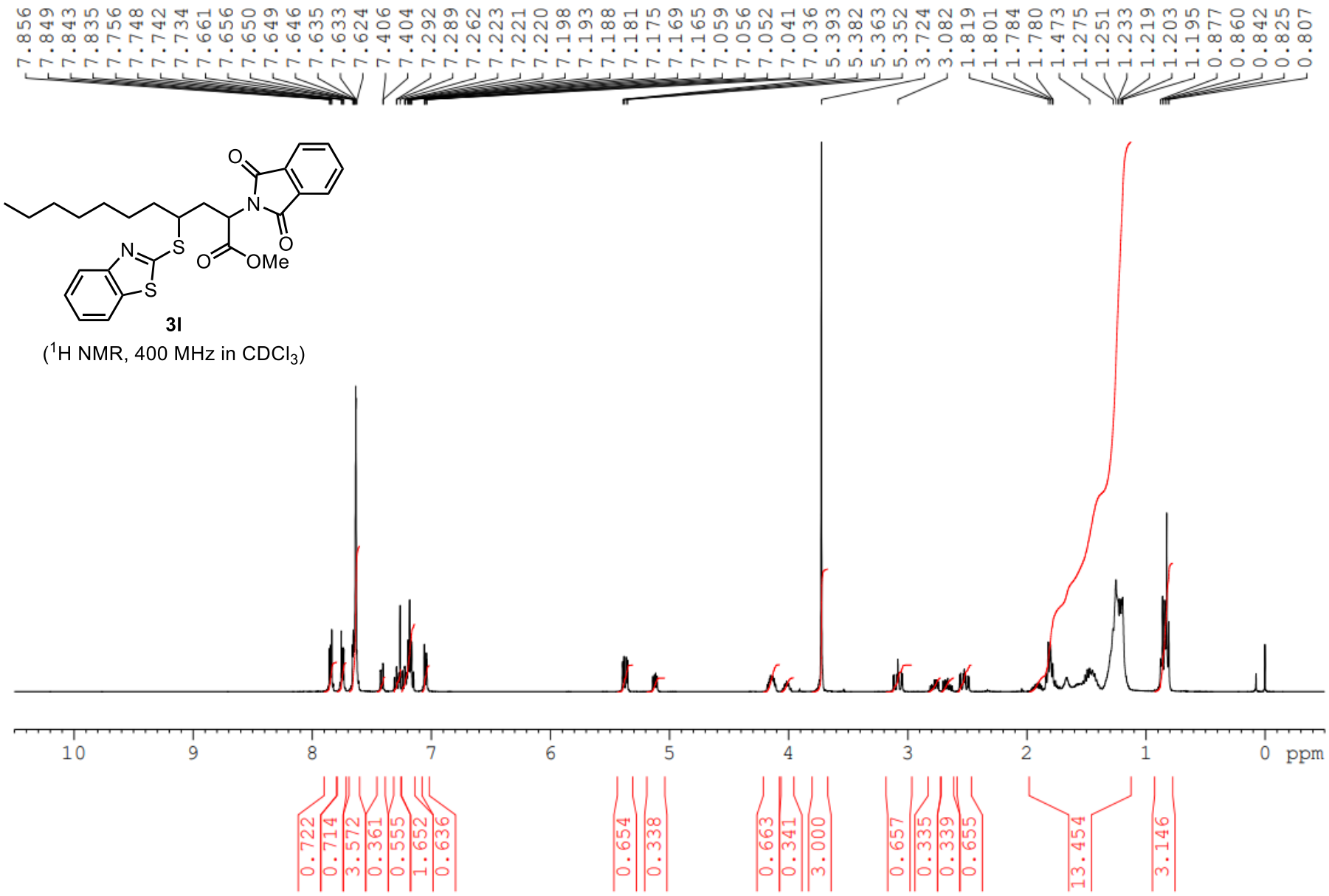


3k

(^{1}H NMR, 400 MHz in $CDCl_3$)

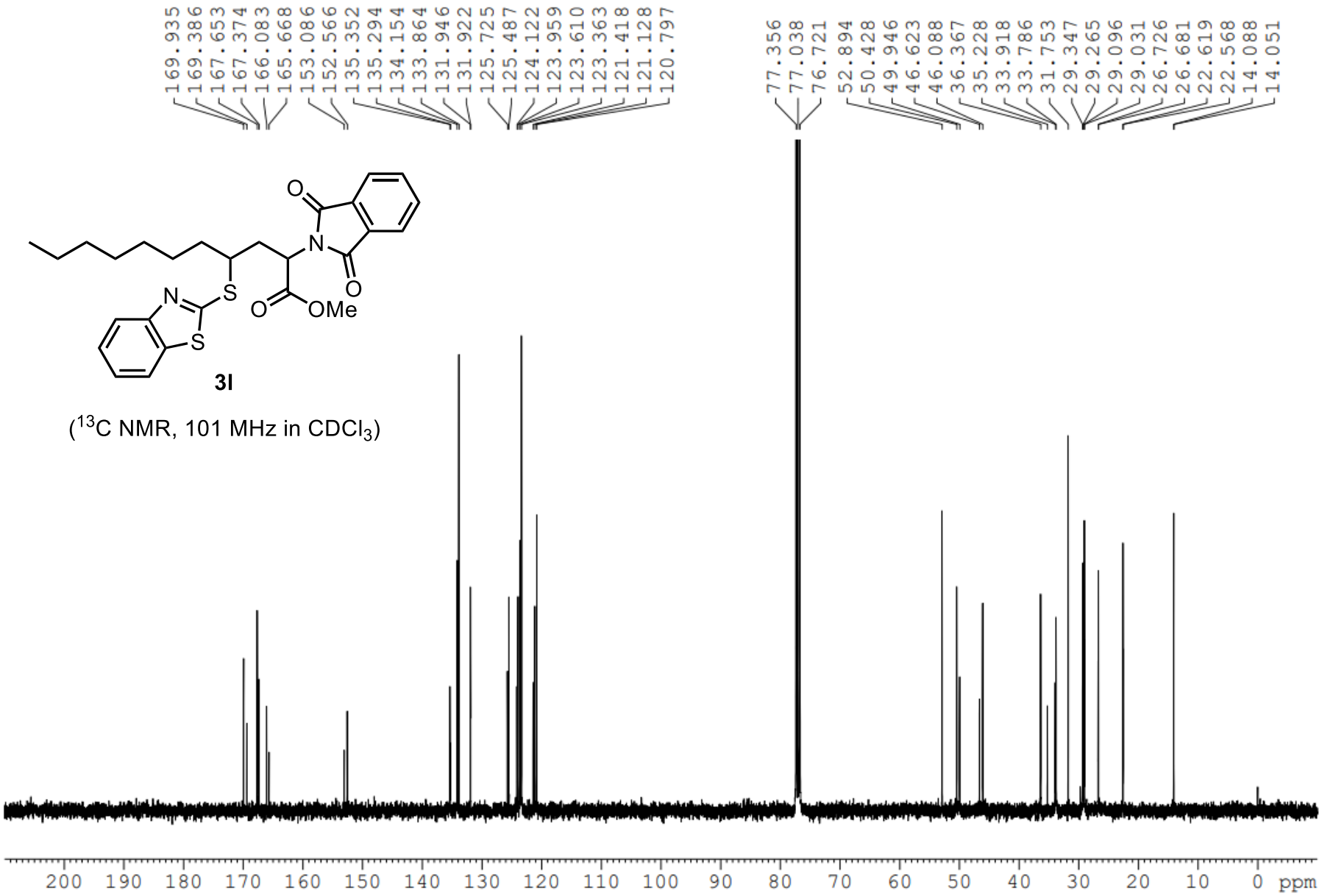


(^{13}C NMR, 101 MHz in $CDCl_3$)



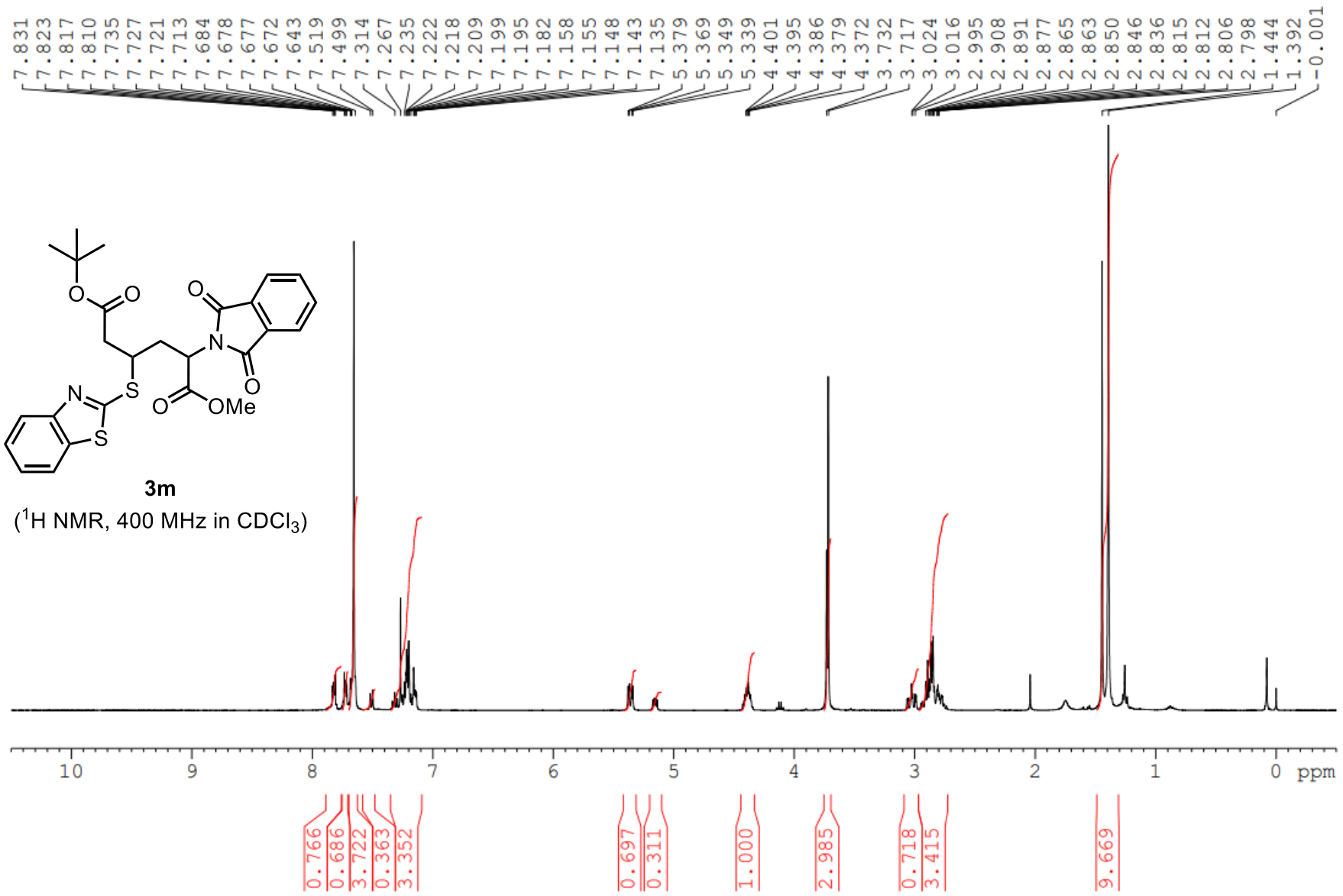
3l

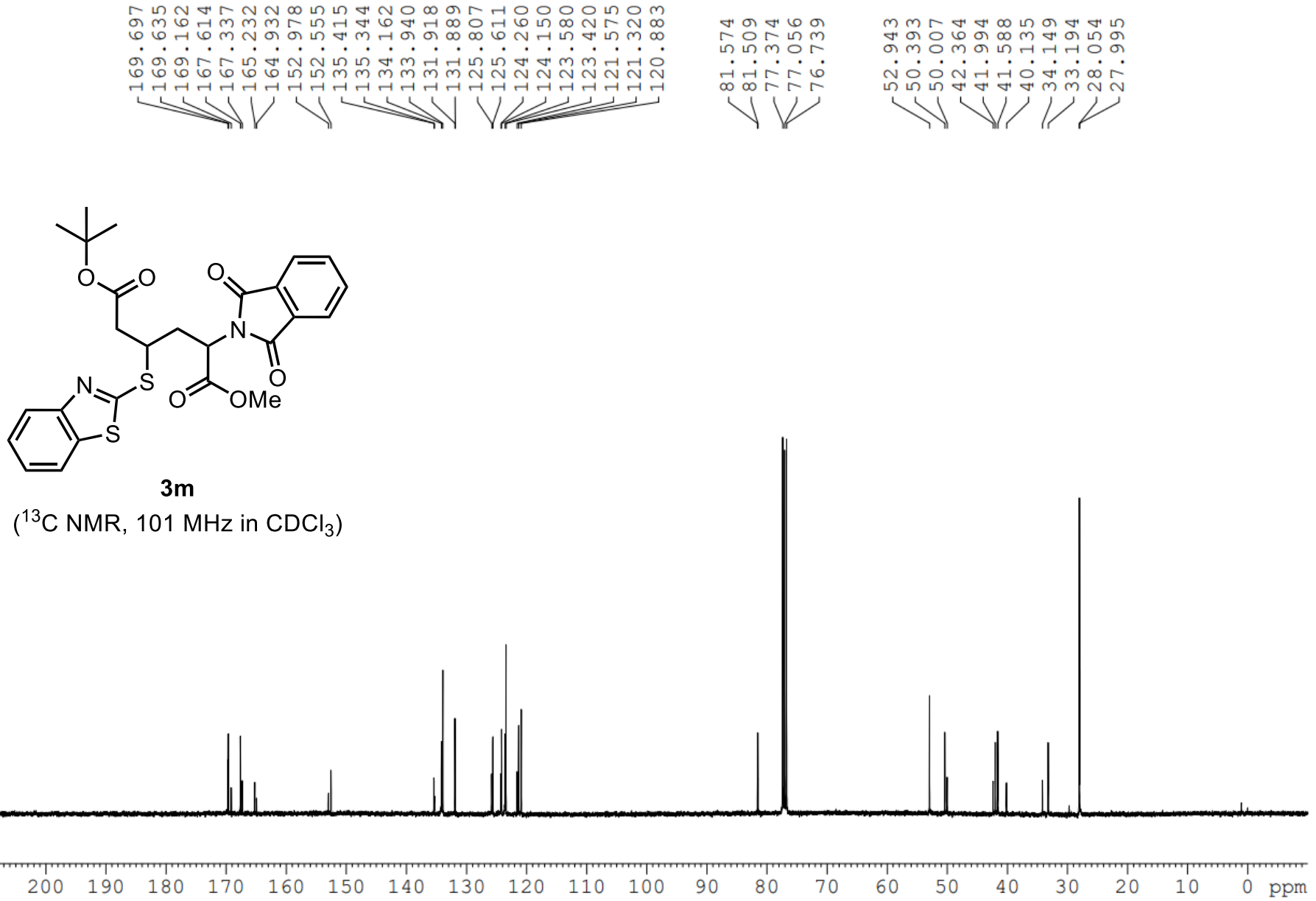
(^{1}H NMR, 400 MHz in $CDCl_3$)



3l

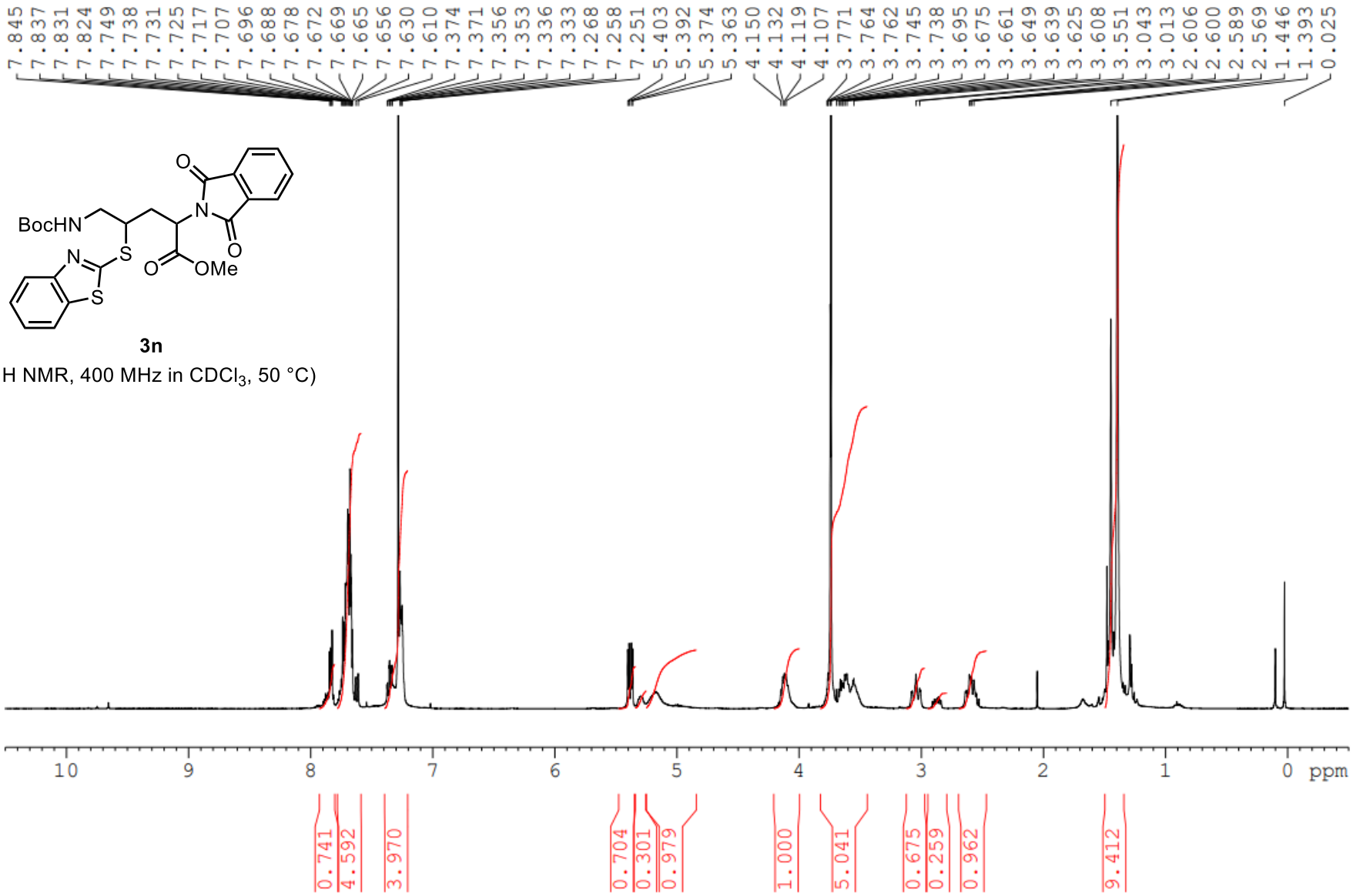
(^{13}C NMR, 101 MHz in $CDCl_3$)


7.831
7.823
7.817
7.810
7.735
7.727
7.721
7.713
7.684
7.678
7.677
7.672
7.643
7.519
7.499
7.314
7.267
7.235
7.222
7.218
7.209
7.199
7.195
7.182
7.158
7.155
7.148
7.143
7.135
5.379
5.369
5.349
5.339
4.401
4.395
4.386
4.379
4.372
3.732
3.717
3.024
3.016
2.995
2.908
2.891
2.877
2.865
2.863
2.850
2.846
2.836
2.815
2.812
2.806
2.798
1.444
1.392
-0.001
O
O
O
N
O
N
S
O
OMe
S
3m
(1H NMR, 400 MHz in CDCl3)
10
9
8
7
6
5
4
3
2
1
0
ppm
0.766
0.686
3.722
0.363
3.352
0.697
0.311
1.000
2.985
0.718
3.415
9.669



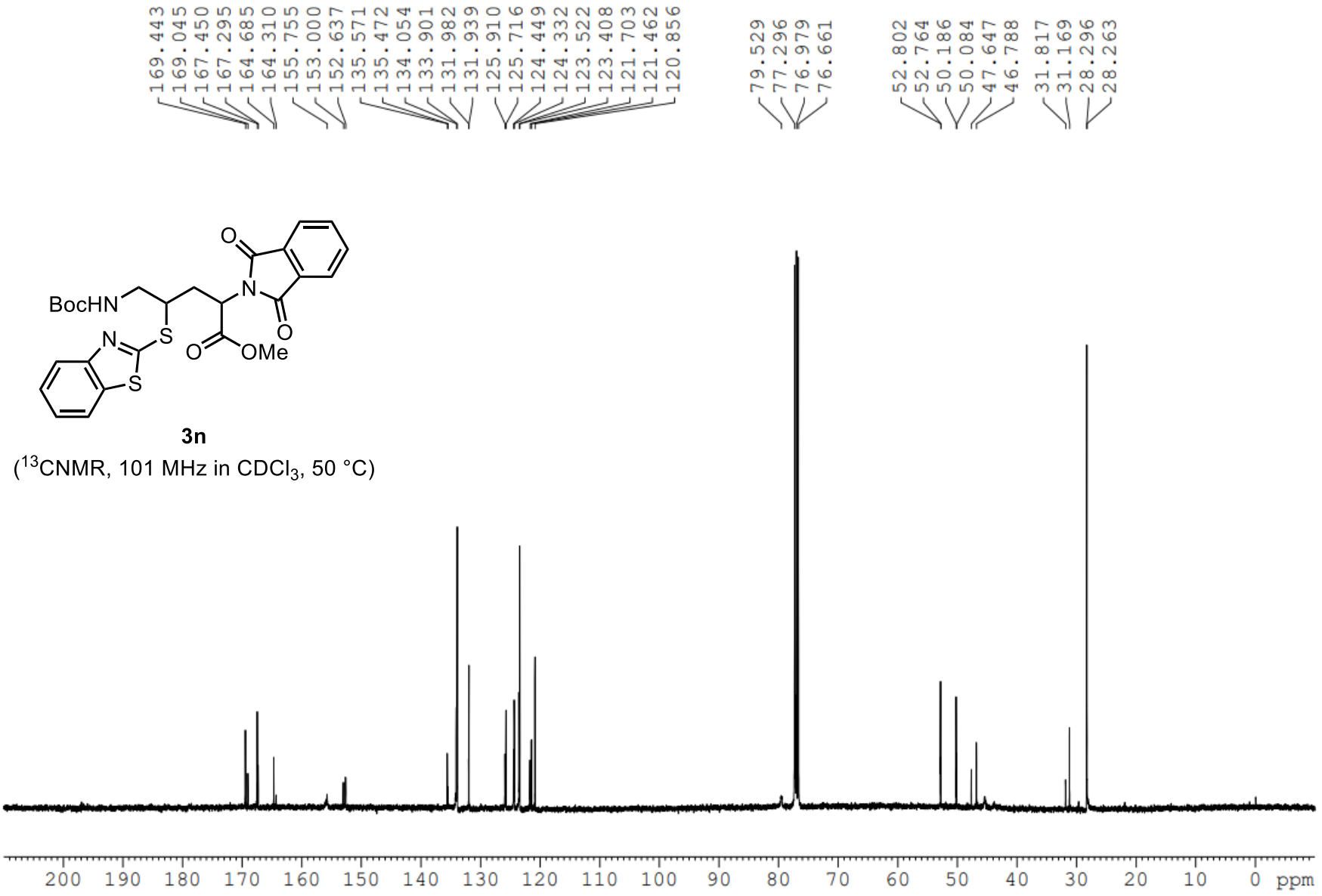
3m

(^{13}C NMR, 101 MHz in $CDCl_3$)



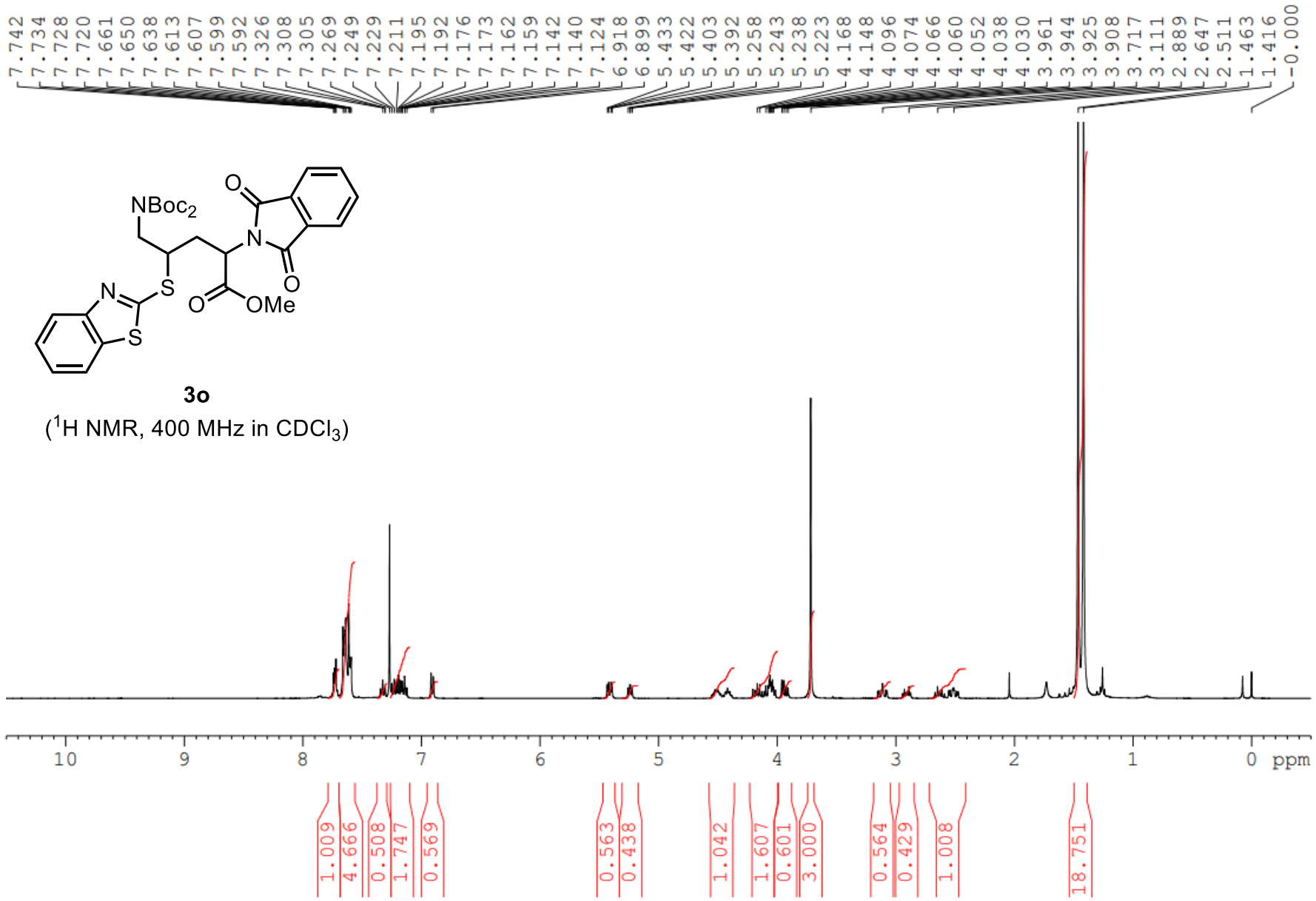
3n

(^{1}H NMR, 400 MHz in $CDCl_3$, 50 °C)



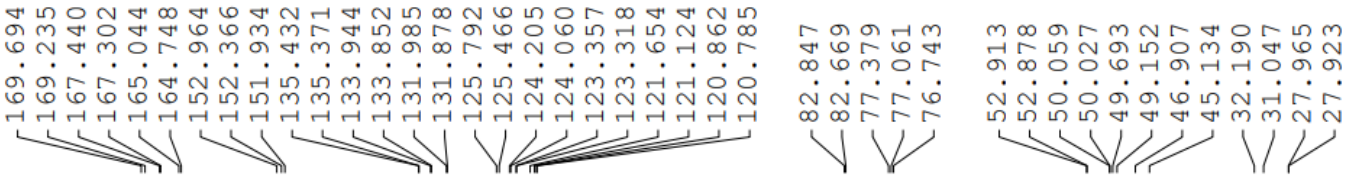
3n

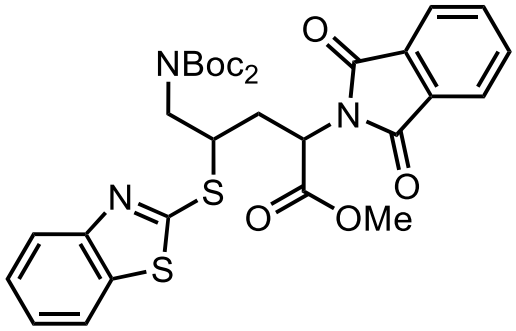
(^{13}CNMR, 101 MHz in $CDCl_3$, 50 °C)



3o

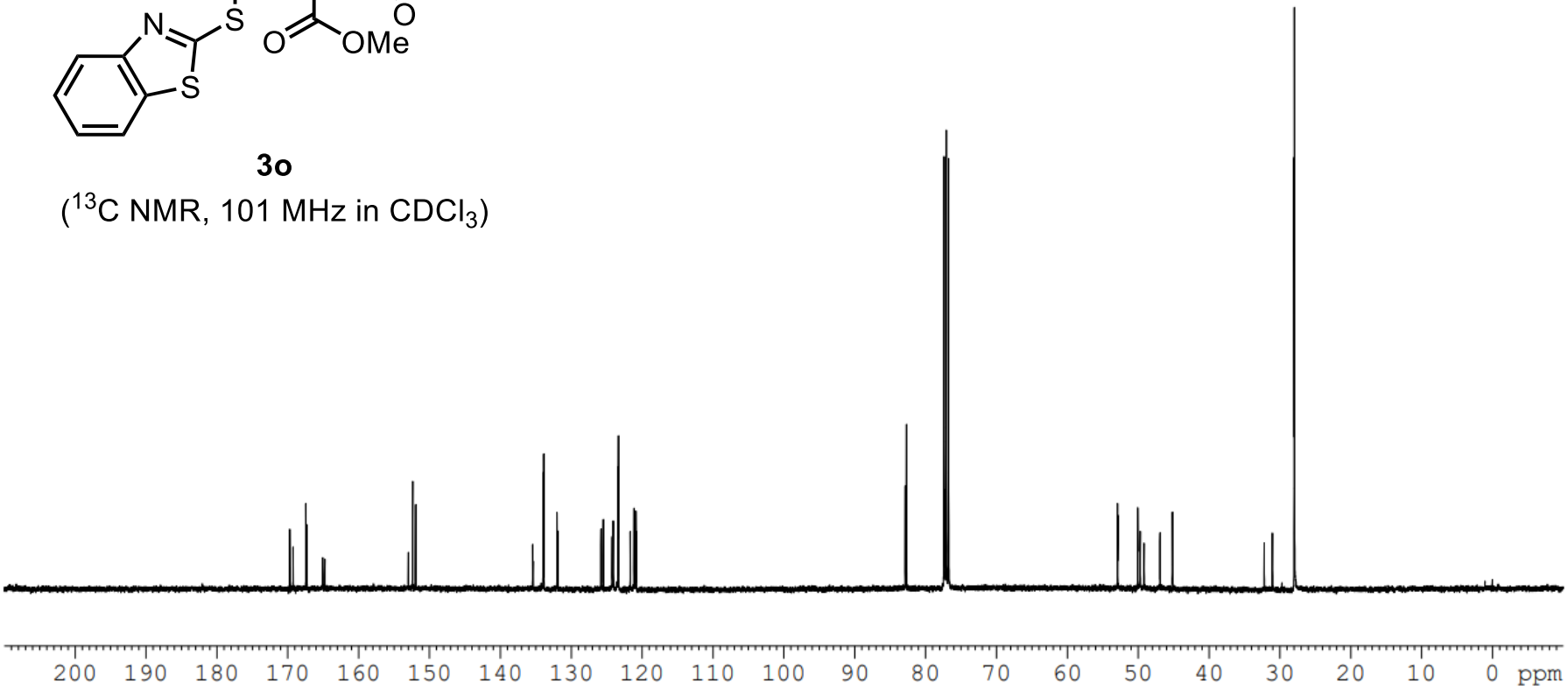
(^{1}H NMR, 400 MHz in $CDCl_3$)

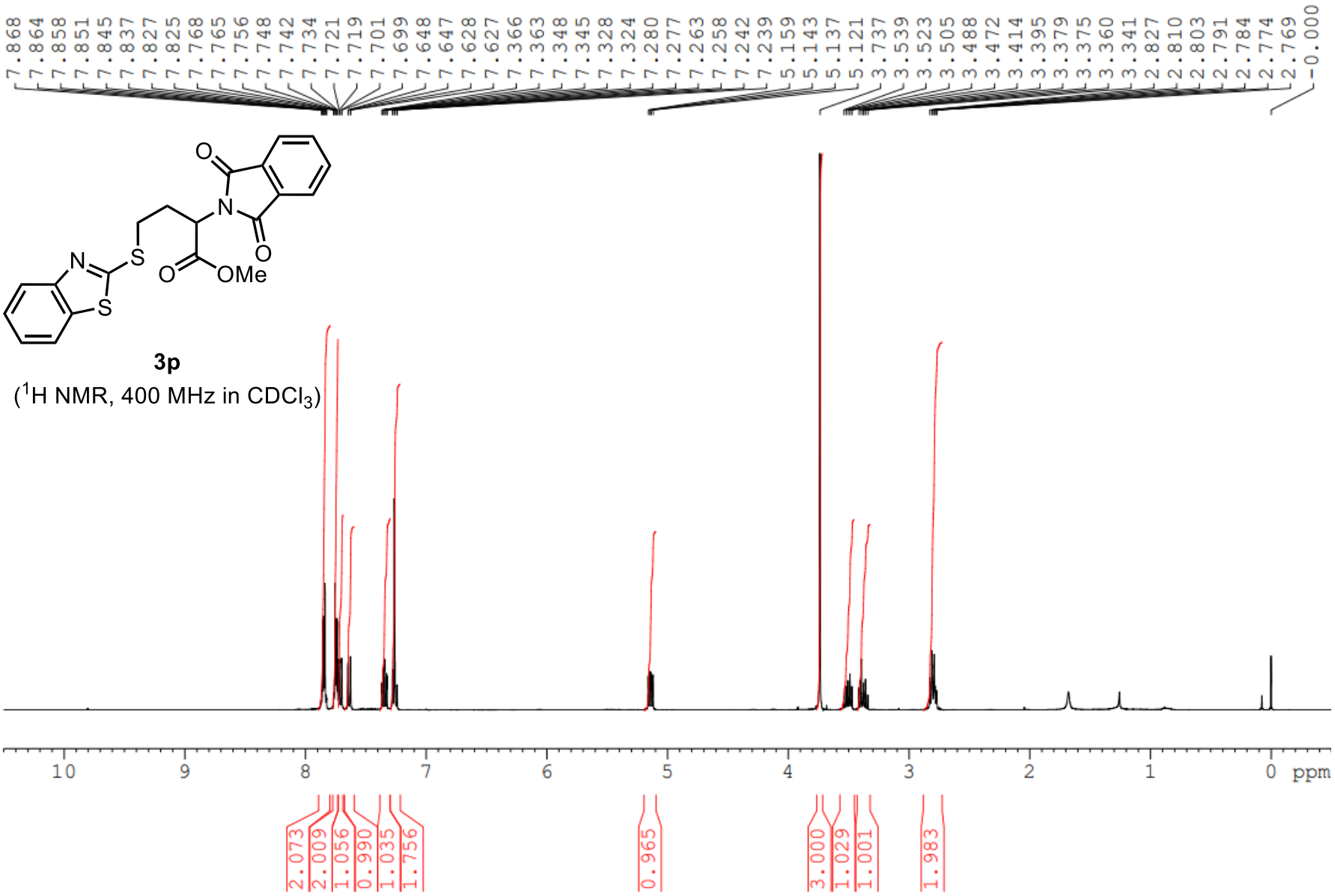




3o

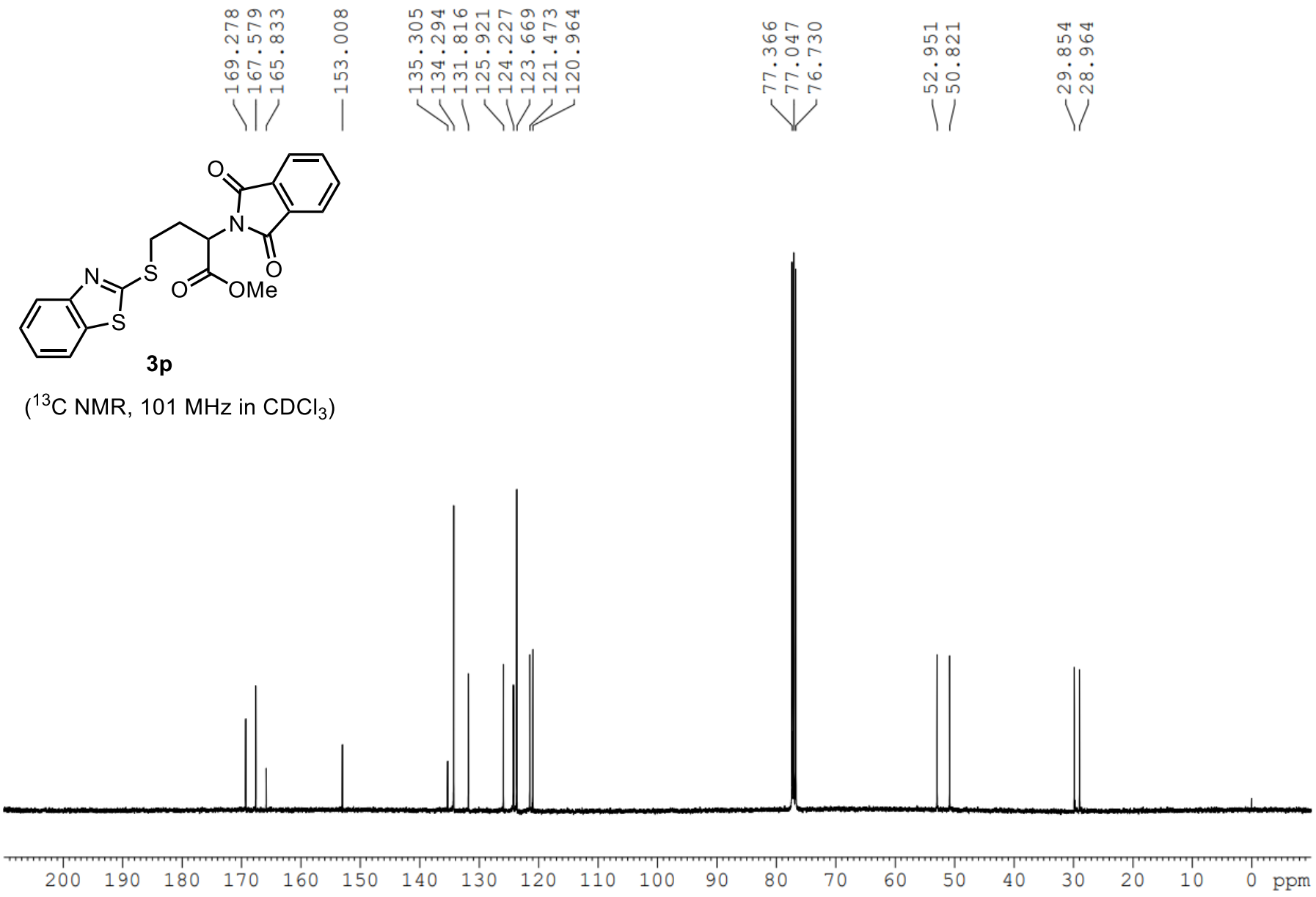
(^{13}C NMR, 101 MHz in $CDCl_3$)





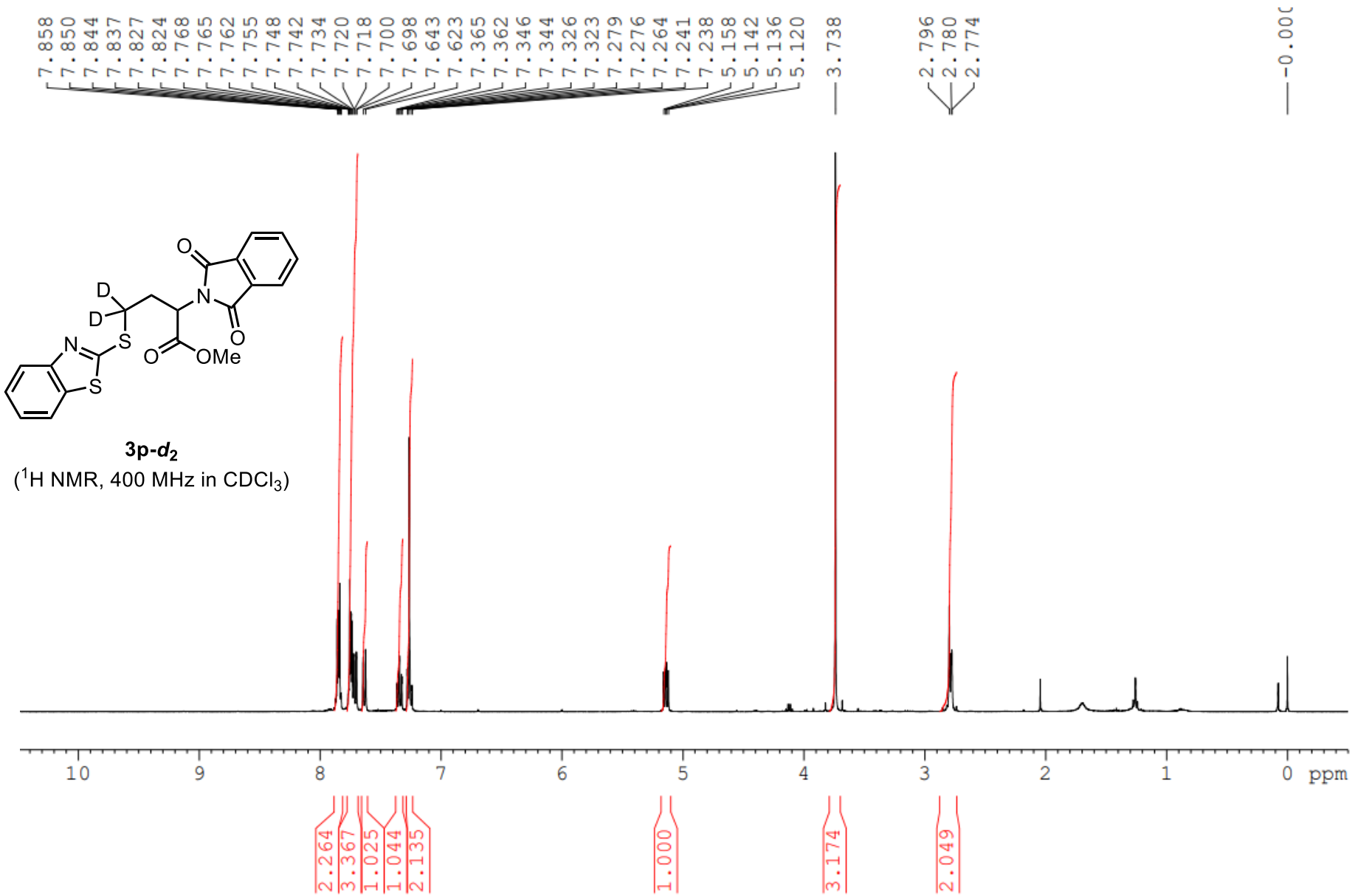
3p

(^{1}H NMR, 400 MHz in $CDCl_3$)



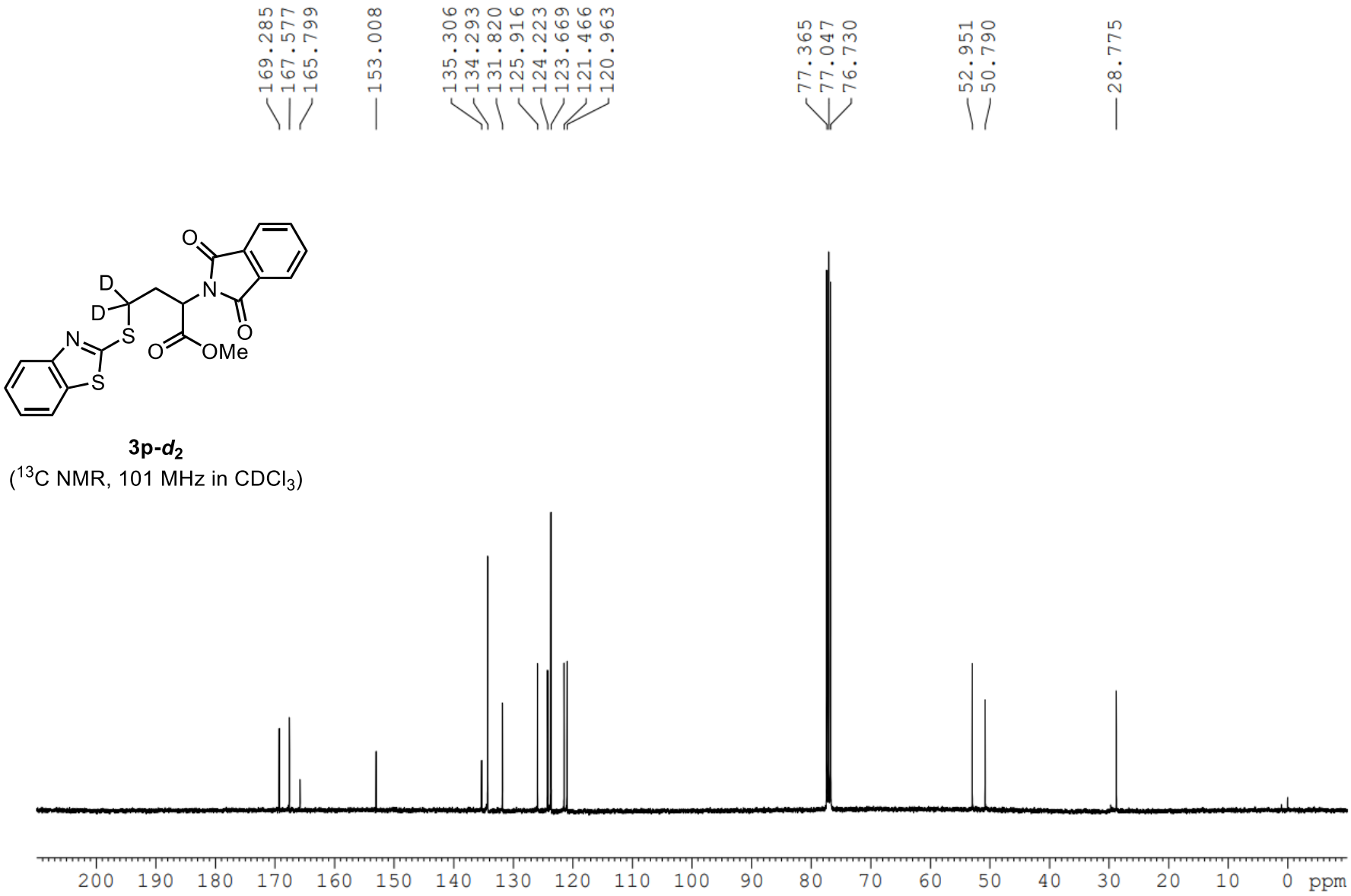
3p

(^{13}C NMR, 101 MHz in $CDCl_3$)



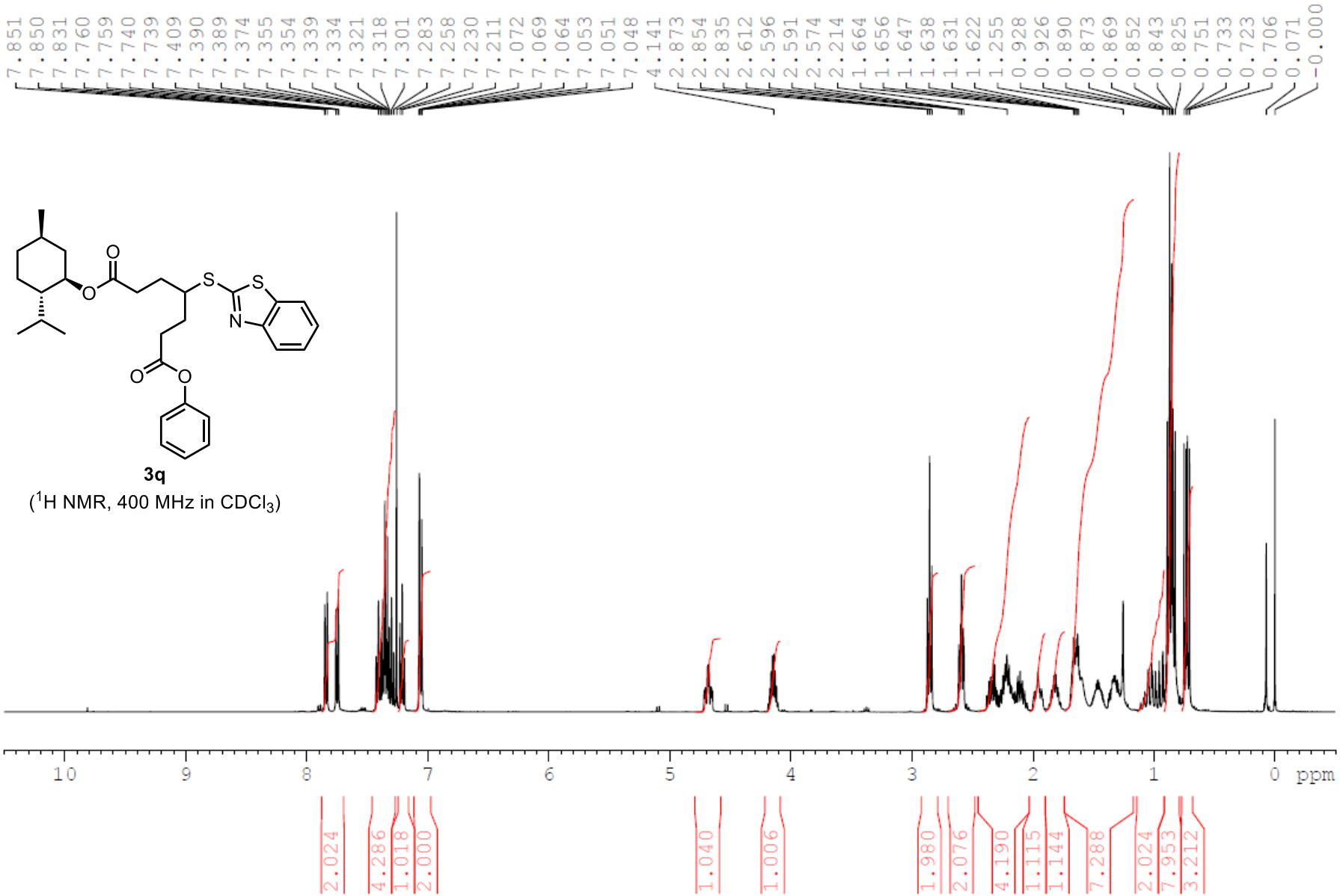
3p-d_2

(^{1}H NMR, 400 MHz in $CDCl_3$)



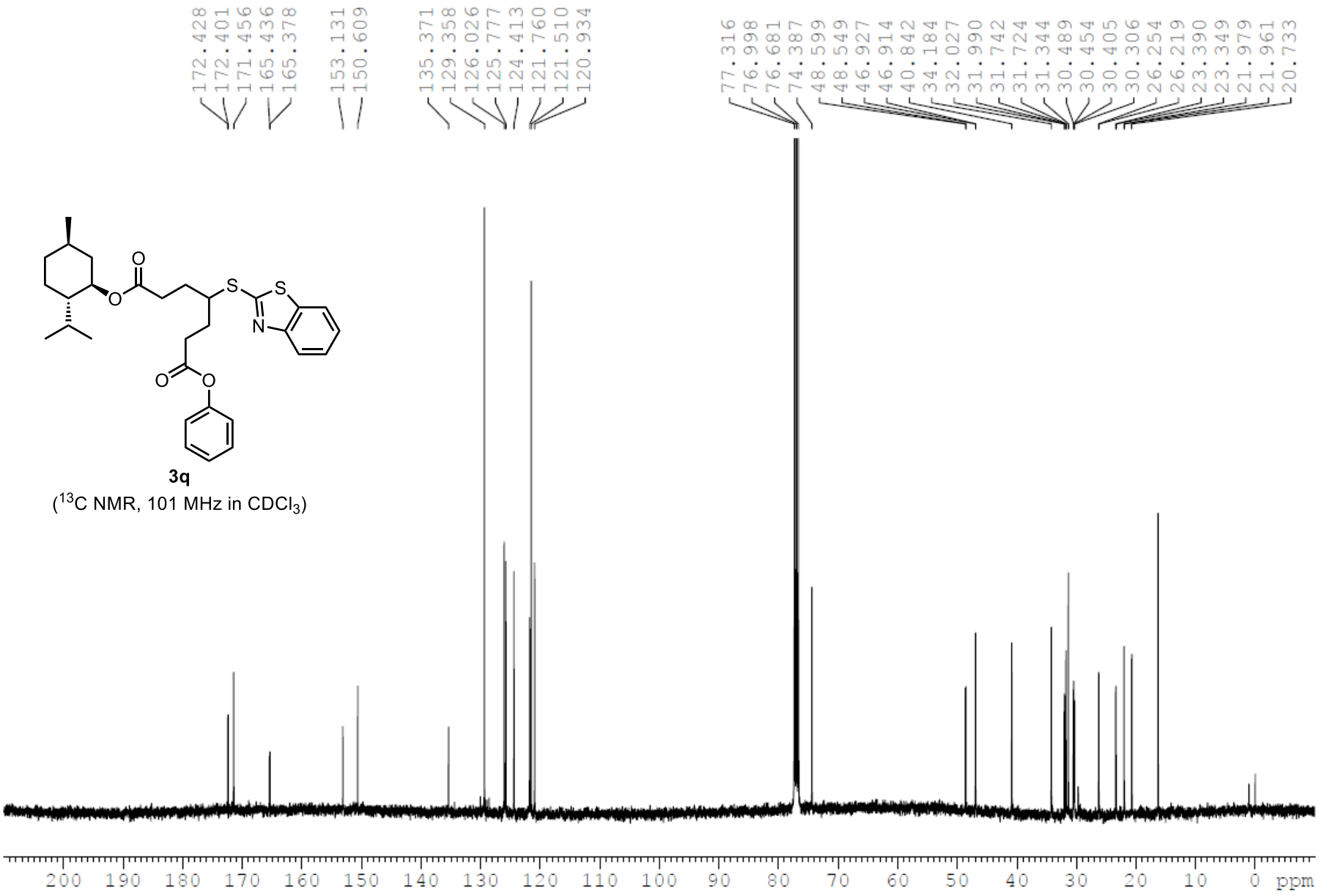
3p-d_2

(^{13}C NMR, 101 MHz in $CDCl_3$)



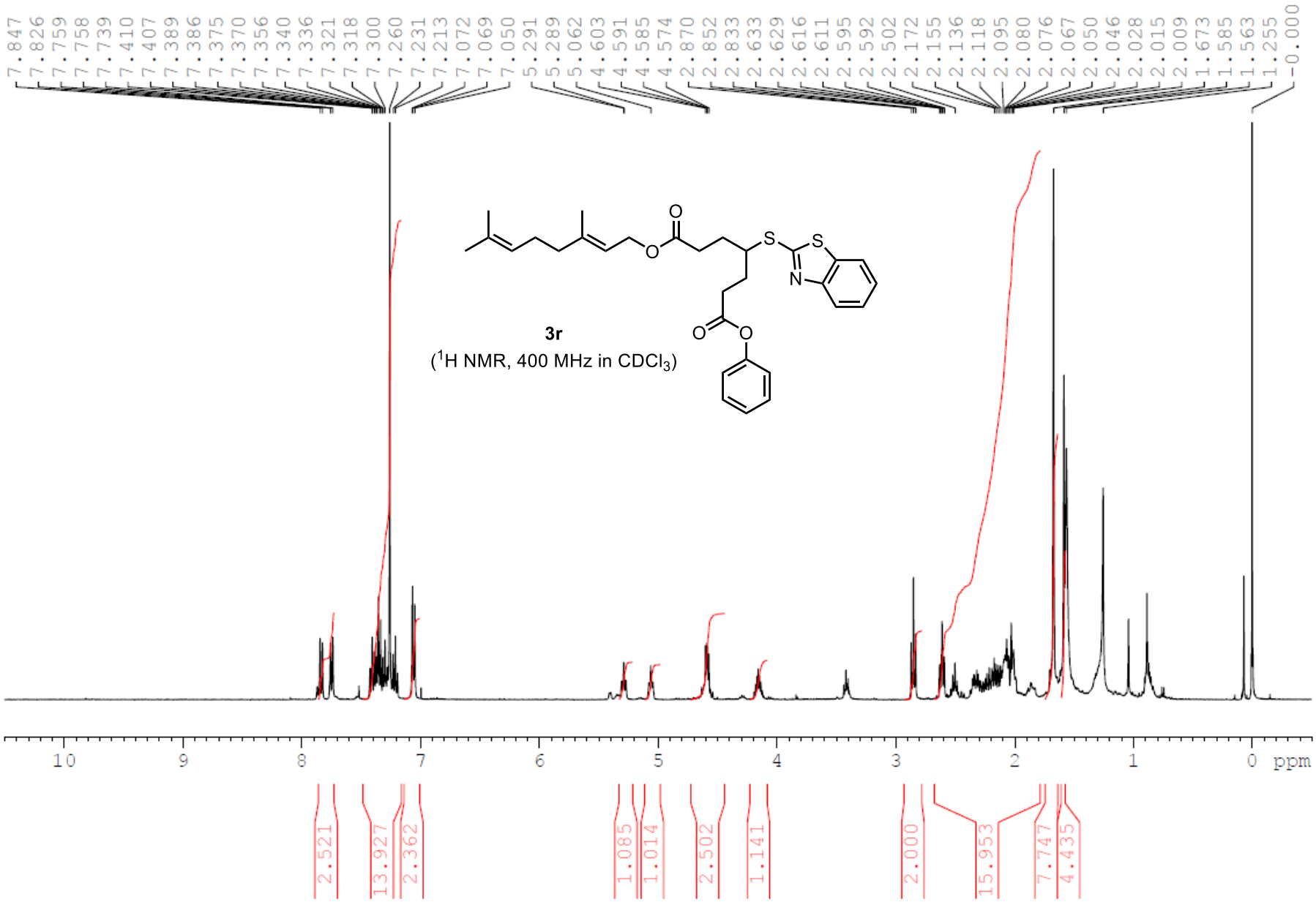
3q

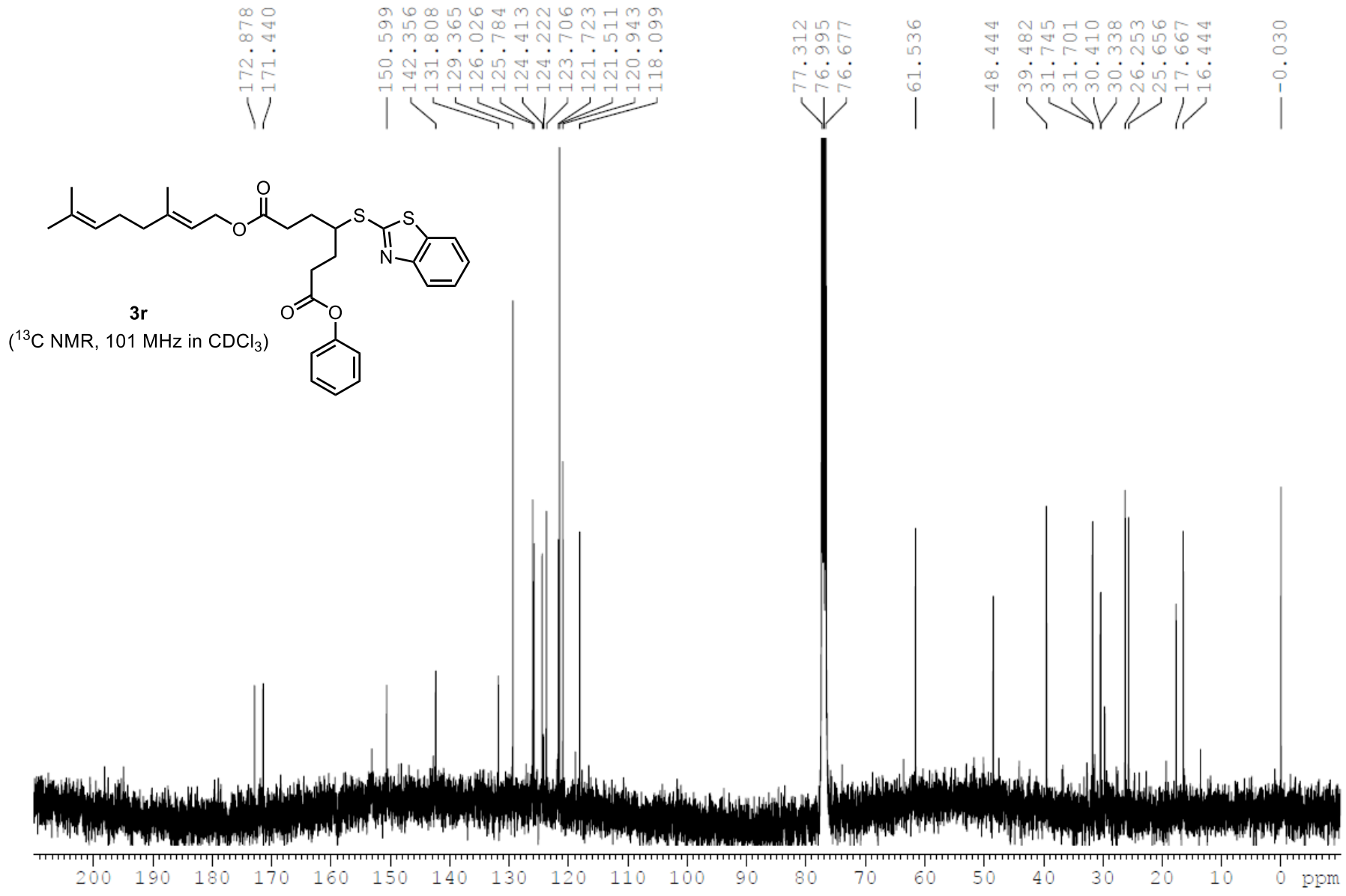
(^{1}H NMR, 400 MHz in $CDCl_3$)



3q

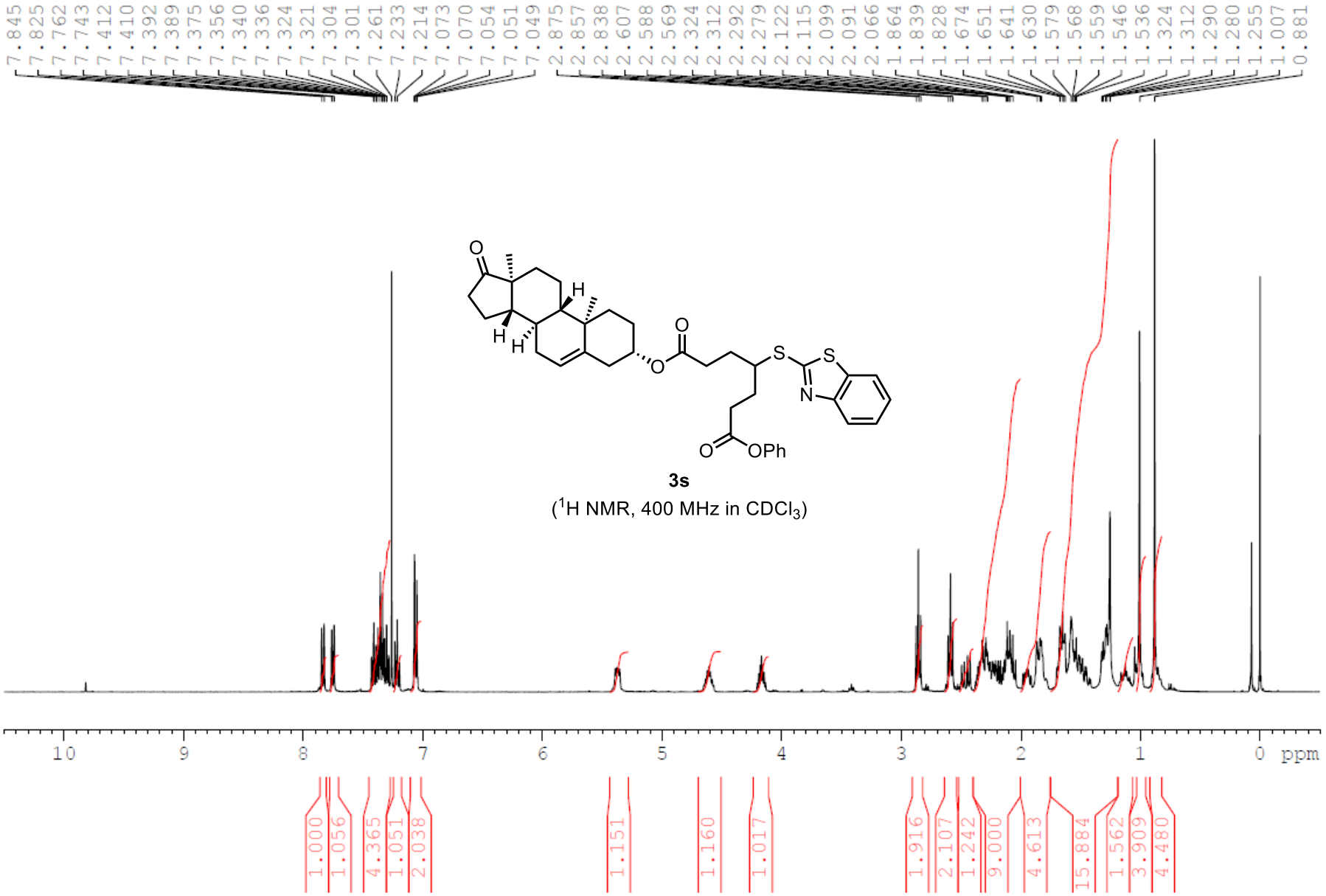
(^{13}C NMR, 101 MHz in $CDCl_3$)


7.847
7.826
7.759
7.758
7.739
7.410
7.407
7.389
7.386
7.375
7.370
7.356
7.340
7.336
7.321
7.318
7.300
7.260
7.231
7.213
7.072
7.069
7.050
5.291
5.289
5.062
4.603
4.591
4.585
4.574
2.870
2.852
2.833
2.633
2.629
2.616
2.611
2.595
2.592
2.502
2.172
2.155
2.136
2.118
2.095
2.080
2.076
2.067
2.050
2.046
2.028
2.015
2.009
1.673
1.585
1.563
1.255
-0.000
O
O
S
S
N
O
O
3r
(^{1}H NMR, 400 MHz in $CDCl_3$)
10
9
8
7
6
5
4
3
2
1
0
ppm
2.521
13.927
2.362
1.085
1.014
2.502
1.141
2.000
15.953
7.747
4.435



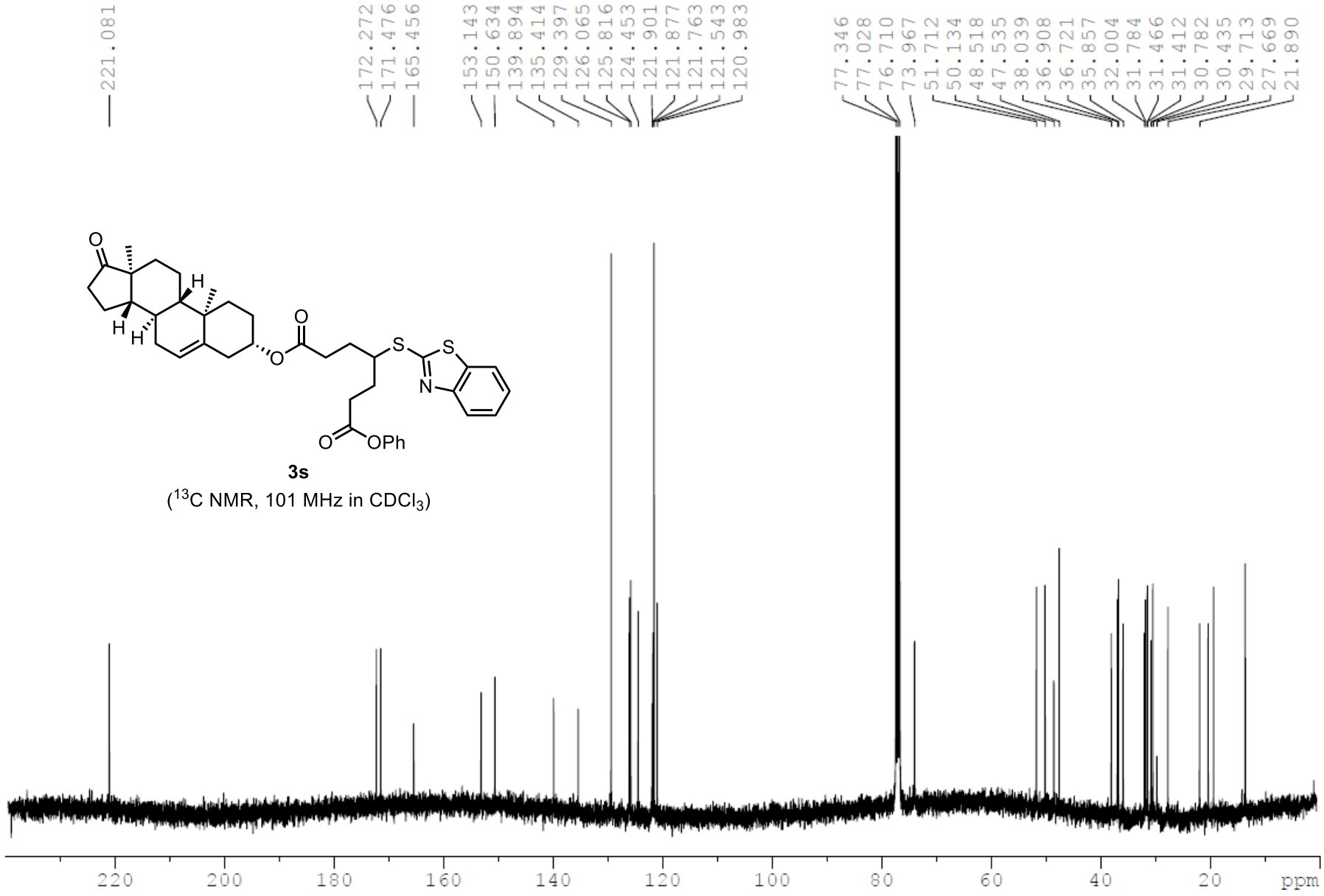
3r

(^{13}C NMR, 101 MHz in $CDCl_3$)



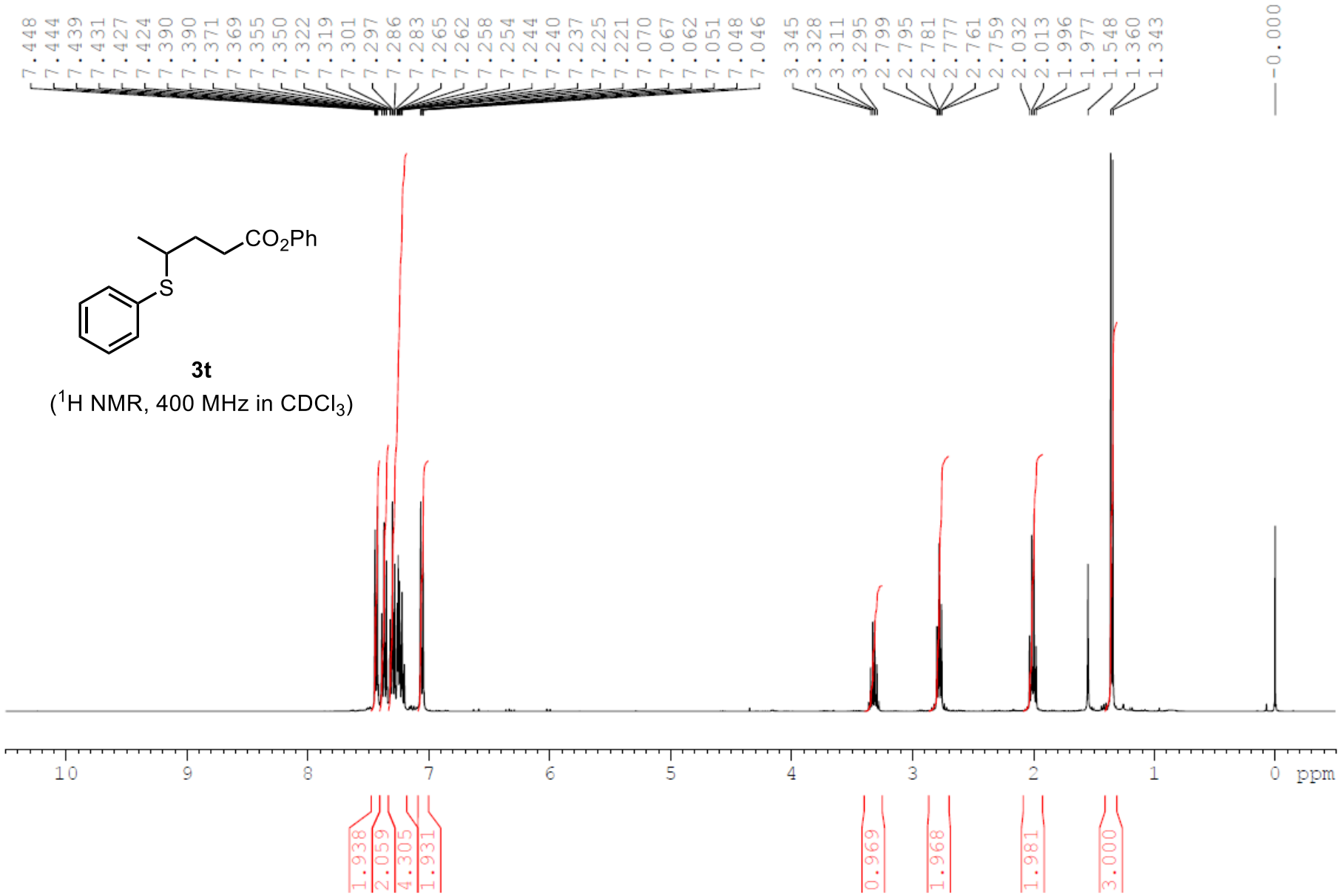
3s

(^{1}H NMR, 400 MHz in $CDCl_3$)



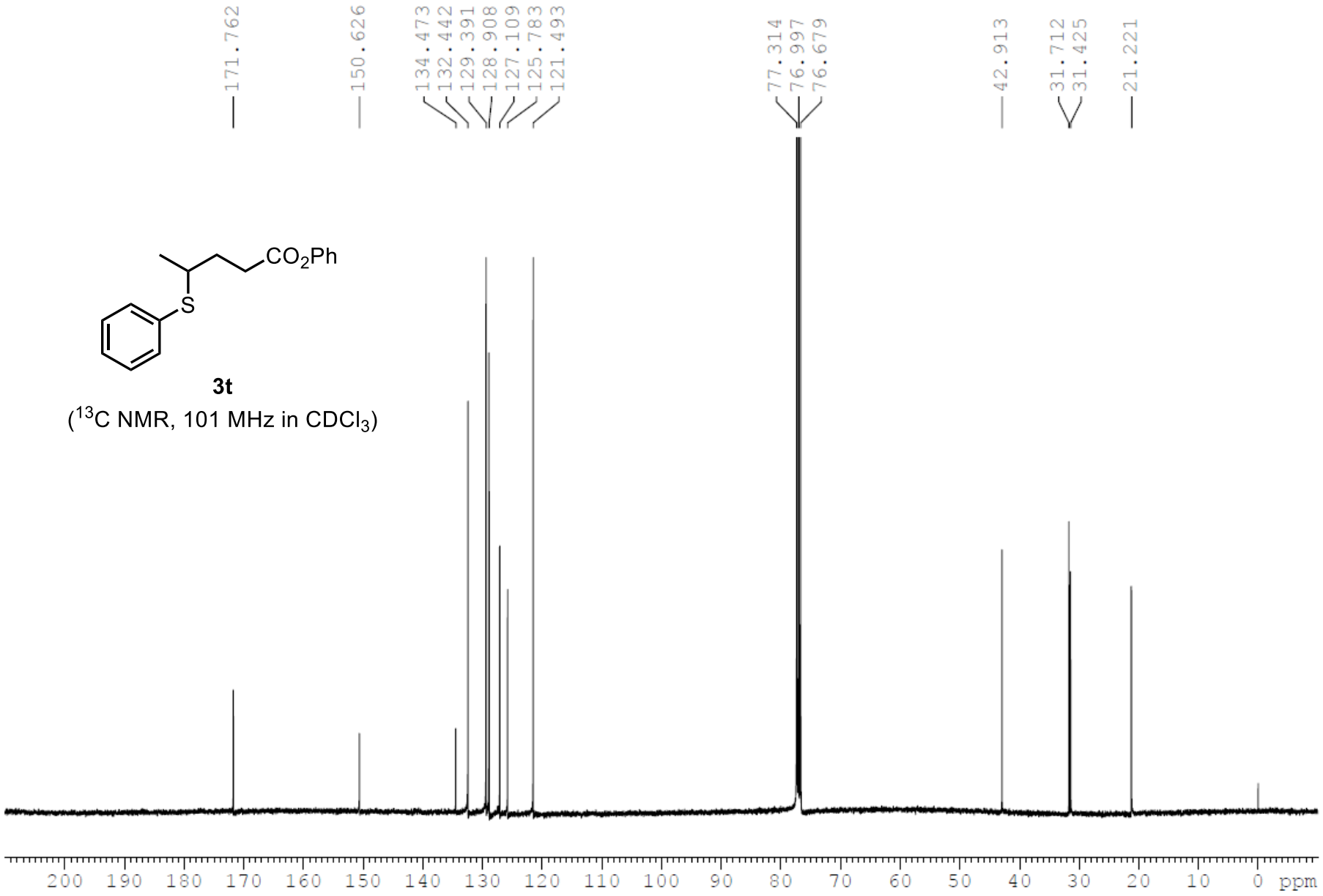
3s

(^{13}C NMR, 101 MHz in $CDCl_3$)



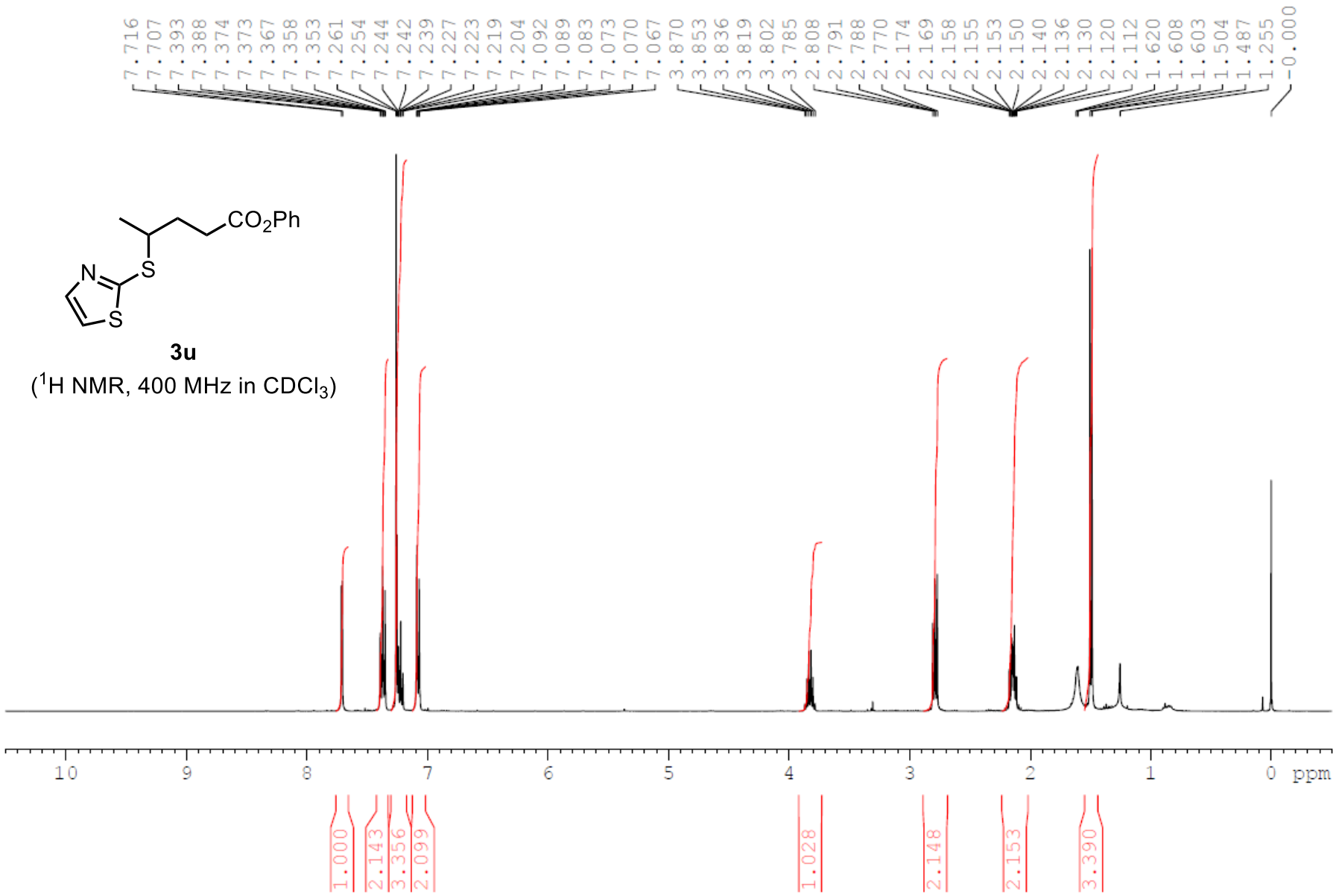
3t

(^{1}H NMR, 400 MHz in $CDCl_3$)



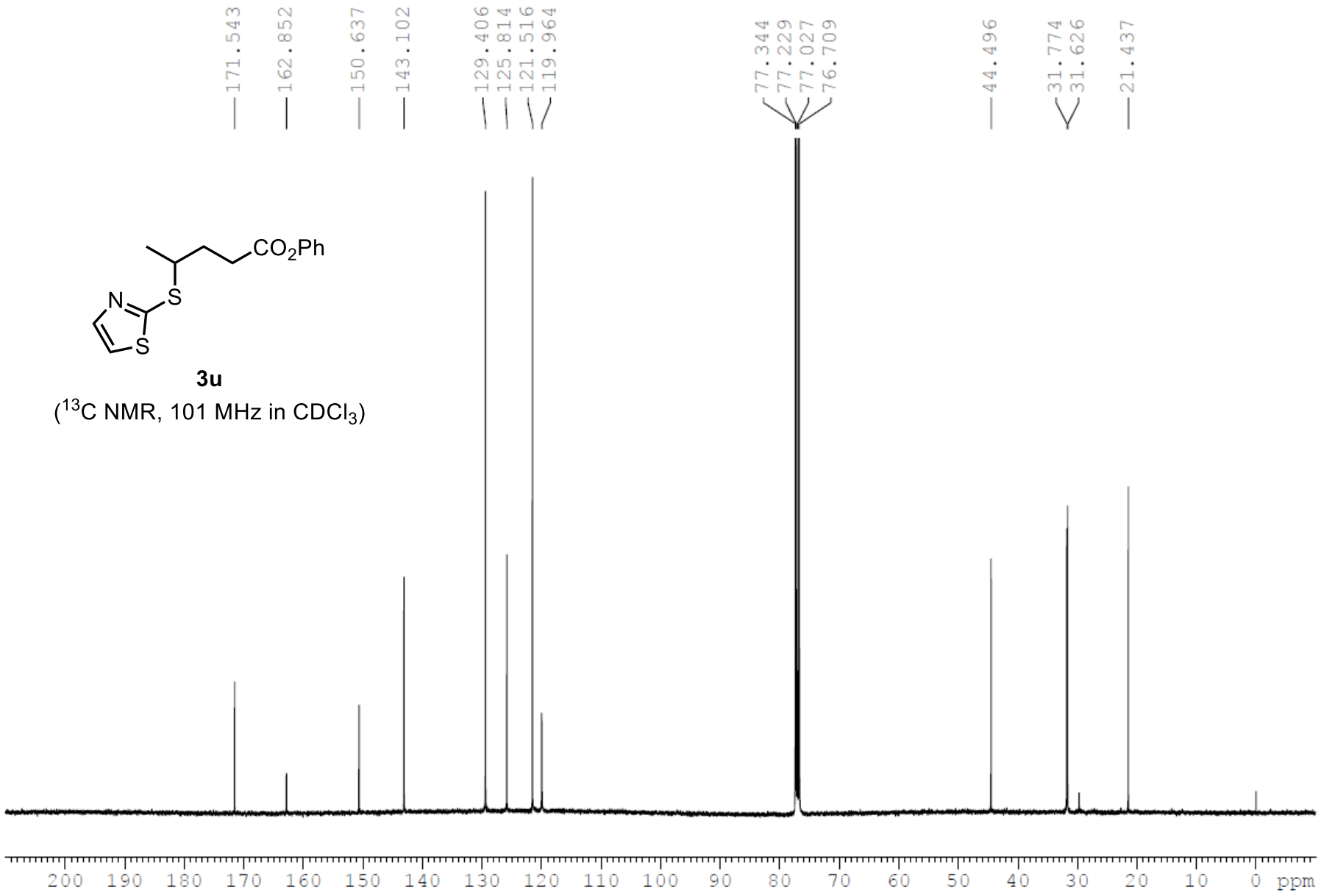
3t

(^{13}C NMR, 101 MHz in $CDCl_3$)



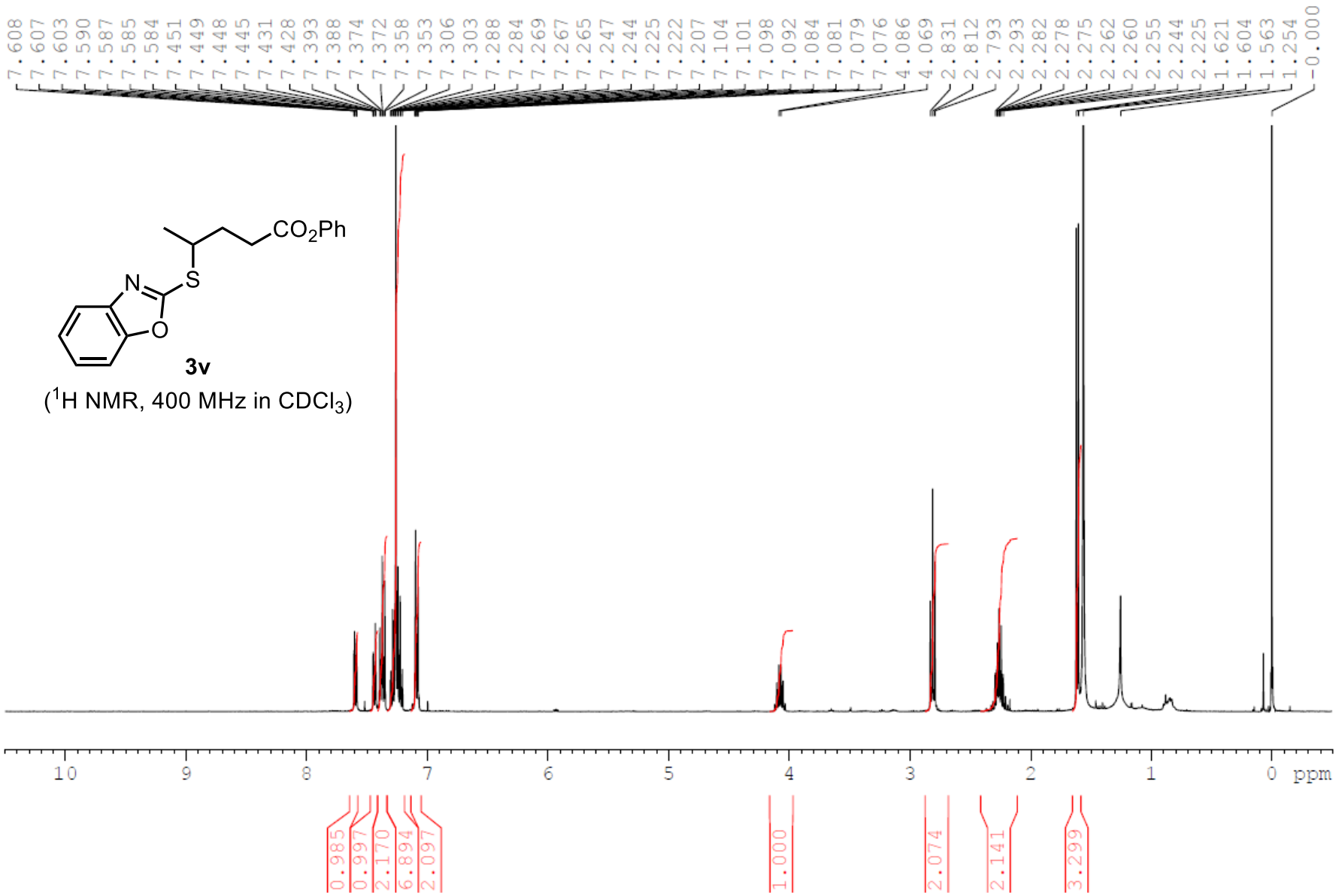
3u

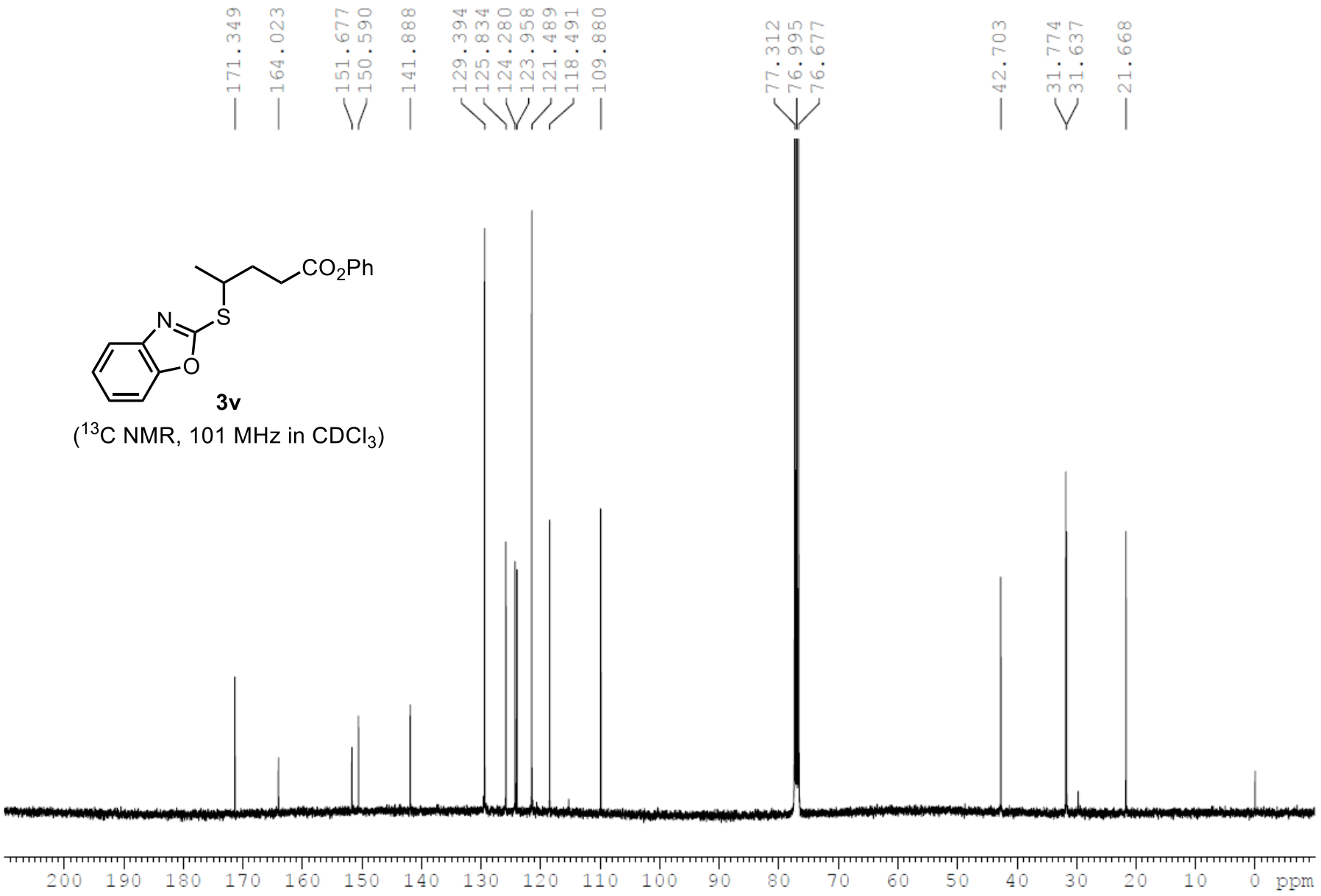
(^{1}H NMR, 400 MHz in $CDCl_3$)



3u

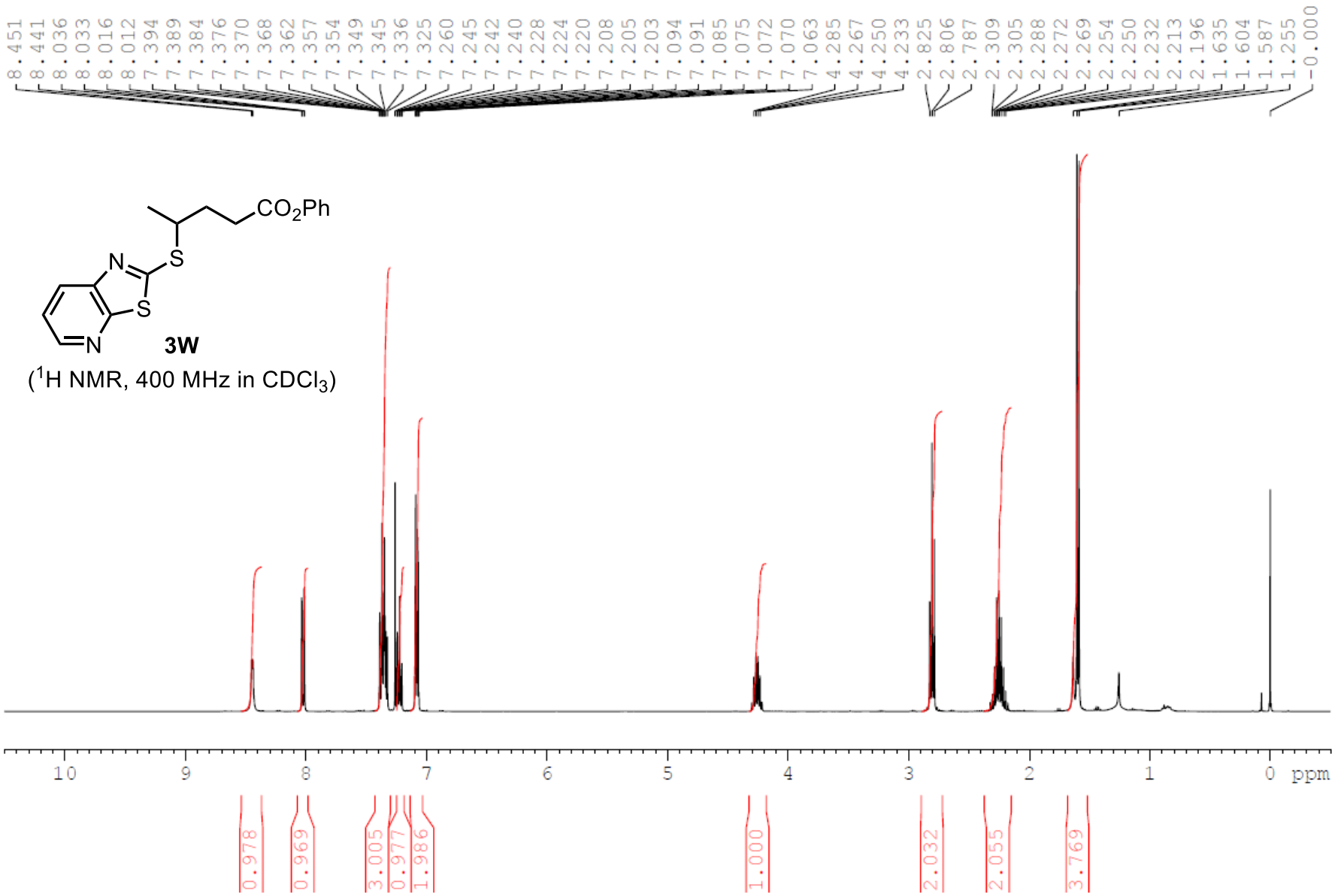
(^{13}C NMR, 101 MHz in $CDCl_3$)

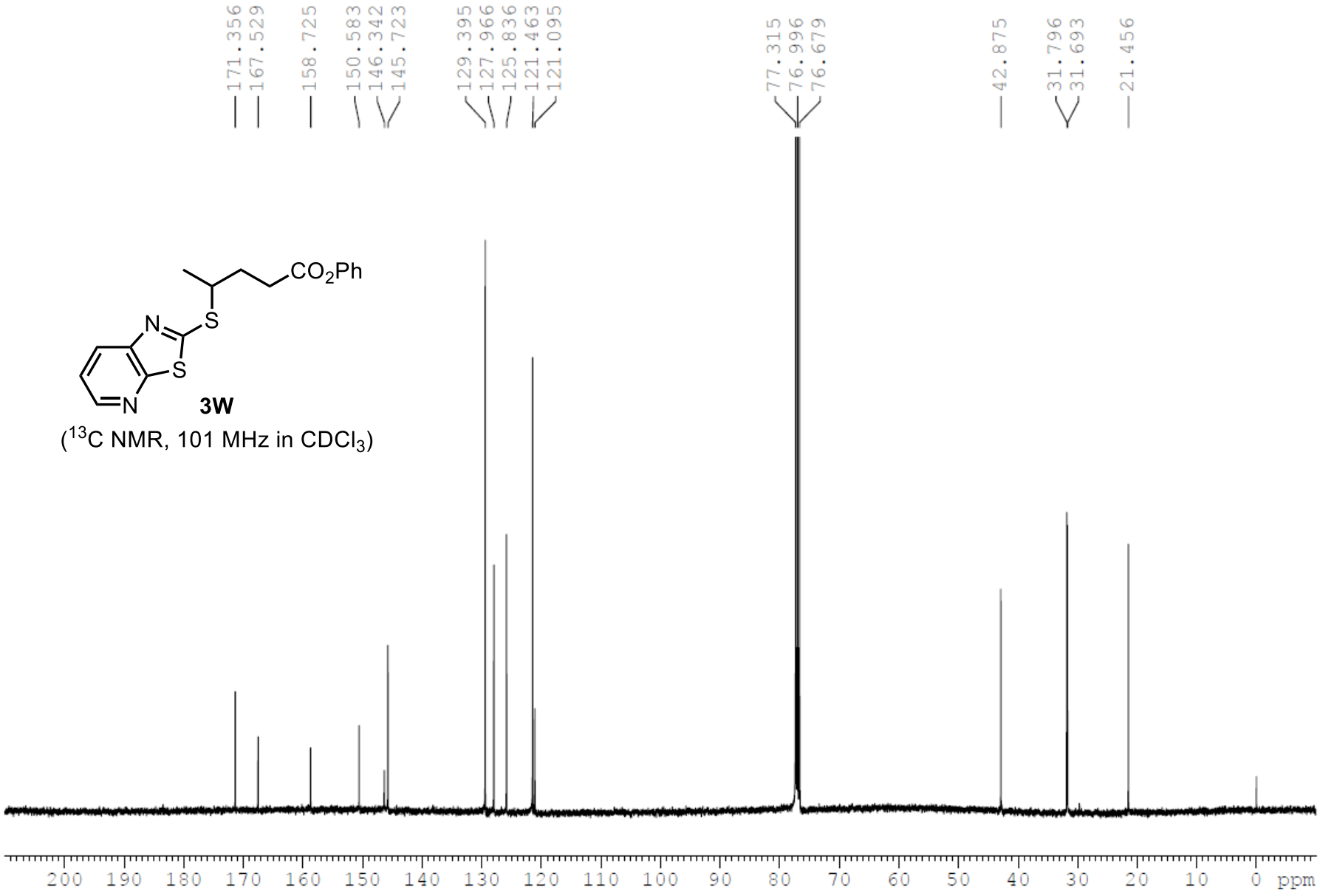

7.608
7.607
7.603
7.590
7.587
7.585
7.584
7.451
7.449
7.448
7.445
7.431
7.428
7.393
7.388
7.374
7.372
7.358
7.353
7.306
7.303
7.288
7.284
7.269
7.267
7.265
7.247
7.244
7.225
7.222
7.207
7.104
7.101
7.098
7.092
7.084
7.081
7.079
7.076
4.086
4.069
2.831
2.812
2.793
2.293
2.282
2.278
2.275
2.262
2.260
2.255
2.244
2.225
1.621
1.604
1.563
1.254
0.000
CO2Ph
N
S
O
3v
(1H NMR, 400 MHz in CDCl3)
10
9
8
7
6
5
4
3
2
1
0
ppm
0.985
0.997
2.170
6.894
2.097
1.000
2.074
2.141
3.299



3v

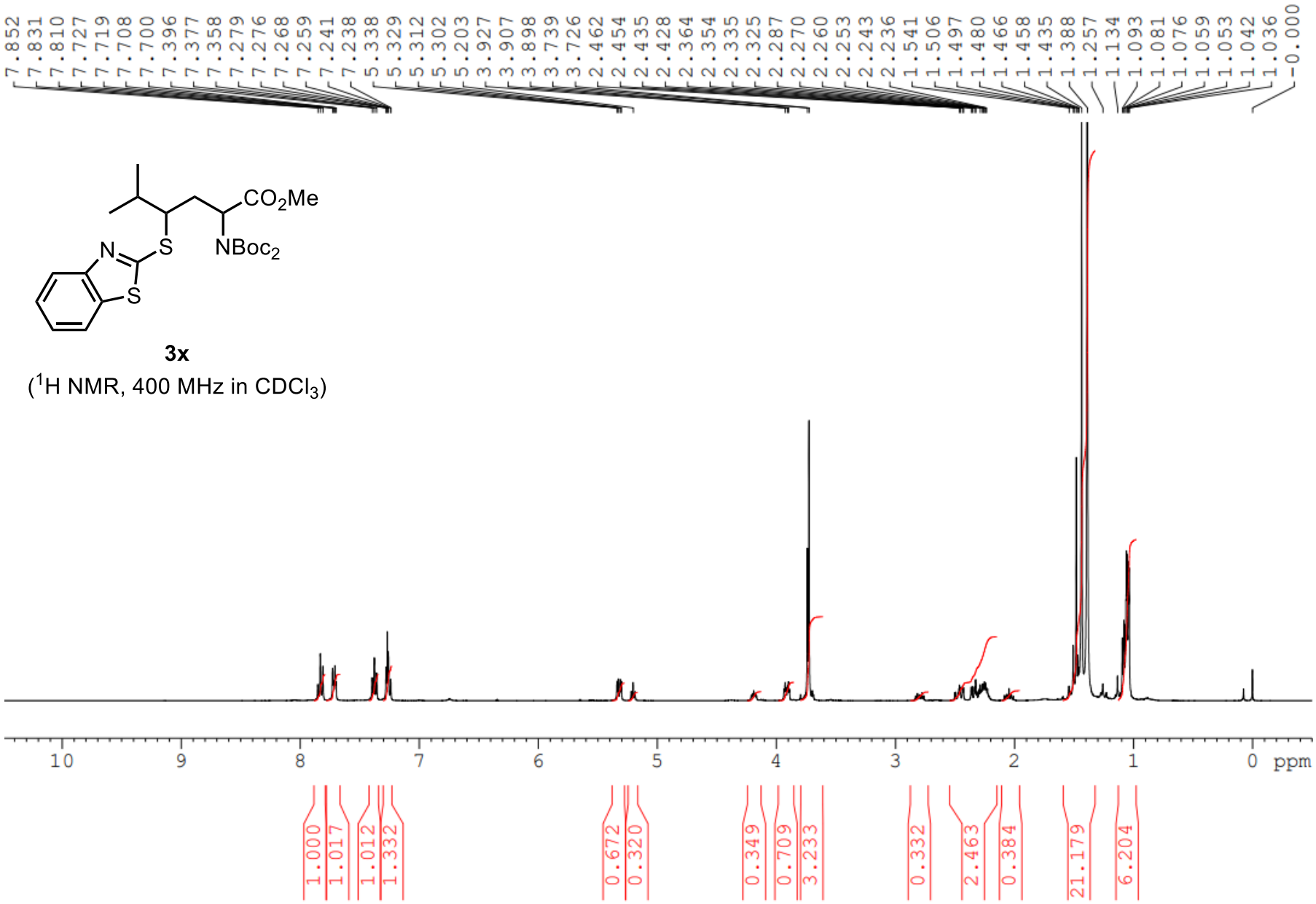
(^{13}C NMR, 101 MHz in $CDCl_3$)


8.451
8.441
8.036
8.033
8.016
8.012
7.394
7.389
7.384
7.376
7.370
7.368
7.362
7.357
7.354
7.349
7.345
7.336
7.325
7.260
7.245
7.242
7.240
7.228
7.224
7.220
7.208
7.205
7.203
7.094
7.091
7.085
7.075
7.072
7.070
7.063
4.285
4.267
4.250
4.233
2.825
2.806
2.787
2.309
2.305
2.288
2.272
2.269
2.254
2.250
2.232
2.213
2.196
1.635
1.604
1.587
1.255
-0.000
CO2Ph
N
S
S
N
3W
(1H NMR, 400 MHz in CDCl3)
10
9
8
7
6
5
4
3
2
1
0
ppm
0.978
0.969
3.005
0.977
1.986
1.000
2.032
2.055
3.769



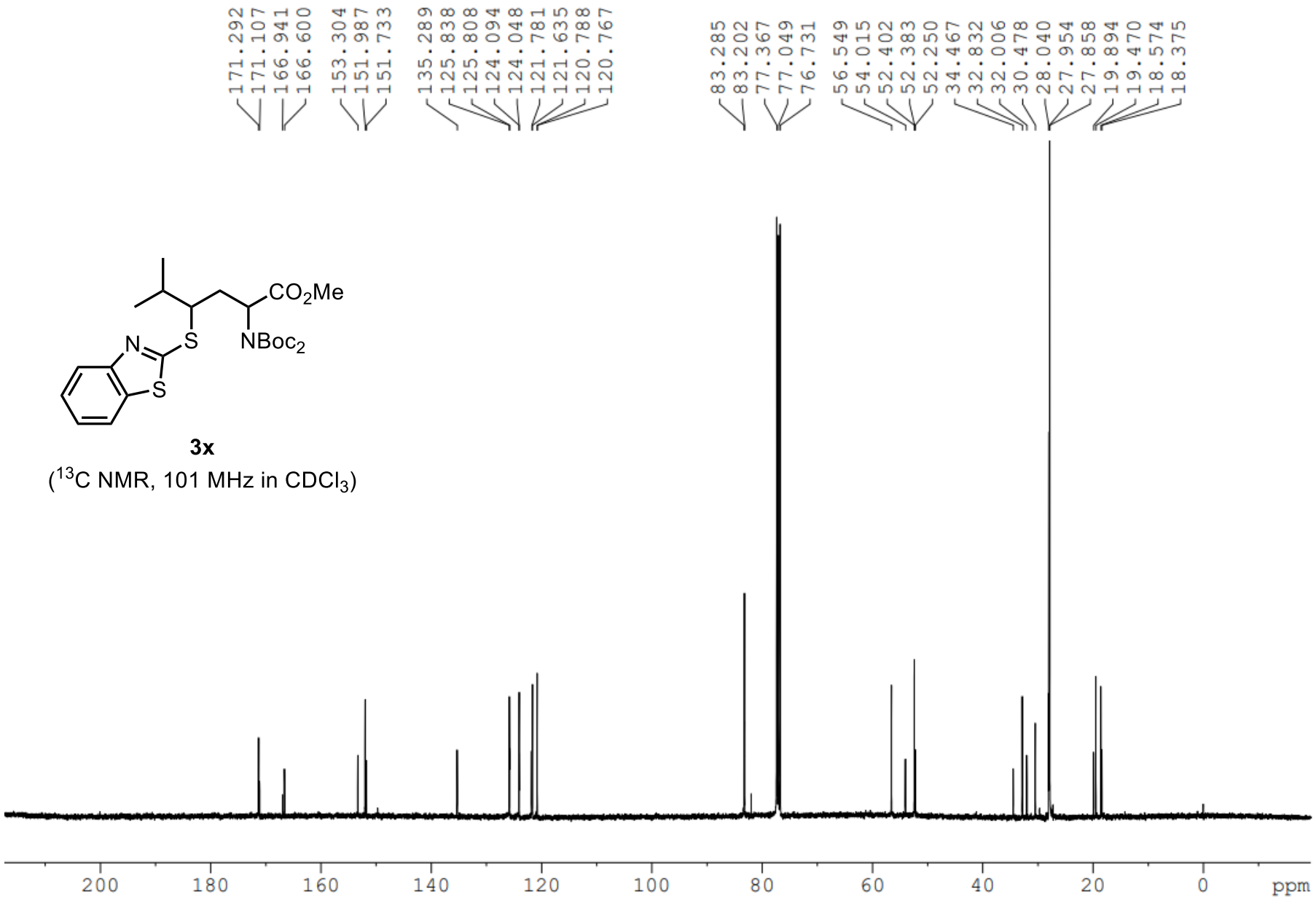
3W

(^{13}C NMR, 101 MHz in $CDCl_3$)



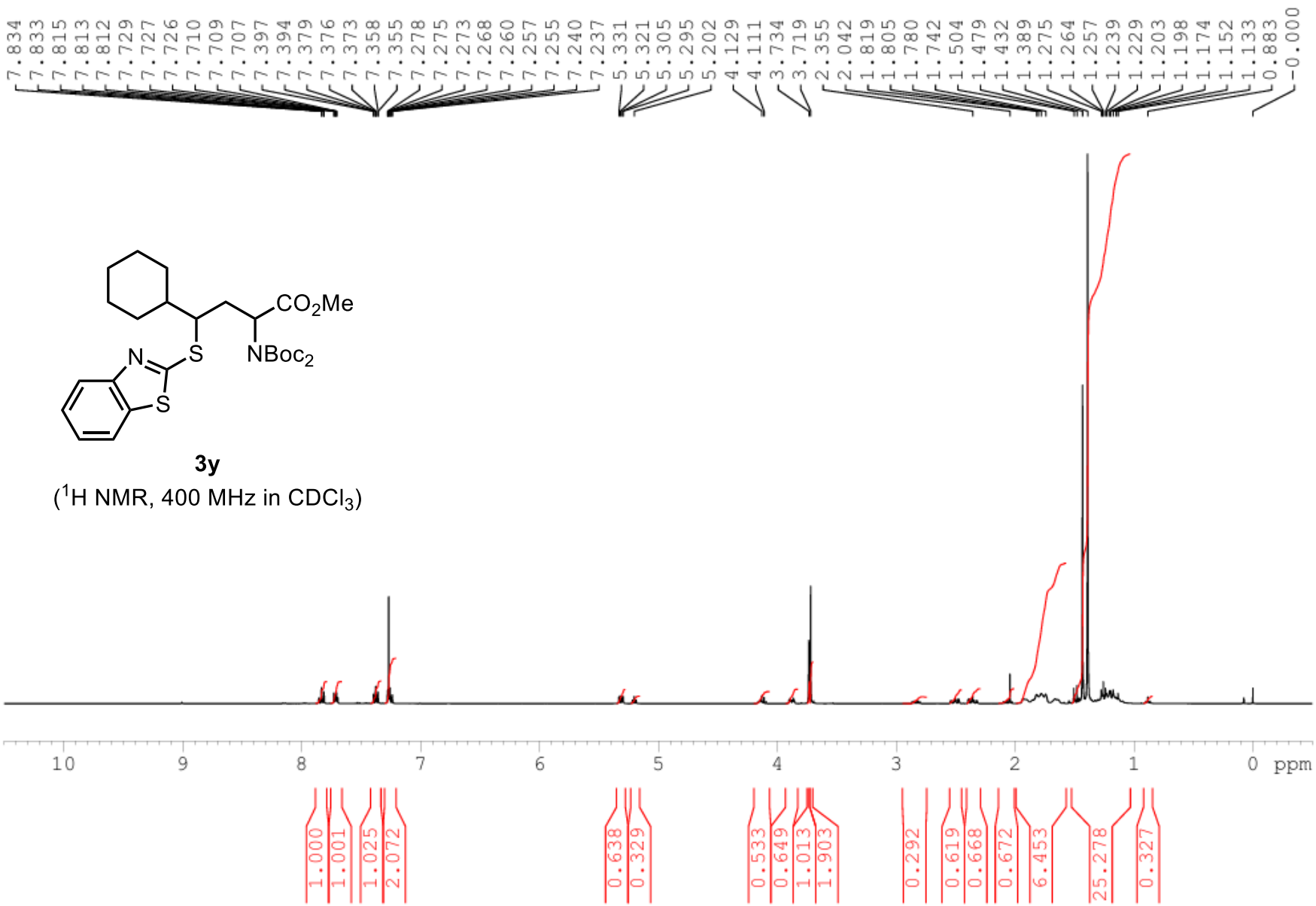
3x

(^{1}H NMR, 400 MHz in $CDCl_3$)



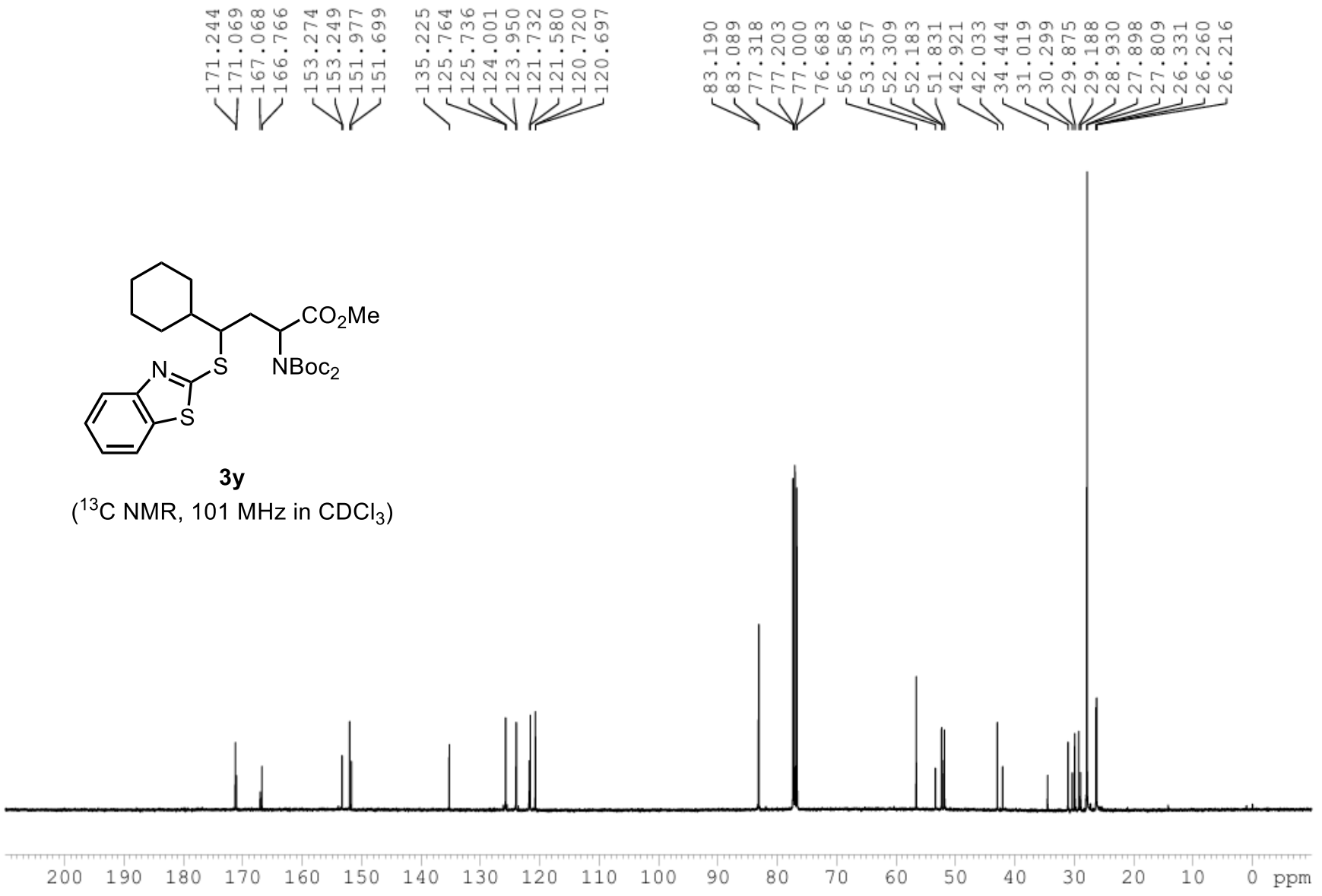
3x

(^{13}C NMR, 101 MHz in $CDCl_3$)



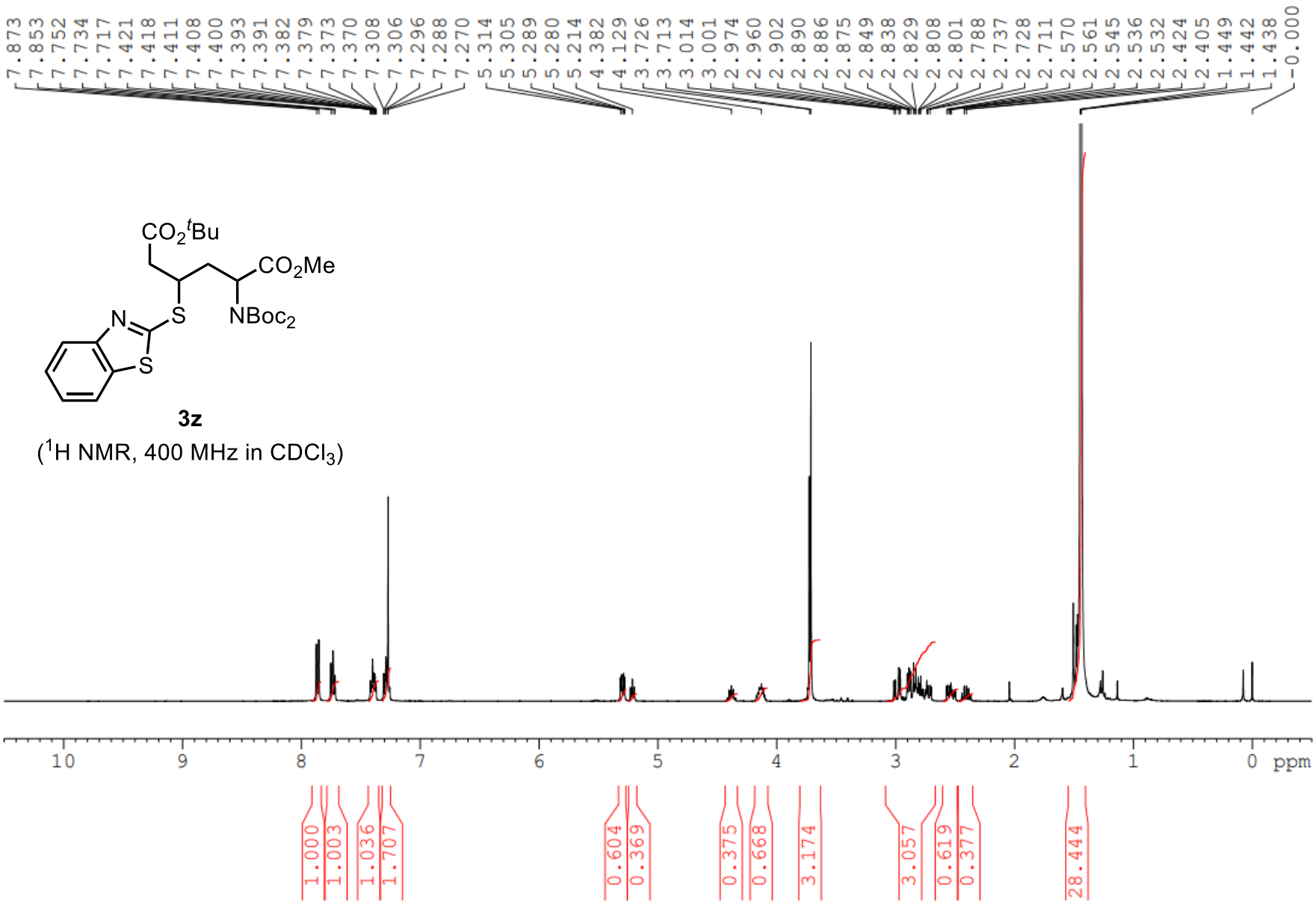
3y

(^{1}H NMR, 400 MHz in $CDCl_3$)



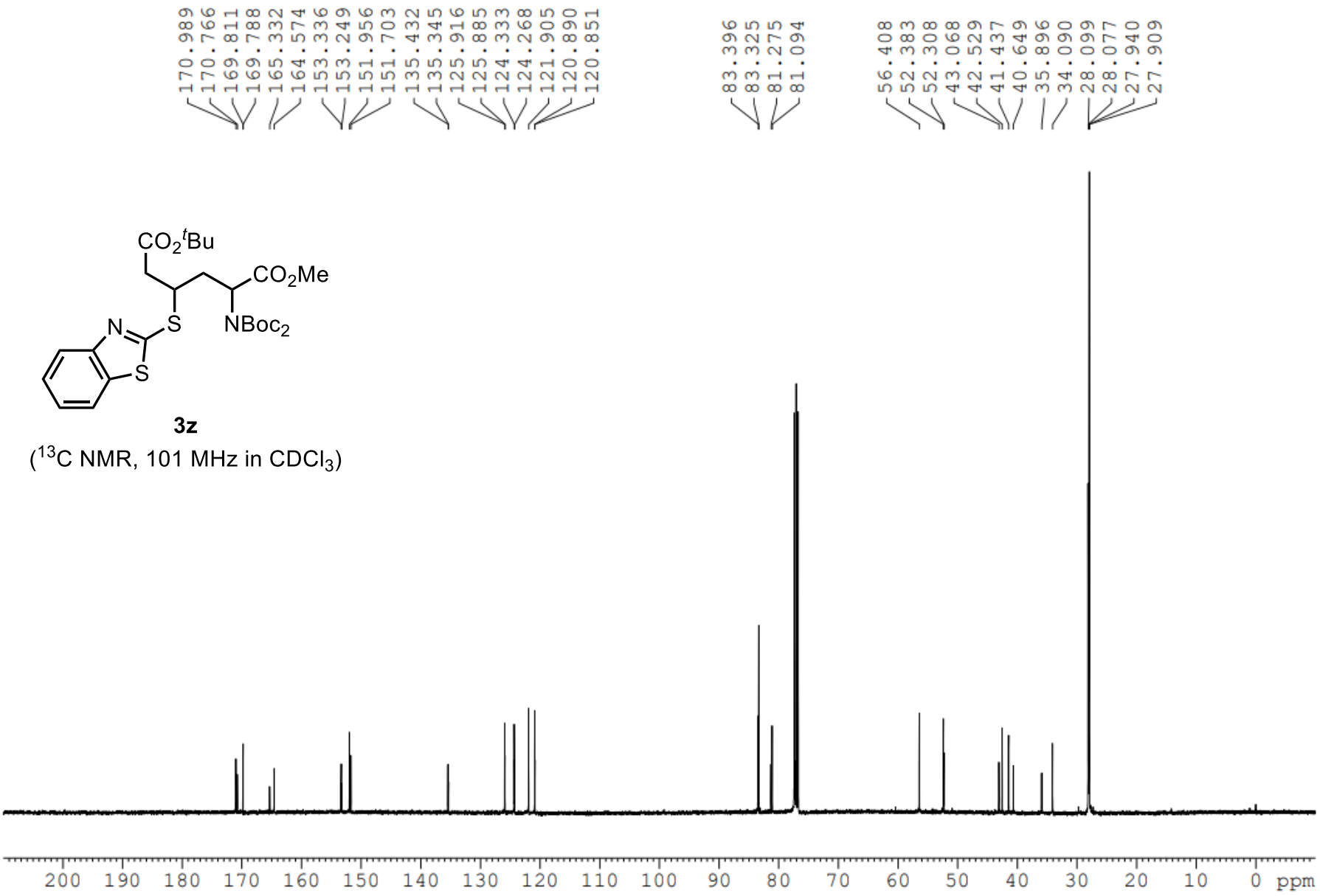
3y

(^{13}C NMR, 101 MHz in $CDCl_3$)



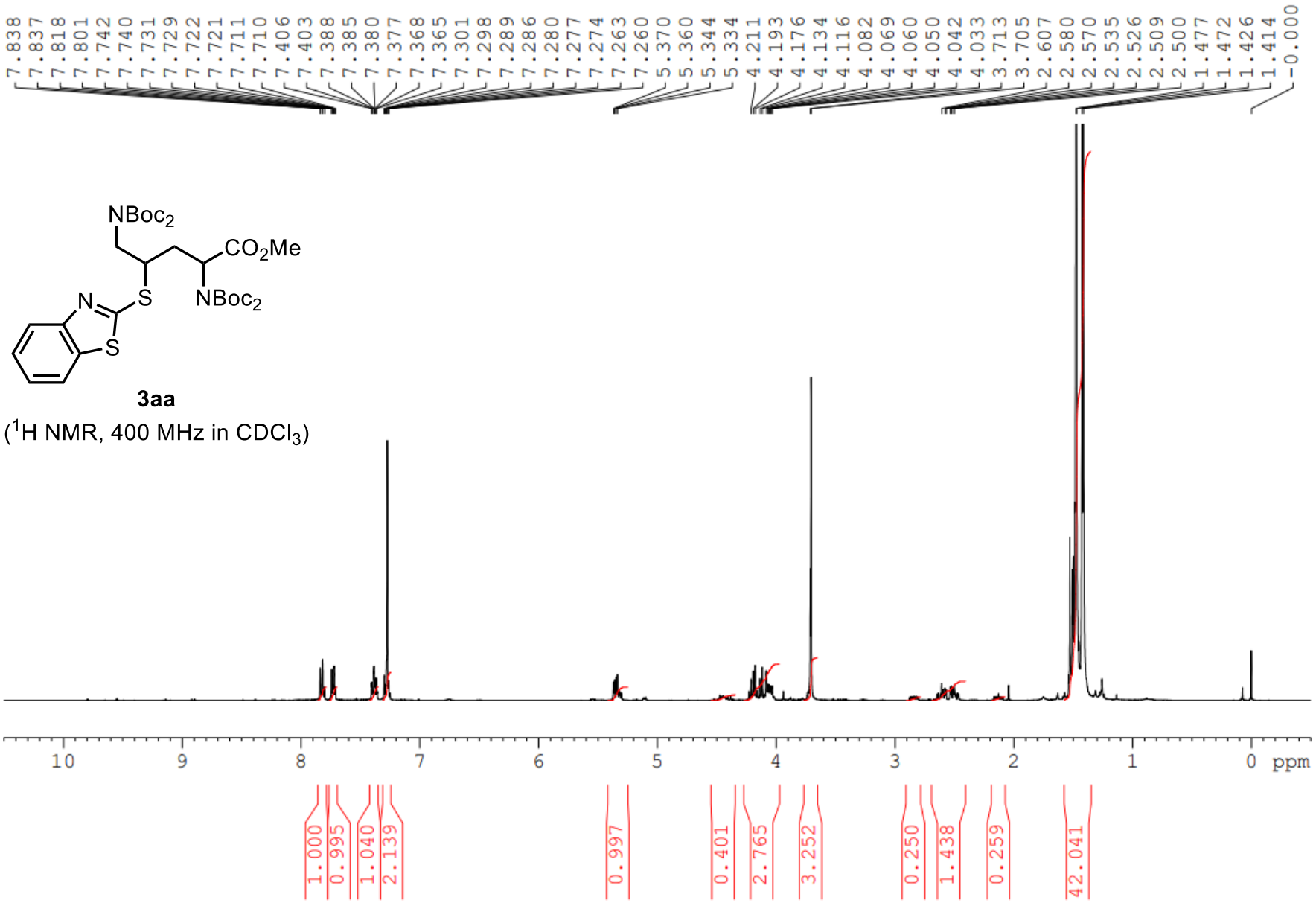
3z

(^{1}H NMR, 400 MHz in $CDCl_3$)



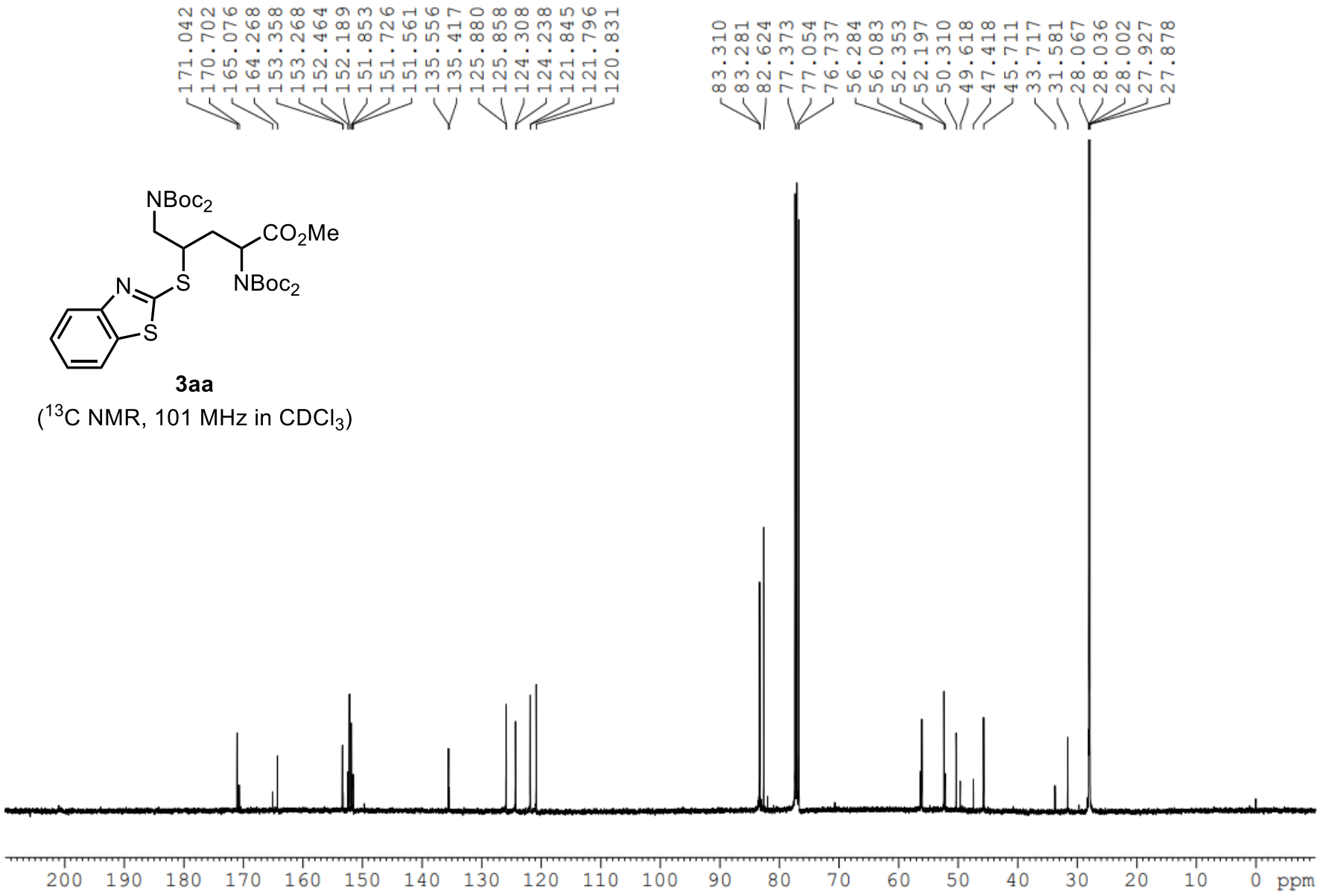
3z

(^{13}C NMR, 101 MHz in $CDCl_3$)



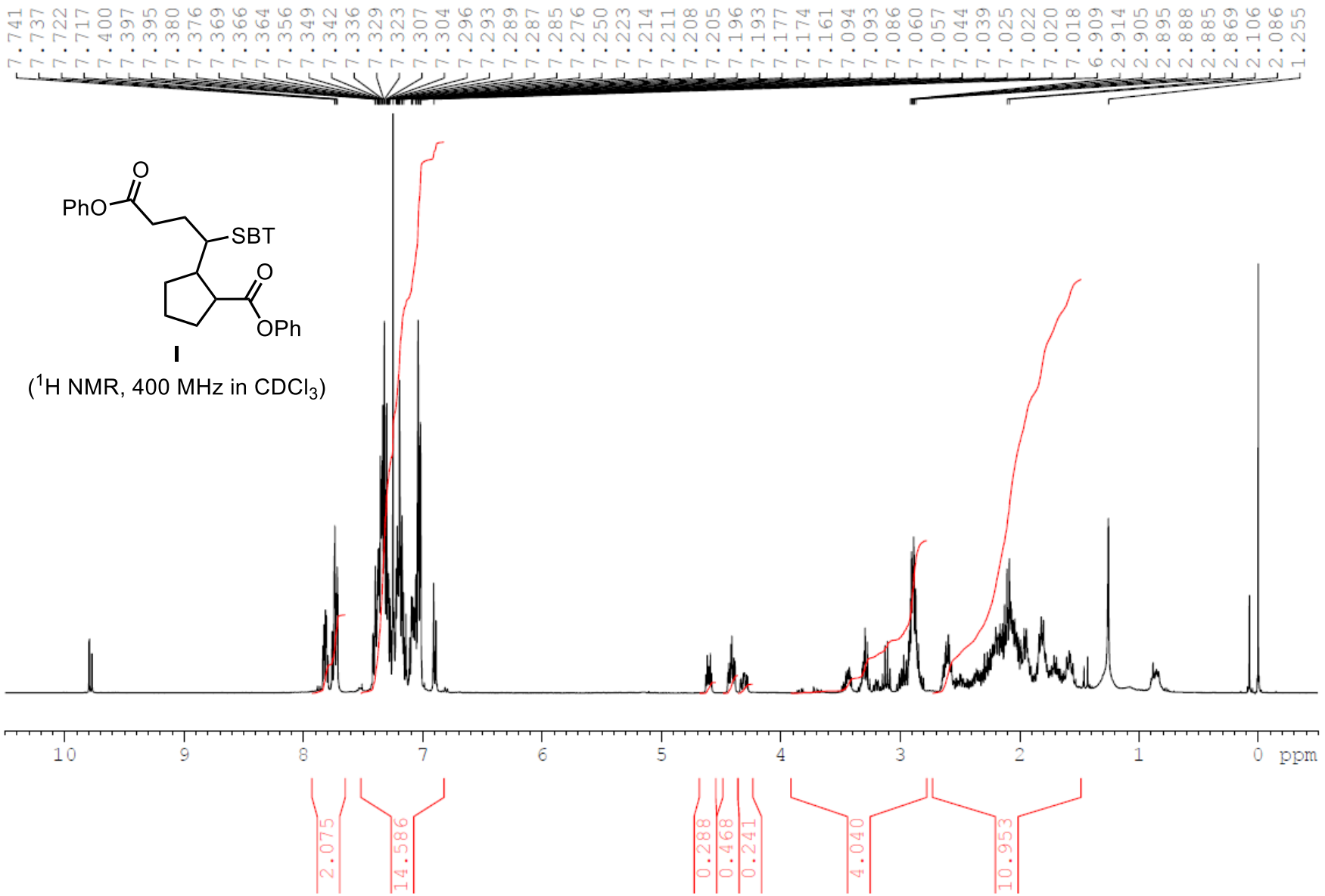
3aa

(^{1}H NMR, 400 MHz in $CDCl_3$)



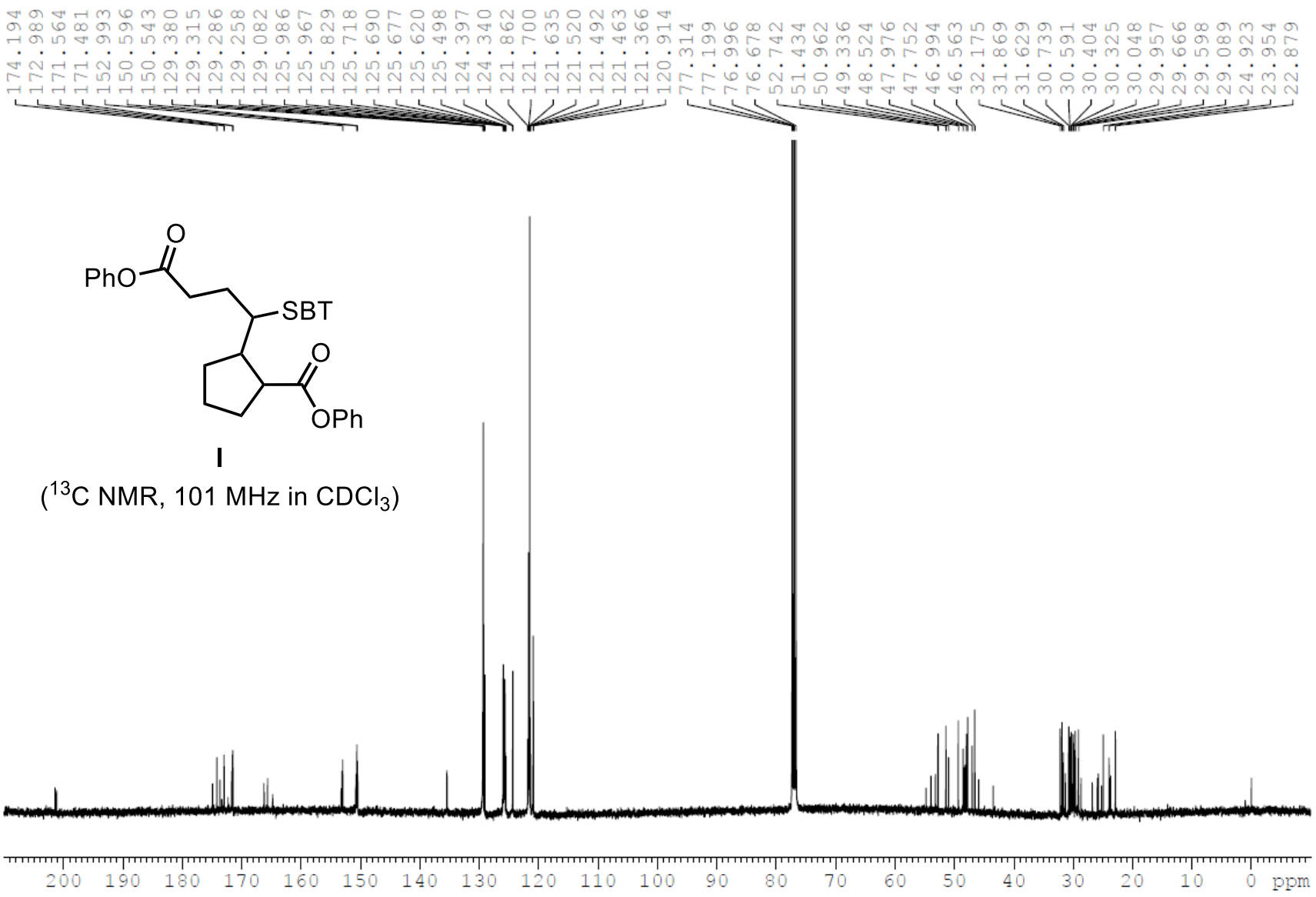
3aa

(^{13}C NMR, 101 MHz in $CDCl_3$)



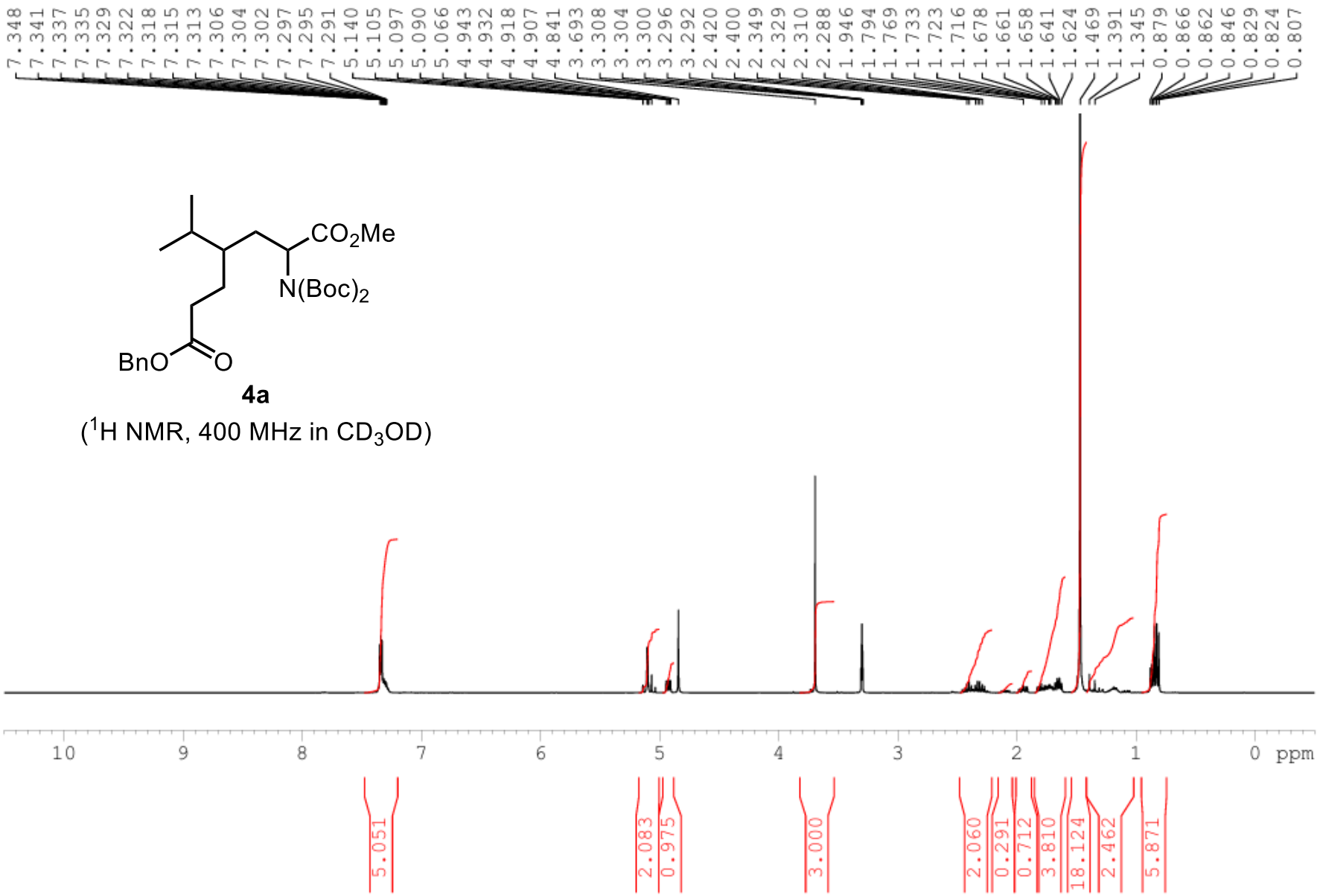
I

(^{1}H NMR, 400 MHz in $CDCl_3$)



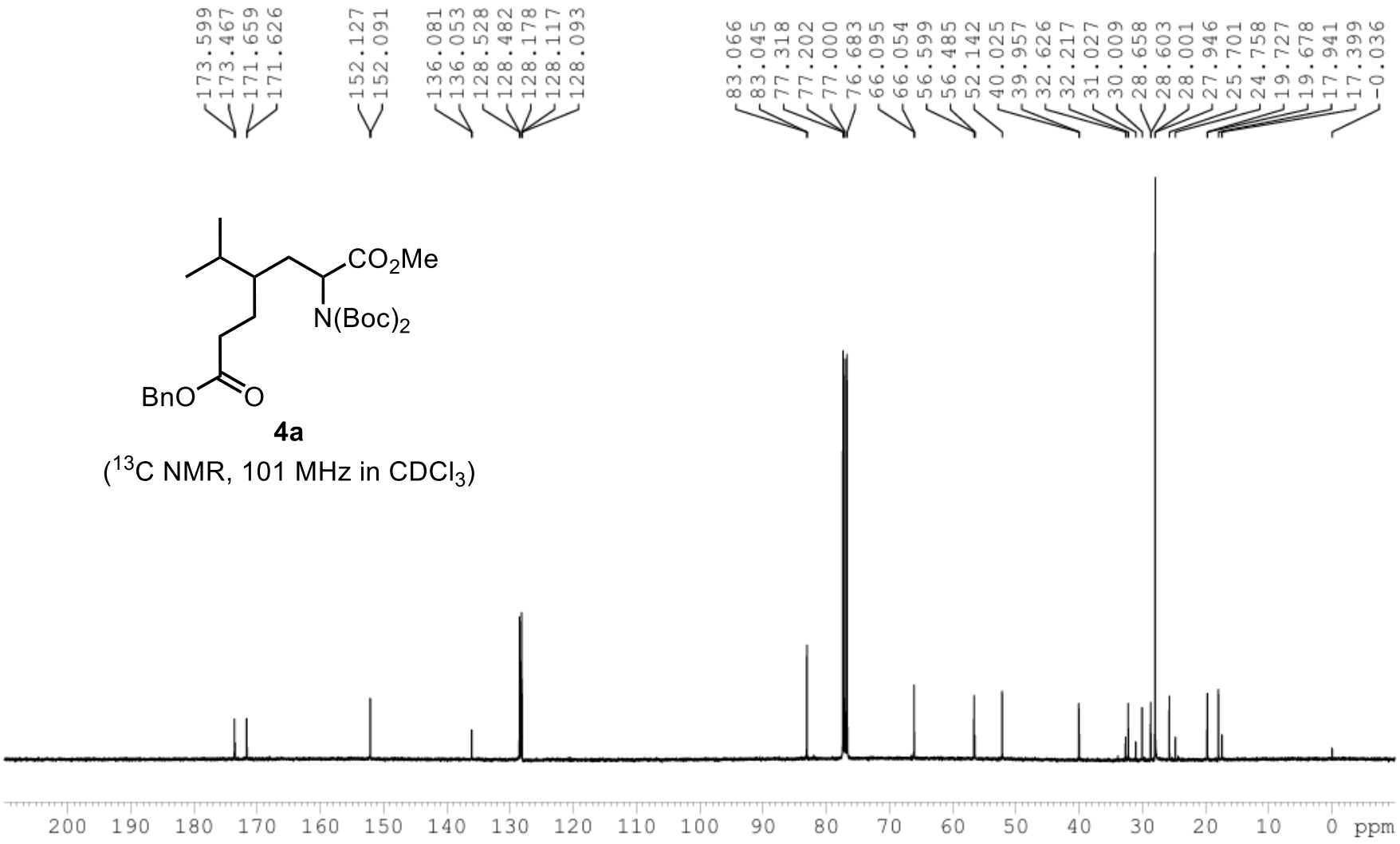
I

(^{13}C NMR, 101 MHz in $CDCl_3$)



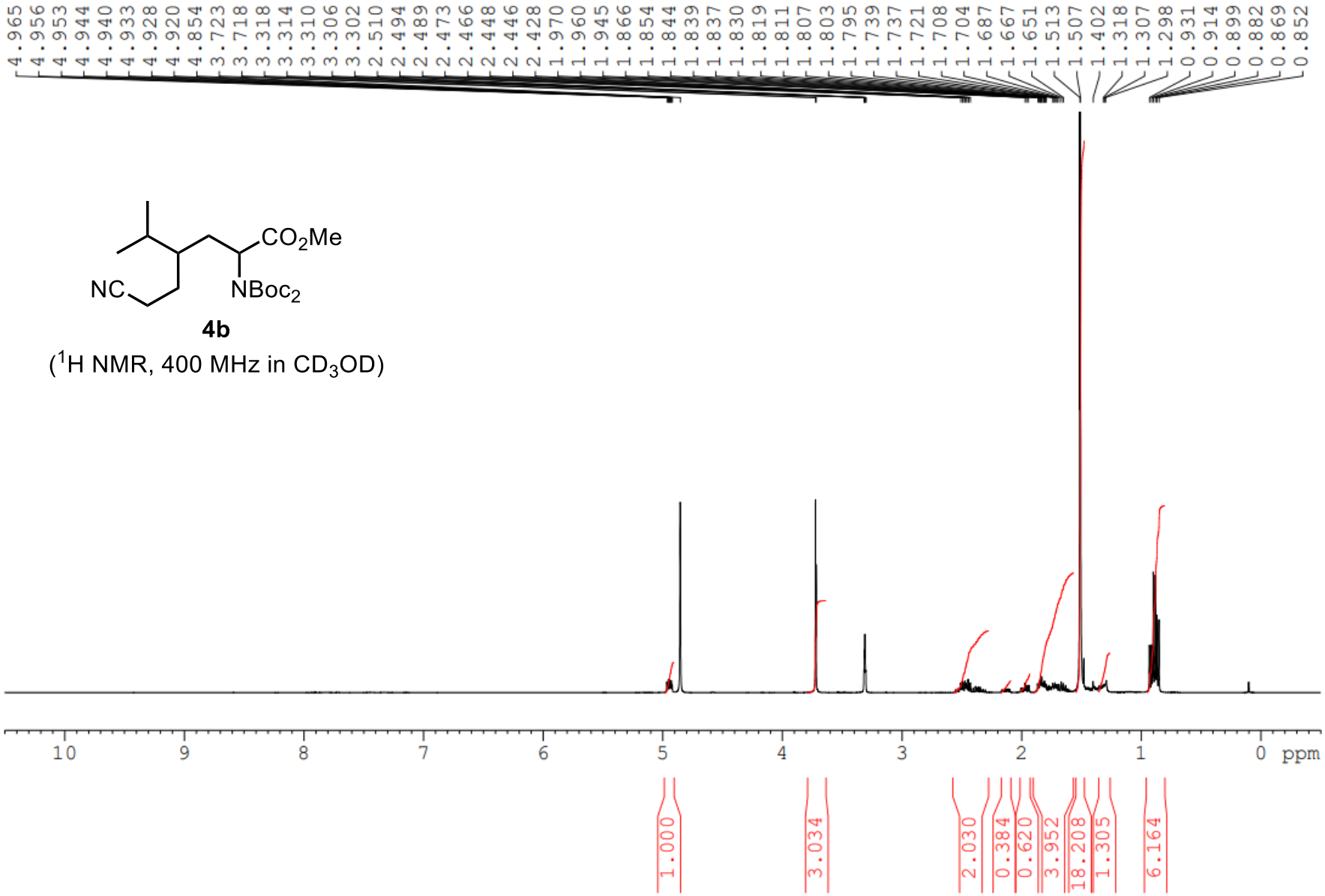
4a

(^{1}H NMR, 400 MHz in CD_3OD)



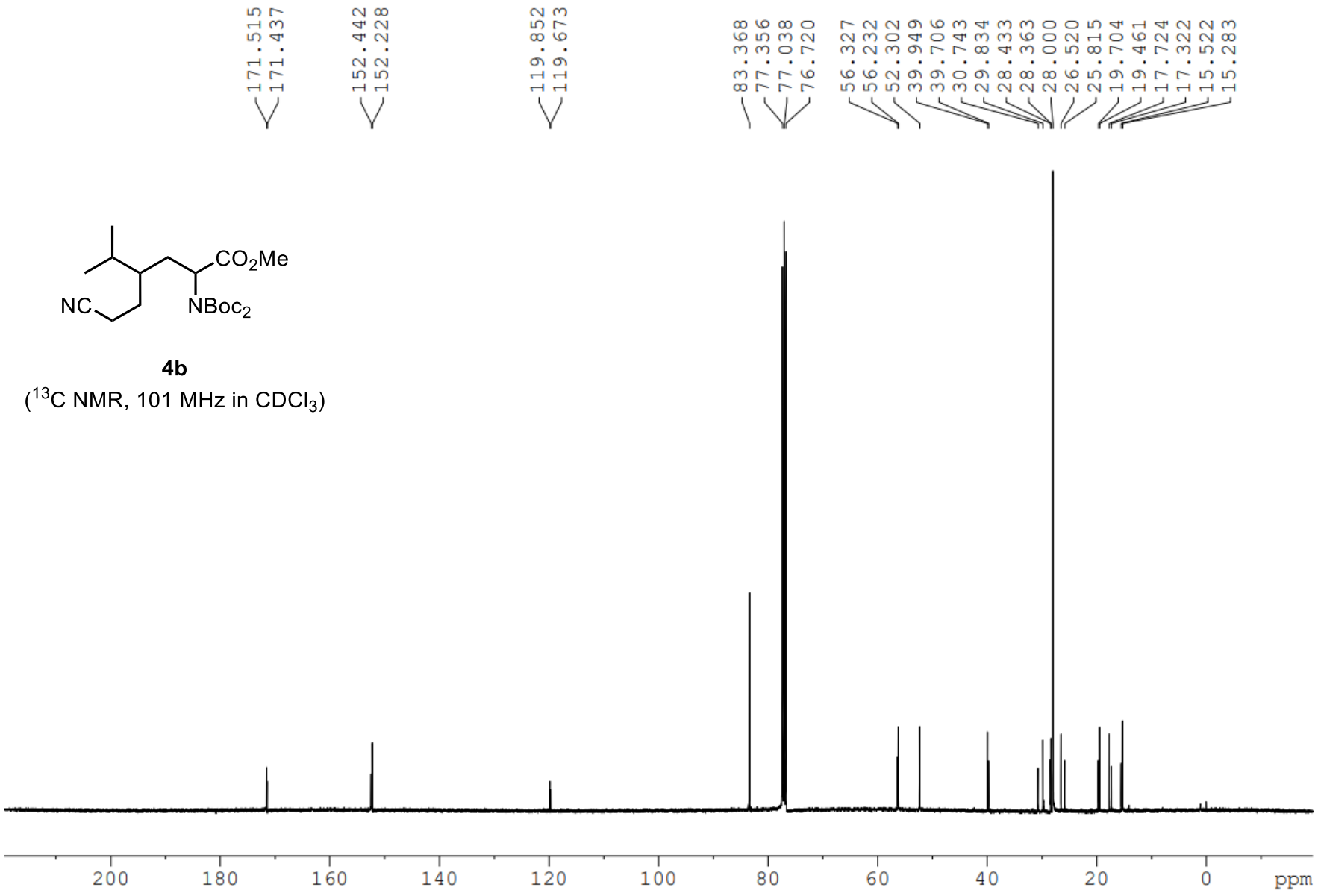
4a

(^{13}C NMR, 101 MHz in $CDCl_3$)



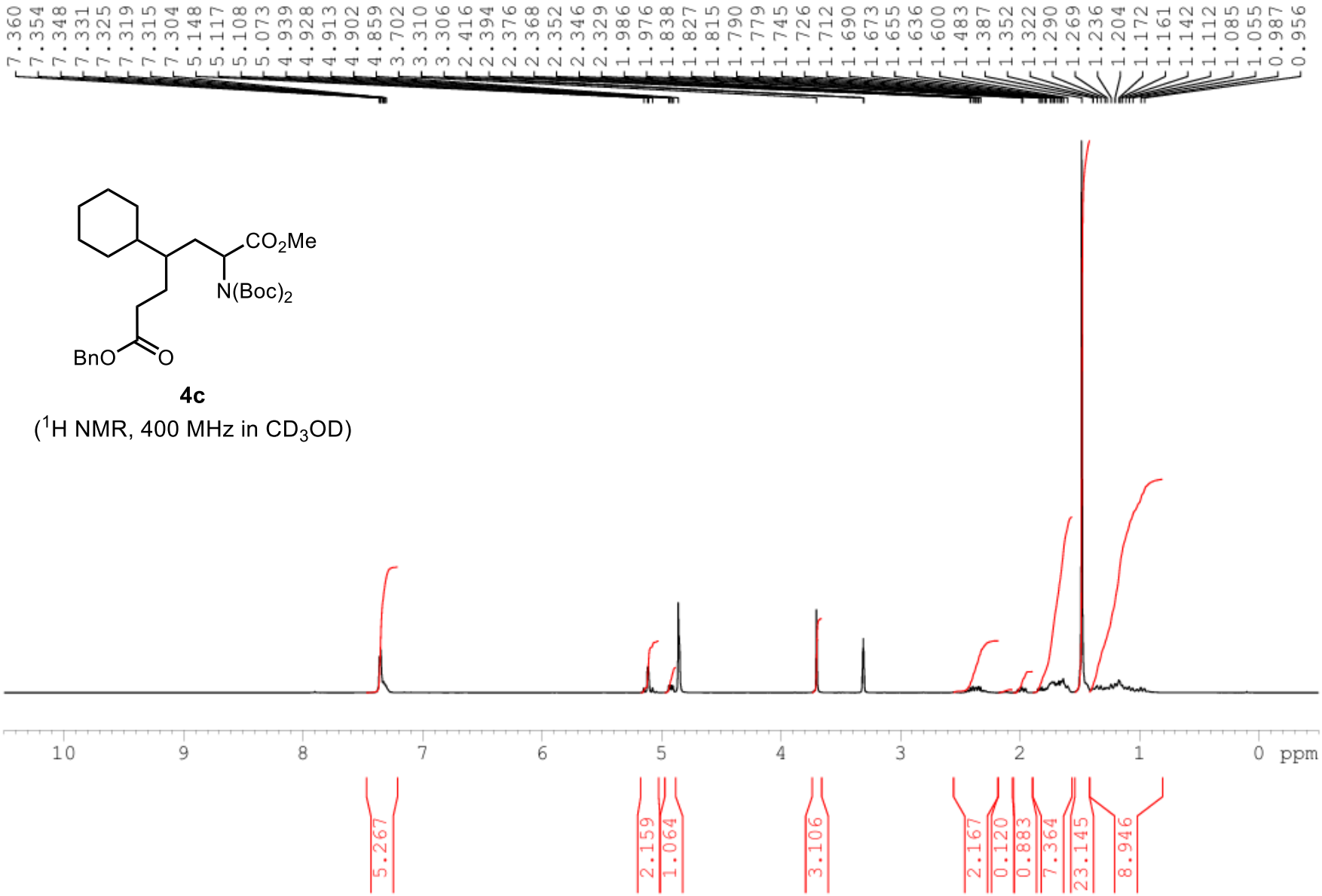
4b

(^{1}H NMR, 400 MHz in CD_3OD)



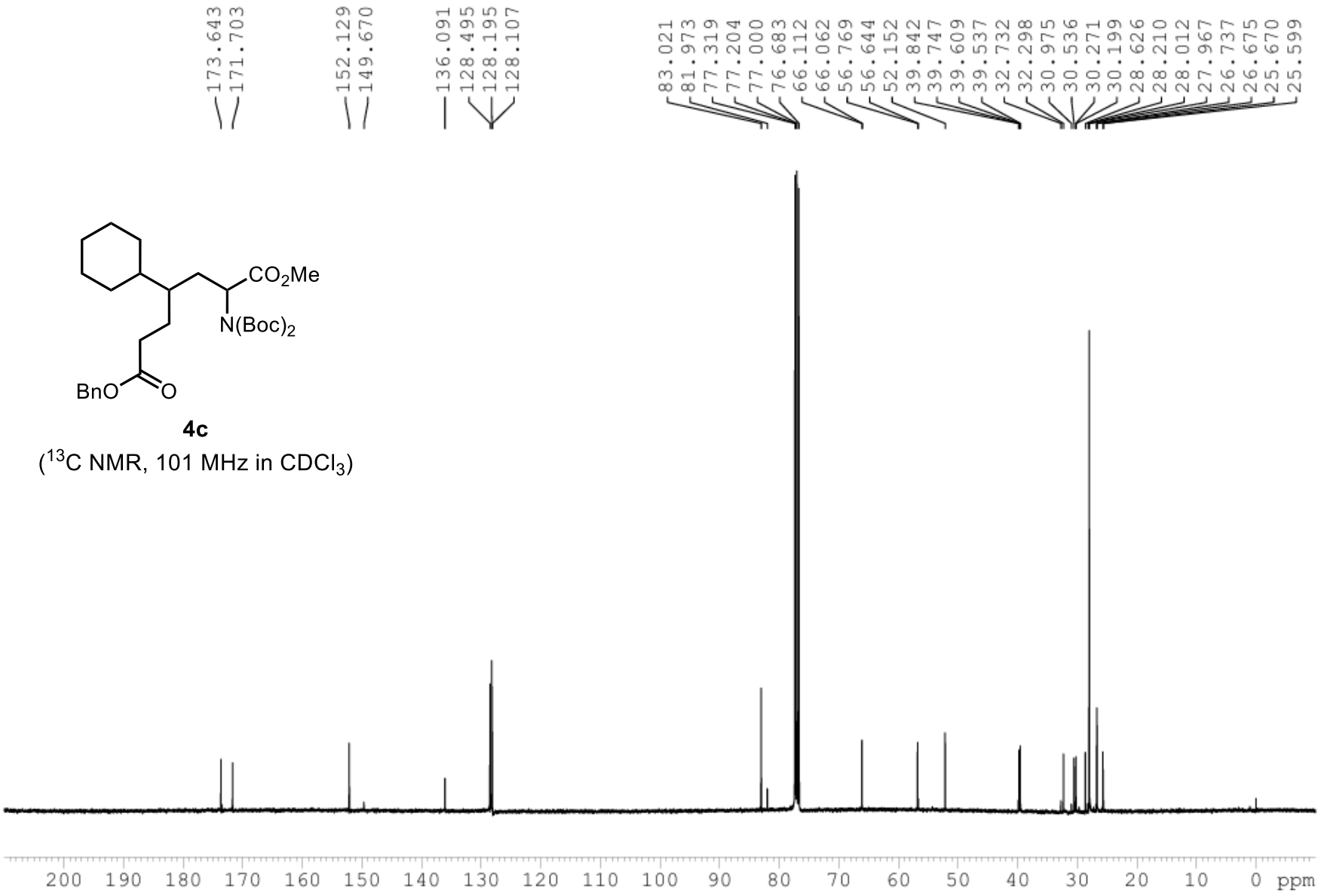
4b

(^{13}C NMR, 101 MHz in $CDCl_3$)



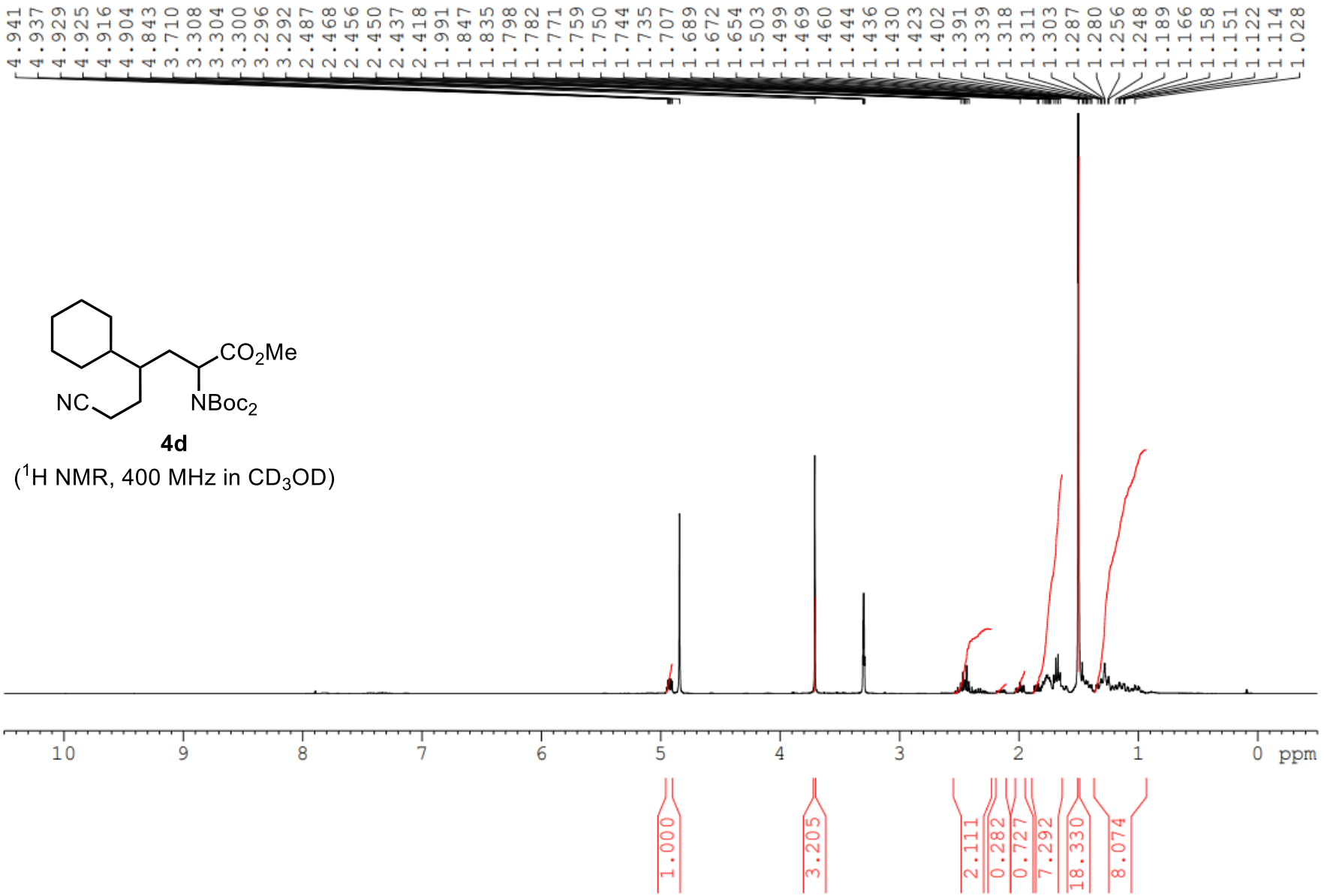
4c

(^{1}H NMR, 400 MHz in CD_3OD)



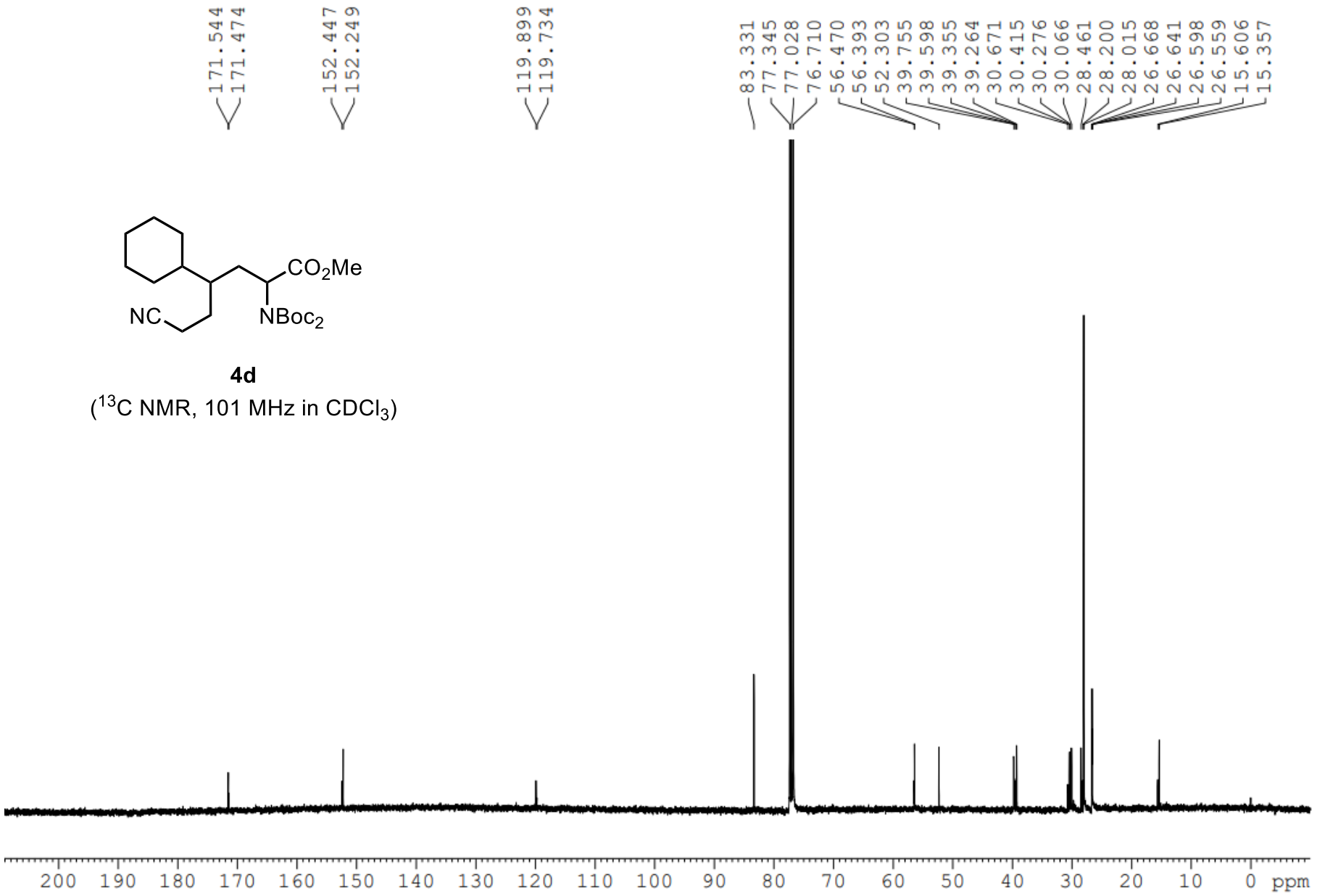
4c

(^{13}C NMR, 101 MHz in $CDCl_3$)



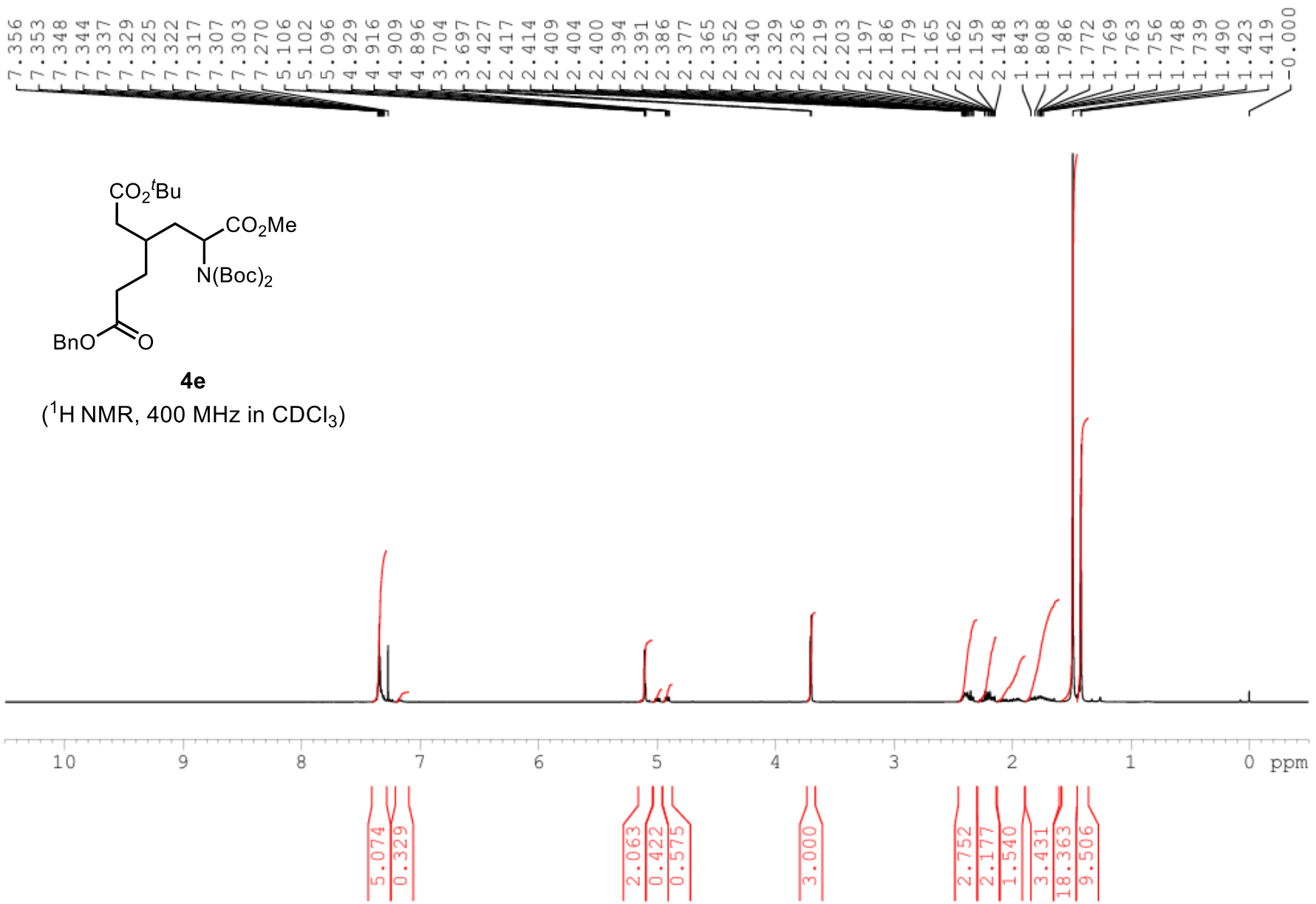
4d

(^{1}H NMR, 400 MHz in CD_3OD)



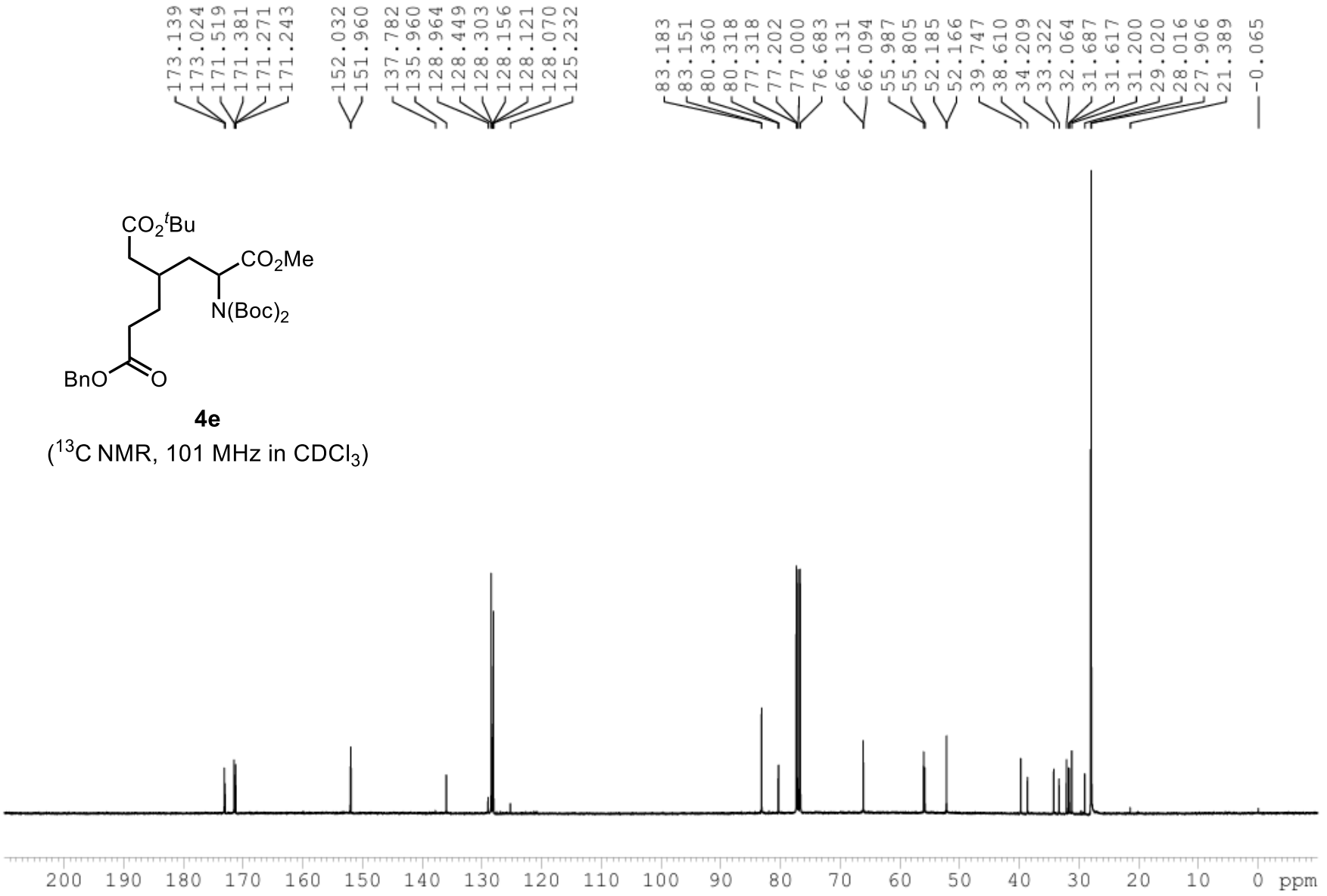
4d

(^{13}C NMR, 101 MHz in $CDCl_3$)



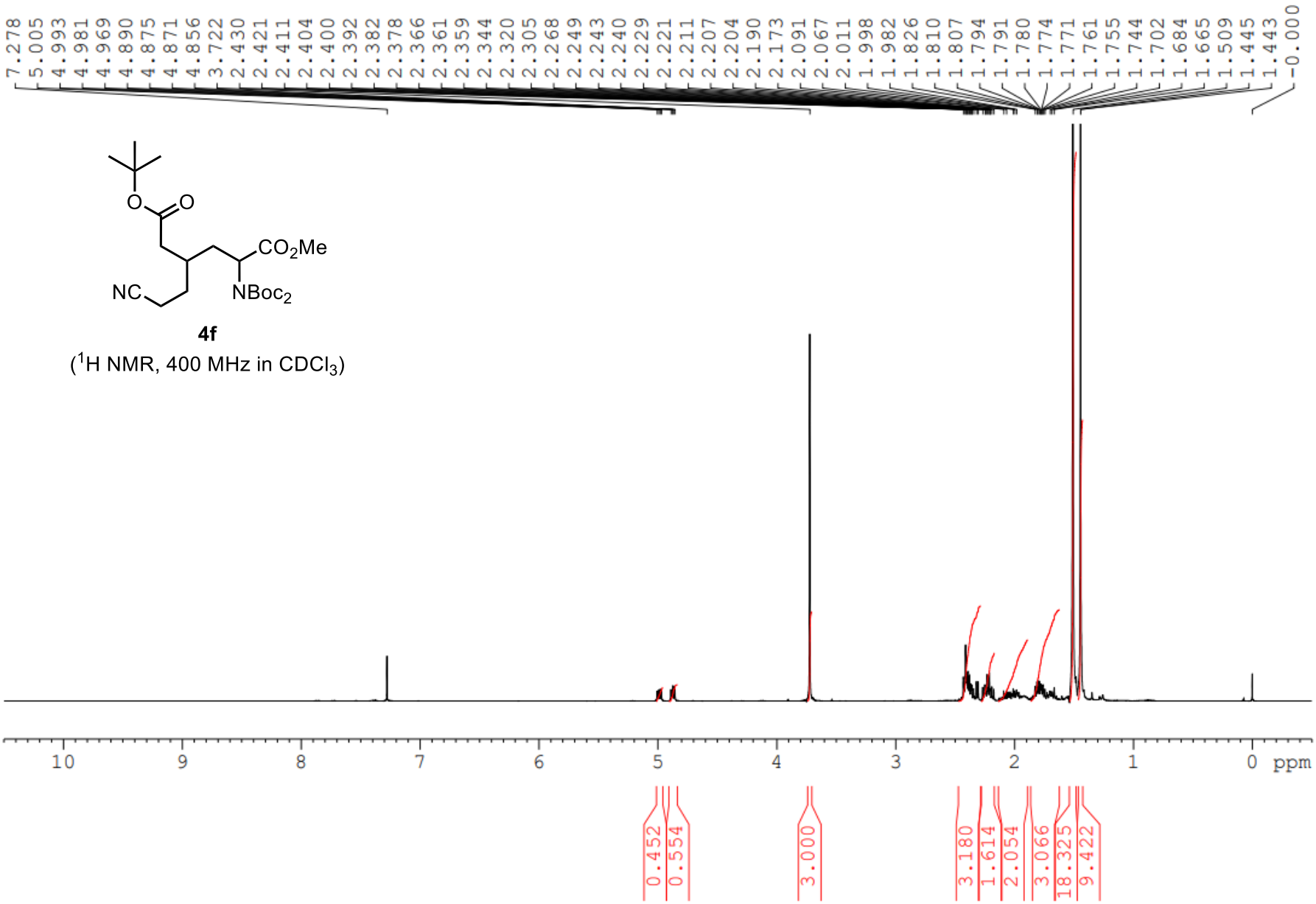
4e

(^{1}H NMR, 400 MHz in $CDCl_3$)



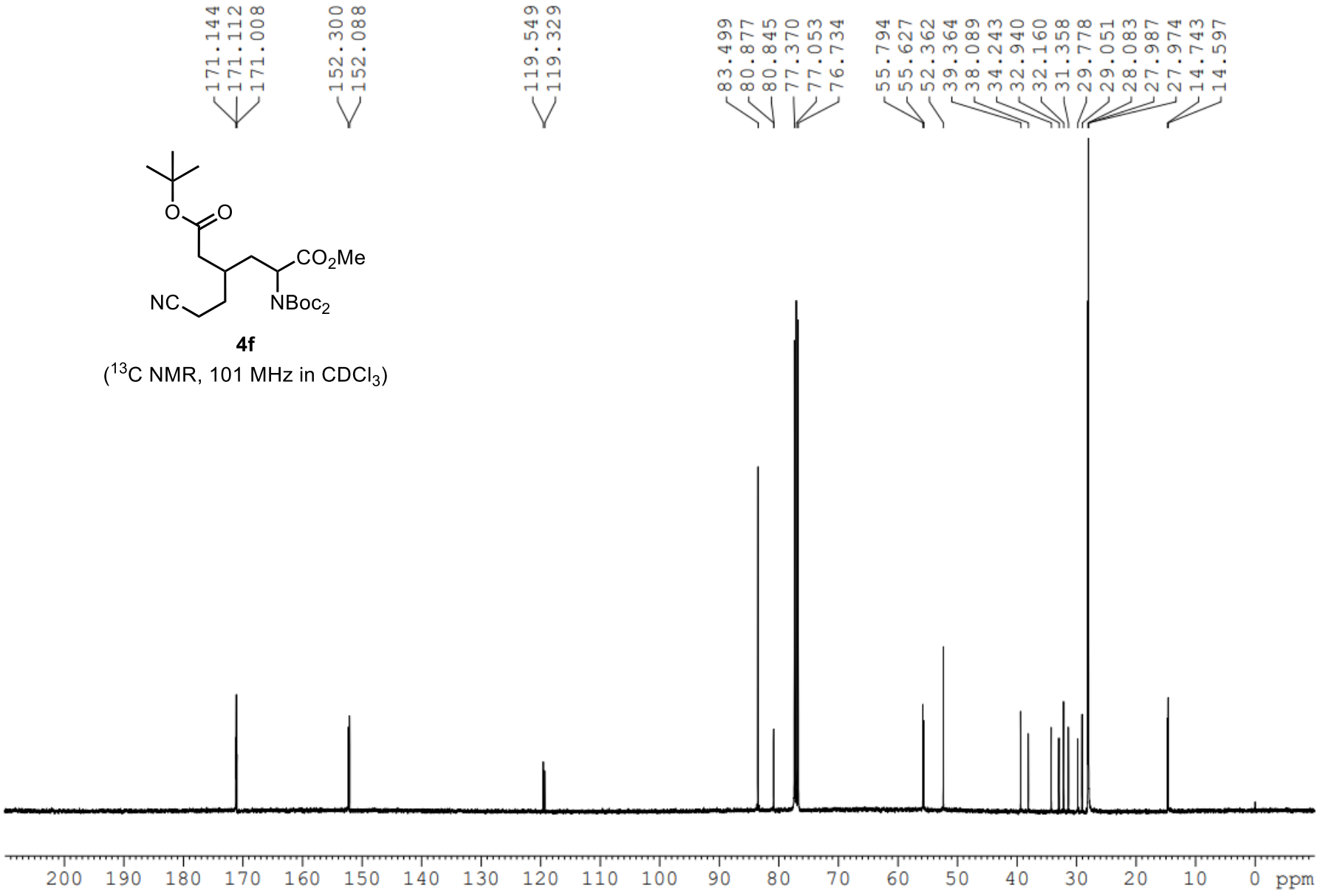
4e

(^{13}C NMR, 101 MHz in $CDCl_3$)



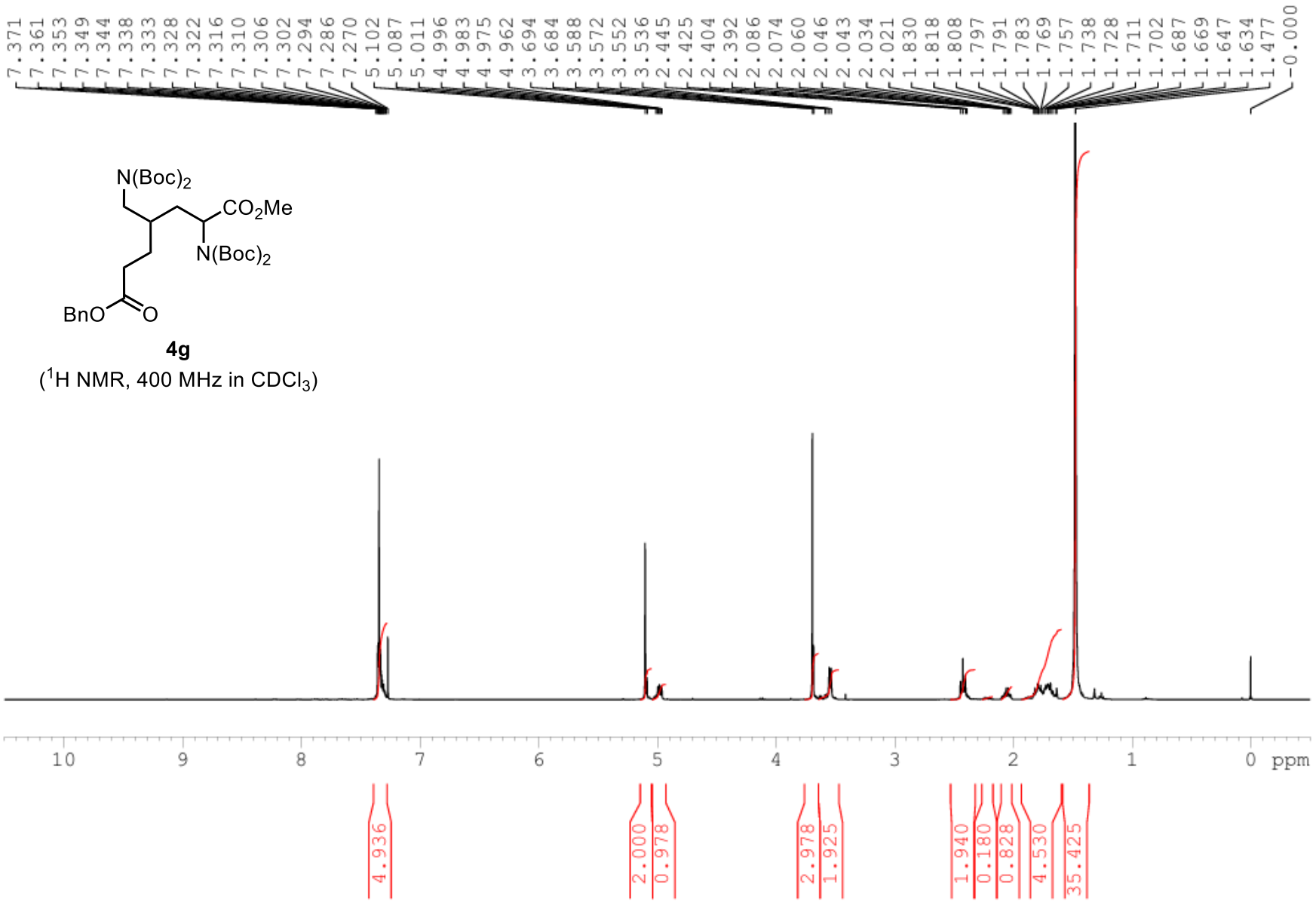
4f

(^{1}H NMR, 400 MHz in $CDCl_3$)



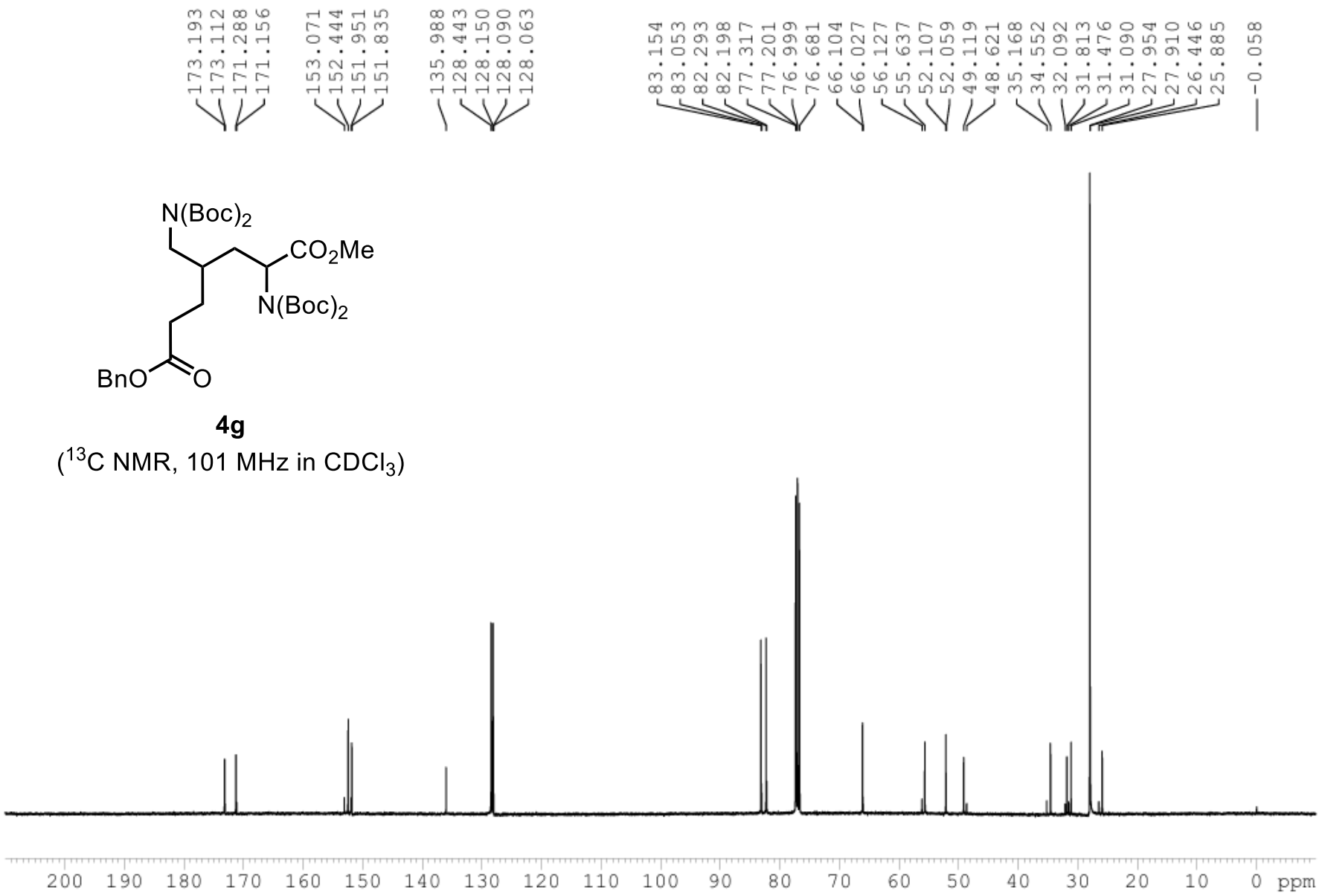
4f

(^{13}C NMR, 101 MHz in $CDCl_3$)



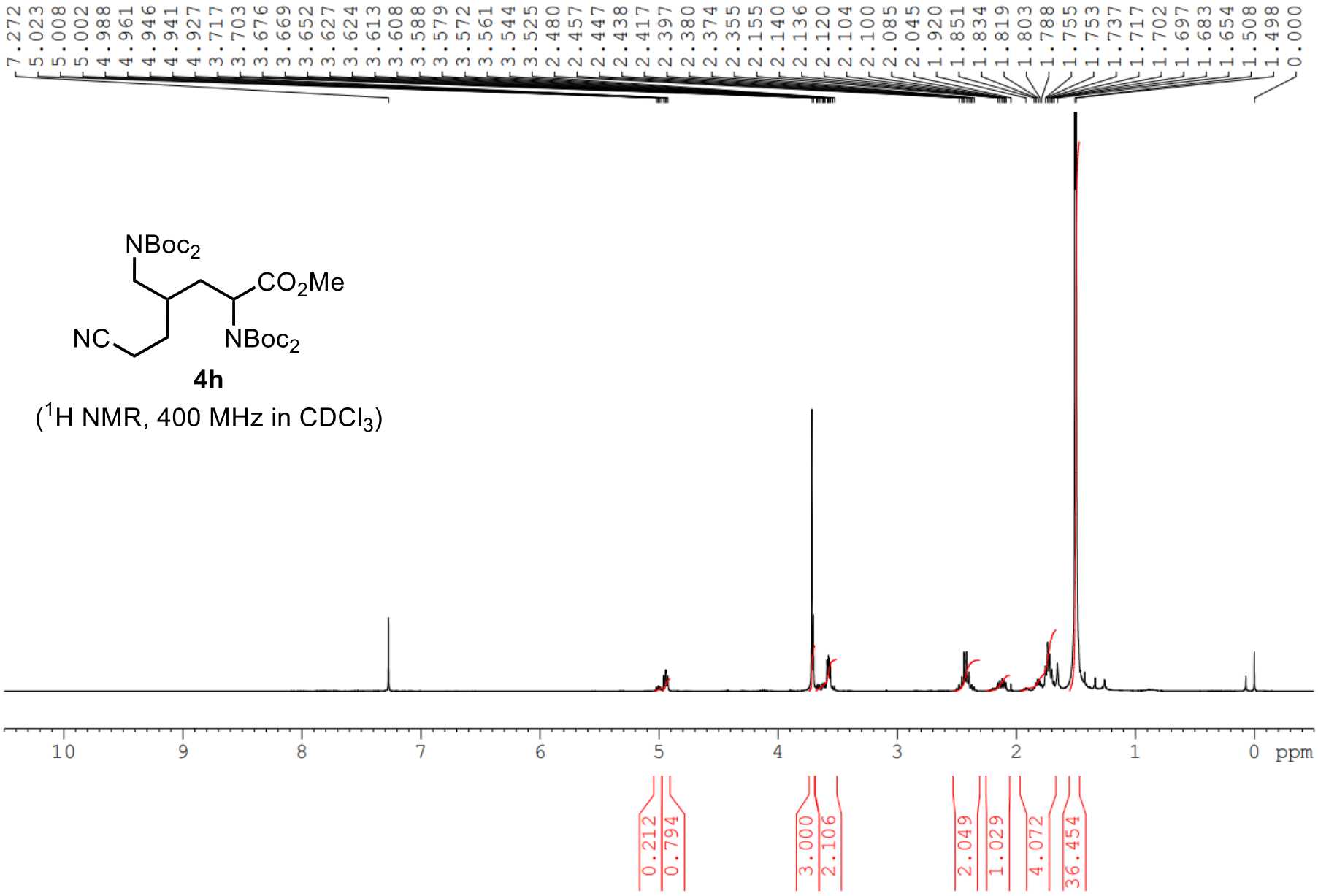
4g

(^{1}H NMR, 400 MHz in $CDCl_3$)



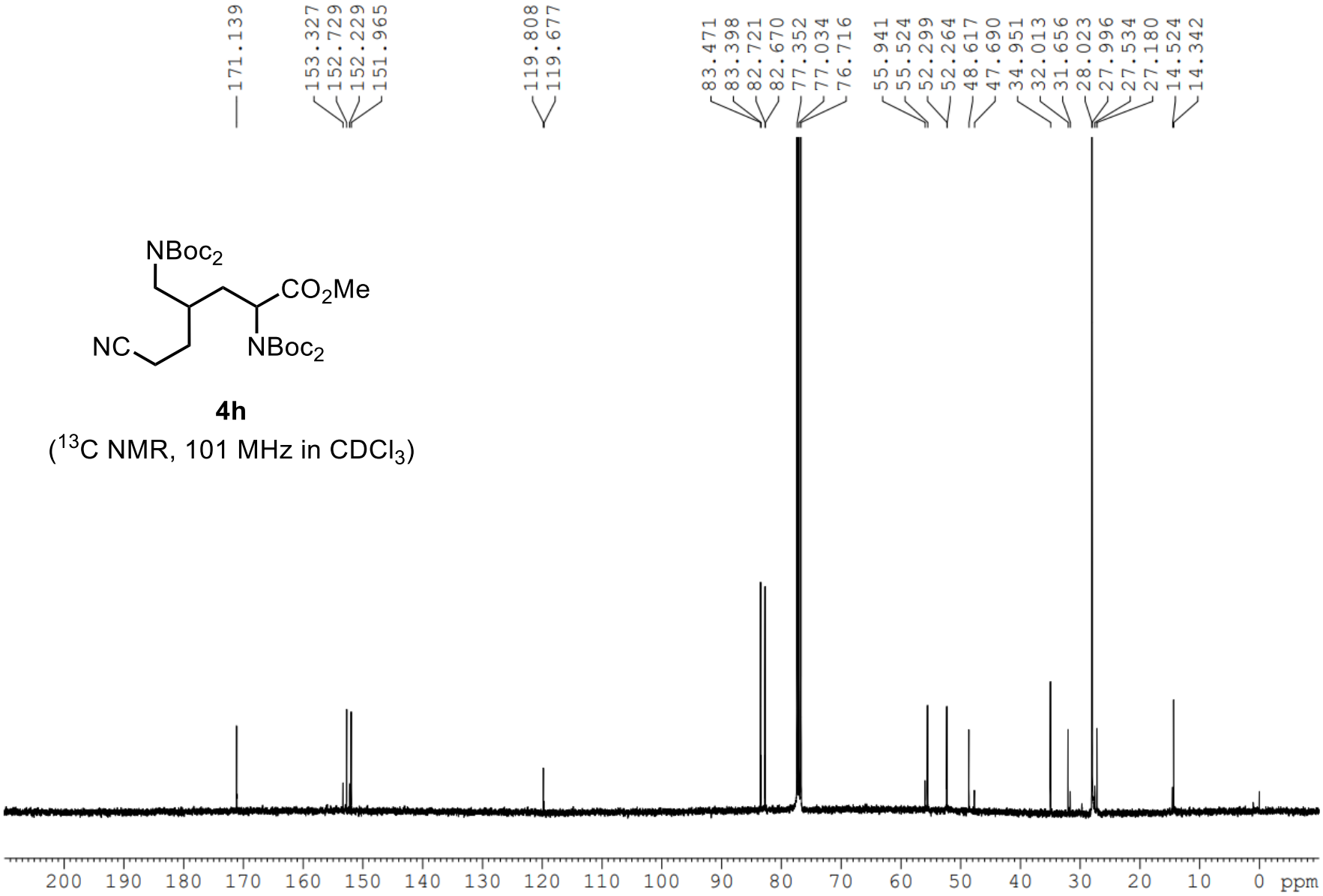
4g

(^{13}C NMR, 101 MHz in $CDCl_3$)



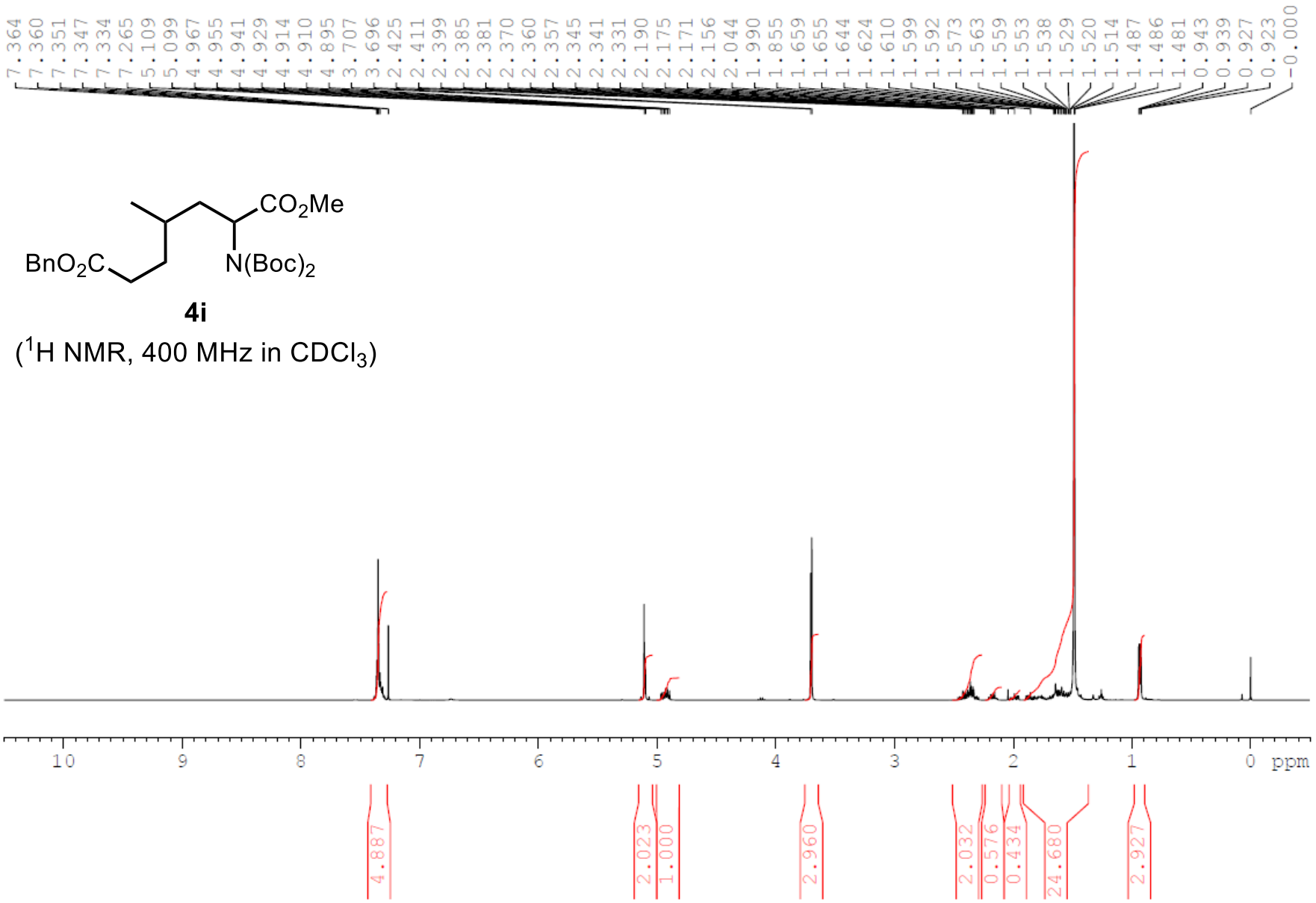
4h

(^{1}H NMR, 400 MHz in $CDCl_3$)



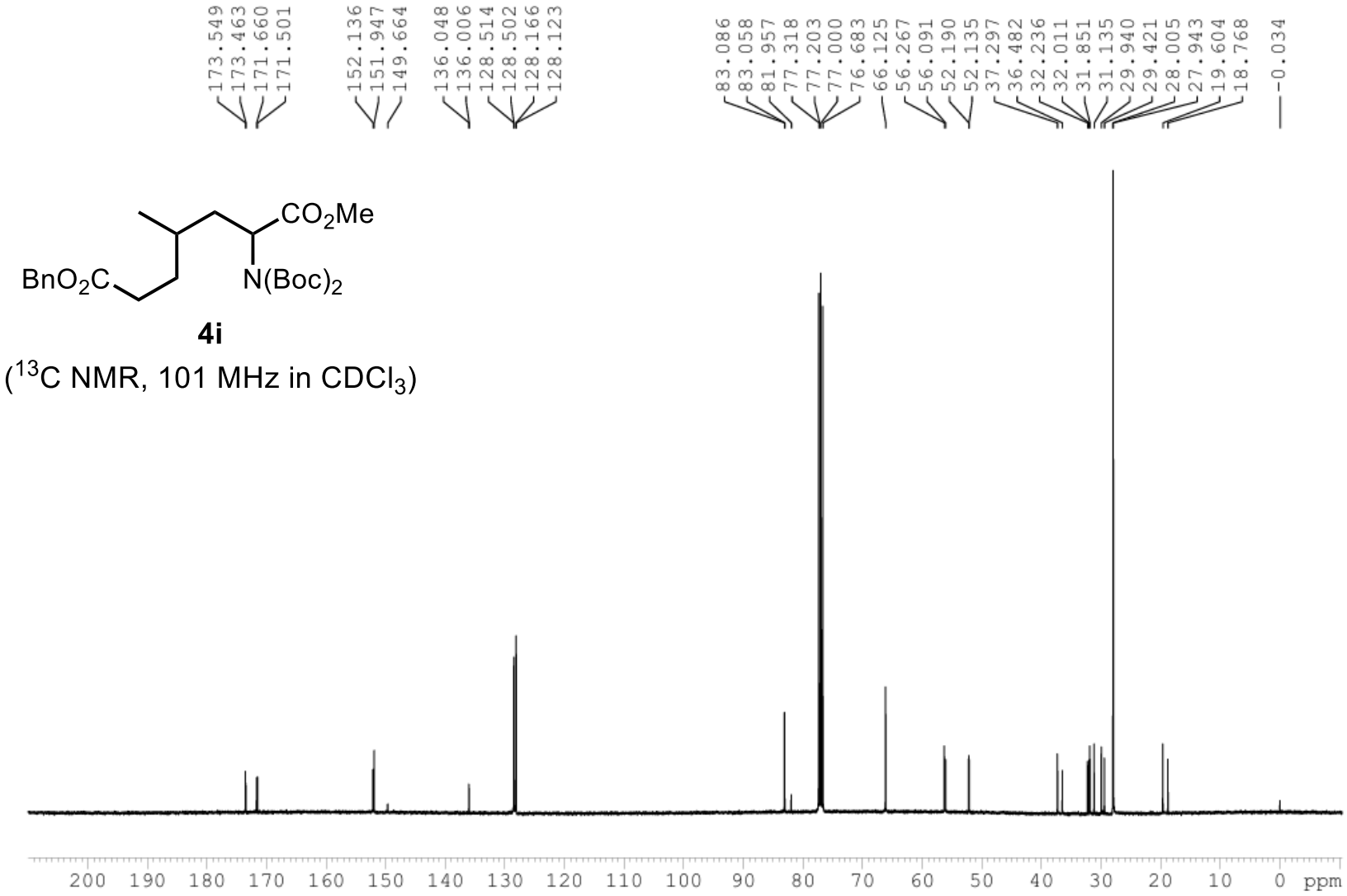
4h

(^{13}C NMR, 101 MHz in $CDCl_3$)



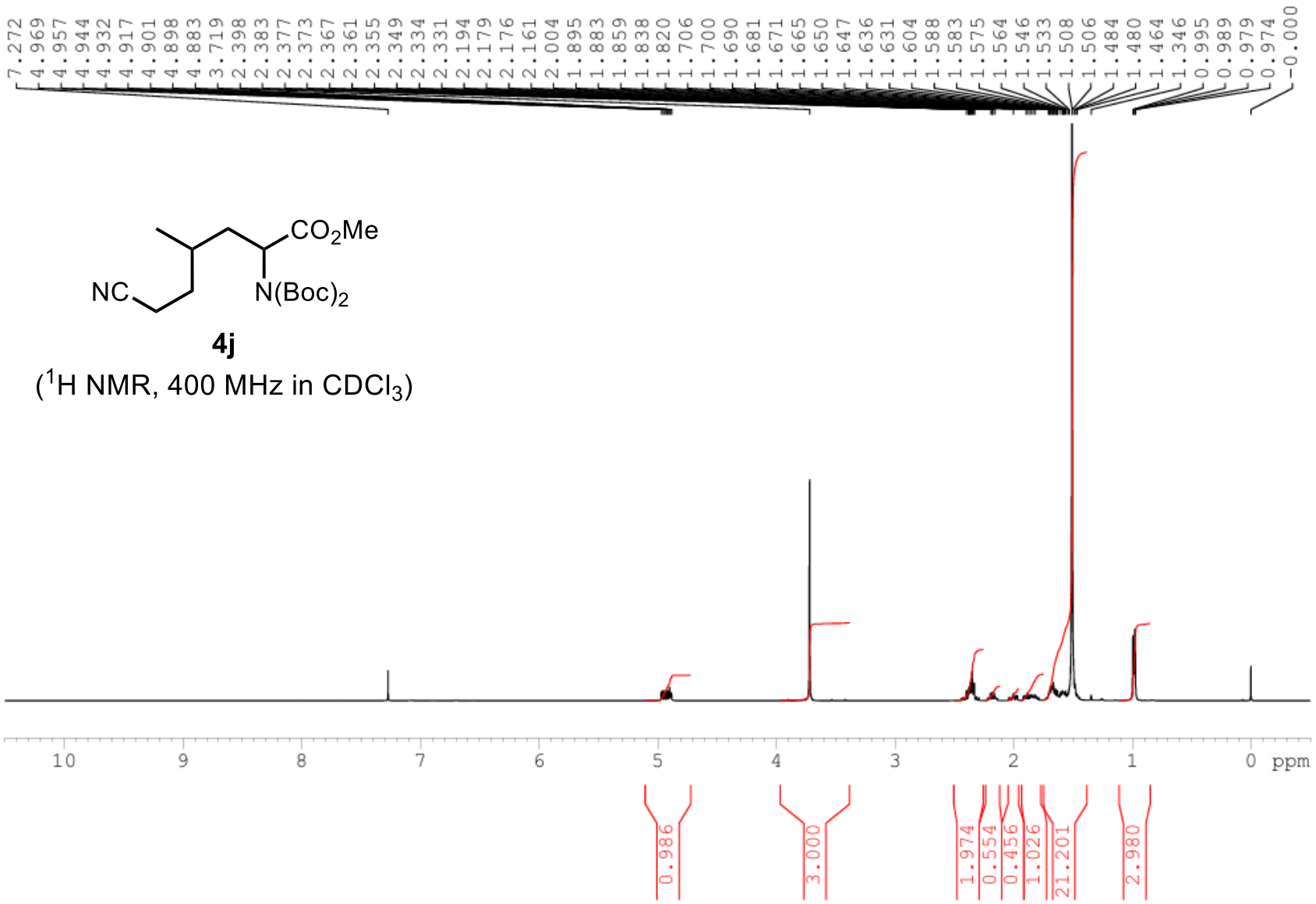
4i

(^{1}H NMR, 400 MHz in $CDCl_3$)



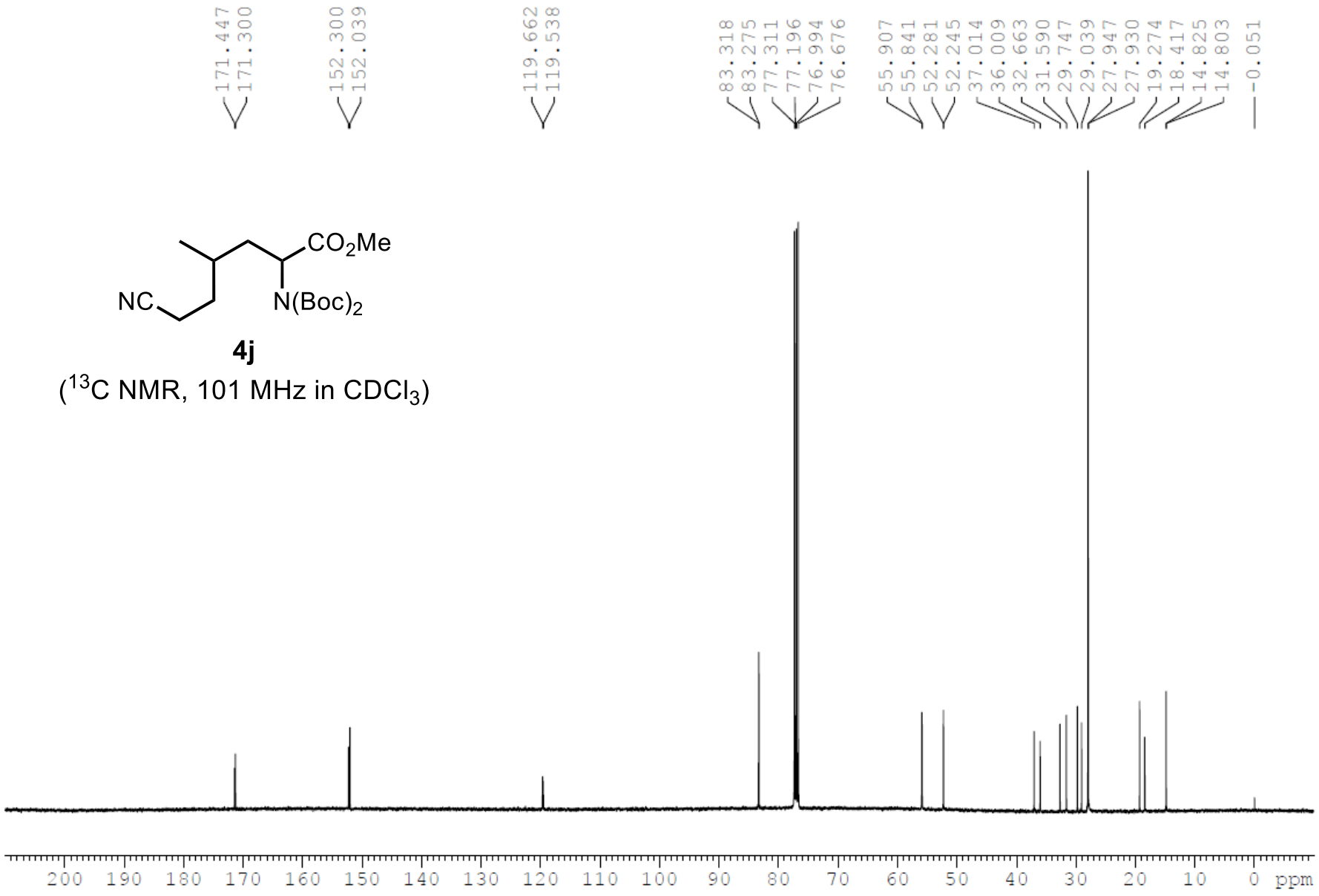
4i

(^{13}C NMR, 101 MHz in $CDCl_3$)



4j

(^{1}H NMR, 400 MHz in $CDCl_3$)



4j

(^{13}C NMR, 101 MHz in $CDCl_3$)